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EOGENETIC AND TELOGENETIC CEMENTATION OF SANDSTONES

EOGENETISCHE EN TELOGENETISCHE CEMENTATIE VAN ZANDSTENEN

(met een samenvatting in het Nederlands)

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR
AAN DE RIJKSUNIVERSITEIT TE UTRECHT,
OP GEZAG VAN DE RECTOR MAGNIFICUS PROF. DR. J.A. VAN GINKEL,
INGEVOLGE HET BESLUIT VAN HET COLLEGE VAN DEKANEN
IN HET OPENBAAR TE VERDEDIGEN
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door

NICOLAAS MOLENAAR

geboren op 18 december 1956 te Utrecht

Promotor: Prof. Dr. S.D. Nio

Co-promotor: Dr. P.L. de Boer

CONTENTS

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SAMENVATTING

INLEIDING

Een van de belangrijkste problemen in de sedimentologie is de voorspelling van de porositeit en de permeabiliteit van klastische sedimenten. Een groot deel van de porositeit gaat gedurende de diagenese verloren door cementatie, dat tevens de voornaamste afname van de permeabiliteit veroorzaakt. Cementatie bepaald ook het al dan niet gebeuren en de intensiteit van vele andere diagenetische processen, zoals mechanische en chemische compactie. Daarom zijn de oorzaken van cementatie van zandsteen en de invloed van cementatie op latere diagenese gekozen als hoofdthema's van het onderzoek, waarvan het onderhavige proefschrift het resultaat is. Hiervoor is onderzoek verricht aan het Onder Eocene Roda Zandsteen Member (Spanje) (hoofdstukken 2 en 3) en de Onder Givetien Nèvremont Formatie (Belgie) (hoofdstukken 4, 5 en 6).

Lithificatie van een sediment wordt vooral veroorzaakt door de neerslag van cement in de poriën tussen klasten. De meest voorkomende soorten cement zijn $CaCO_3$ (calciet) en SiO_2 (kwarts). Neerslag van calciet of kwarts cement in klastische sedimenten is dan ook één van de voornaamste oorzaken van het verloren gaan van de oorspronkelijke porositeit en permeabiliteit. De twee laatste eigenschappen bepalen in hoeverre een sediment (vervuild) water, olie en/of gas kan bevatten en ook of deze zich door dat sediment kunnen verplaatsen. Hoewel cementatie een zeer belangrijk proces is, zijn er nog steeds vele vragen omtrent de oorzaken van de cementatie van zandsteen. Enkele van deze vragen betreffen:

- *de herkomst van de cement materialen;*
- *de oorsprong van de oplossing die deze materialen aandraagt en de reacties veroorzaakt, d.w.z. het soort poriënwater;*
- *de drijvende kracht achter de beweging van deze oplossing door het sediment;*
- *de uiteindelijke oorzaken van de (lokale) neerslag van cement.*

De meeste soorten poriënwater bevatten slechts zeer geringe hoeveelheden calciet en kwarts in oplossing. Daarom zijn grote hoeveelheden van dat water nodig om voldoende materiaal voor cementatie aan te voeren. Met toenemende begravingsdiepte wordt dit steeds moeilijker, aangezien alleen al door mechanische compactie de permeabiliteit van het sediment afneemt hetgeen de stroming van oplossingen bemoeilijkt. Aan of dicht onder het sediment oppervlak doet zich dit probleem nog niet voor. Direct na afzetting zijn de meeste zandstenen immers nog zeer poreus en permeabel. Ook is het water aan de oppervlakte veelal verzadigd aan calciet en/of kwarts (respectievelijk zeewater in de sub-tropische zone en rivierwater). Voorts is er een drijvende kracht aanwezig in de vorm van getijdenbewegingen, kuststromingen en stromingen van continentaal grondwater. Deze drie factoren maken dat ondiep mariene en terrestrische milieus ideaal zijn voor een vroege cementatie van

zanden. Veel cementen blijken dan ook áán of nabij het sediment-water of sediment-lucht oppervlak zijn gevormd, zoals aan de hand van twee voorbeelden aangetoond zal worden in de volgende hoofdstukken.

In tegenstelling tot de tijd welke beschikbaar is bij diepe begraving, is de tijd voor cementatie aan of nabij het sediment oppervlak zeer gering. Vroeg of laat treedt hetzij erosie op of doorgaande sedimentatie brengt het betreffende zand buiten het milieu dat geschikt is voor cementatie. Daarom is vroeg cement veelal niet volledig en heeft het een heterogene verdeling: d.w.z. het cement is gebonden aan bijvoorbeeld horizonten die pauses in de (klastische) sedimentatie representeren (bodems of "abandonment surfaces"), aan zones met een primair relatief hoge permeabiliteit, aan plaatsen waar relatief veel kernen voor chemische neerslag van cement aanwezig waren, of combinaties daarvan. In een zandsteen met veel litische ductiele klasten kan deze heterogeniteit nog verder geaccentueerd worden door mechanische compactie van de niet of minder sterk gecementeerde zones tijdens begraving van dat sediment. In een kwartsrijke zandsteen is dit effect minder groot: de meeste klasten zijn immers stabiel en rigide. Hier echter kan in een later stadium bij diepere begraving druk oplossing plaatsvinden in de niet door vroeg cement gestabiliseerde zones.

Een groot voordeel van gedifferentieerd gecementeerde zandstenen ligt in het feit dat op macroscopische schaal verschillen in de diagenese zichtbaar zijn, welke een gedetailleerde bemonstering van de verschillende zones mogelijk maken. Immers, deze verschillen in diagenese representeren verschillen in één of meer van de factoren die de cementatie bepaald hebben. Verschillen zijn terug te leiden tot initiële verschillen in de structuur (gelaagdheid of laminatie), textuur (korrel pakking of vorm), samenstelling (hoeveelheid cement kernen). Veelal hangen ze samen met variaties in de sedimentatie snelheid. Laterale en/of vertikale variaties in één of meer van deze parameters in een klastische sequentie hebben de vroege cementatie in bepaalde zones geïnduceerd, of in andere zones tegengehouden. Door de verschillen tussen de diverse zones in een klastisch sedimentair lichaam te bestuderen zijn konklusies te trekken over de oorzaken van cementatie.

Daartoe zijn twee zandsteen formaties bestudeerd:

1- *de Onder Eocene Roda Zandsteen Member (Spanje) (hoofdstukken 2 en 3). Deze formatie vertoont een sterke heterogeniteit in samenstelling en een differentiële resistentie tegen recente verwering. In ontsluitingen manifesteert zich deze differentiële resistentie door de aanwezigheid van harde lagen of nodulen in een omringende zandsteen, die minder resistent is tegen de huidige verwering.*

2- *de Onder Givetien Nèvremont Formatie (Belgie) (hoofdstukken 4, 5 en 6).*

De studie van deze twee voorbeelden heeft geleid tot een aantal conclusies over cementatie:

- *Indien geen geschikte kernen aanwezig zijn vindt meestal geen neerslag*

van cement plaats. D.w.z. er vindt geen precipitatie van kwartscement plaats indien kwarts klasten afwezig zijn of als de kwarts klasten door kleihuidjes bedekt zijn en indien er geen kalkklasten zijn vindt geen vroege kalkcementatie plaats.

- *De tijd is een zeer belangrijke factor: vandaar dat vroege cementatie gebonden is aan pauses in klastische cementatie.*
- *Tijdens die pauses kunnen veranderingen in het sediment plaatsvinden: er ontwikkelen zich zones met een verhoogd gehalte aan carbonaat componenten (door productie van biogene kalk in het mariene milieu) die als cement kern kunnen dienen, terwijl in een continentale omgeving de kernen juist afgeschermd worden door infiltratie van kleien en ijzeroxyden (c.q. de vorming van cutans).*
- *De vroege cementatie heeft een grote invloed op de latere diagenese: gestabiliseerde zones worden gevormd, die, alhoewel ze initiële zones met verlaagde permeabiliteit vormen, in een later stadium hun permeabiliteit juist weer bewaren doordat compactie wordt tegengegaan door het neergeslagen cement.*

HOOFDSTUKKEN 2 EN 3

Het onderste Member van de Givetien Nèvremont Formatie bestaat uit fluviatiele zandstenen en conglomeraten die voornamelijk opgebouwd zijn uit kwarts componenten. In deze klastische sedimenten komen aantal pedogene verschijnselen voor, zoals:

- lagen met calciet "glaebules" en nodulaire "calcrete";
- "gley" verschijnselen, gekenmerkt door hematiet segregaties, die een vlekkigheid door geprononceerde verschillen in kleur veroorzaken;
- wortel horizonten;
- cutans, veroorzaakt door mechanische infiltratie van klei en/of ijzerhydroxyden;
- graafgangen en vooral "striotubules".

Hieruit werd geconcludeerd dat het klimaat ten tijde van bodemvorming semi-aride was. Het bron gebied van de klastische sedimenten was waarschijnlijk het chemisch intensief verweerde Brabant Massief, hetgeen de mineralogisch rijpe samenstelling van de sedimenten verklaard.

De gehele diagenese werd sterk beinvloed door het terrestrische depositionele milieu. Vooral de infiltratie van klei mineralen, zoals kaoliniet en illiet, hebben voor de diagenese bepaald. Deze infiltratie vond plaats langs vroegere wortelgangen en andere meer permeabele zones in het zand. Hierdoor werden lokaal de kwartskorrels bedekt door kleihuidjes (ook wel klei cutans of "argillans" genoemd). Overal waar deze kleihuidjes dik genoeg waren en de korrels volledig omhuld hadden, kon geen kwarts cement neerslaan. Een eerste fase van kwarts cementatie vond aan de oppervlakte plaats, hetgeen duidelijk gedemonstreerd wordt door het lokaal voorkomen van kleihuidjes bovenop kwartscement. Op deze plaatsen was de zandsteen ruim voldoende gestabiliseerd om latere mechanische en chemische compactie te weerstaan. Namelijk overal

waar de kleihuidjes de vroege kwarts cementatie verhinderd hebben, is gedurende de diepere begraving chemische compactie opgetreden in de vorm van druk oplossing tussen kwartskorrels onderling, hetgeen juist bevorderd werd door de kleihuidjes tussen de korrels. De lithificatie van de sedimenten is bewerkstelligd door een combinatie van kwarts cementatie en compactie. De zeer heterogene verdeling van beide processen werd voornamelijk bepaald door de heterogeniteit van mechanische infiltratie van klei boven de waterspiegel.

De bron van het kwarts cement was zoet water, dat aan de oppervlakte meestal oververzadigd is aan kwarts. Wanneer voldoende tijd beschikbaar is, zoals tijdens een stop in klastische sedimentatie hier geïndiceerd door de bodemverschijnselen, kan aan de oppervlakte een lokaal vrijwel volledige cementatie door kwarts plaatsvinden. In de meeste gevallen is de vroegtijdige karakter van de cementatie niet meer te bewijzen, aangezien de meeste kwartsrijke sedimenten vrijwel ongevoelig zijn voor mechanische en soms ook voor chemische compactie. Compactie en het verloren gaan van primaire porositeit kan anders namelijk gebruikt worden als graadmeter voor het tijdstip van sediment stabilisatie. In de Nèvremont Formatie is door de afwisseling in bodemvorming, kwartscementatie en hernieuwde bodemvorming de oppervlakte nabije aard van de kwarts cementatie goed bewijsbaar.

HOOFDSTUKKEN 4, 5 EN 6

De textuur en samenstelling van de zanden van het Onder Eocene Roda Zandsteen Member (Tremp-Graus Bekken in de zuidelijke Pyreneeën) zijn kort na afzetting door diagenese gemodificeerd. Sedimentatie van deze zanden vond plaats onder invloed van eb-getijdenstromingen door grote zich verplaatsende ribbels en/of duinen. Van tijd tot tijd, stopte de sedimentatie en vond vroege diagenese plaats, zoals;

- bioturbatie en verrijking van het zand met kalkige korrels;
- mechanische infiltratie van fijnkorrelig kalkig matrix materiaal;
- de neerslag van een kalk cement direct rond de kalkkorrels en de kalkige matrix.

Door deze processen werden de bovenste lagen van de depositionele lichamen veranderd in verharde kalkige lagen die "hardgrounds" genoemd kunnen worden. Door de aanwezigheid van het vroege cement, dat het zand stabiliseerde, konden deze lagen de mechanische compactie tijdens begraving weerstaan. In de lagen zonder vroeg cement ging de porositeit en permeabiliteit door mechanische deformatie van zachte sedimentaire klasten echter volledig verloren. Vroege diagenese resulteerde dus in een sterke differentiatie van de permeabiliteit in de betreffende zandsteen lichamen. Deze differentiatie werd nog versterkt door latere diagenese.

Na een eerste fase van begraving, brachten opheffing en erosie in het noordelijke deel van het onderzochte gebied het Roda Zandsteen Member weer gedeeltelijk aan de oppervlakte. Hierdoor kon zoet water in de zandsteen

indringen en werd de rest van de poriën gevuld met een grof kristallijn laag-magnesium calciet cement. Deze cementatie was het eerst voltooid in de vroeg gecementeerde zones. Gelijk met deze cementatie werden alle kalkcomponenten bestaande uit aragoniet en hoog-magnesium calciet vervangen door laag magnesium calciet, soms met het bewaard blijven van de oorspronkelijke interne textuur, maar soms met de ontwikkeling van een nieuwe textuur uit grotere kristallen.

Het carbonaat cement is dus zeer heterogeen verdeeld. Soms uit zich dat door harde nodulen en/of lagen, die resistent zijn tegen verwering. Hier is de vroege cementatie en dus de vorming van de "hardgrounds" begonnen, doordat de omstandigheden voor cementatie ideaal waren. Wanneer de klastische sedimentatie lang genoeg stilstond, konden deze nodulen aaneengroeien tot continue lagen.

De nodulen kunnen informatie geven omtrent de factoren die de cementatie beinvloed of bepaald hebben. Het blijkt dat een aantal factoren zoals de korrel-sortering en de hoeveelheid kalkig materiaal lokaal optimaal waren. Op deze plaatsen, nu vaak nog gerepresenteerd door nodulen, begon de vroege cementatie.

CHAPTER 1

EOGENETIC AND TELOGENETIC CEMENTATION OF SANDSTONES

N. MOLENAAR

INTRODUCTION

The present study concentrates on a major problem in many sedimentological studies, the prediction of porosity and permeability properties of sandstone unit in the subsurface: i.e., the destruction, preservation, and enhancement of porosity and permeability in subsequent diagenetic stages.

Porosity and permeability properties of a sandstone, are, above all, related to cementation and thus to the factors controlling cementation. In addition, compaction is an important, usually complementary, process. It is governed by the clastic composition of the sediment and by the timing of cementation. Cementation usually retards or even stops compaction. Cementation is the main cause of porosity reduction in sandstones, especially in sandstones composed of rigid grains. Calcite and quartz commonly are the most important cementing minerals (Blatt, 1979). Calcite frequently constitutes the main or exclusive cement mineral in marine sandstones. In addition, quartz can be important in continental and mixed marine-continental settings.

For any substantial cementation, many volumes of interstitial water have to percolate through the sediment in order to supply the materials needed (e.g., Blatt, 1979). With increasing burial depth, the permeability of most sandstones decreases through compaction, through authigenesis or replacement and, of course, also by cementation. Unless dissolution occurs, the flow of interstitial solutions thus becomes progressively inhibited, and the time needed for cementation by chemicals introduced from outside the pertinent sand body increases to a geologically unacceptable length (Blatt, 1979). Therefore, bulk cementation during deep burial is strongly conflicting. A main problem in understanding cementation is thus the way in which the cementing minerals are brought into the sandstones (Land, 1984).

EARLY CEMENTATION

Near the surface the conditions for cementation are, theoretically, far more feasible than at depth. The primary porosity and permeability are still high near the surface. Moreover, flow rates of interstitial water are high near the sediment-water or the sediment-air interface, given the proper setting. Shallow-subtidal to supratidal environments have suitable conditions, as do have continental settings. Thus, near the surface the conditions are excellent for the supply of large amounts of marine or meteoric water through a sand-body. Tidal

and wave action or topographic relief can act as the driving force behind the movement of the interstitial waters. Therefore, a relation is to be expected between pauses in sedimentation and early cementation and/or the formation of hardgrounds. This subject will be elaborated in most of the next chapters.

Can early cements be recognized by typical features in their distribution or habit? In general, one would expect a relatively homogeneous distribution of cement throughout a sandstone body, if it is introduced during deep burial conditions. Then, physical conditions, such as temperature or partial gas-pressures, are similar throughout a sedimentary body, and sufficient time is available for the completion of diagenetic processes, even if conditions are not optimal. To the contrary, if cementation occurs during shallow burial or pre-burial, the distribution of cement is likely to be spatially inhomogeneous and bound to particular periods and horizons in which the effects of interstitial water movements are intensified (Chapters 3, 4 and 6).

THE AFFILIATION BETWEEN EARLY DIAGENESIS AND DEPOSITIONAL ENVIRONMENT

The composition of clastic sediments, mineralogically and texturally, is primarily the result of tectonic setting (e.g., Dickinson, Lawton & Inman, 1986), weathering (i.e. the climate) (Suttner & Dutta, 1986; Grantham & Velbel, 1988) and mineralogical partitioning during transport and deposition (Hayes, 1979; Basu, 1985; Valloni, 1985). Subsequent diagenesis can modify the primary composition. The primary fabric (porosity and permeability), the detrital composition and the parameters related to the depositional environment (such as the rate of sedimentation and the residence time in a certain chemical environment, the overall chemistry of the water, the activity of in- and epi-fauna) control early modifying processes and subsequent diagenesis (Füchtbauer, 1983). These processes change the porosity and permeability, the composition of the sediment and its interstitial water. Early diagenesis is thus partly controlled by depositional processes and environment (e.g., Hayes, 1979).

Especially the permeability controls the rate of the early diagenetic processes. It also determines if processes are governed by supply from outside, either through sea or fresh water, or by the composition of the interstitial water (and by fractionation through dissolution-reprecipitation reactions), respectively in coarse-grained or fine-grained sediments. The latter will tend to constitute an internal chemical environment controlled by clastic composition, interstitial water and the fractionation between the two. Coarse-grained deposits, such as sandstones, have in general a relatively high permeability, and fractionation of interstitial water through mineral-water reactions is subordinate to the large flow through the pores. Especially here, the reactions during early diagenesis are strongly influenced by the depositional environment at and near the sediment surface.

In the subsequent chapters (2 and 4) it will be shown that often the

impact of the depositional environment on diagenesis is impressive. The study of the resulting diagenetic features can therefore contribute to a correct interpretation of the depositional environment.

THE TELOGENETIC REALM

After folding and faulting, denudation and partial truncation of a sedimentary sequence, can bring sediments again to the surface. Hydraulic heads of meteoric water are formed and sandstone bodies are recharged and flushed with meteoric water, causing a state of disequilibrium. Flow rates of interstitial fluids increase, since permeability and porosity increase through relaxation of the rock. After a long burial diagenesis or in case of an initially marine mineralogy, minerals will not be in equilibrium with surface conditions. Also here, diagenesis is controlled by the porosity and permeability patterns in the sandstones (Chapter 7).

DIFFERENTIALLY CEMENTED SANDSTONES

In the present study, the two problems about cementation will be attacked from an unorthodox angle of view: looking at the diagenesis of sandstones which have been differentially cemented with calcite or quartz.

Often the degree of cementation of sandstones is highly variable. Spatial inhomogeneity of the degree of cementation can be manifested by well-cemented horizons, layers, and, in the extreme case, lenses and nodular horizons occurring in less well-cemented sandstone bodies. Despite of the fact that such differential cementation in sandstones is a quite common feature, apart from a description of the phenomenon not much attention has been paid to it (e.g., Johnson & Swett, 1974; Berners, 1985; Ardanese et al., 1987; Hudson & Andrews, 1987; Pirrie, 1987; Bryant, Kantorowicz & Love, 1988; McBride, 1988). A sandstone body, displaying differences in the degree and appearance of the lithification on a medium- to small-scale, has an identical burial history. The presence of well-cemented horizons or nodules (differential cementation) depends on a suite of environmental conditions and sedimentary parameters, such as sediment composition, texture and porosity and permeability patterns. The dispersion of cement in such a sandstone, homogeneous or inhomogeneous, thus yields information about the local internal controlling factors on cementation processes, since the external conditions were similar. On a detailed scale, many parameters of the sediment, being potential controlling factors on cementation, can be qualitatively and quantitatively studied. If certain parameters do show significant differences between well-cemented and less-cemented zones, these should be considered as possible determining or constraining factors. Differences of character and composition between nodules and surrounding rock suggest a causal relationship with differential cementation. Primary differences may be obliterated by later diagenesis but also may have been accentuated. This may especially be the case, when early diagenesis has

affected and modified the permeability. Then, later diagenesis will be constrained by these superimposed permeability patterns.

Two inhomogeneously cemented sandstone formations were studied. Their diagenesis will be described and interpreted in the next chapters. They are the Lower Eocene Roda Sandstone Member (Spain) and the Lower Givetian (Upper Middle Devonian) Nèvremont Formation (Belgium). The study focused upon lithification through carbonate or quartz cementation, and compaction. The relation between clastic sedimentary facies, sources and early diagenesis, the constraints of early diagenesis on later diagenesis and causes and timing of cementation processes will be discussed.

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INTERMEZZO 1: INTRODUCTION FOR CHAPTERS 2 AND 3: EARLY QUARTZ CEMENTATION

SOURCES OF QUARTZ CEMENT

Conversion of clay minerals

An important first possible source for silica authigenesis is the conversion of clay minerals. Illite, chlorite and quartz can be the products of the conversion of smectites and interlayered smectite-illite clay minerals at intermediate burial depths (e.g., Towe, 1962; Heling, 1978; Hoffman & Hower, 1979; Eslinger & Sellars, 1981). This process yields silica in solution, amongst other elements. The amount of silica provided by the illitization process depends on the kind of reaction involved (Boles & Franks, 1979). This process is of importance in clayey sediments and possibly also in shallow-marine fine-grained carbonates. The latter sediments may act as a closed system in which authigenesis of euhedral crystals can act as an effective silica sink (Molenaar & de Jong, 1987).

It is, as yet, not clear if the silica liberated during clay mineral conversion in clayey sediments is able to escape the pertinent sedimentary system. Probably, fine-grained sequences act as a closed system with respect to silica (Land, 1984). If these sequences are open, the produced silica could provoke cementation in surrounding coarse-grained clastics. Clayey sediments intercalated within sandstone sequences probably are open with respect to silica and other elements (Füchtbauer, 1967; Moncure, Lahann & Siebert, 1984). If the silica liberated is precipitated in the near vicinity as authigenic clay and silt-sized quartz, the clayey sediment virtually acts as a closed system. In that case, this process cannot be a source of quartz cements in coarse-grained sediments.

The most common theory about the origin of silt- or clay-sized quartz (smaller than 50 μm) is that it has been derived from normal plutonic or metamorphic source rocks through chemical weathering and through a process of breaking and mechanical abrasion of larger crystals (Nahon & Trompette, 1982). If this fine-grained quartz indeed had a common origin, then they should have similar characteristics as coarse-grained quartz. However, fine-grained quartz has a heavier oxygen isotopic composition than coarse-grained quartz and heavier also than the most common plutonic and metamorphic source rocks (Blatt, 1987). This would indicate a relatively low temperature during crystallization of the fine-grained quartz, such as during diagenetic conditions at low to intermediate burial depths. The $\delta\ ^{18}O$ of coarse-grained quartz, to the contrary, has a range and mean similar to that of plutonic and metamorphic rocks. These differences of $\delta\ ^{18}O$ suggest that fine-grained quartz may be the product of erosion of authigenic quartz in fine-grained sediments. Yeh and Savin (1979) showed that significant amounts of silica indeed are precipitated

within shales during burial diagenesis. The crystal-size of the authigenic phase is likely to be determined by the texture of the sediment, i.e. small pores in clayey sediments induce fine-grained authigenic quartz. This implies that these sediments are a closed system for silica.

Pressure solution, stylolitization and dissolution of silicates

A second possible mechanism of silica release are pressure solution and stylolitization in siliciclastic sediments during meso-diagenesis (e.g., Houseknecht, 1988). The process of stylolitization itself creates permeability barriers for the materials liberated by dissolution through the accumulation of insoluble material along stylolitic seams. However, on the other hand, extensive pressure solution or stylolitization itself forms evidence for the openness of the system with respect to the dissolved silica.

During mesogenesis silica can be released through intrastratal solution of silicates or dissolution of quartz during high temperature conditions. The solubility of quartz increases with increasing temperature (e.g., Morey, Fournier & Rowe, 1962), and also with increasing pressure (Fournier & Potter, 1982; summary of Williams & Crerar, 1985). Therefore, ascending warm silica enriched formation waters become supersaturated with respect to quartz in the cooler shallow burial realm. As a consequence, quartz cement would precipitate in shallow buried sandstones. The prerequisite for this process is a mechanism to move the enriched formation waters out of the source rocks. The mentioned processes are active when mechanical compaction already has been accomplished. Therefore, only thermal convection could be such an agency.

Dissolution of biogenic opal-A

A third process which releases silica is the dissolution of biogenic opal-A after oxidation of the protecting organic coatings. These organic coatings strongly reduce the solubility of biogenic opal (Hurd, 1972). When the host-rock has a fine-grained texture and thus a low permeability, this may cause a rapid establishment of anoxic conditions below the sediment-water interface, and thus a preservation of the protecting organic coatings. If not, biogenic opal would easily and rapidly dissolve in the uppermost sediment layer and the silica would be released into the watercolumn again.

Biogenic opal constituting diatom and radiolarian frustules is most abundant in pelagic calcareous deposits. Since pelagic oozes initially have a very high porosity, mechanical compaction will release huge amounts of interstitial pore waters from the carbonate during initial stages of burial. Silica rich interstitial waters can thus theoretically be released out of pelagic calcareous host rocks through compaction, if the dissolution is an early diagenetic process. Here the question arises if these systems are open or closed with respect to dissolved silica. Mechanical compaction of pelagic deposits is restricted to the

uppermost few hundreds meters of burial. Further lithification is accomplished rapidly, depending on the original composition and grain-size of the pelagic sediment, through dissolution and reprecipitation (Garrison, 1981). Moreover, in case of dissolution of opal-A the solubility of opal-CT, chalcedonic quartz or mega-quartz will be exceeded. During later diagenesis, with increased temperatures, eventually all opal-A and opal-CT is replaced by stable quartz, a process thought to produce chert nodules in pelagic carbonate rocks. (e.g., Rad & Roesch, 1974; Wise & Weaver, 1974; Brueckner & Snyder, 1985). The frequent occurrence of silica accumulations in chert layers and nodules or in chalcedony cement in pelagic carbonates (Jørgensen, 1986) suggests that these sediments form a closed system with respect to silica. The development of chert probably acts as an effective sink for all the dissolved biogenic opal excluding dissolution of biogenic opal-A as a source for sandstone quartz cementation.

Meteoric water

An important source of silica is meteoric water under (near) surface conditions, representing the most likely source of silica:

- meteoric water is usually supersaturated with respect to quartz,
- the sand(stone) is still highly permeable,
- sufficient amounts of water can easily flush through the sand.

Often several of the required conditions for extensive cementation are thus accomplished in near surface settings. A further prerequisite for early of near surface cementation is the availability of time in order to flush sufficient amounts of meteoric water through the sandstone. Even if the permeability is not very high, or the rate of flow of interstitial water is low, cementation can occur if sufficient time is available. Thus, cementation is expected to be frequently related to continental sandstone settings and paleosol development. This latter will be discussed in chapters 2 and 3.

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CHAPTER 2

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PALAEOPEDOGENIC FEATURES AND THEIR PALAEOCLIMATOLOGICAL SIGNIFICANCE FOR THE NEVREMONT FORMATION (LOWER GIVETIAN), THE NORTHERN ARDENNES, BELGIUM.

N. MOLENAAR

ABSTRACT

The lower member of the Nèvremont Formation is characterized by the frequent occurrence of pedogenic features, which suggest intermittent exposure of the fluvial depositional environment. The evidence for pedogenesis comprises horizons of calcite glaebules and nodular calcrete, hematite segregation, resulting in pronounced colour mottling, and the formation of palaeosolic root-horizons with root tubes, cutanic features, burrows and striotubules. Based upon the presence of these features, it is suggested that the climate was semi-arid. The source area of the quartz-rich parent clastic sediment was presumably subjected to intensive chemical weathering, resulting in mature quartzose sediments, with illite and kaolinite as dominant clay minerals.

INTRODUCTION

Descriptive studies of the Devonian sediments in the northern Belgian Ardennes have resulted in a well-established stratigraphic framework (Coen-Aubert, 1974). However, little is known of the depositional environments, especially for the Middle Devonian. Sedimentation during the Early Givetian was probably strongly influenced by the presence of the London-Brabant Massif, situated north of the Dinant Basin, and perhaps by the Stavelot Massif (Tsien, 1979), situated southeast of the Vesdre Basin. The first was a pronounced high during most of post-Caledonian Paleozoic time (Coen-Aubert, 1974; Ziegler, 1979). During the earliest Givetian this high probably formed a landmass that was part of the Old Red Continent.

The Givetian in the northeastern part of the Dinant Basin and the western part of the Vesdre Basin (Fig. 1) can be subdivided into two formations (Fig. 2), the lowest being the Nèvremont Formation (Coen-Aubert, 1974). The lower part of the Nèvremont Formation consists of quartzose clastics, the upper

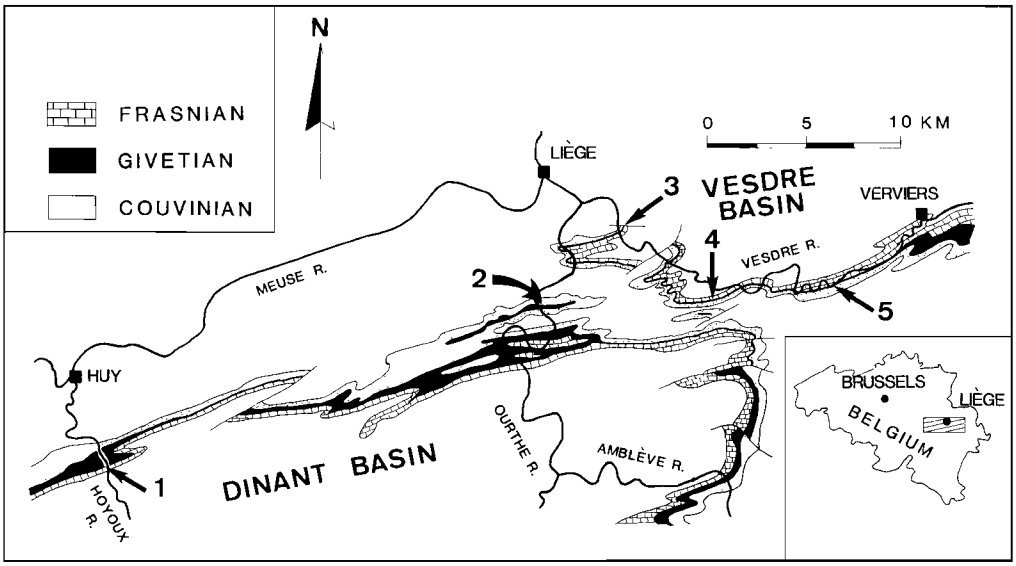

Figure 1: *Sample Locations and general distribution of the Couvinian, Givetian and Frasnian in the northern part of the Dinant Basin and the western part of the Vesdre Basin. Thickness of Member 1 or the exposed part of Member 1 is indicated in brackets.*

AGE/FORMATION				LITHOLOGY
UPPER DEVONIAN	FRASNIAN			CYCLIC BIOSTROMAL LIMESTONES (BIOSPARITES-MICRITES)
MIDDLE DEVONIAN	GIVETIAN	ROUX F.		DOLOMITES
		NEVREMONT F.	MEMBER 3	DOLOMITES, SILICICLASTIC DOLOMITES
			MEMBER 2	PELLETOIDAL-FENESTRAL LIMESTONES, SILICICLASTIC DOLOMITES
			MEMBER 1	VARIEGATED ARENITES AND CONGLOMERATES
	COUVINIAN			RED SHALES, ARENITES AND CONGLOMERATES

Figure 2: *General stratigraphy and lithology; after Kasig and Neumann-Malhkau (1969), Coen-Aubert (1974) and measured sections (Fig. 1).*

part is composed of limestones or dolomites. The lower member of the Nèvremont Formation, which will be referred to as Member 1, is composed of a variegated clastic sequence. This sequence consists of interbedded red, grey and mottled conglomerates, arenites and clastic wackes. The composition is predominantly quartzose, although carbonate grains may be an important constituent in the upper part of Member 1.

The aim of this paper is to establish a depositional environment for the lower part of the Nèvremont Formation by means of interpretation of early diagenetic features. Furthermore, evidence will be given for the presence of pedogenic features comparable to those in recent soils. Paleosols might be expected since terrestrial plants developed during the Early Devonian. However, with the exception of the description of Old Red Sandstone calcretes by Allen (1974) and Leeder (1975), few Devonian paleosols have been described so far (McPherson, 1979; Ortlam, 1980).

Samples were studied from exposures at Barse-Vierset (1), Tilff (2), Prayon (3), Trooz-Fraipont (4), and Les Mazures (5) (Fig. 1) by means of petrographical study of a 100 thin sections, X-ray diffraction study and scanning electron microscopy.

DESCRIPTION AND INTERPRETATION

Host rock

The clastics constituting Member 1 in the studied exposures are quartz-arenites or lithic arenites, conglomerates, and wackes, in descending order of frequency. X-ray diffraction studies show that illite and kaolinite are the main clay minerals, occurring in various proportions, while chlorite occurs in minor amounts. The clastics build up sheet-like or lenticular layers, consisting internally of broad, shallow scour and fill deposits with low-angle cross-lamination or horizontal lamination. Locally, they may be arranged in thinning-upward and fining-upward sequences. The siliciclastics were probably eroded from rocks cropping out in the London-Brabant Massif, as indicated by the presence of some tourmaline-quarzite clasts (Kasig, 1969).

The sediments are lithified predominantly by quartz-cementation in the quartzose terrestrial deposits, or by both quartz and calcite-cementation in the presumably lacustrine and shallow marine clastics (Molenaar, 1986). The cementation occurred partly penecontemporaneously, and partly during burial diagenesis, as witnessed by, respectively, the lack of or presence of compactional features. Locally hematite may form a cementing agent and a pigment.

The sediments of Member 1 possess a high mineralogical maturity. Framework components of the arenites are predominantly quartz. Lithic fragments, such as phyllitic-clayey rock-fragments, siltite, arenite and

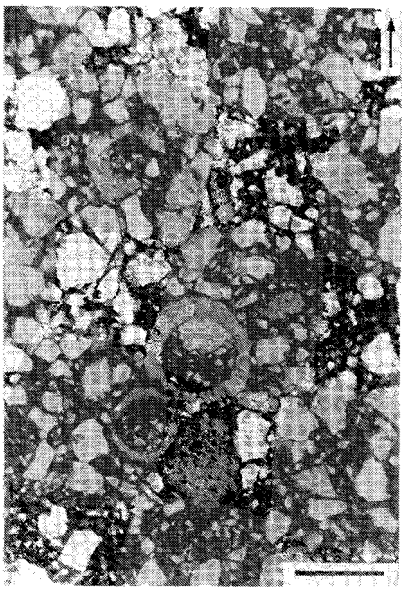

Figure 3: *Slightly reworked gyrogonites (G) with internal geopetal sediment and geopetal accumulation of matrix on top of clastic grains. The arrow indicates the stratigraphic facing. The mechanically infiltrated matrix is iron rich. The sediment is a sublithic arenite-wacke from a lacustrine intercalation with some carbonate clasts and calcite cement. Plane polarized light. Scale bar is 1 mm.*

metaquartzite rock-fragments and carbonate (bio)clasts occur in varying percentages. These carbonate (bio)clasts occur in several layers in the upper part of the sequence. The fossil content points to some lacustrine intercalations and (reworked) marine incursions towards the top of Member 1. Gyrogonites, i.e. calcified female fructifications of charophytes (Fig. 3), and peloids indicate lacustrine conditions, whilst worn bioclasts, brachiopod fragments and fossiliferous limestone fragments are relics of the marine incursions. The quartz grains may be second cycle, as indicated by the presence of some worn overgrowths. Quartz grains show an embayed surface in several wackes, probably caused by superficial dissolution. The roundness of the quartz grains varies from very angular to well rounded, or it may be totally obscured by quartz overgrowths or marginal replacement by ferric oxides. Sorting also displays a large range. Arenites are well sorted to very poorly sorted, while the conglomerates are nearly always poorly or very poorly sorted. This variable textural immaturity and the range in mineralogical maturity (mature to sub-mature) were probably caused by extensive mechanical mixing of the sediments. Vadose diagenesis was active during relatively long periods of slow sedimentation or pauses in sedimentation, as indicated by the presence of the various pedological features described in this paper. Apart from roots and plant fragments, other fossil remains are scarce.

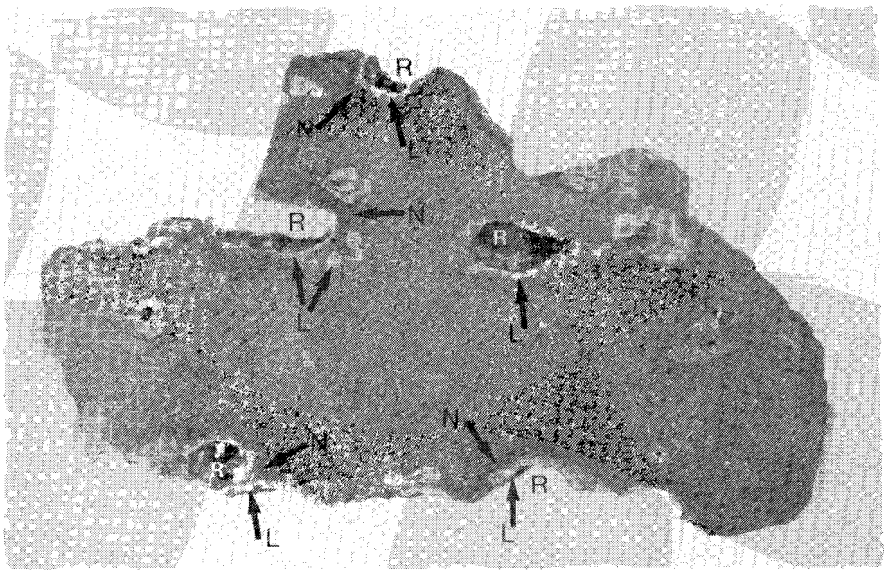

Figure 4: *Photograph of hand sample showing rootchannels (R), light brown leached zones (L), brown neoferrans (N), and greyish brown porous arenite with clay cutans dispersed throughout the sediment. Sample is 16 cm long and 9 cm high.*

Root channels

Dispersed throughout the conglomeratic and arenitic sediments are tubular structures or systems of branching tubes, which are interpreted as being caused by root-penetrations. These tubes are empty or they may still be filled with organic material, now carbonized. The former root tubes are arranged in horizons approximately parallel to the bedding, and probably mark the palaeopedomorphic surfaces. They have been traced over a distance of several hundred meters near section 4. The root-tube horizons at several stratigraphic levels in sections 1 and 4 indicate a former vegetation-cover.

Root tubes, with a maximum diameter of 2 cm, formed a path along which other processes occurred preferentially. One of these processes was the segregation of iron compounds. This resulted in bleached zones along the channels and dark red iron enrichment zones or neoferrans, which show distinct inner margins towards the channel and vague outer margins. These bleached zones and neoferrans are clearly visible in Fig. 4.

Burrows and striotubules

In several samples the sediment is disturbed by striotubules (Fig. 5).

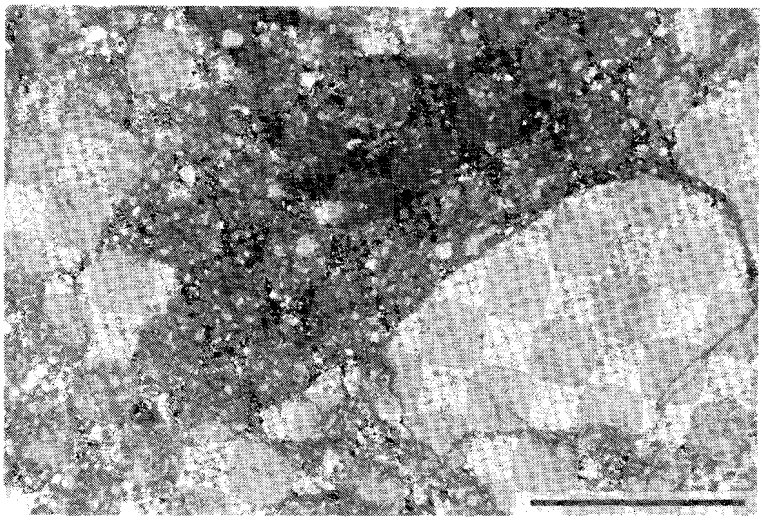

Figure 5: *Photomicrograph from thin section showing a striotubules and some calcrete glaebules. Glaebules seem to be displaced somewhat by the burrowing agent. Crossed nicols. Scale bar is 1 mm.*

These are striated (animal) burrows. Similar features have been described by Buurman (1980). Visibility of these structures is sometimes enhanced by iron and manganese oxides separations. In several samples burrowing caused clearly visible mixing of primary clayey and sandy laminae. These burrows may be partly filled with gypsum or barite.

Clay illuviation

Illuviation cutans, composed of clay-sized material, are common in many of the sandstones as well as the conglomerates. However, in the conglomerates and the wackes this feature seems to be restricted to former permeable channels, because many conglomerates have a low porosity due to the presence of a primary, i.e. detrital, clay matrix. Apart from some detrital clay in the arenites, occurring as matrix and/or clasts, clay may be present around grains and bordering vugs. Clay flakes, predominantly illite and kaolinite, are aligned with their (001) planes parallel to grain-boundaries and vug-boundaries (Figs. 6B, 6C), forming a birefringent fabric, i.e. a clay-cutan (Fig. 6A). Permeability may be greatly reduced, creating an impermeable layer or horizon.

In vugs and larger pores these cutans, referred to as void-argillans (Brewer, 1964), are often mammillated, as variations in thickness of the cutan result in curved cutanic surfaces. Owing to compaction in the wackes, argillans (presumably former void argillans) were squeezed into irregular masses still

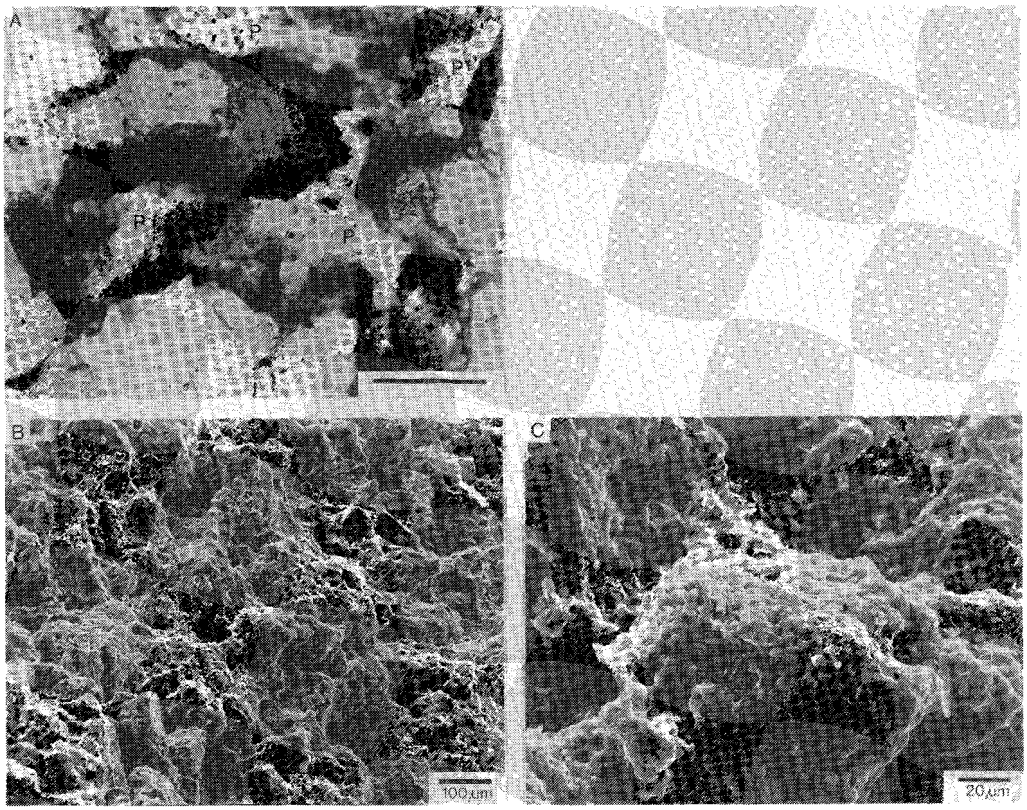

Figure 6: *Example of arenite with mechanically infiltrated clay forming clay cutans.* **6A**: *oriented birefringent clay around very angular quartz clasts, one with worn overgrowth, and mammilated argillans inside and bordering larger vughs with reduced primary porosity (P). Partly crossed nicols. Scale bar is 0.1 mm.* **6B**: *Scanning electron microphotograph of the same sample showing the clay cutans. Secondary electron image.* **6C**: *detail of 6 B: oriented clay-platelets parallel to the quartz grain surface. Secondary electron image.*

possessing a birefringent fabric. In other cases the irregular clayey masses are compacted clay-filled burrows or clay lenses between sand-filled burrows.

Clay-cutans are the result of mechanical infiltration in a formerly porous sediment (Teruggi & Andreis, 1971; Brewer, 1972; Walker, 1978). Above or near the former watertable or above impermeable layers the clay-sized material was flushed in and remained in the pores when downward flux with clay particles in suspension stagnated and the water evaporated.

Clay illuviation is a process restricted to the vadose zone or the zone of

fluctuating groundwater-table (Teruggi & Andreis, 1971; Walker et al., 1978). Clay-cutans are very frequently observed in paleosols (Terugi and Andreis, 1971). However, soil formation is not a prerequisite, since they may also form in (semi) arid regions without other pedogenic processes (Walker et al., 1978). Their relationship with paleosols is sometimes clearly demonstrated by former root tubes with clay-cutans (Fig. 7) or by the presence of other pedogenic features. The thickness of the cutans is probably mainly dependent on the diameter of the connections between pores, which is a function of sorting and packing of the sediment. Since the distribution of sorting and packing is inhomogeneous, thicknesses of cutans display a similarly irregular distribution. The settling of clay particles is likely to have obstructed small pore connections. This contributed to arrest the downward flux. In this case, porosity would be partly preserved. The thickness of the cutans is probably also affected by the duration of the interruption of sedimentation. A long interruption, and thus a long residence in the vadose or uppermost phreatic zone, would allow more clay to be moved downward. In general, this occurs in conjunction with the formation of paleosols, since paleosol development typically represents a major break in the sedimentation. Whenever clay-cutans were thick enough, and completely enclosed the framework components, they prevented later cementation (Heald & Larese, 1974). This resulted in a friable and porous sediment.

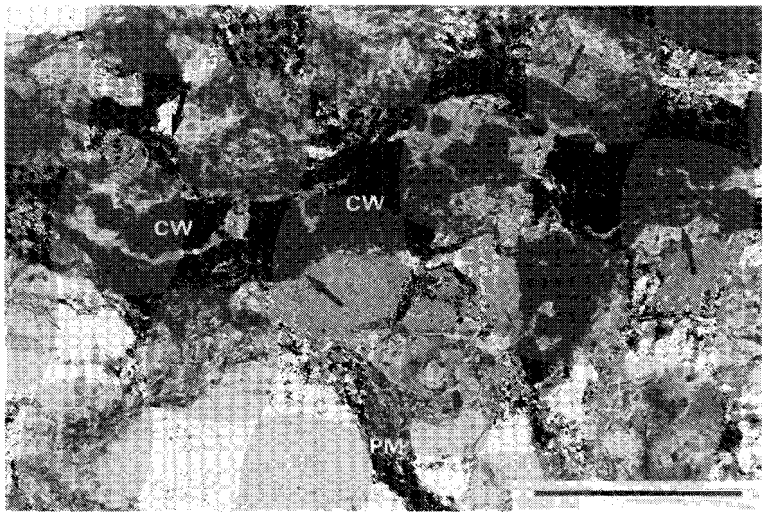

Figure 7: *Photomicrograph of root tube with carbonized wood fragments (CW) and clay cutans (indicated with arrows) around the former rootlet in an arenite with some primary clay matrix (PM). Plane polarized light. Scale bar is 1 mm.*

Hematite

Iron (oxi)hydrate compounds, now converted to hematite as identified by X-ray diffractometry, were not present in the sediment at the time of deposition, apart from some hematitic clasts in conglomerates and as clay-sized matrix in some wackes at the top of fining-upward sequences. Iron compounds are manganese-rich as is shown by energy dispersive X-ray analyses (EDAX) connected to an scanning electron microscopy (SEM).

The iron and manganese (oxi)hydrates were also flushed in mechanically. Mechanical infiltration usually took place concurrently with clay infiltration, which occurred in at least two phases: one phase penecontemporaneously and a second phase after partial quartz-cementation. The infiltrated, i.e. illuviated, iron and manganese compounds occur in cutans around framework grains, dispersed throughout the sediment or along permeable channels. They form ferrans (as a separate phase) or ferri-argillans (together with clay minerals) (Brewer, 1964). Locally, the iron and manganese compounds may thus form the cementing material, partly or completely filling the pores. The occurrence of geopetal structures indicates the mechanical mode of infiltration (Fig. 3). Frequently, both mechanical infiltration and chemical infiltration and/or redistribution (gleying) are controlled by the presence of permeable channels such as root tubes or burrows, causing a mottled distribution of clay and hematite in the sediment.

However, iron and manganese infiltration cannot be attributed to pedogenic processes with certainty, since infiltration could have occurred above the watertable regardless of the presence of a soil. The only prerequisite for this process is a lowered groundwater level.

Apart from detrital supply, intrastratal solution of ferro-magnesian minerals in a chemically immature sediment is capable of introducing iron-manganese compounds into the sediment, and of causing red colouration (Walker, 1967; Morad, 1983). However, because of the high mineralogical maturity of the sediments of Member 1, and the almost total lack of ferro-magnesian mineral grains and authigenesis of clay-minerals, which would be a result of intrastratal solution, this can be ignored as a source for iron-maganese compounds. Infiltration probably accounts for (nearly) all the iron and manganese compounds.

Mottling and ferric glaebules

Colour mottling is a common feature in many of the arenites and wackes. Mottles occur as light grey to greenish mottles, frequently vermicular, within a reddish matrix. The mottles may have either diffuse or distinct boundaries. In several samples they are clearly associated with former root tubes, i.e. a bleached zone around the tube.

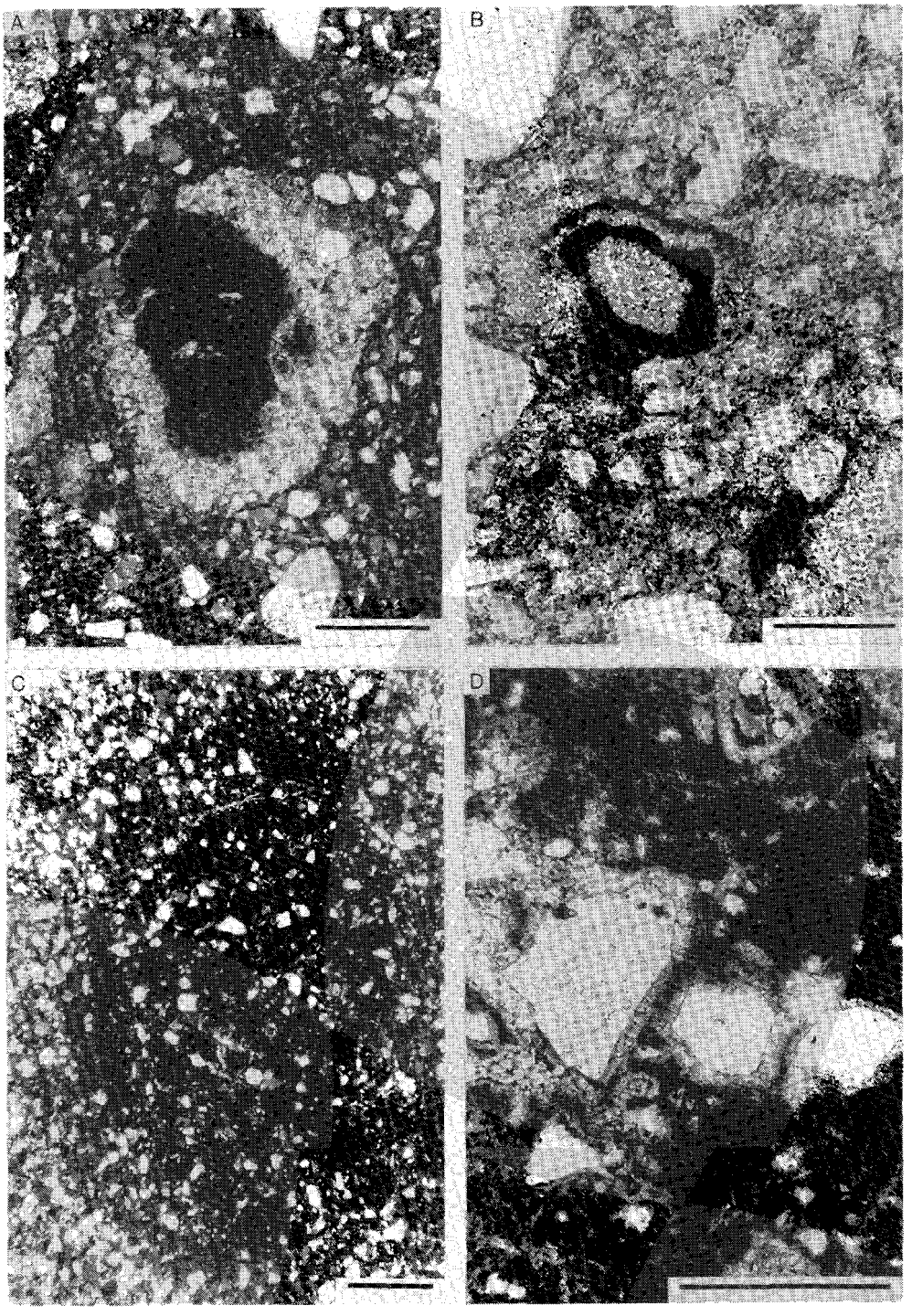
A
B
C
D

Figure 8: *Photomicrographs showing examples of compound pedogenic glaebules.*
8A: *Photomicrograph of a ferric-calcite compound glaebule with a ferric nucleus in a wacke. Scale bar is 0.2 mm.* **8B**: *Small concentric laminated compound ferric-calcite glaebule. Plane polarized light. Scale bar is 0.2 mm.*
8C: *Large concentric laminated compound ferric-calicite glaebule with glaebular halo and high content of clastic quartz grains. Partly crossed nicols. Scale bar is 1 mm.* **8D**: *Detail of Figure 8 C. Calcite coated quartz grains, i.e. calcitans, inside the glaebule. Plane polarized light. Scale bar is 0.5 mm.*

After infiltration the iron and manganese oxi-hydrates were subjected to two modifications: redistribution (gleying), and recrystallization, causing red colouring. Redistribution of the iron and manganese compounds was a fairly common process in the wackes as well as in the arenites. This resulted in a pronounced colour mottling, i.e. light grey to greenish greyish spots caused by removal of these compounds. Especially along preferred water channels, such as burrows and former root tubes redistribution and consequently mottling was very frequent. Figure 4 shows an example of the leaching and the resulting bleached zones around former root tubes, with dark colored neoferrans-mangans.

Segregation-processes, i.e. the redistribution of the iron-manganese compounds, were caused by pseudogleying (Buurman, 1980). Pseudogleying occurs above or near a low groundwater level. Periodic wetting of the soil occurred predominantly downward along permeable channels, such as root tubes and burrows. The greater part of the soil above this low groundwater level was thus oxidized, while wetted channels periodically possessed a reducing micro-environment (Buurman, 1980). In these channels, iron and manganese compounds became reduced and thus soluble. Leaching and eventual reprecipitation in the oxidized parts of the soil was the consequence (Fig. 4). The pseudogleying resulted in a red matrix with leached greyish spots.

In some samples segregation processes caused concentration of the iron (and manganese) oxides in small massive ferric nodules (Fig. 10), often combined with calcite, forming compound calcite-ferric glaebules (Fig. 8A, 8B, 8C and Fig. 10). The ferric nodules do not possess an internal fabric and mostly have a similar or slightly lower content of clastic grains as compared to the matrix. The size of the ferric glaebules in the wackes (up to 1 mm.) shows that they were not in hydrodynamic equilibrium with the coarse siliciclastics. Frequently they grade outwards into the sediment, possessing a diffuse boundary or a glaebular halo. In contrast, the compound glaebules are often concentrically layered (Fig. 8C) with one or more thin hematitic laminae (Fig. 8B), or a hematitic nucleus (Fig. 8A).

The diffuse glaebular boundaries and the association with mottled host rocks suggest that the redistribution of iron-manganese, which sometimes culminated in the formation of glaebules, can be interpreted as mainly due to pedogenic accretionary processes (Brewer & Sleeman, 1974).

Colour

Present rock colours vary from greyish-red and pale orange-red, or light to very light grey. The red colouring is caused by the amount of iron-oxides and their distribution. In the clayey-silty matrix of the wackes and in some conglomerates primary pigment, i.e. detrital clay sized iron-oxides, might have been present. In the arenites, most of the iron compounds were infiltrated as primary matrix content is very low. Subsequently the iron was redistributed by pseudogleying.

After (re)precipitation and subsequent oxidation, the iron oxides were converted into hematite, which constitutes the red pigment; the so-called aging (Turner, 1980). This conversion to hematite could be partly of pedogenic nature in semi-arid and arid climates (Walker, 1967; van Houten, 1973; Bown & Kraus, 1981). However, diagenetic conversion of part of the iron compounds and/or hematite into (re)crystallized cement is indicated by replacement of quartz clasts, authigenic quartz overgrowths, and quartz cement by hematite crystals. The present colour distribution is thus the result of penecontemporaneous processes, partly pedogenic, as well as of burial diagenesis.

Calcite and compound glaebules

In the upper part of the fining-upward sequences, glaebules (cf. Brewer, 1964) are a fairly common feature. The host-rock is usually a greyish-red coloured wacke, and occasionally an arenite. In a few cases reworked nodules and other pedorelicts such as papules (Brewer & Sleeman, 1964; Brewer, 1972) were observed.

Concurrent with, or shortly after the infiltration of iron compounds, calcite supply and precipitation took place. This caused the development of whitish calcite glaebules. The glaebules range in diameter from 0.1 to 1.5 mm and are massive micritic or microsparitic nodules, or they may alternatively be concentrically laminated. In the latter case they are called concretions (Brewer, 1964). Sometimes the glaebules may be compound, i.e. they may possess some hematitic laminae or a hematite nucleus (Fig. 8). The hematite was probably precipitated periodically during reducing conditions in a still-porous calcite nodule (Chakravarty et al., 1982).

The concentric habit is caused by an alternation of calcitic and hematitic laminae in the compound glaebules or by a slight variation in the size of calcite crystal: the glaebule nuclei are often sparitic while the outer laminae or layer are micritic to microsparitic. In the latter case, the laminations are diffuse and the concentric habit is faint. Most calcite glaebules have a distinct boundary, whilst the larger compound glaebules tend to have diffuse boundaries and glaebular halos (Fig. 10).

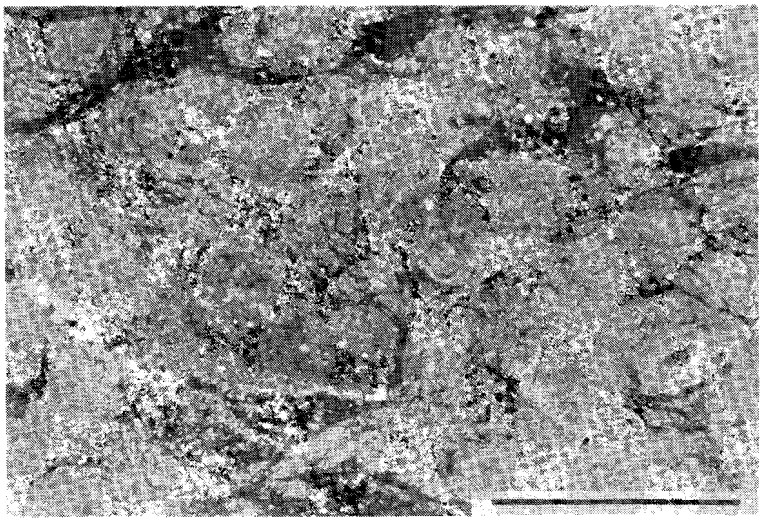

Figure 9: *Calcrete nodule with circular cracks and craze planes, composed of coalescent calcite glaebules. Crossed nicols. Scale bar is 1 mm.*

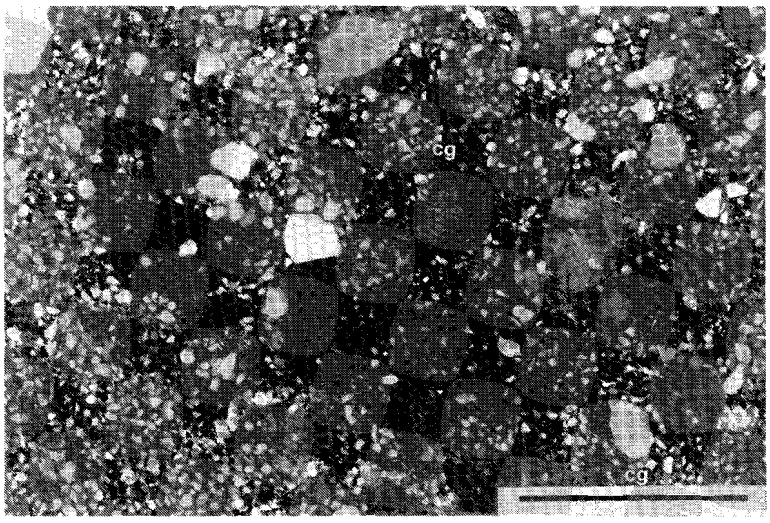

Figure 10: *Ferric glaebules with undifferentiated fabric and diffuse boundaries (FG) and some low magnesium calcite glaebules (CG) and compound ferric-calcite glaebules (FCG) in a poorly sorted wacke. Partly crossed nicols. Scale bar is 1 mm.*

In the fining-upward sequence (section 2 and 4) the number and size of the glaebules increase towards the top. In the uppermost level, the glaebules are clustered together forming calcrete nodules up to 1.5 cm in size (Fig. 9) (Nagtegaal, 1967; Reeves, 1970; Allen, 1974; Steel, 1974). The constituent glaebules are separated from each other by thin films of clayey material where stylolitization may have occurred preferentially during burial diagenesis. Owing to shallow burial compaction or to the stylolitization, several nodules tend to have their long axes parallel to the bedding.

Nodule growth was displacive as indicated by the lower percentage, or even the total absence, of clastic grains inside the nodules. If (quartz) grains are present, an occurrence which is generally restricted to compound glaebules, they may be enveloped by a single calcite crust (Fig. 8D), a feature characteristic of calcrete (Nagtegaal, 1967). This crust, called calcitan (Jongerius & Rutherford, 1979), is composed of wedge-shaped microsparite-sized calcite crystals, oriented with their long axes perpendicular to the grain surface.

The larger glaebules may be dissected by curved or irregular cracks, now filled by microsparite-sized calcite, sparite-sized calcite, hematite, and occasionally by gypsum-anhydrite. These cracks were caused by desiccation, since evidence of dissolution is absent. Along the margins of the cracks (if calcite filled) the glaebule shows crystal enlargement into microsparite or sparite. Glaebules and calcrete nodules do not occur together with root tubes.

The fact that calcite glaebules grade into nodular calcrete and display a broad range in size; the displacement of the host rock by the calcite glaebules; the disruption of calcite glaebules by striotubules; the presence of desiccation cracks; and the glaebular halos around several larger compound glaebules all suggest that the glaebules are orthic pedogenic features, i.e. that they are formed in situ during a pre-burial stage.

GENERAL INTERPRETATION AND DISCUSSION

According to the internal organization into sheet-like or lenticular layers with shallow internal scour-and-fill structures and horizontal or subhorizontal lamination and arrangement of layers in thinning-upward and fining-upward sequences, Member 1 is thought to consist of (distal) sheetflood-deposits, stream channel deposits and crevasse splay-deposits. The arenites in which mechanical infiltration occurred were probably deposited in the interchannel areas or in the abandoned part of a coastal alluvial plain. The fluvial and terrestrial nature of the deposits is confirmed by the root-horizons, glaebule-horizons, and by the vadose illuviation. That the coastline was in the vicinity appears from some marine intercalations, with a high content of clastic carbonate towards the top of Member 1. These carbonate grains probably originated from marine lagoonal influxes. Thus it is likely that the pertinent area belonged to the southeastern edge of the Givetian Old Red Continent.

Usually, features, such as the root-horizons and the glaebule-horizons as well as the colouration, are arranged parallel to the bedding. Especially in Location 4, several horizons could be traced over a distance of several hundreds of meters. This suggests that the bedding was likewise parallel to the palaeomorphic surface and the associated palaeo-groundwater level. The various processes apparently occurred during the absence of major tectonic movements and erosion (Dorn, 1960; Bless et al., 1980).

Most of the pedogenic features are dispersed throughout the sections and, perhaps with the exception of the fining-upward sequences (section 2 and 4), they never compose a complete paleosol profile. This may indicate a slow subsidence of a fairly stable continental margin with continuous local reworking of the sediments and soils.

A number of the processes are thus penecontemporaneous but not necessarily pedogenic: in particular the mechanical clay and iron-manganese infiltration. Others are definitely pedogenic and also occurred in the vadose to very shallow phreatic zone: part of the clay and iron-manganese infiltration; the calcite infiltration and segregation, combined with ferro-manganiferous oxides in glaebules and compound glaebules; the separation of ferro-manganiferous oxides by gleying. Conversion to hematite is in part a burial diagenetic process.

A low groundwater level is indicated by the process of pseudogleying, which points to an oxidized dry soil (Buurman, 1980), as well as by the infiltration of clay minerals and iron-manganese compounds with downward flow of water (Walker et al., 1978). Furthermore, a low groundwater level is a prerequisite for the formation of nodular calcrete and calcite glaebules, since these are only stable in a largely dry soil. The presence of the calcrete nodule horizons and/or calcite glaebules also indicates a low and highly periodical (seasonal) precipitation with net evaporation and a fairly high temperature (Nagtegaal, 1967). The ferric oxide lamination in the compound glaebules were caused by mobilization of iron (and manganese) compounds during wet and thus reducing periods. Subsequent precipitation occurred after preferential evaporation of still porous calcite nodules. They also point to alternating dry and wet periods (Sehgal & Stoops, 1972; Chakravarty et al., 1982). Apart from the pseudogley, the cracks in the calcrete nodules caused by in situ brecciation also seem to point to an alternate wetting and drying of the sediment (paleosol) (Freytet, 1973). A semi-arid climate is also indicated by the precipitation of calcium sulphates in former burrows and by the occurrence of ferric glaebules (e.g., Gallahar et al., 1974).

However, the calcrete does not progress beyond the first stage of calcrete formation (stage 1 of Leeder, 1975), i.e. small nodules dispersed throughout the host sediment (Wieder & Yaalon, 1982). Furthermore, it does not occur concurrently with illuviated materials and root tubes. Accumulation of pedogenic calcrete is controlled by such factors as time, topography, climate and chemical factors, i.e. the supply of calcium carbonate in case of siliciclastic and non- calcareous sediments. Since the sedimentation rate was very low in

this area, enough time was available for the potential formation of calcrete. During the Givetian, a period of approximately 5 million years (Odin, 1982), 10 to 70 m of sediment were deposited in the studied area. When the topographic gradient is too high and/or rainfall is too high, the calcium carbonate constituents are flushed out of the sediment. However, the sedimentary structures suggest shallow, relatively low energy fluvial channels on a flat coastal alluvial plain. A low relief is also indicated by some marine incursions in Member 1. Thus, a more conclusive explanation of stage 1 of calcrete formation is that the precipitation was somewhat higher than ideal circumstances, as is also suggested by the various levels with traces of vegetation and by the mineralogical composition of the clastics.

The supply of iron and manganese (oxi)hydrates (in solution or bound to clay minerals) and the high mineralogical maturity (Suttner et al., 1981) could be explained by intensive chemical leaching and weathering in the source area. This resulted in the quartzose composition of the clastics.

CONCLUSIONS

Member 1, constituting the lower part of the Nèvremont Formation, is characterized by the presence of pedogenic features. These are pseudogley, glaebules, nodular calcrete and root horizons.

Early vadose diagenesis and clay and iron-manganese illuviation played an important role. This diagenesis might have been associated in part with paleosols. Diagenesis and pedogenesis are indicative of a semi-arid climate, while the composition of the sediments and the illuviated iron-manganese compounds suggest intensive weathering in the source area.

Based on the terrestrial character of Member 1, the Old Red Continent extended into the western part of the Vesdre Basin during the earliest Givetian.

The colour of the variegated sediments is of post-depositional nature, i.e. formed partly during pre-burial stage and partly during burial diagenesis.

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CHAPTER 3

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THE INTERRELATION BETWEEN CLAY INFILTRATION, QUARTZ CEMENTATION AND COMPACTION IN LOWER GIVETIAN TERRESTRIAL SANDSTONES, NORTHERN ARDENNES, BELGIUM.

N. MOLENAAR

ABSTRACT

Terrestrial siliciclastic deposits of the lower part of the Nèvremont Formation (Lower Givetian) in the Belgian Ardennes include sandstones and conglomerates, all of which have a predominantly quartzose composition. Diagenesis of these clastic sediments was strongly influenced by the terrestrial depositional environment. Postdepositional alterations range from pre-burial to a deep-burial realm. Pedogenic processes include mechanical infiltration of clay minerals often associated with iron compounds. Infiltration occurred along permeable water channels, created by both pedoturbation and bioturbation. This clay-sized material formed cutans which enveloped detrital framework grains or surrounded the permeable vugs and channels. Thick cutans prevented the nucleation of quartz cement, which in other places frequently filled nearly all available pore spaces and caused the lithification of many of the sediments during early burial diagenesis. The relation between cutanic features and early burial quartz cement suggests that the necessary silica was most probably derived from chemical weathering in the source area and at the depositional surface. Only minor amounts of quartz cement were formed during intermediate to deep-burial stages. The silica for this second-cementation phase was produced by intergranular pressure solution and clay mineral diagenesis. Furthermore, various stages of mechanical compaction and pressure solution were observed, depending on the amount and timing of the introduction of quartz cement. Compaction played an important role in the diagenesis whenever cementation was absent or not completed during early burial. The cutanic features and the occurrence of detrital matrix partly controlled the distribution of quartz cement and compaction.

INTRODUCTION

Megaquartz is one of the most frequently occurring cementing materials in sandstones. Despite of many research, the time of introduction of quartz cement and the source of the silica is still matter of discussion. Previous authors assumed that most of the silica necessary for quartz cement in sandstones was provided by pressure solution of detrital quartz grains. However, as was stated by Sibley and Blatt (1976) and Pittman (1979), pressure solution plays a far less important role than has been previously assumed. Furthermore, the presence of megaquartz as cement suggests a low silica concentration. Therefore, large quantities of solution are needed to provide the silica, a fact which is difficult to account for during burial conditions and associated low permeabilities (Blatt, 1979; Land, 1984).

The purpose of this study is to determine the factors controlling the irregular distribution of matrix, cement, and compaction features in Givetian sandstones; to show the interrelations of the various diagenetic processes which caused these phenomena; and to discuss possible silica sources.

Detailed sampling was carried out in five sections through the lower siliciclastic member of the Nèvremont Formation, referred to as Member 1, the locations of which are shown in Figure 1. Diagenetic features were studied mainly by means of thin section and X-ray diffractometry.

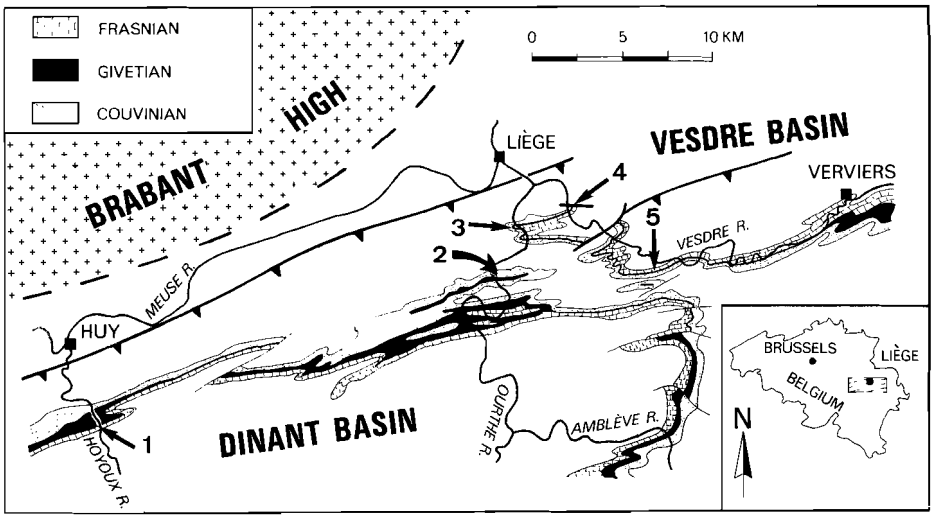

Figure 1: *Location of sections and general geographical distribution of the Couvinian, Givetian and Frasnian in the northern part of the Dinant Basin and the western part of the Vesdre Basin. Numbers refer to the section locations: 1- Barse-Vierset; 2- Tilff; 3- Colonster; 4- Prayon; 5- Trooz-Fraipont.*

STRATIGRAPHY AND GEOLOGICAL SETTING

The Lower Givetian Nèvremont Formation (Coen-Aubert, 1974) is part of the sedimentary sequence of the western part of the Vesdre Basin and the northeastern part of the Dinant Basin (Fig. 1). During the Early and most of the Middle Devonian, this area was part of the Old Red Continent (Tsien, 1974; Bless et al., 1980), as is indicated by nondeposition or by terrestrial clastic sedimentation. A tripartite subdivision can be made in the Lower Givetian in this area (D'Heure, 1969): a basal variegated siliciclastic member (Member 1), a transitional carbonate-siliciclastic member (Member 2), and an upper carbonate member (Fig. 2). The lagoonal and shallow-marine carbonate sedimentation (Kasig, 1980), which continued into the Upper-Frasnian (Kasig & Neumann-Mahlkau, 1969), terminated the terrestrial and clastic sedimentation. A transgression towards the north, which eventually reached onto the Brabant High during the Middle and Upper Frasnian, caused this shift in sedimentary environment.

The burial depth increased continuously until the onset of the Variscan orogeny in the Stephanian. The maximum burial depth attained by Member 1 was approximately 2.5 km for the western part of the Vesdre Basin and approximately 3 km for the area near section 1 (Fourmarier, 1954). After the Variscan folding and uplifting, disconformable deposition of Upper Cretaceous sediments and some Tertiary sediments took place, followed by Tertiary uplifting and denudation, both of which still continue. The Variscan orogeny caused a northward-thrust movement of the Dinant-Vesdre thrust sheet of undetermined amount. The exact position during deposition relative to the hinterland, the Brabant High, is thus not known.

GENERAL DESCRIPTION AND PETROGRAPHY

The base of the Givetian Nèvremont Formation consists of an alternation of red and gray, locally mottled, clast-supported granule conglomerates and medium to coarse-grained sandstones. The color mottling is caused by the irregular distribution of clay and/or iron oxides, which will be discussed below.

Deposition of the sediments of Member 1 occurred in a terrestrial environment. This is apparent from the specific assemblage of sedimentary structures, root horizons, and paleosols with various pedogenic features (Molenaar, 1984). Very shallow channeling, resulting in the lateral wedging out of layers, is frequently observed. The internal bedding structures are horizontal lamination and low-angle cross-bedding. The whole sequence, constituting Member 1, is fining upwards. The siliciclastic deposits wedge out towards the south. The clastics are (distal) sheetflood, stream channel, and/or crevasse-splay deposits. The fossil content points to the occurrence of some lacustrine intercalations and clastic-marine incursions towards the top of Member 1. The marine incursions together with the adjacent terrestrial deposits indicate that deposition occurred on an alluvial plain in the vicinity of the coast.

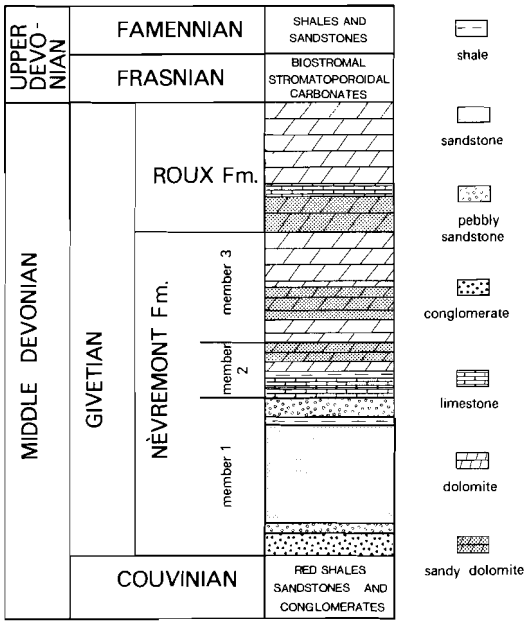

Figure 2: *Lithostratigraphic column of the Givetian at location 5 (Trooz-Fraipont), representative for the eastern part of the Vesdre Basin. The general lithology of the Middle and Upper Devonian is also indicated for the area concerned. At location 5 the Givetian attains a total thickness of 56 m.*

Striotubules, that is, striated animal burrows in soil horizons (Buurman, 1980), and former root channels indicate pedoturbation. The resulting mechanical mixing of the sediment not only disturbed or even totally obscured primary sedimentary structures, but probably also caused the textural immaturity in most of the affected layers. The latter are characterized by very poor sorting and a bimodal to polymodal grain-size distribution, and by alternating areas of tightly packed and more openly packed detrital grains. Areas with a matrix-supported texture are dispersed throughout a well sorted framework-supported arenite. Especially the wackes are devoid of primary sedimentary structures, probably because they tend to form the top of a sedimentary unit, and thus may have been subjected to extensive pedoturbation or bioturbation. The sorting in the undisturbed internal bedding structures is good.

The sandstones are mineralogically very mature, and can be classified as quartz arenites and quartz wackes, and lithic arenites and lithic wackes, depending on matrix content (Travis, 1970). The conglomerates are polymictic. Monocrystalline quartz is the main framework component (44 to 71 %); minor components are polycrystalline quartz, chert, phyllite, and sandstone fragments (Table 1). The lithic grain content varies from 4 to 19 % and averages 10 %.

Some of the quartz grain are resedimented, or even polycycled, as is indicated by worn overgrowths (Figs. 3A, 4A). Optical extinction ranges from nearly straight to strongly undulose and semicomposite. Feldspar is almost totally absent. Accessory heavy minerals are tourmaline, zircon, rutile, ilmenite, and occasionally pyroxenes. Limestone clasts mark the lacustrine and marine influxes.

SAMPLE NUMBER	DETRITAL GRAINS										
	monoquartz	polyquartz	sandstone chert	phyllite	total	detrital matrix	cutans	quartz cement	porosity	minus (cement + cutans) porosity	total
PR1	51	3	7	1	62	5	3	30	0	33	100
PR2	48	7	3	2	60	4	2	31	4	37	101
PR3	56	1	3	1	61	3	0	34	3	37	101
PR4	50	5	1	1	57	2	13	27	2	42	101
PR5	49	5	0	2	56	0	12	32	0	44	100
PR6	48	10	6	1	65	0	4	22	8	34	99
PR7	55	3	1	0	59	19	8	3	12	23	101
PR8	53	5	2	0	60	0	18	8	15	41	101
PR9	66	12	2	0	80	0	11	8	1	20	100
PR10	52	8	0	0	60	0	14	4	23	41	101
PR11	69	10	0	0	79	0	20	1	0	21	100
PR12	71	11	0	0	82	0	14	2	1	17	99
PR13	66	5	1	0	72	0	19	9	0	28	100
PR14	55	19	0	0	74	21	0	4	0	4	99
PR18	58	9	6	0	73	7	12	8	0	20	100
PR19	44	14	0	0	58	6	0	36	0	36	100
PR20	59	7	2	0	68	24	0	7	0	7	99
PR21A	52	4	0	3	59	5	0	36	0	36	100
PR21B	55	9	1	0	65	22	0	12	0	12	99

Table 1: *Results of point counting (200 to 600 points) of several thin sections of samples from location 4 (Prayon).*

MATRIX

The clay sized matrix consist of illite and kaolinite in varying ratios, and minor amounts of hematite and chlorite. Silt-sized quartz grains may also

be a matrix component. The total matrix content is highly variable (3 to 27 %, mean is 14 %), as is its distribution. The irregular distribution of matrix causes part of the color mottling. Two kinds of matrix may be distinguished.

A first kind of matrix material (up to 24 %, mean content is 6 %) has been observed in the sandstones, especially in fining-upwards sequences, and in some of the conglomerates. The lack of any preferred orientation of clay minerals, the occurrence of matrix-supported fabrics and the polymodal grain-size distribution make evident the detrital nature of this matrix. The polymodal grain-size distribution is likely to have been accentuated by mechanical mixing.

Furthermore, geopetal accumulation of matrix or the presence of oriented structures in the matrix, that is, cutanic phenomena, indicate a second kind of matrix that must have been introduced in the sediment after the deposition of the sand fraction. This kind of matrix may occur abundantly, although it may be very irregularly distributed, in the well-sorted and coarser portions of the sandstones. Due to pedoturbation and/or bioturbation and the infiltration processes, the matrix frequently has an irregular distribution. Both processes have probably caused some, if not most, of the textural immaturity.

MECHANICAL INFILTRATION

As stated above, clay occurs not only in the form of detrital matrix, but also as coatings around framework components (up to 20 %, mean content is 8 %), and is present along the margins of larger pores and vugs. The coatings are formed by clay particles oriented tangentially to the coated surfaces, causing a birefringent fabric (Figs. 3A, 3B). In the larger voids these coatings, called clay cutans or argillans (Brewer, 1964), vary (strongly) in thickness, resulting in mammillated cutans.

Locally, the cutans may enclose the grains totally; in other places they occur as interrupted coatings or merely block the pore connections. The cutans occur mainly in permeable portions of the sandstones or in permeable channels, such as burrows and former root channels, or their immediate surroundings (Fig. 6). In some well-sorted, medium- to coarse-sand-sized samples, cutans are dispersed throughout a larger volume of the sediment and appear to be unrelated to any specific, originally permeable sedimentary feature. The grain-size distribution is strongly bimodal.

The predominant clay minerals constituting the cutans are illite and kaolinite, as was demonstrated with X-ray diffractometry. Iron oxyhydrates were frequently sedimented concurrently with clay minerals, and may even form ferri-argillans (Brewer, 1964). The oxyhydrates were carried downward in suspension or bound to the clay minerals.

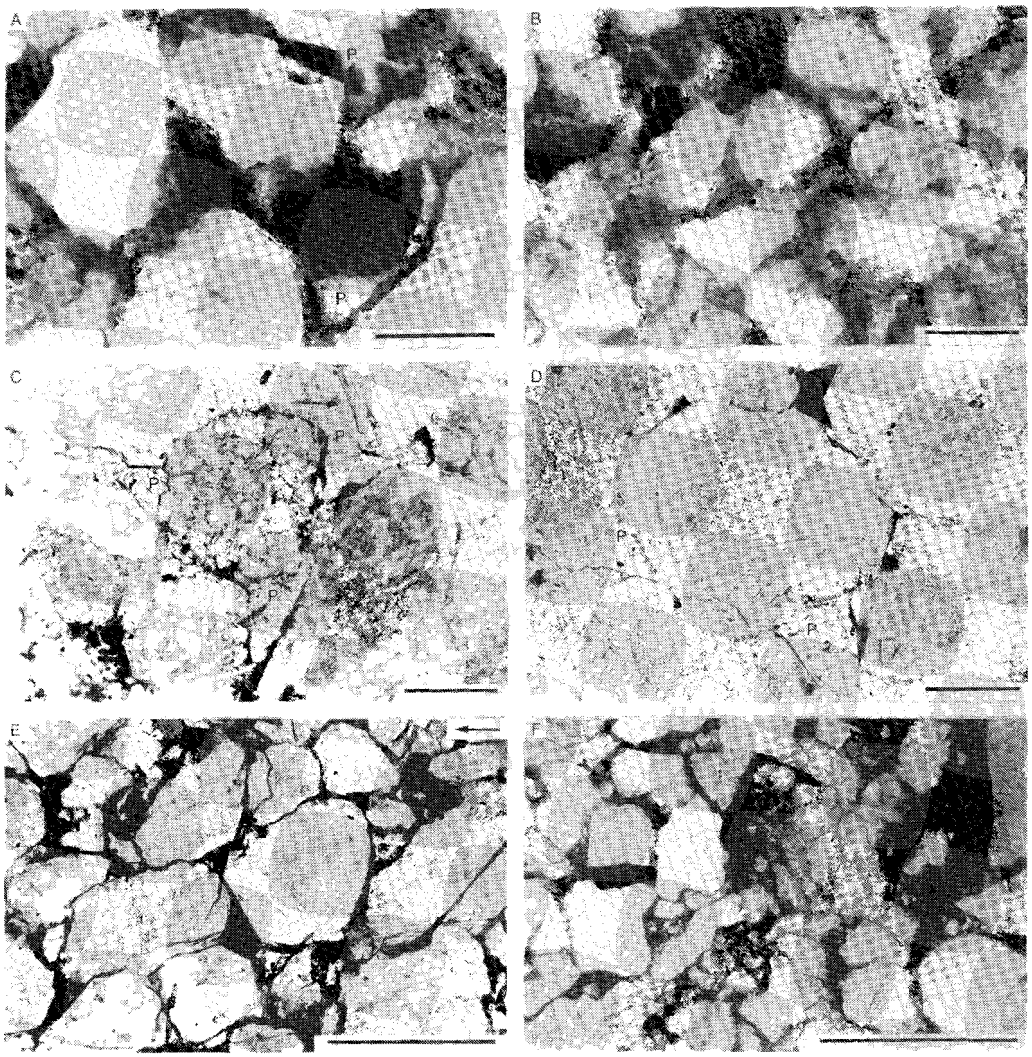

Figure 3: *Photomicrographs of thin sections showing examples of infiltration by clay and/or iron compounds.*

3A and 3B: *Detail of vadose, mechanically infiltrated clay, constituting birefringent clay cutans (argillans) around quartz grains and in voids of a quartz arenite. Some of the quartz grains show multiple abraded overgrowths. The primary interparticle porosity (P) was moderately reduced by the cutans, which prevented later cementation. Scale bars are 0.1 mm. 3A. Partly crossed nicols; 3B: plane polarized light.*

3C and 3D: *two examples of clay mechanically infiltrated after the formation of quartz overgrowths. Overgrowth precipitation occurred during very early burial, as indicated by the point contacts between detrital grains. Reduced primary*

interparticle porosity remained (P). Clay cutans are indicated by arrows. Many of the quartz grains are cloudy because of the large amounts of vacuoles. Grains are probably derived from hydrothermal quartz veins. Note the absence of overgrowths around the sandstone grain in the centre of microphotograph 3C. The scale bars are 0.1 mm. Plane polarized light.
3E*: Several stages of iron oxide precipitation alternating with quartz cementation. Scale bar is 0.5 mm. Plane polarized light.*
3F*: Geopetal accumulation of silty, iron-rich clay matrix on top of detrital grains. Some meniscus-like features are also indicative of the post-depositional vadose infiltration of this matrix. Sample is a lithic arenite (LF = lithic grain) with carbonate clasts and some calcite cement from a lacustrine intercalation. The arrow indicates the stratigraphic facing. Scale bar is 0.5 mm. Plane polarized light.*

The (clay) cutans are the result of mechanical infiltration into the sediment (Kessler, 1971; Walker et al., 1978). Downward-percolating surface water such as floodwater or rainwater is able to carry clay-sized material into the sediment. This material, in the present case consisting of clay minerals and/or iron oxyhydrates, sedimented either upon evaporation of the water, or upon diffusion into capillaries (Brewer, 1972). Moreover, several samples showed geopetal accumulations on top of detrital grains and meniscus-like accumulations of iron-rich material (Fig. 3F), attesting to the vadose nature of the infiltration. Similar features were described by Kessler (1978) for eolian sandstones.

The process of infiltration is characteristic of the vadose zone or the uppermost phreatic zone of a fluctuating water-table (Terrugi & Andreis, 1971; Brewer, 1972). Frequently, zones of high permeability, such as were the mentioned sedimentary burrows or former root channels, became preferential paths for the infiltration of suspensions and solutions either during soil formation or during the pre-burial diagenesis. Usually, the amount of cutanic material decreases away from the infiltration channels. In some samples cutans are dispersed throughout a larger volume of the sediment and appear to be unrelated to any specific originally permeable sedimentary feature. The area of infiltration is then probably dependent on factors such as sorting and grain size, which determine the permeability.

Cutans are frequently observed in recent and fossil soils (Terrugi & Andreis, 1971). In several samples, clay infiltrations was obviously related to root channels, and was thus (partly) associated with paleosol development. However, soil formation is not a prerequisite, since cutanic features as occur in semiarid regions in the absence of soils (Walker et al., 1978; Kessler, 1978).

Obviously infiltration was one of the first processes to occur in the arenites because it was restricted to the uppermost pre-burial zones. It occurred both before and after the formation of quartz overgrowths (Figs. 3C, 3D).

FERRUGINIZATION

Iron oxides, locally enriched in manganese and titanium oxides, are not exclusively related to infiltrated clay or detrital matrix, but may also occur as a separate cementing agent (Fig. 3E). More frequently, however, they are disseminated throughout the sediment, suggesting a detrital origin, or they occur in the form of diffuse nodules or neoferrans. Furthermore, iron accumulations are related to particular infiltration channels and form ferrans or ferri-argillans bordering the vug/channel boundaries (Fig. 6). Occasionally, these ferrans consist of tabular hematite crystals up to 50 μ, and occur on quartz overgrowths. Usually the ferrans are composed of very finely grained, opaque hematite.

The clustered occurrence of iron compounds, now present as hematite, causes the mottled character of many sediments of Member 1. This mottling is partly primary and is caused by the introduction of iron compounds into the sediment (detrital or infiltrated). Furthermore, the occurrence of diffuse nodules and neoferrans in several samples demonstrates that the iron compounds were partly redistributed after their sedimentation or infiltration. The redistribution, which resulted in a red sediment with greyish leached spots, was observed most frequently in the wackes, which often form the top of the fluvial fining-upwards sequences, but also in the arenites. It was probably pseudogleying that caused the color mottling noted above, as is indicated by the predominance of red colors. Soluble, reduced iron compounds were leached out from periodically wetted and reducing parts of the soil. Segregation and reprecipitation in oxidized areas of the soil occurred later. This kind of remobilization and reprecipitation of iron oxyhydrates is a purely pedogenic process (Buurman, 1980). It is characteristic of dry paleosols, which are only periodically wetted. Both the pseudogleying and the mechanical infiltration of matrix indicate a low groundwater level.

Hematite is the coloring agent. The iron compounds were converted to (coarser) crystalline hematite, a process called aging (Walker, 1967; Turner, 1980). This must have happened (partly) during burial diagenesis, as is shown by the fact that hematite crystals corrode and replace authigenic quartz cement and quartz clasts.

QUARTZ CEMENT

Mega-quartz is the main cementing material in most arenites and clast-supported conglomerates. Only minor amounts of microcrystalline quartz were observed. The amount of quartz cement found is, however, highly variable, and its distribution is irregular, even on a microscopic scale. The amount of quartz cement and the nature of contacts between framework components makes it possible to distinguish two kinds of cement.

A first kind of quartz cement usually forms optically continuous

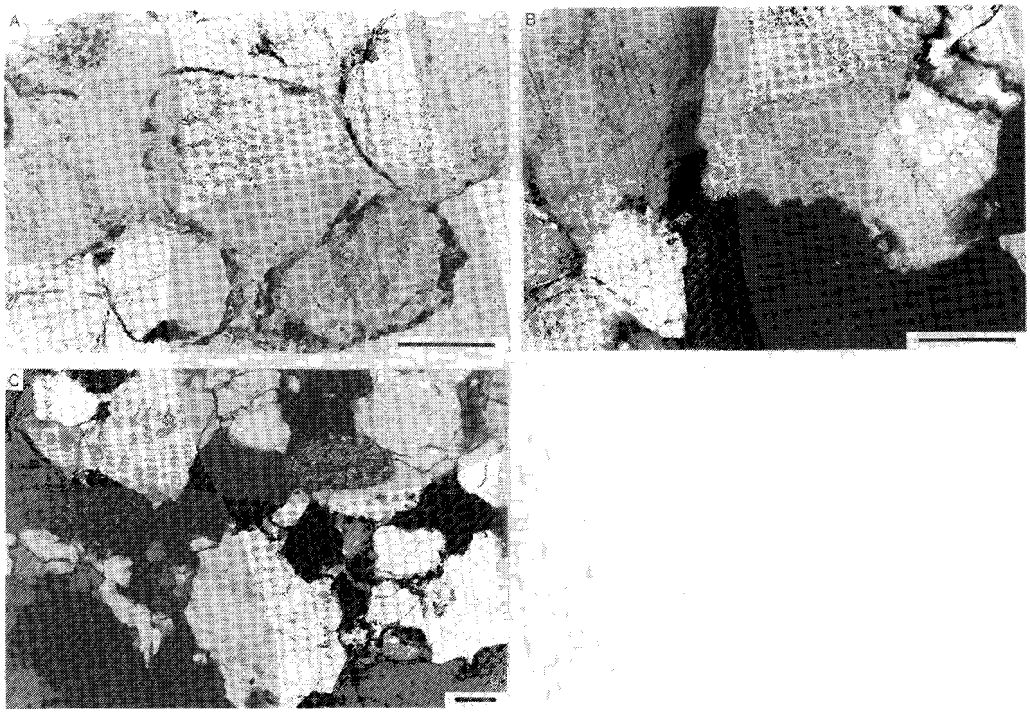

Figure 4: *Examples of quartz overgrowths. Scale bars are 0.1 mm.* **4A**: *Point contacts between detrital quartz grains, some of them with abraded detrital overgrowths, indicate that overgrowth precipitation was precompactional. The outlines of the quartz grains are clearly visible from the dust and the small amounts of infiltrated clay. Plane polarized light.* **4B**: *Some of the overgrowths, especially the one in the center of the photomicrograph, show interpenetrating mutual boundaries quite similar to sutured contacts due to pressure solution. Grains are nearly "floating" as in 4A. Crossed nicols.* **4C**: *Quartz arenite with some lithic clayey fragments, not deformed by mechanical compaction. Early burial quartz overgrowths have lithified and stabilized the arenite inhibiting compaction. Crossed nicols.*

overgrowths on detrital quartz grains, which usually display point contacts (Fig. 4A). The overgrowths are crystallographic in accordance with the crystallinity of the quartz nuclei, that is, their undulosity, as was also described by Waugh (1970). This indicates the detrital, strained nature of many of the quartz grains. The boundaries between overgrowths may be diffuse or straight and distinct, and are mostly anhedral whenever the overgrowths fill the total available pore space. Euhedral terminations are observed in residual pore spaces. Occasionally quartz overgrowths may show "sutured" contacts due to interpenetration of the boundaries (Fig. 4B). Percentages of quartz cement are high, up to 36 %, while the minus cutan + cement porosity accounts for values up to 44 %.

Furthermore, quartz occurs as a cement that is optically distinguishable from the surrounding quartz grains, which clearly display compactional features. Usually, detrital matrix or cutans are present; the latter tend to envelop the grains totally. The percentages of quartz cement and minus cutan + cement porosity are far less than in samples with the previously described overgrowths, confirming the occurrence of compaction and pressure solution.

This strongly suggests that quartz was precipitated in at least two separate phases. Apparently, a large part of the quartz cement was early diagenetic or perhaps penecontemporaneous. Penecontemporaneous precipitation is evident by the absence of compaction in the pertinent samples, as is indicated by the point contacts between detrital grains (Figs. 4A, 4C), and by the large amount of quartz cement (up to 36 % in section 4 near Prayon; see Table 1) and the large minus (cement and cutan) porosity values, that is, the porosity before infiltration and cementation. A second phase of vadose mechanical infiltration of clay and iron oxyhydrates, which was frequently observed in section 4 near Prayon, followed the formation of relatively thin quartz overgrowths. This also points to the very early precipitation of the quartz as well. The absence of any structures common to vadose cements, which may be observed in carbonate as well as silica cements (Meyer, 1984), such as microstalactitic features, suggests precipitation in the phreatic zone. This is in accordance with the predominance of megaquartz, which indicates low Si concentrations.

A second stage of quartz precipitation was observed in samples which also show features indicative of intermediate to strong compaction: ductile lithic grains are bent, and rigid grains show long contacts. In this case, quartz cement is restricted to the space left between sutured and strained detrital grains. Whenever the quartz cement was introduced during deep burial, following compaction and substantial pressure solution, grain contacts are concavo-convex and sutured.

The infiltrated clay-sized material, clay minerals and/or iron compounds, must have prevented quartz from nucleation on the detrital quartz grain, as was observed previously by Heald and Larese (1974). Nucleation was prevented only where cutans were thick enough and completely surrounded the detrital grains, which is especially the case with ferri-argillans. Since the amount of cutanic material usually decreases away from the infiltration channels, the possibility for quartz nucleation increases with increasing distance from these channels (Fig. 7). This probably indicates a low nucleation rate for overgrowths, or it may indicate that pores were blocked by cutanic clay and remained isolated during further diagenesis.

Thus, albeit that the early burial quartz cementation was usually restricted to parts of the framework where grain coatings were absent or incomplete and where there was no primary clay matrix, it is always associated with features indicative of mechanical infiltration.

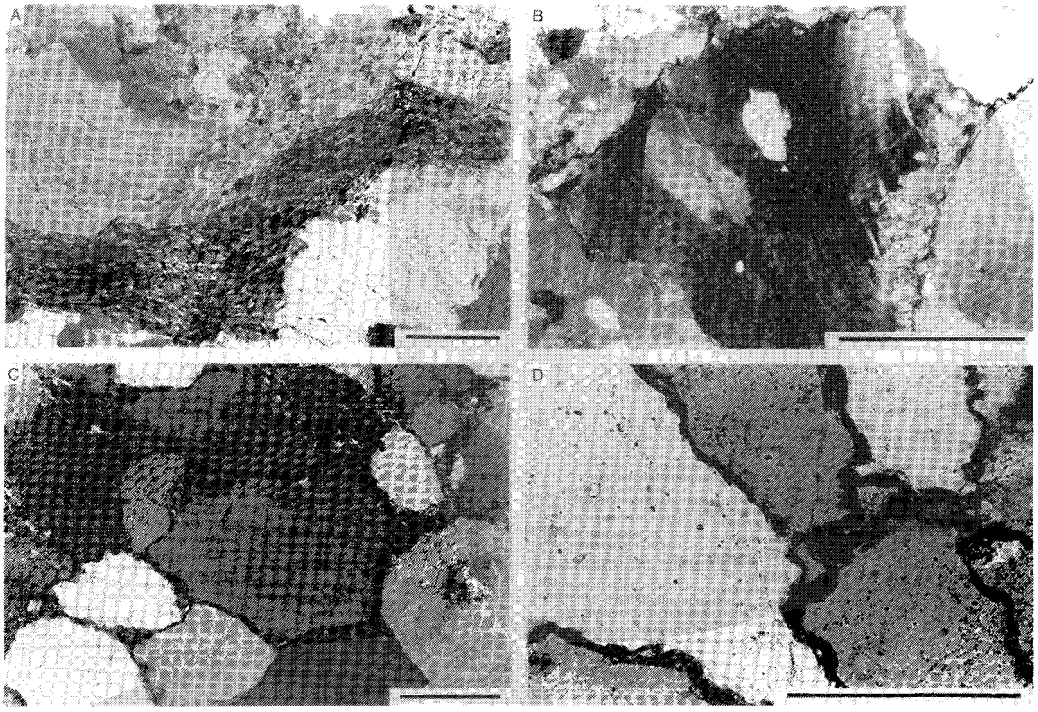

Figure 5: *Examples of compactional features.* **5A**: *A more advanced compaction squeezed the phyllitic grains between the rigid quartz grains in a sublithic arenite. Scale bar is 0.1 mm; partly crossed nicols.* **5B**: *Detrital grains are strained and have sutured contacts due to pressure solution; a lithic granule conglomerate composed predominantly of polycrystalline quartz grains and sandstone clasts. Scale bar is 1 mm. Partly crossed nicols.* **5C**: *Practically complete fitting, sutured fabric in a quartz arenite with clay cutans around the clasts. Small remaining pores are filled with quartz cement. Scale bar is 0.1 mm. Partly crossed nicols.* **5D**: *Detail of photomicrograph 5C showing quartz cement in remaining pores and the lineated arrangement of the clay particles in the cutans. Scale bar is 0.1 mm. Partly crossed nicols.*

COMPACTION FEATURES

The degree of compaction varies considerably, ranging from nearly uncompacted to very strongly compacted sediments, with a sutured grain fabric (Fig. 5). The observed compactional features are due to two processes: mechanical compaction and chemical compaction. Below a burial depth of 1,000 to 1,500 m, pressure solution is the dominant process, whereas above this depth, mechanical compaction is more important (Füchtbauer, 1967; Nagtegaal, 1978). With the exception of the wackes, the sediments constituting Member 1 are very stable and resistant to mechanical compaction. This is due to the

predominantly quartzose composition. However, mechanical less stable components are present in varying proportions. These less stable grains account for most of the lithic detritus, particularly the clayey and phyllitic clasts, the siltite-arenite clasts (which often have a clayey matrix), and the micritic carbonate grains. Compaction is manifested by plastic deformation of these ductile grains (Fig. 5A). As the burial depth increased, these grains first became bent and were subsequently squeezed. A low degree of compaction is indicated by long grain contacts and the slight bending of ductile grains around rigid (quartz) grains, or even around quartz overgrowths (Fig. 5A). After progressive compaction, these ductile grains became squeezed between quartz clasts, forming a dispersed pseudo-matrix. The amount of plastic deformation and framework collapse was dependent upon the amount of lithic fragments and on the time of introduction and quantity of cement, that is, the stabilization of the framework. Because of the large differences in these factors, plastic deformation also occurred to a variable extent.

In the case of more rigid grains, the mechanical compaction caused nearly floating and point contacts to become long contacts and caused the fracturing of rigid framework components. Eventually, this resulted in strained quartz grains with undulose extinction and even semicomposite undulose extinction. Microfractures and bohm lamellae may cross both grains and cement in small areas, which were cemented during early burial. The microfractures in quartz grains were healed by quartz cement. In the heavy minerals, however, fractures remained unhealed.

Chemical compaction resulted in the formation of dissolutional contacts: microstylolitic contacts in the clast-supported frameworks. These are concavo-convex and sutured grain contacts, both caused by pressure solution. In arenites and conglomerates, detrital clay and occasionally cutanic clay are squeezed between sutured clasts. In the absence of clay matrix or clay cutans, pressure solution is less evident, although sutured contacts may be present as well. Thus, the presence of clayey material was not a prerequisite for pressure solution, since pressure solution also occurred in clay-free sediments. However, the presence of clay may have facilitated pressure solution, as was also suggested by Sibley and Blatt (1976). In the wackes, chemical compaction resulted in marginally corroded clasts and a faint slaty or fracture cleavage.

Apart from the presence of detrital clay matrix, the course of compactional processes and of the pressure solution was controlled by the infiltration processes and by the time at which the cement was introduced. The variable extent of development of cutanic features caused the range in the degree of compaction and the character of compactional processes. Clay infiltration, quartz cementation, and compaction are thus intimately related. Wherever appreciable quartz cementation took place during early diagenesis and filled nearly all the available pore spaces, compactional features are practically absent, that is, the framework was stabilized in the early burial realm. However, if the amount of early burial quartz cementation was limited, compaction was not inhibited. If hardly any or no precompactional quartz cement was

precipitated, compaction progressed with increasing burial depth, eventually resulting in a framework with pressure-soluted components (Figs. 5B, 5C, 5D).

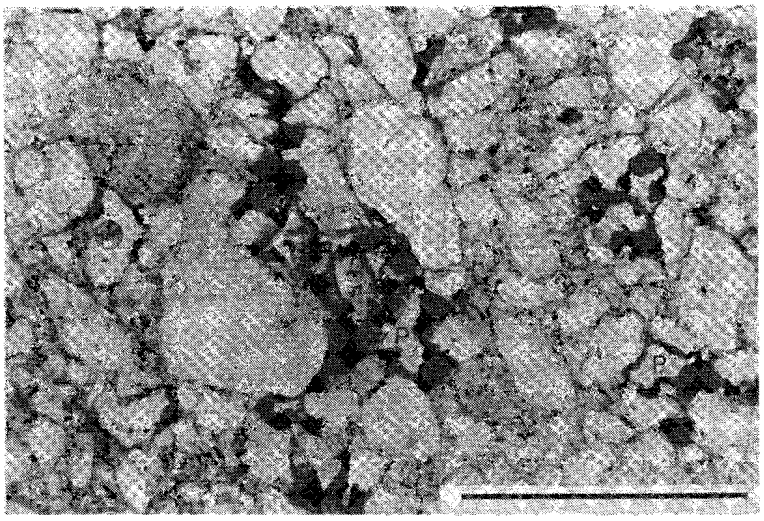

Figure 6: *The porosity in this sandstone with detrital matrix is completely associated with channels caused by pedoturbation and/or bioturbation. These channels are bordered by ferri-argillans. Scale bar is 0.5 mm. Plane polarized light.*

POROSITY

In many samples no observable porosity remained, owing to a combination of infiltration, quartz cementation and/or compaction. Whenever clay and/or hematite cutans were thick enough and entirely enclosed the grains, voids or channels, no cementation occurred or cementation was stopped. However, of these voids/channels has a large diameter, or if the cutans were dispersed throughout a large volume of sediment, the framework was not stable enough to resist compaction. The porosity was then almost totally destroyed during burial by compaction and strong pressure solution, resulting in sutured or concavo-convex grain contacts. Porosity remained if early diagenetic quartz cement stabilized the framework sufficiently to counteract the compaction but did not fill the pores completely. Thus, in sediments were cutans occur in small volumes of sediment, a reduced, secondary channel-like porosity, caused by pedoturbation and bioturbation, or a primary, reduced interparticle porosity, remained. This remaining porosity (with a maximum value of 23 %; see Table 1) is dispersed irregularly and in patches throughout the rock, owing to its relation to former root channels or other vadose infiltration channels. This kind of channel-like porosity also occurs in sandstones with detrital matrix but

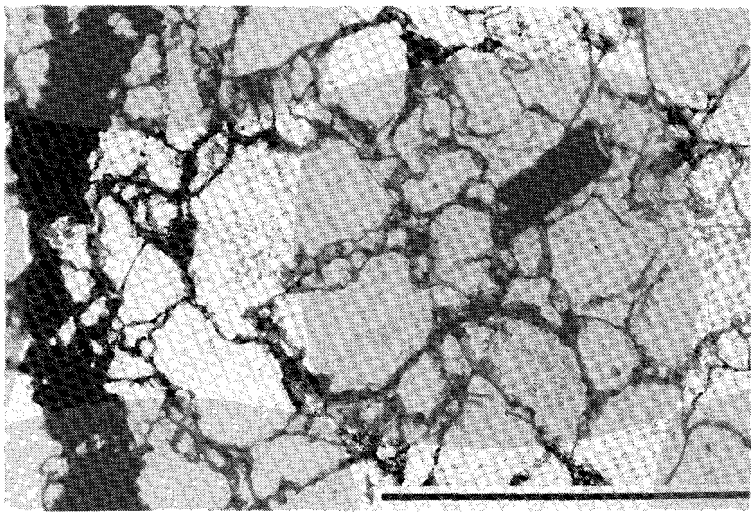

Figure 7: *Channel, approximately parallel to the bedding, filled with clay and iron oxides. Ferri-argillan content decreases with increasing distance from the main channel. Grain contacts change from sutured to long and eventually (out of the picture) to point contacts. The amount of quartz cement and overgrowths increases away from the main channel. Scale bar is 0.5 mm. Plane polarized light.*

usually was reduced by mechanical compaction (Fig. 6). Original porosity in arenites without detrital clay matrix must have attained a maximum of 44 % (minus cement + cutan porosity) in the Prayon section.

ORIGIN OF SILICA CEMENTS

Quartz cement and compactional features are scattered randomly throughout the sediment. The most likely factors controlling the distribution are the cutanic features, the occurrence of detrital matrix, and the availability if silica in solution. Since there were at least two precipitation phases, this indicates that the silica sources were most probably of a different nature.

Intrastratal solution

Silica is unlikely to have been supplied by intrastratal solution of feldspars and ferro-magnesian minerals, the latter of which may be an important source for authigenic iron minerals (Walker, 1967; Morad, 1983). Whenever unstable minerals are present (as accessories), they are generally relatively fresh and unweathered. Features indicative of intrastratal solution, such as dissolutional features of unstable minerals (Walker, 1967; Morad, 1983) and

associated clay-mineral authigenesis and framework collapse structures (Nagtegaal, 1978), are absent. Moreover, the observed hematite is of detrital origin, or it was introduced into the sediment by mechanical infiltration. It is not indicative of intrastratal solution. Thus, the high mineralogical maturity is not due to intrastratal solution, which thus can be ruled out as a source of silica.

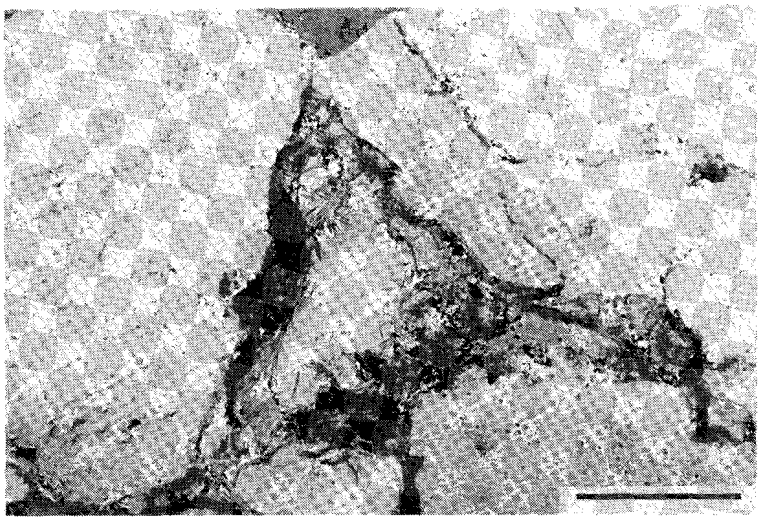

Figure 8: *Authigenic chlorite, grown on a clay cutan. Scale bar is 0.1 mm. Plane polarized light.*

Clay mineral conversion

Another possible silica source is the conversion of clay minerals during burial in Member 1 or in the underlying Couvinian shales. The illitic clay component of the detrital clay matrix, and occasionally of the cutans, underwent some recrystallization, as shown by the coarseness of illite crystals in several samples. Perhaps some of the illite was formed by the conversion of a smectite or a mixed-layer smectite-illite, which are reactive and thus relatively unstable clay minerals. They are absent according to the diffractograms. Furthermore, authigenic chlorite occurs in the few conglomerates and arenites (Fig. 8) that show substantial pressure solution. The authigenic nature of the chlorite is evident since chlorite is found only in residual pore space in pressolved samples and because the crystals are delicate (rims or randomly oriented crystal clusters), and could never have survived transport (Wilson & Pittman, 1977). Illite, chlorite and quartz are often the products of the conversion of smectites and interlayered smectite-illite clay minerals

(Hoffman & Hower, 1979). The amount of silica provided by the illitization process depends on the kind of reaction involved, that is, the amount of external aluminium supply (Boles & Franks, 1979). However, this reaction is typical of the intermediate to deep burial realm, since it requires a temperature of at least 40 to 50 °C (Hoffman & Hower, 1979; Heling, 1978; Eslinger & Sellars, 1981). This corresponds to a burial depth of approximately 1,300 to 1,600 m. Thus, clay-mineral conversions could only have been capable of yielding silica for the second phase of burial quartz cementation. The occurrence of authigenic chlorite together with authigenic quartz in the presence of detrital or cutanic clay, all of which occur in residual pores in pressure soluted frameworks, suggests that this reaction may have taken place. Furthermore, pressure solution must have provided additional silica in the same samples in the same reaches of burial depth.

Underlying clayey formations may also have supplied additional silica during burial. However, since the permeability was strongly destroyed at that time, pressure solution and clay-mineral diagenesis in the rock itself probably account for the silica for the second quartz cementation. Moreover, the "openness" of clayey formations with respect to silica is still a matter of debate (Land, 1984).

Superficial quartz cementation

It is striking that the early diagenetic quartz cement seems to be restricted to those clastics in which cutanic features are also present. This indicates that the depositional environment has a major influence on the cementation patterns. Probably this was due to the availability of silica during terrestrial weathering. Continental water contains up to 30 ppm silica in solution, far above the saturation value of quartz, which is approximately 6 ppm at surface temperatures.

The most likely source of the bulk of the quartz cement, which is mainly pre-burial, is the clastic hinterland. This was probably the Brabant High (Kasig & Neumann-Mahlkau, 1969), a part of the Old Red Continent. Because of the large amounts of clastic sediment of the Lower Devonian and the Couvinian, and the absence of major tectonic movements, the products of this source area are likely to have been mature. The mineralogical maturity of the clastics in Member 1 points to intensive chemical weathering in the source area, since transport has only minor influence on mineralogical maturity (Suttner et al., 1981). The chemical weathering in a stable source area, and even in the depositional area, as well, might have yielded silica-bearing solutions. This is supported by the presence of angular quartz grains (caused by chemical etching) in the parts of the sediment where cutans are well developed. Chemical weathering, and even intrastratal solution, combined with continuous reworking of the sediments in the depositional area, could have been an additional source. The reworking prevented the preservation of intrastratal solution relics. Reworking could have been an important process, because of the low

sedimentation rate in the studied area. During the 5 m.y. of the Givetian (Odin, 1982) only 10 to 70 m of sediment have accumulated (Coen-Aubert, 1974). The introduction of a large amount of cement is compatible with (near) surface conditions, because of the amounts of solution needed to precipitate the cement. Therefore, besides other factors, low sedimentation rates may be an important factor favoring quartz as cement. The absence of microcrystalline and fibrous quartz varieties, indicating a low silica saturation, and the presence of hydromorphic pedogenic features, suggest a semiarid climate.

Superficial quartz cementation is observed in silcretes in both arid/semiarid and humid areas (Riezebos, 1974), the latter related to deep weathering profiles (Summerfield, 1983a, b). Most silcretes are composed of crypto- and microcrystalline or fibrous quartz varieties (Smale, 1973; Summerfield, 1983a). Quartz overgrowths may occur but seem to be restricted to quartzarenites in nonweathering profiles. Experiments showed that megaquartz can precipitate at surface conditions without any intermediate opal or chalcedony phases (Mackenzie & Gees, 1971; Paragassu, 1972). The climate and the composition and texture of the host rock are controlling factors on the kind of quartz precipitated during early or preburial diagenesis. This suggest that the depositional environment might play a major role in sandstone diagenesis.

The importance of intergranular pressure solution is merely dependent on the amount of cement and the time of its introduction (for example, the time at which the framework becomes stabilized and can counteract compaction). This cement can be provided by sources both inside and outside the pertinent deposit.

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INTERMEZZO 2: INTRODUCTION FOR CHAPTERS 4, 5 AND 6: EARLY $CaCO_3$ CEMENTATION

FACTORS CONTROLLING EARLY $CACO_3$ CEMENTATION

Several factors are important for the development of early $CaCO_3$ cement in sandstones. They are:

- the presence of suitable nuclei for precipitation of cement;
- the presence of water supersaturated with respect to $CaCO_3$, i.e. the sources of the cement material, either external or internal;
- the continuous replenishment of such supersaturated water, i.e. the supply of cement materials;
- the availability of sufficient time in order to have a noticeable amount of cement.

These factors will be treated subsequently. They give insight into the factors controlling cementation.

NUCLEI

The mineralogy of $CaCO_3$ cement, aragonite, high- or low-magnesian calcite, tends to reflect the mineralogical composition of the clastic components (e.g., Macintyre et al., 1968; Winland, 1971; Alexandersson, 1972), and even the orientation of the constituting crystals (Sandberg, 1985). Precipitation of cement is enhanced by the presence of suitable nuclei, either in the form of detrital clasts or matrix. This implies that in general the possibility for cementation increases with increasing content of carbonate clasts. Therefore, conditions, during which the amount of nuclei is increased, favour the development of (early) $CaCO_3$ cement. In a shallow marine environment, a sand can be modified towards a more carbonatic composition during pauses in sedimentation, which allow cementation to start and control the local onset of cementation (Chapter 4 and 5).

SOURCES OF CEMENTING MATERIALS

External sources

Normal sea water in the (sub-)tropical climate zones is saturated with respect to $CaCO_3$ and is thus a potential source for cement. Supersaturation of sea water with respect to $CaCO_3$ can be enhanced by several mechanisms:

- an increase of temperature, which causes a decrease of the solubility of

CO_2 and thus of $CaCO_3$;
- stirring of the water through tides and waves causing a decrease of the CO_2 concentration;
- evaporation of sea water;
- mixing of sea and fresh water;
- photosynthetic activity.

Supersaturation is thus found in almost all (sub-)tropical shallow seas.

Internal sources

Carbonate clasts may become a source for cementation through dissolution and reprecipitation. The $CaCO_3$ minerals precipitated in the marine environment will remain (meta-)stable as long as the buried marine interstitial water does not undergo chemical changes. However, in case of a recharge with fresh water through a hydrostatic head, these minerals can become unstable and dissolve. Fresh water usually is not saturated with respect to $CaCO_3$. During mixing with marine water the activity of Ca^{2+} and the dissolved carbonate species increases. Furthermore, through the introduction of oxidizing water protective organic coatings around biogenic carbonate clasts are decomposed, increasing their dissolution potential (Feazel & Schatzinger, 1985). If the system is not completely open, because of a not too high flow rate, then the water will, as a consequence, become supersaturated with respect to low-magnesian calcite. This may precipitate as a replacement but also as a cement. For ongoing replacement of aragonite by calcite, the volume of minerals increases with approximately 8 %. This can happen in an early stage, but also after burial and subsequent denudation (Chapter 6).

SUPPLY OF CEMENTING MATERIALS

The mechanism to move the dissolved material for cementation through the sand is of extreme importance, and cementation will be dependent on the presence of such mechanisms and/or on the permeability (e.g., Harris, Kendall & Lerche, 1985). Possible mechanisms are waves, tides, currents or evaporation. Early cementation would then be restricted to the shallow subtidal and the intertidal zones. Especially a depositional environment subject to tides is a favourable setting for early cementation, because of the well-sorted sand deposits and their high permeability. Sea water is continuously pumped through the upper part of the sediment by tidal action. Intermittent evaporation periods can increase the degree of supersaturation. A further effect of the continuous replenishment of the water is the high degree of oxygen saturation and the degradation of organic coatings which may shield nuclei for precipitation of cement.

The effectiveness of the pumping action decreases during the precipitation of early cements and through continuing sedimentation and burial. Cementation blocks the connections between pores and thus lowers the

permeability. Also the diffusion rate is reduced due to the decrease in permeability (Klinkenberg, 1951). Sedimentation brings the pertinent sediment interval out of reach of effective movement of interstitial water. Therefore the degree of supersaturation and the rate of supply of cementing materials decrease rapidly below the sediment surface. As a result of the decreasing nucleation rate, the crystal size of early cement tends to increase from the nucleation point towards the centre of the pore: the so-called drusy cement (e.g., Sandberg, 1985).

TIME

The migration of sea water through the sandstone is controlled by the permeability: supply will thus be most efficient in the most permeable sandstones. Environments hostile to abundant live, such as the intertidal zones, will retain their originally well-sorted texture. Here, early cementation will be most rapid. Cementation will take more time in the deeper subtidal zones, where abundant life decreases permeability through burrowing and thought the introduction of fine-grained material into the sandstone. The time needed for cementation increases here, although the biological activity itself may cause introduction of sea water into the sandstone, which counteracts the decrease of permeability. Here, cement is associated with pauses in sedimentation or periods of extremely low sedimentation rate when sufficient time is available (e.g., Chapter 4; Molenaar, in prep.).

CAUSES OF DIFFERENTIAL $CACO_3$ CEMENTATION

The general lack of time does not allow early diagenetic processes to go to completion. Their initiation is, as has been shown before, dependent on a set of environmental conditions and also on a suite of sedimentary parameters. Therefore, early diagenetic features tend to be irregularly distributed throughout the affected horizons, causing variations in the degree of cementation throughout a sedimentary sequence and also in a lateral sense. An example of such small-scale irregularities are horizons containing well-cemented weathering resistant nodules.

There are several possibilities for explaining these spatial inhomogeneities:

- The occurrence of stratigraphically and spatially discrete pauses in the clastic sedimentation. These pauses may be associated with processes creating inhomogeneities in texture and composition, as is shown in chapters 4 and 5.

- Periodic changes in sedimentation rate and associated alternation of the residence time of the sediment within a certain chemical environment, e.g. a variable time of residence in the oxidizing zone, or in the

sulphate reducing zone before reaching the fermentation zone.

- Alternations in local hydrodynamic, climatic and/or environmental conditions. In consequence this causes either small-scale variations in primary composition (such as the mineralogy of clasts, the matrix content, and the porosity and permeability), or a change in the effectiveness of the pumping action of sea water through the uppermost layers of the sediment.

Large-scale cycles or changes in the sedimentary sequence may be caused by variations in the petrographic composition of framework components through a change in basin-setting or source area through periodic tectonic activity etc.

CONCLUSION

The above discussed suite of conditions enables to predict, in a crude sense, the occurrence of favourable depositional and diagenetic environments for early cementation of sandstones at or near the sediment-water surface. However, the fact that sedimentary parameters controlling the early diagenetic processes are so numerous makes a reliable prediction ambiguous.

An example of a sandstone sequence deposited in a suitable setting, i.e. a shallow-marine tide-dominated environment, will be treated in the next chapters.

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CHAPTER 4

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EARLY DIAGENETIC ALTERATION OF SHALLOW-MARINE MIXED SANDSTONES: AN EXAMPLE FROM THE LOWER EOCENE RODA SANDSTONE MEMBER, TREMP-GRAUS BASIN, SPAIN.

N. MOLENAAR

& G.P. van de BILT, E.R. van den HOEK OSTENDE & S.D. NIO

ABSTRACT

A Lower Eocene shallow-marine sandstone complex, composed of calcareous quartzose arkoses, partly was modified by diagenesis relatively short after deposition. The sandstone complex forms the lower member of the Roda Formation, which represents part of the Palaeogene fill of the Tremp-Graus Basin in the southern Pyrenees, Spain. Early diagenesis comprised the introduction of matrix into the sandstone framework through mechanical infiltration and bioturbation, and the precipitation of a, mainly aragonitic, rim-cement. This early diagenetic modification occurred in the uppermost parts of sandstone bodies, beneath abandonment surfaces. The early cement stabilized the sandstone framework, and counteracted mechanical compaction. In sandstones lacking this early cement, on the other hand, mechanical compaction severely reduced the primary porosity during a first burial phase, causing the development of a tightly compacted fabric. Mechanical compaction was highly effective because of a high content of ductile grains. Afterwards, two major erosional phases truncated the sandstone complex in the northern part of the area studied. Probably through the introduction of meteoric water, unstable carbonate phases, such as aragonite and high-magnesian calcite, were replaced by low-magnesian calcite, whereas a contemporaneous second calcite cement generation was precipitated. After the erosional phases, the sandstones were buried once again until recent uplift and denudation brought them to the surface.

INTRODUCTION

Many shallow-marine sandstones are potential reservoir rocks due to their relatively homogeneous nature with respect to porosity and permeability patterns. The Lower Eocene Roda Sandstone Formation in the south-central Pyrenean basin (Tremp-Graus Basin) (Fig. 1) consists of several vertically

stacked sandstone bodies with maximum thicknesses of about 30 metres, interbedded with silty marls. These deposits were formed in a shallow marine tidally influenced environment (Yang & Nio, 1985). These sandstone bodies, deposited on a shallow shelf area, are characterized by well-preserved cosets of large-scale to giant cross-bedding up to 10 metres high. Despite of the high energetic depositional conditions, resulting in giant low-to high-angle cross-bedded cosets, the sandstones are not homogeneous with respect to texture and composition. Instead, they display a distinct differential resistance against weathering. Resistant horizons alternate with less resistant friable ones. The resistant well-indurated horizons are partly enriched in matrix and bioclasts and display intense burrowing. Here, the sandstone can be characterized as a matrix and bioclast-rich sandy limestone. These sandy limestones are related to major truncation horizons within the sandstone bodies, which we interprete as abandonment surfaces. Contrary to this, the bulk of the sandstones are well-sorted arenites. However, even here well-cemented horizons alternate with friable horizons. This distinctly different behaviour against weathering is related to the amount of carbonate cement.

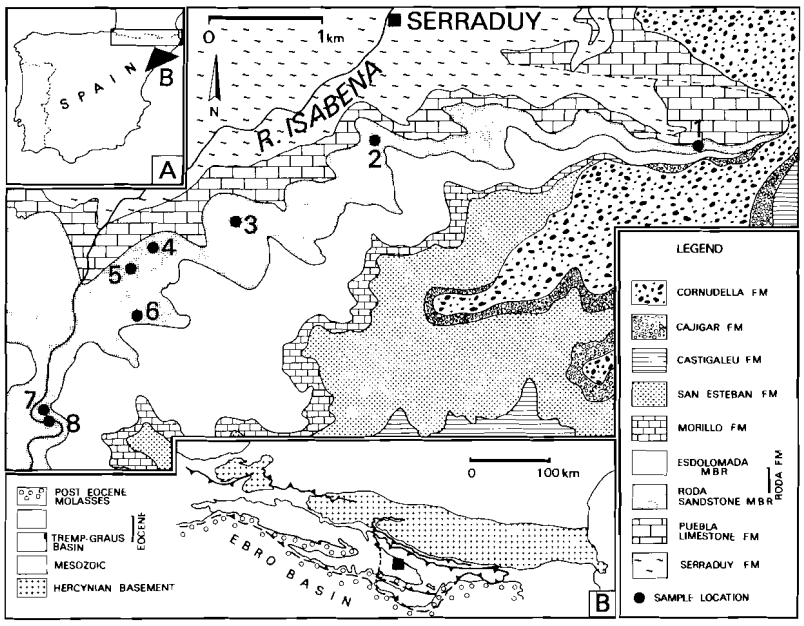


Figure 1: *Geological sketch map of the northern part of the Isábena valley, southern Pyrenees. Spain. Numbers refer to locations of outcrops that have been sampled. Two cores have been drilled near location 6. The map location in Spain and in the Pyrenees is shown on the insets A and B, respectively.*

The sandstones have been examined in order to develop a genetic model, mainly by standard thin-section petrography. This model should list the features characteristic for the various processes and explain the occurrence of the indurated and texturally and compositionally modified horizons. Moreover, the relation between the rate of sedimentation and the various processes will be described. To explain the differential cementation, several possibilities will be considered, such as changes in clastic supply, grain-size distribution, and variations in sedimentation rate.

GEOLOGICAL SETTING AND STRATIGRAPHY

The outcrops studied are located in the Tremp-Graus Basin, which forms part of the south-central segment of the southern Pyrenean foreland basin (Fig. 1). In general terms, the structure of this foreland basin resulted from a collisional event between the Iberian continental plate and the stable European mega-plate, beneath which it was underthrusted. This underthrusting gave rise to a linked thrust system dominated by southward overthrust movements (Williams, 1985; Camara & Klimowitz, 1985). This thin-skinned thrust system, with oblique and lateral ramps, brought about the fragmentation of the originally interconnected parts of the southern Pyrenean foreland basin. Since the thin-skinned tectonic activity was penecontemporaneous with sedimentation, the Paleogene fill of the Tremp-Graus Basin displays marked tectonically induced patterns (Ori & Friend, 1984; Puigdefabregas & Souquet, 1986). Also the sedimentation pattern of the Roda Formation was influenced by tectonic movements, which probably triggered the intermittent supply of terrigenous clastics.

The lithostratigraphic subdivision of the Paleogene Tremp-Graus Basin fill in the Isábena valley (Figs. 1 and 2) was first established by Mey et al. (1968) and Schaub (1973), and modified by Nijman and Nio (1975). The Roda Formation forms part of this Paleogene fill. It consists of a succession of shallow-marine mixed siliciclastic-carbonate deposits. Its formation was preceded and followed by long periods of stable basin conditions, reflected by the deposition of two marine limestone formations (the Morillo and Puebla Limestone Formations) (Fig. 2). The Roda Formation of the Isábena valley is subdivided into two sandstone members, the Roda Sandstone Member - the lower one - and the Esdolomada Member, separated by several siliciclastic limestone layers. These sandy limestones represent a major period of strongly reduced supply of siliciclastic sediments, which represents periods of stable basin conditions. The basal part of the Roda Sandstone Member is composed of silty and sandy shales, with several thin intercalations of sandy limestone. The upper part of this member, attaining a thickness of approximately 40 to 65 metres, consists of several major medium-to-coarse grained sandstone bodies, separated by sandy-to-silty marl and siltstone intervals. The sandstone bodies of the Roda Sandstone Member display a progradational pattern in predominantly southwest direction.

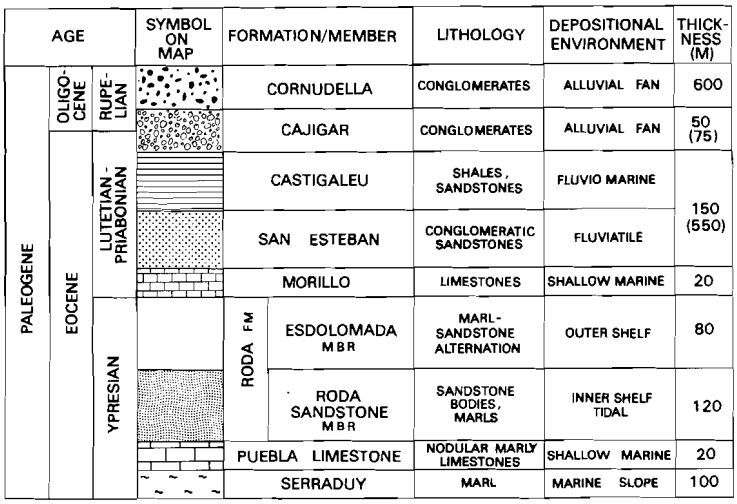


Figure 2: *Schematic lithostratigraphic column of the Tremp-Graus Basin in the Isábena Valley, also showing the interpretation of the depositional environments.*

BURIAL HISTORY

The burial history of this part of the Tremp-Graus Basin could be reconstructed, which is a prerequisite for the development of a diagenetic model. Tectonic activity along the northern margin of the Tremp-Graus Basin finally resulted in the construction of a fan-delta complex, constituting the San Esteban and Castigaleu Formations. During the late Middle Eocene, tilting and uplifting of the northern margin of the Tremp-Graus Basin resulted in widespread erosion of the San Esteban Formation and, in the northeastern part of the Isábena Valley, of the Roda Sandstone Member as well (Figs. 1 and 2). The estimated maximum burial depth of the Roda Sandstone Member before erosion was 650 metres, probably less in the northern part of the area studied. The period of tectonic activity is marked by a major unconformity. It is overlain by the Cajigar Formation, which consists mainly of distal alluvial fan deposits. A stratigraphic higher unconformity resulted from a second period of tectonic activity, that initiated the formation of large proximal alluvial fan complexes of the Cornudella Formation. The Roda Sandstone Member attained maximum burial depths during the second phase of burial of at least 450 metres in the north and 900 metres in the south of the study area, at the end of this phase of continental sedimentation.

STUDIED FACIES

The studies on diagenesis were carried out on the following facies of the Roda Sandstone Member:

1- A by-passing facies, consisting of coarse-grained sands, representing lag deposits. This facies is characterized by a succession of thin sandstone bodies displaying numerous abandonment surfaces. The major processes responsible for this depositional facies, were wave action and longshore currents.

2- An inner shelf facies. Sedimentary structures comprise well defined cosets of very large low-angle cross-bedding with set heights of 3 to 4 metres and cosets of megaripple cross-bedding with set heights of 0.2 to 0.6 metres. Deposition occurred by migrating sandwaves. Major mechanisms included tidal currents and longshore currents. Abandonment surfaces are very frequent.

3- An estuary mouth facies, which is characterized by the occurrence of very large to giant cosets of high-angle and low-angle cross-bedding with set heights up to 10 metres, reflecting transverse sand bars deposited by ebb-dominated tidal currents. The abandonment surfaces are well defined and more widely spaced than in facies 1 and 2.

4- An estuary channel facies is characterized by several fining-upward sequences, representing the lateral migration of tidal channels and shoals. The channel deposits display well defined cosets of tabular mega-cross-bedding, containing complete tidal bundle sequences (Nio et al., 1983; Yang and Nio, 1985). Burrowing features are restricted to the uppermost parts of the channel deposits. Abandonment surfaces are less well developed than in the other facies.

Low overall sedimentation rates characterize facies 1, whereas facies 4 was rapidly deposited. Sedimentation was strongly intermittent in facies 2 and 3, due to interruptions in the progradation of sandwaves and transverse bars. Reactivation surfaces probably reflect major storms, which eroded and changed the morphology of the depositional lobes. Thus, parts of the sandstone bodies have been rapidly deposited, whereas other parts were devoid of sedimentation for longer periods. Biogenic activity was important during periods of low sedimentation rate or non-deposition. The different segments of the sandstone bodies, defined by distinct stages in the depositional cycle are separated by major abandonment surfaces due to major storm truncations. These abandonment surfaces are typically underlain by burrowed bioclastic wackes and/or matrix rich arenites. Pronounced abandonment surfaces are especially developed in the uppermost parts of depositional sequences, representing degradational stages of sandwaves and bars.

Outcrops sometimes show nodules. These are usually ovoid, with long

axes of 15 to 150 cm in length. Horizons of nodules, clearly associated with abandonment surfaces, occur parallel to them, whereas the long axes of nodules are arranged parallel to the low-angle or high-angle cross-bedding. The nodules sometimes display distinct outlines but also gradually merge into the surrounding host rock.

METHODOLOGY

In the two major sandstone bodies of the Roda Sandstone Member, 125 samples have been taken from eight outcrops. Additional samples have been obtained from two short cores (Fig. 1). The texture, composition and diagenetic features of 131 samples have been qualitatively determined by means of thin-section petrography. Thin-sections were partly stained for the discrimination of ferroan carbonate, according to the method of Dickson (1966). Clastic composition and diagenetic features were quantified by thin-section point counting.

The carbonate mineralogy was determined through X-ray diffractometry (XRD) of powder preparates, whereas oriented glass-mounted preparates of the fraction smaller than 50 μm were used for clay mineral determination.

The total carbonate content was determined by atomic absorption spectrophotometric (AAS) analyses of the Ca, Mg and Sr content of the bulk carbonate.

The grain-size distributions of the siliciclastic components of several samples, separated from the sediment through HCl treatment, have been measured by means of a Malvern 3600D laser particle sizer.

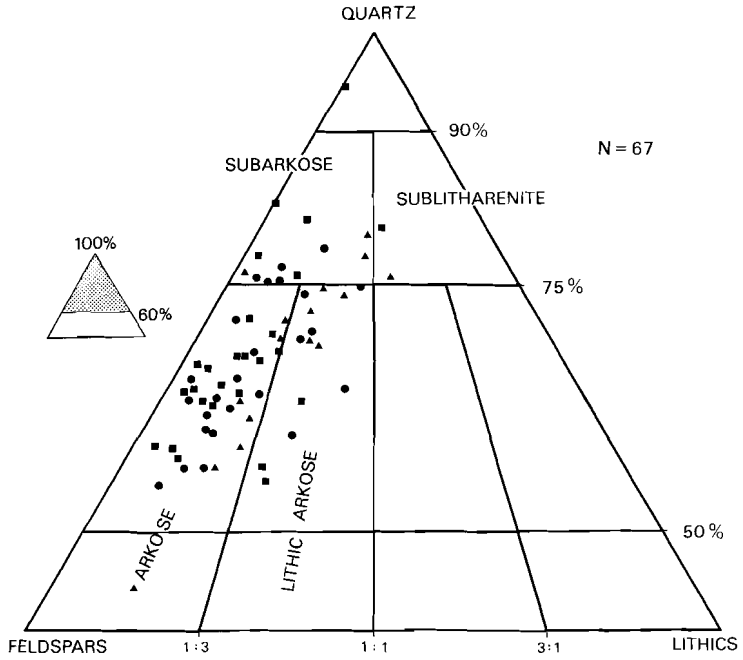
SANDSTONE PETROGRAPHY

Clastic components

With regard to the siliciclastic components, most of the sandstones can be classified as (quartzose) arkoses, using the classification system of Folk (1968) (Fig. 3A). Some, however, may be classified as sandy peloidal or bioclastic packstones to wackestones, considering their high content of various kinds of carbonate clasts (Fig. 3B).

The primary detrital terrigenous input into the basin consisted of siliciclastics, mainly quartz and feldspar (K-feldspar and plagioclase), and lithic extrabasinal clasts, such as biotite, chlorite and some muscovite flakes, mixed siliciclastic-carbonate siltstone and sandstone clasts, chert grains, and sparse recrystallized limestone clasts. The feldspars range from fresh to strongly vacuolized, and display a variable degree of replacement by a mixture of illite and kaolinite. The large variability of vacuolization and clay replacement points

A


QUARTZ
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SUBLITHARENITE
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ARKOSE
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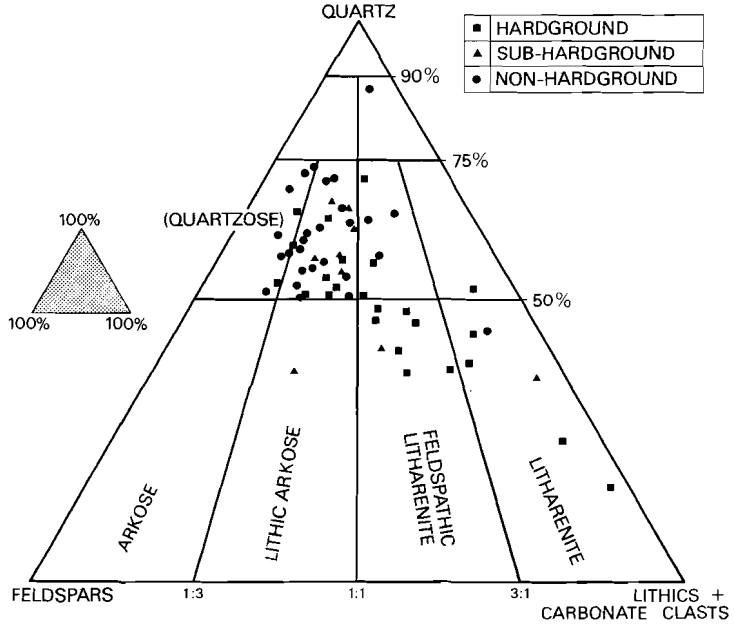
3:1
LITHICS

B


QUARTZ
HARDGROUND
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90%
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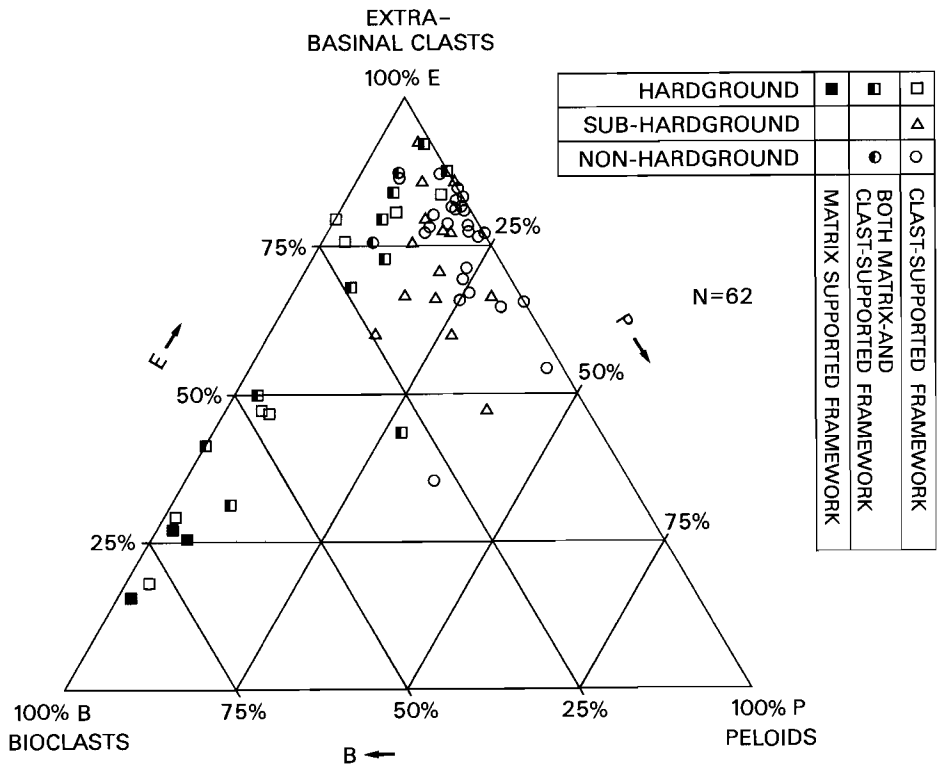

Figure 3: *Compositional triangular diagrams based upon percentages obtained by thin-section pointcounting of 300 to 400 points; N=67.*

3A: *Triangular QLF diagram (A) of the sandstones of the Lower Roda Formation, according to the modified classification of Folk (1968). A: Q- mono- and polycrystalline quartz; L- mixed siliciclastic-carbonate clasts, siltstone and sandstone clasts, biotite, chlorite and chert grains; F- microcline, orthoclase and plagioclase. The prefix quartzose can be added if the percentage quartz is more than 50. The relative amounts of the various terrigenous components is the same throughout the sandstone bodies. There is thus no distinction between hardgrounds and non-hardgrounds with respect to their siliciclastic composition. Hardgrounds do not represent changes in siliciclastic supply. The changes through preburial processes have modified a primarily compositionally homogeneous sediment.*

3B: *Triangular diagram including the intrabasinal carbonate clasts (peloids and bioclasts) in the lithic fraction (L). Note the distinct shift, especially from the hardgrounds.*

3C: *Triangular diagram with emphasis on the carbonate grains; E- extrabasinal clasts (siliciclastics, mixed siliciclastic-carbonate clasts); P- peloids; B- bioclasts. P and B are mainly intrabasinal.*

to the inherited nature of these features from weathering in the source area.

The relative amount of the various quartzes, feldspars and lithic components is the same throughout the sandstone bodies (cf. QLF triangular diagram of Fig. 3A). Moreover, the grain-size distributions of the siliciclastic components display similar range for all types of sandstone, irrespective of any preburial changes (Fig. 12). The linear relation between the 25 % and 75 % percentile values indicates that there were no major changes in terrestrial supply of siliciclastics.

Within the basin, carbonate intraclasts, such as peloids, sometimes containing siliciclastic silt, and bioclasts were introduced into the depositional system (Fig. 3C). Some of the peloids can be identified as grapestones, i.e. cemented faecal pellets, whereas the origin of others is not clear. These carbonate clasts must have been produced on abandonment surfaces and outside the areas of sand deposition. Large benthonic foraminifera (alveolinids, miliolinids, nummulitids, assilinids, discocyclinids), agglutinated foraminifera, gastropods, bivalves and echinoids constitute the bulk of the in-situ and/or intrabasinally reworked bioclastic components.

Texture

Below abandonment surfaces bioturbation features are frequent. In the bioturbated facies, the axes of elongated or platy clasts exhibit a random orientation, in contrast to the undisturbed parts where a strong lineation, approximately parallel to the bedding surfaces, and sometimes a separation in laminae exist. Furthermore, matrix is present in the sediment below the abandonment surfaces, thereby decreasing the sorting of the sandstones. This matrix is mainly composed of carbonate micrite with a low content of clay minerals (illite, smectite and kaolinite). Matrix is virtually absent in other parts of the sandstone, i.e. not immediately below abandonment surfaces. There, the sorting is fair to good, and the grain-size distribution is unimodal. Thus, the degree of bioturbation, and the obliteration of original primary depositional structures increased during periods of low sedimentation rate or non-sedimentation, since part of the fauna was infaunal.

Matrix

Apart from an enrichment in bioclastic material and the obliteration of primary texture through bioturbation, parts of the sandstone below abandonment surfaces usually contain abundant matrix. This intrabasinally produced carbonate matrix was introduced into the sediment by two distinct processes, each manifested by characteristic features.

A first kind of matrix accumulated on top of clasts and in pore throats in framework-supported parts of the sandstone (Fig. 4). Usually, it does not fill

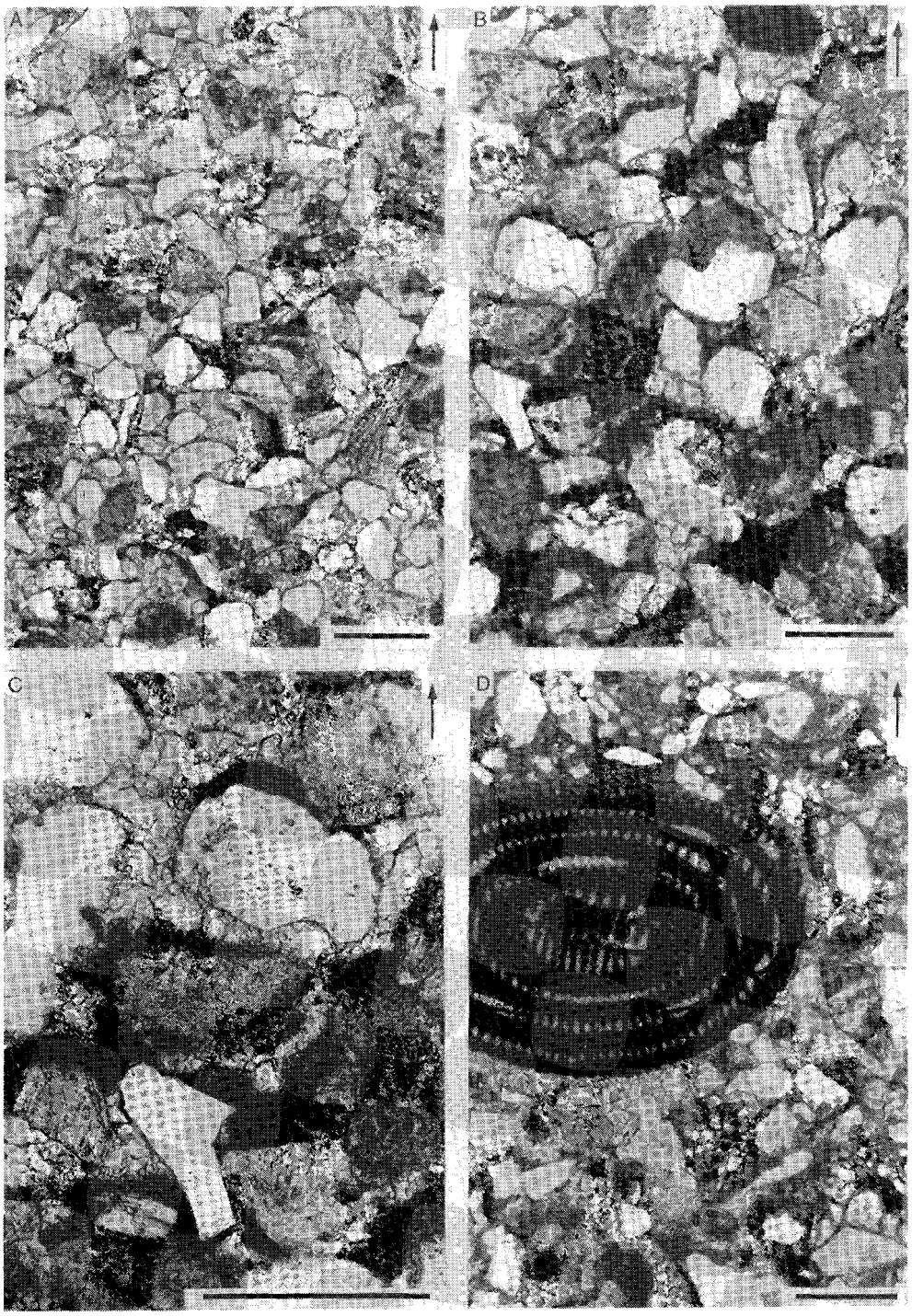
A
B
C
D

Figure 4: *Photomicrographs of thin sections showing the effect of matrix infiltration and early cementation below abandonment surfaces (i.e. hardgrounds and sub-hardgrounds). The arrow indicates the stratigraphic facing. Plane polarized light. Scale bars are 0.5 mm.*
4A: *Sandstone with clast supported framework, infiltrated matrix and first precompactional rim-cement. Sub-hardground. Compactional features are absent.*
4B and 4C: *Details of infiltrated matrix present on top of clasts in sub-hardgrounds. The rim cementation was of later date than the matrix infiltration.*
4D: *Hardground with slight enrichment of bioclasts; an alveolinid test is visible on the photomicrograph. The large test served as an umbrella with respect to matrix infiltration, resulting in a shelter structure. Above the test the pore spaces are locally completely filled with matrix.*

the entire pore space. The grain-size distribution in the affected intervals is strongly bimodal, reflecting the occurrence of fine-grained micritic matrix between the well-sorted framework components. Further distinct features are geopetal, shelter and umbrella structures, a decrease of matrix content beneath an abandonment surface with increasing distance from this surface. This matrix is interpreted as having been deposited by mechanical infiltration from the sediment-water interface into the sandstone framework.

A second type of matrix occurs in sandstones with a distorted fabric, e.g., where the depositional lineation of the clasts and lamination are disturbed by bioturbation. Frequently, this matrix displays a spot-like distribution throughout the sandstone, completely filling the interstitial pores. The framework in the most intensely affected parts of the sandstone body is matrix supported. There the content of bioclasts usually is high (Fig. 5). Also in discrete burrows the sandstone has a matrix-supported fabric. The grain-size distribution in the matrix containing parts is polymodal. This is described to a strong mechanical mixing of individual laminae and layers. Except for burrowed segments of the sandstone, matrix does not totally fill the primary pores of the particle framework. This kind of matrix is interpreted as having being introduced through bioturbation.

As the bulk matrix content decreases with increasing depth from the palaeo abandonment surfaces to a finally virtually absence of matrix, so its character changes from mixed biogenically and mechanically introduced to solely mechanically infiltrated. Thus, sorting beneath an abandonment surface ranges from strongly polymodal in parts of the sandstone affected by both processes, to strongly bimodal in parts that have only suffered mechanical infiltration, and finally to unimodal in absence of matrix. Below major abandonment surfaces both processes were active, whereas below minor abandonment surfaces, i.e. where the sedimentation stop was short, infiltration was the dominant process. Matrix is thus present in all parts of the sandstone that underwent periods of non-deposition.

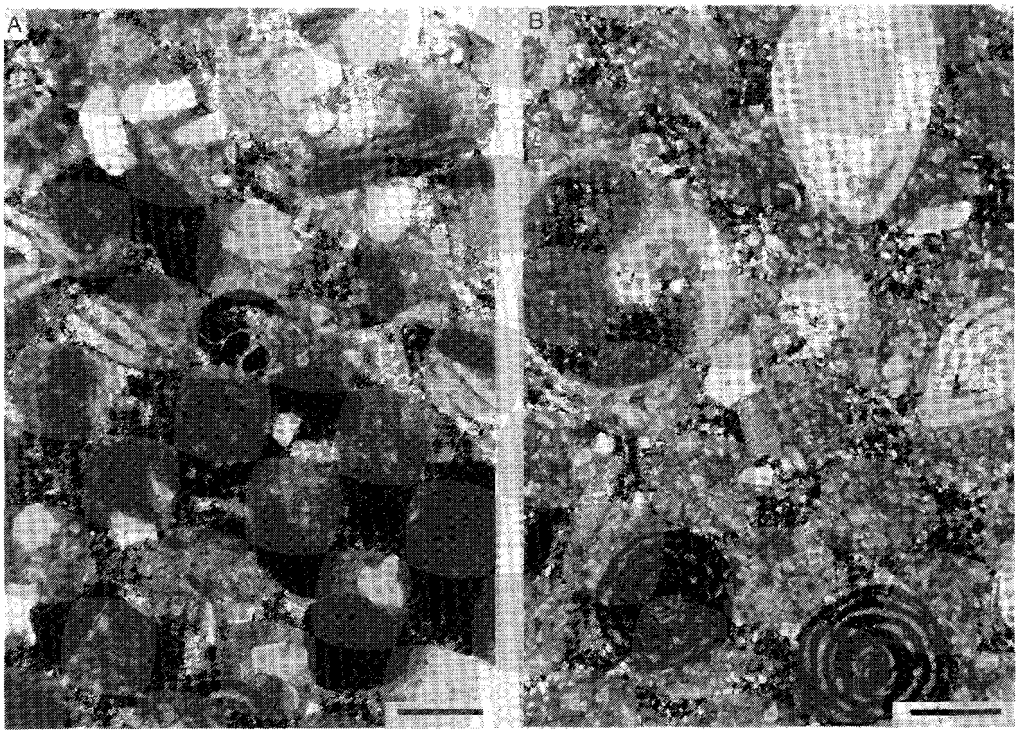

Figure 5: *Examples of hardgrounds showing infiltrated matrix, enrichment of bioclasts, and a polymodal grain-size distributions. Most of the primary texture of the sediment has been destroyed by bioturbation below an abandonment surface. In photomicrograph 5A most of the matrix has been introduced into the sediment by infiltration, in contrast to 5B, where mechanical mixing dominated. Fossils are mainly nummulitids, miliolinids and alveolinids, and a calcite replaced gastropod shell in 5B. Plane polarized light. Scale bars are 1 mm.*

DIAGENESIS

Rim-cementation

Most sandstones are tightly cemented by calcite, although in several layers an effective porosity is still present (averaging 4.3 % ± 2.0; N=29). This is a reduced primary interparticle porosity. Two major kinds of carbonate cement can be distinguished with respect to the time of their introduction and their shape.

A first generation of carbonate cement coats grains (Fig. 6), especially carbonate grains which probably provided suitable precipitation nuclei, but also siliciclastic grains if the first cement generation is abundant. Usually, this type

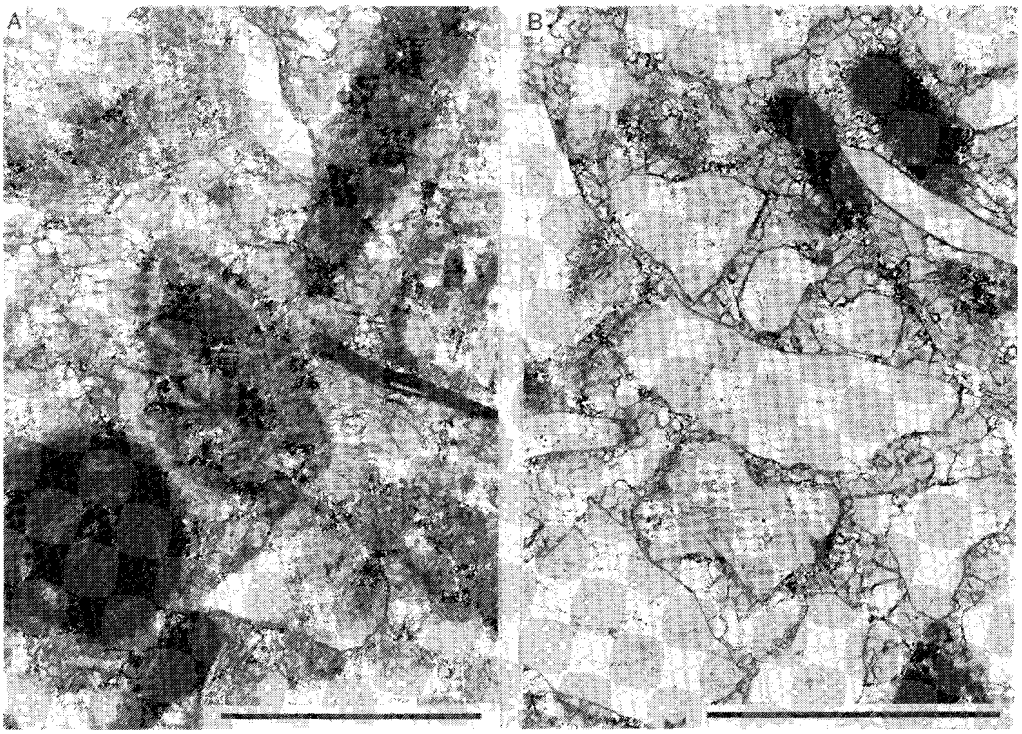

Figure 6A and 6B: *Photomicrograph of thin sections showing the two types of cement of major importance: a precompactional (aragonite) rim-cement, replaced by low-magnesian calcite, and the second burial cement, consisting of a more or less equigranular low-magnesian calcite sparite. In the sample 6A the first cement was aragonite, especially rimming carbonate grains. In 6B the rim-cement has been precipitated around both carbonate and siliciclastics. Plane polarized light. Scale bars are 0.5 mm.*

of cement is present in sandstones that also contain infiltrated matrix; it has been precipitated after infiltration since it also encloses the matrix. This cement, only accounting for 1 to 5 % (averaging 2 %) of the rock volume, is now composed of ferroan low-magnesian calcite. Frequently, this rim-cement exhibits a fibrous habit. In very few samples a radial fibrous texture, recognizable by inclusion patterns and an undulose extinction, is present in the low-magnesian calcite. The first rim-cement around rare echinoid fragments typically has developed as syntaxial overgrowths. In some samples, the first carbonate cement generation is a granular rim-cement. Here, the rim-cement tends to display a gradual transition to the second cement generation.

The fibrous crystal form points to a primary aragonite mineralogy (Fig. 6A) that has been replaced pseudomorphously by a ferroan low-magnesian calcite

during diagenesis. It is suggested that the mineralogy and structure of the rim-cement were determined by the mineralogical composition of the enclosed grain. The gradual transition of the granular rim-cement into the second cement generation suggests a non-pseudomorphous replacement of a former mineralogically unstable rim-cement during precipitation of the second cement. Rim-cement occurs in sandstones below abandonment surfaces that were also affcted by matrix and bioclast enrichment and bioturbation. It is therefore concluded that it represents a marine cementation phase, which is confirmed by the primary aragonitic composition.

About half of the sampled sandstones (51.2 %) have been modified by early diagenesis including matrix infiltration and precipitation of the first generation of cement; 48.8 % of the sandstones sampled remained unaffected, except for some minor bioturbation. Nearly all nodules possess the first cement as well as infiltrated matrix.

Compaction

Mechanical compaction features were found in those sandstones, in which the rim-cement is absent (e.g., Fig. 7). Mechanical compaction is manifested by bent, broken and mechanically exfoliated and ferroan calcite sparite filled biotite grains, plastically deformed ductile grains (such as peloids and siltstone clasts) and concavo-convex contacts between ductile and rigid framework components, e.g., between peloids and quartz or feldspar grains. Intensely illitized and vacuolized feldspar grains also have behaved like ductile grains. Fragile bioclasts are sometimes found to have been broken. In the most extreme case, ductile grains form a semi-matrix (Fig. 7B), whereas rigid siliciclastic grains display brittle fracture. Although, features indicative of pressure dissolution between siliciclastic grains or carbonate grains were not found. Most of the reduction in total volume was accomplished through plastic deformation only. Compaction was fairly effective in reducing the primary porosity because of the high percentage of ductile grains (cf. Nagtegaal, 1978). The very ductile behaviour of the peloids points to their largely non-lithified character, reflecting their assumed intrabasinal origin.

Mechanical compaction features were not observed or are not apparent in sandstones where the rim-cement is present (Fig. 5 and 6). A distinct difference exists in the amount of compaction, calculated from the minus-cement porosity, in framework-supported sandstones between samples with the first cement (± 0 % compaction) and samples without the rim-cement (an average of 24 % compaction). The near absence of compaction and the high minus-cement porosity (or minus-cement and infiltrated matrix porosity), with a mean value of 40 %, is indicative of a very early and pre-compactional introduction of this first cement. The rim-cemented sandstones were sufficiently lithified to counteract mechanical compaction.

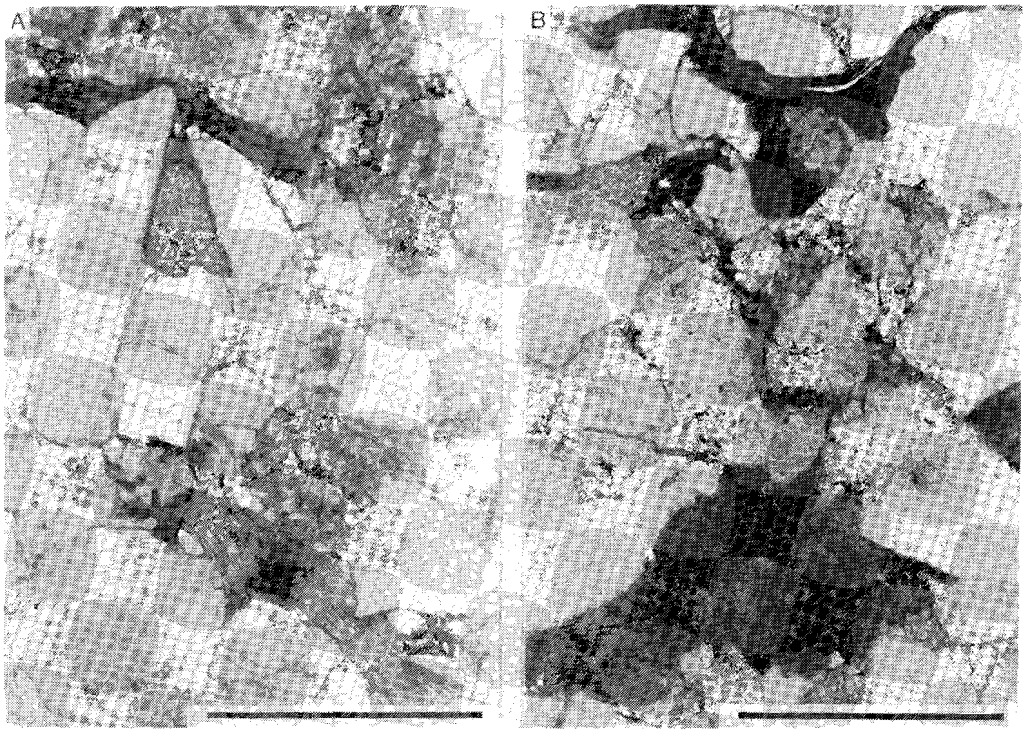

Figure 7: *Photomicrographs of thin sections. Compactional features are present in a sandstone without a first cement. Features are kinked biotite flakes, concavo-convex contacts between rigid and ductile grains. Note the deformation of ductile micrite grains towards a pseudomatrix. Plane polarized light. Scale bar is 0.5 mm.*

Sparite cementation

After precipitation of a first generation of cement, represented by the rim-cement, a second generation cement consisting of calcite sparite was introduced into the residual pores (Fig. 7). The second generation of cement also fills cracks in rigid framework components and occasionally partly replaces plagioclase feldspar clasts. It is a blocky, more or less equigranular low-magnesian ferroan calcite, ranging from 0.02 to 1 mm in crystal diameter. In sandstones that display compactional features, the second cement frequently exhibits a sub-poikilotopic habit, almost enclosing individual framework components. The smaller crystal-size of the sparite cement in non-compacted sandstones points to a higher saturation of the interstitial water with respect to calcite in the parts of the sandstone below abandonment surfaces than in the sandstones which were affected by compaction.

The second cement phase is present in all sandstones, however in strongly varying percentages. Before the second cement was precipitated, compaction reduced the primary porosity in portions of the sandstone bodies where the first cement generation was lacking and where the framework thus was not stabilized during early diagenesis. Therefore, and because of the filling of brittle fractured clasts, the second cement can be inferred to have been precipitated only after burial compaction.

There is no distinction between sandstones lacking the early diagenetic cement in the northern and southern parts of the area with respect to the minus-cement porosity, in spite of the fact that the southern part was buried deeper during the second burial phase. The compaction of the not modified sandstones in the northern area (23.4 % ± 7.1, N=11; sections 1, 2 and 3) is not significantly different from that in the southern area (22.3 % ± 6.1, N=10; sections 6, 7 and 8). This is either an indication of the introduction of the second cement and the resulting ultimate stabilization of the sandstone framework before subsequently reaching the maximum depth of the second burial, or of the effectiveness of compaction during the first burial which was adequate to stabilize the framework sufficiently, possibly combined with strain hardening of the peloids.

Replacement of carbonate constituents

In addition to matrix and diagenetic cements and replacements, carbonate occurs as detrital extrabasinal clasts usually containing some quartz silt, intrabasinal peloids, bioclasts. Low-magnesian calcite is the only carbonate mineral present, as was indicated by both XRD and AAS analyses. However, both high-magnesian calcite and aragonite must have been originally present as constituents of bioclasts and probably also as micrite. Aragonite was a primary constituent; it occurred in gastropod shells and as an early rim-cement. Aragonite shells, which are virtually restricted in occurrence to the major abandonment surfaces, have been leached and subsequently filled with blocky or drusy low-magnesian calcite, without collapse or infiltration structures. Porcellaneous tests of benthonic foraminifera, such as alveolinids and miliolinids, were originally composed of high-magnesian calcite. This has been replaced by micrite to sparite-sized low-magnesian calcite. Other carbonate clasts of uncertain primary mineralogy and origin have been replaced by sparite. The replacive sparite often merges into the sparry cement, filling the primary interparticle interstices. Where complete replacement has occurred, only vague margins of the former clasts, outlined by some micritic dust, indicate their presence. Microsparitized peloids merge into the microsparitized matrix.

Neomorphic replacement has especially affected the micrite matrix, resulting in extensive microsparitization, probably because of a low clay mineral content (Bausch, 1968); micrite peloids in many of the samples have also been affected. The microsparitization suggests that the primary matrix and peloids consisted mainly of metastable aragonite and/or high-magnesian calcite, formed

biogenically.

Diagenesis resulted in the neomorphic replacement of aragonite and high-magnesian calcite by low-magnesian calcite. All inferred aragonite and high-magnesian calcite particles have been replaced by low-magnesian calcite, frequently resulting in microsparitization of former the micrite. Dissolution and precipitation were instantaneous, as is indicated by the absence of collapse structures even in case of larger replaced shells below abandonment surfaces, and by the pseudomorphous nature of the replacement of aragonite rim-cement. This indicates that the sediment had already been stabilized by cementation in hardgrounds and sub-hardgrounds, or by compaction in the case of non-hardgrounds. Replacement and the precipitation of the second cement are therefore manifestations of the same diagenetic event. The inferred sequence of diagenetic processes is shown in Fig. 8.

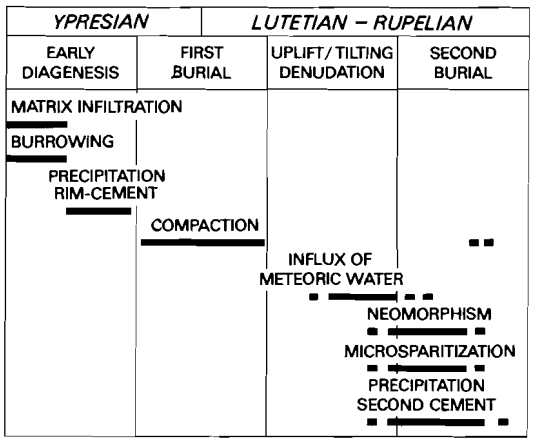

Figure 8: *Relative timing of various events and diagenetic processes in the Roda Sandstone Member.*

RECOGNITION OF HARDGROUNDS

Several features are characteristical for hardgrounds. The early diagenetic processes responsible for these features determined a distinct behaviour of the various parts of the sandstone bodies during later meso- and telo-diagenesis, i.e. a differential susceptibility for mechanical compaction, and thus a different possible degree of second cementation, and, moreover, a different behaviour upon subaireal exposure.

Criteria for the recognition of abandonment surfaces are given in Fig. 9, and quantified in Table 1. A distinction can be made between major abandonment surfaces, i.e. the affected parts below abandonment surfaces,

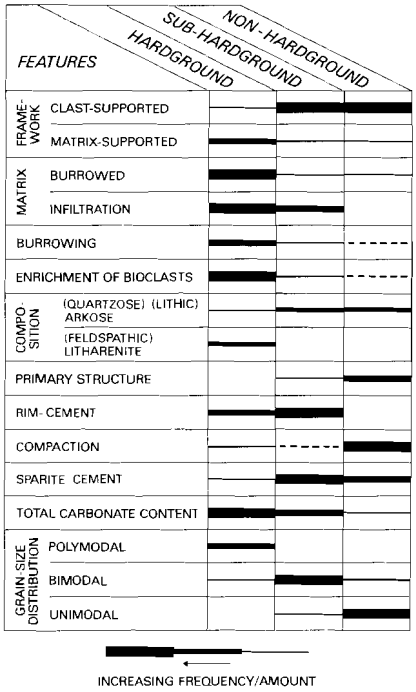

Figure 9: *Summary of features and criteria characteristic of hardgrounds, sub-hardgrounds and sandstones not affected by early diagenesis. The thickness of a bar is proportional to the importance of the process or feature.*

(informally called hardgrounds) and minor abandonment surfaces (called sub-hardgrounds). The latter constitute either the lower parts of hardgrounds, or represent a beginning stage of hardground formation. Where the period of abandonment was short, bioturbation and the enrichment of bioclasts were minor, and matrix infiltration was a first and obviously fast process operating below the abandonment surfaces. Where the supply of sediment was strongly intermittent, not only the upper layer of a depositional lobe was modified by the processes mentioned, but also the upper parts of mega high-angle and especially low-angle fore-sets were affected. However, bioturbation may have occurred as well on and in the toe-sets of mega-cross-bedded sets, albeit in the absence of other preburial processes. The variation of several parameters below an abandonment surface with increasing depth is depicted in Fig. 10. The sandstone composition was modified into a wacke and eventually into a sandy bioclastic limestone (Fig. 3B), almost without changing the original grain-size distrubution (Fig. 12), as the amount of reworked intrabasinal or in situ produced carbonate clasts increased. The content of non-reworked bioclasts increased in proportion to the timespan of non-deposition. The total content of carbonate is higher towards abandonment surfaces, due to a combined increase

in content of matrix, bioclasts and cement. The relation between diagenetic processes and sedimentation rates is shown in Fig 11.

FEATURES		HARDGROUNDS	SUB-HARDGROUNDS	NON-HARDGROUNDS
FRAME-WORK	CLAST-SUPPORTED	17.5 %	96.3 %	93.1 %
	MATRIX-SUPPORTED	20.0 %	0.0 %	0.0 %
	COMBINATION	62.5 %	3.7 %	6.1 %
MATRIX	INFILTRATED	33.3 %	7.7 %	17.9 %
	BURROWED	28.6 %	46.2 %	0.0 %
	COMBINATION	38.1 %	0.0 %	0.0 %
	NONE	0.0 %	46.2 %	82.0 %
	RIM-CEMENT	37.5 %	100.0 %	3.0 %
	NODULES	22.5 %	50.0 %	4.7 %
ABSOLUTE PERCENTAGES	MATRIX %	27.6	6.2	4.3
	BIOCLASTS %	20.9	5.0	4.0
	PELOIDS %	4.1	9.9	16.0
	EXTRABASINAL CLASTS %	35.1	40.8	59.0
	SPARITE CEMENT %	11.7	37.1	16.1
	TOTAL CARBONATE %	59.3	55.3	36.5
	EFFECTIVE POROSITY %	2.7	3.0	5.0
	COMPACTION %	2.0	0.0	24.0

Table 1: *Quantification of various characteristics in hardgrounds, sub-hardgrounds and non-hardgrounds. Percentages have been obtained by point counting of thin sections.*

Macroscopically a tripartition in the sandstones can be made based upon resistance against weathering, texture and composition of the sandstone. A discrimination is possible between friable well-sorted arenites, well-sorted indurated arenites, and weathering resistant matrix and bioclast rich wackes to sandy bioclastic limestones. This tripartition largely coincides with the subdivision into non-hardgrounds, sub-hardgrounds and hardgrounds. The different behaviour to weathering is caused by different amounts of carbonate cement, and the amount of semi-matrix that is mainly composed of compacted ductile peloids. Due to the abundant presence of swelling-montmorrillonites, the non-hardgrounds become friable upon weathering and more susceptible to further dissolution.

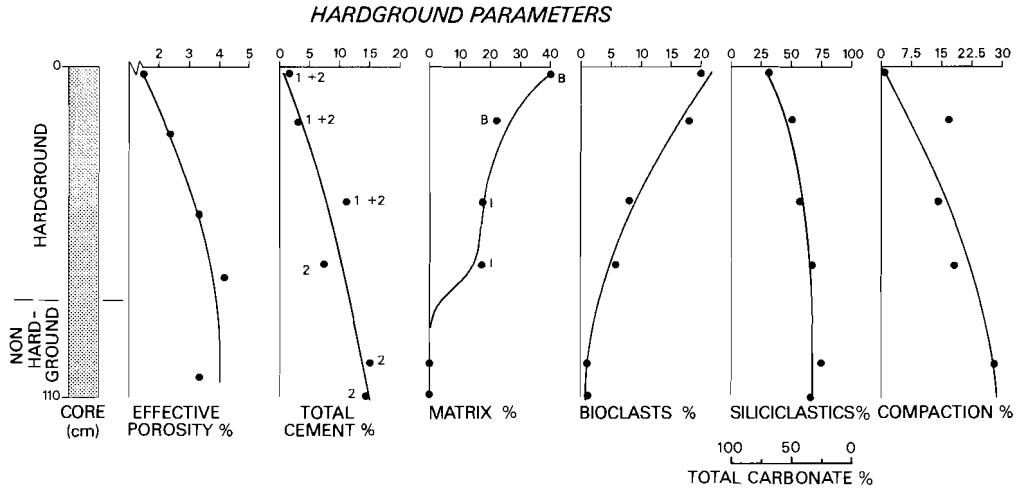

Figure 10: *The variation of several parameters below a hardground surface (core taken from a major hardground). 1: rim-cement; 2: second sparite cement phase; B: burrowed matrix; I: infiltrated matrix.*

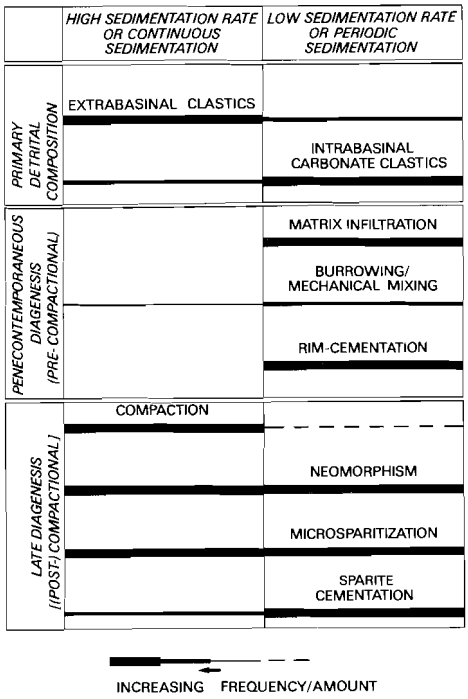

Figure 11: *Relationship of diagenetic processes and sedimentation rate.*

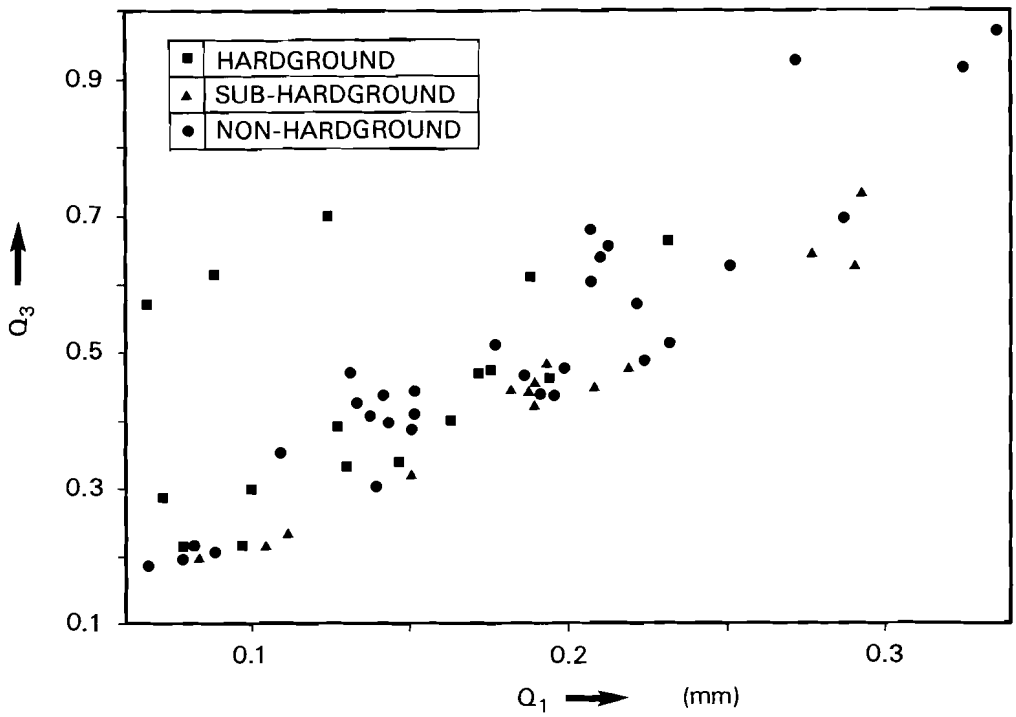

Figure 12: *The grain-size distributions, expressed as the 25 % and the 75 % percentile values, measured on HCl insoluble residues. They show similar ranges for all kinds of sandstone irrespective of any preburial changes below abandonment surfaces. The presence of matrix has practically no influence on the grain-size distrubution, since matrix is mainly composed of carbonate micrite, containing practically no clay minerals. Variations in grain-size were locally influenced by hydraulic conditions and sedimentation processes, not by post-depositional modifications.*

DISCUSSION

The percentage of peloids is lower below major abandonment surfaces than in non-affected horizons (Fig. 3C). This points to the fact that part of the matrix probably was derived from the destruction of former peloids through bioturbation. Another part of the matrix might have been derived from bio-erosion and mechanical abrasion of bioclasts or degradation of skeletons after death and decomposition of the organic binding material on the abandonment surfaces. Furthermore, matrix may have been generated through mechanical disturbance of a premature hardground, which had been slightly lithified by a beginning rim-cementation. Since the rim-cement, which consists of small crystals, preferentially nucleated on carbonate clasts, a beginning

stage of hardground development was still friable and might have been bioturbated. These disintegrated cement crystals could have been incorporated within the sediment as matrix.

Probably, the amount of infiltrated matrix was dependent on the original sizes of the connections between pores, thus on the grain-size distribution and on the absolute grain-sizes. Since the infiltrated matrix blocked the pore connections, infiltration can only account for a certain enrichment in matrix. Furthermore, in the most enriched parts of the sandstone, the permeability has been severely reduced. This counteracted the flow of interstitial water supplying chemicals needed for the rim-cementation. To a certain degree, both processes are mutually exclusive. When the abandonment of the depositional surface was of long duration, the upper part of the sediment eventually became completely burrowed, and was modified to a matrix-supported impermeable layer, blocking any cementation below. Yet, diffusion was enhanced through bioturbation. The depth of this intense modification was probably dependent on the kind of infauna present. Contrary to mechanical mixing, infiltration was a rapid process, since it was completed before the precipitation of the first generation of cement.

The fact that parts of the sandstone bodies below abandonment surfaces have been modified by extensive matrix infiltration can be explained by the lack of evidence of intensive winnowing by wave action of the fine material from these surfaces. The presence of a diversified fauna is in conformity with the absence of high energy conditions. It can therefore be assumed that the early diagenesis occurred in sediments which were, at that time, below the fair weather wave-base. Since features indicative of the pertinent processes have been observed in many intervals of the sandstone bodies other than the major capping abandonment surfaces, this could account for the fact that deposition of most of the sandstones took place below the fair weather wave-base. The truncation of the sandstone bodies probably occurred during heavy storm periods.

A large volume of water supersaturated with respect to calcite was necessary to provide the amount of solutes for precipitation of the second cement generation. Since there were distinct differences in porosity and permeability at the time of introduction of the second cement, it seems insurmountable that there has to be a relationship between the porosity and permeability patterns and cementation. Major hardgrounds had a low permeability due to the high amounts of matrix present. However, a very high minus-cement porosity still existed in the sub-hardgrounds due to the compaction-counteracting effect of the first cement phase. Parts of the sandstone bodies not affected by penecontemporaneous diagenesis, already had an intermediate porosity and a low permeability due to mechanical compaction. In these non-hardgrounds the permeability was especially decreased by the presence of pore-obstructing semi-matrix, constituted by compacted ductile peloids. Thus, at the time of precipitation of the second cement generation, the sub-hardgrounds represented the most porous parts of the sandstone. Any flow

of interstitial water, carrying the solutes for the second cementation phase, would preferentially take place in those parts of the sandstone bodies where a small amount of precompactional cement was present. This cement counteracted compaction, and consequently percentages of infiltrated matrix were low. Moreover, supersaturation with respect to calcite was higher in the more porous parts of the sandstone bodies, causing a higher nucleation rate and a small crystal-size of an equigranular cement. As a consequence of the lower permeabilities of non-hardgrounds and hardgrounds, those parts of the sandstone have been cemented later, or at least the cementation was completed later. The non-hardgrounds represent parts of the sandstone being cemented later than sub-hardgrounds at lower supersaturations, which caused the development of a sub-poikilotopic cement.

Mixed siliciclastic-carbonate arenaceous sediments are highly susceptible for mechanical as well as chemical compaction. In fact all sandstones with a high amount of ductile grains are susceptible to mechanical compaction and may suffer framework collapse upon burial. These deposits seem to be less favourable for hydrocarbon accumulation, because of the expected low porosity and permeability even after a burial of a few hundreds of metres only. However, if there are stops in the sedimentation, early diagenetic cementation may cause the development of intervals within the sandstone bodies which have a stabilized framework. Especially if there are periods with low but continuous sedimentation, cementation can keep place with sedimentation, resulting in thick stabilized horizons. Since carbonate clasts, such as peloids and bioclasts, are preferential nucleation sites for the precipitation of cement, hardgrounds are likely to originate more easily, and probably exclusively, in a sandstone complex containing carbonate clasts. Furthermore, depositional surfaces of a sandstone, that contains abundant soft intrabasinal carbonate clasts, should have a higher stability against the rolling of particles. The threshold for erosion is thus higher than in purely inhabitated siliciclastic sandstones. The period of non-deposition is likely to be longer in siliciclastic sandstones to produce a hardground.

CONCLUSIONS

The parts of the sandstone bodies below abandonment surfaces are characterized by several processes:

- bioturbation;
- the infiltration and mixing of matrix, and
- the precipitation of a penecontemporaneous rim-cement.

These surface layers were thus stabilized and may be called hardgrounds. Other parts of the sandstone, which had not been stabilized by the first cement, were compacted mechanically. A second generation of cement, composed of sparry calcite, was precipitated after compaction. Little or no time has elapsed between neomorphic changes and precipitation of the second cement.

The porosity and permeability patterns in the sandstone complex were to

a large extent controlled by the spatial distribution of the processes, which caused changes in the texture and composition of the sandstones during early diagenesis.

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CHAPTER 5

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ORIGIN OF NODULES IN MIXED SILICICLASTIC-CARBONATE SANDSTONES, THE LOWER EOCENE RODA SANDSTONE MEMBER, SOUTHERN PYRENEES, SPAIN.

N. MOLENAAR & A.W. MARTINIUS

ABSTRACT

Calcite cement is inhomogeneously distributed in the Eocene Roda Sandstone Member. Strongly cemented nodules and layers, intercalated within less well-lithified sandstones, are common. The nodules yield valuable information about the factors that controlled the onset and the degree of cementation. Nearly all nodules are associated with abandonment surfaces, formed when sedimentation ceased for a variable length of time. The nodules represent a first stage in the development of continuous hardgrounds. The initiation of hardground formation was dependent on a combination of several parameters, such as grain-sorting and the presence and amount of carbonate nucleon centres. Hardground formation began at distinct points, now manifested by nodules, aggrading into layers in cases where sedimentation had ceased for a sufficient length of time. The resulting variability in the amount of cement determines the present-day difference in weathering behaviour between nodules and of the adjacent, less well cemented sandstones.

INTRODUCTION

Nodular features in carbonate and fine-grained siliciclastic sediments have received much attention. Most nodules are richer in carbonate than the surrounding sediments. Some authors concluded that nodules in carbonate formed late in diagenesis (e.g., Bjørlykke, 1973), although an early diagenetic origin has been put forward more frequently (e.g., Jenkyns, 1974; Mullins et al., 1980; Möller and Kvingan, 1988). In siliciclastic pelites, early diagenetic processes related to decomposition of organic material are thought to be the cause of the development of nodules or concretions (e.g., Curtis and Coleman, 1986). Concretions in siliclastic pelites may growth during early diagenesis as well as after some mechanical compaction (Raiswell, 1971). So far, very little attention has been paid to the occurrence of nodules in sandstones (e.g., Garrison et al., 1969; Chafetz, 1979; Pirrie, 1987; McBride, 1988). The Lower Eocene Roda Sandstone Member is an example of a sandstone displaying nodular structures.

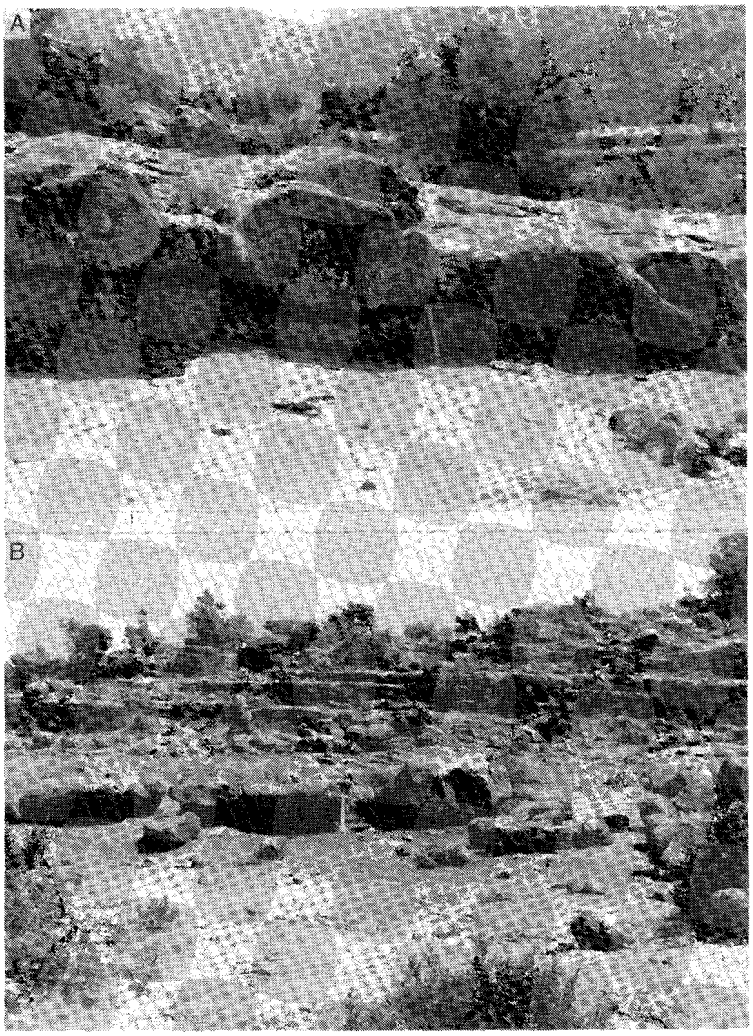


Figure 1: *Outcrops of the Roda Sandstone Member showing nodular features. Photograph 1A shows a well lithified layer with internal nodular structures. Photograph 1B displays discrete nodules in horizons interbedded with poorly-lithified sandstones that are more less resistant to weathering.*

Weathering-resistant layers and nodular layers, as well as horizons with isolated nodules, appear in outcrops of the Roda Sandstone Member (Fig. 1). Its nodular appearance indicates locally inhomogeneous lithification. The distribution of carbonate cement was studied in order to better understand the causes of sandstone cementation.

In general, a uniformously dispersed occurrence of cement does not yield many clues about its source and causes of cementation. An irregular and inhomogeneous distribution of cement, such as displayed by cemented nodules, lenses or horizons alternating with non- or less-cemented horizons, can provide information about the factors controlling cementation. In the latter case, it is likely that sediment parameters and/or environmental conditions initiated cementation at distinct spots, or inhibited the development of cement elsewhere. If such inhomogeneities are visible in outcrops, e.g., by differential weathering patterns, it is possible to accurately sample the variably cemented parts of a sandstone body. If nodules are indeed caused by differences in the diagenetic processes, their presence must reflect the variability of local sedimentary parameters, such as grain-sorting and the amount of carbonate cement-nuclei present.

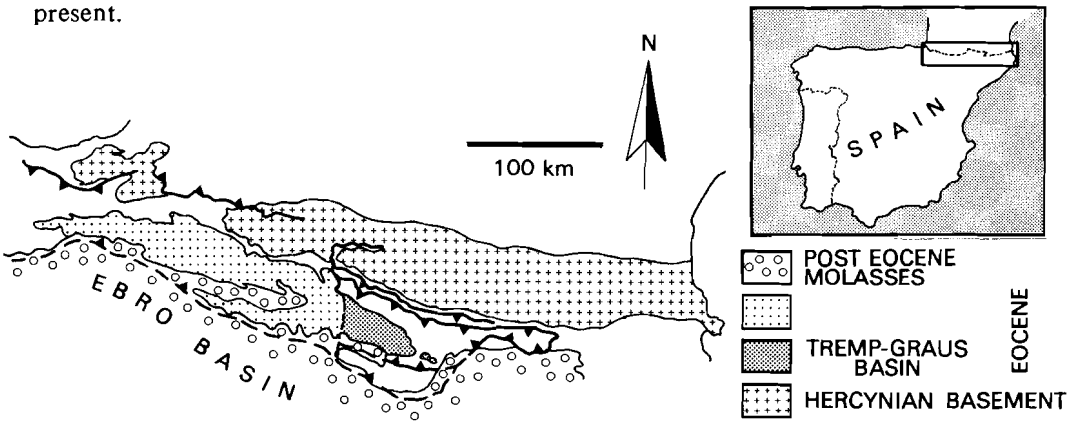


Figure 2: *Location and general geologic setting of the Tremp-Graus Basin in Spain. Sample location are along the river Isabena between Roda d'Isábena and Serraduy.*

Geological setting

The Tremp-Graus Basin forms part of the southern Pyrenean foreland basin which was fragmented due to southward thrusting during the Paleogene (Williams, 1985) (Fig. 2). Thrusting took place contemporaneously with sedimentation in the Tremp-Graus basin, (Ori and Friend 1984). This tectonic movement probably triggered major clastic influxes into the basin, such as the deposition of the Roda Sandstone Member. The Lower Eocene Roda Sandstone Member consists of a sequence of tide-dominated shallow-marine mixed siliciclastic-carbonate sandstones separated by sandy or silty marls (Nijman and Nio, 1975). Its basal part consists of silty to sandy marls with thin sandy limestone layers. The upper part is approximately 40-65 m thick and contains up to five vertically stacked sandstone bodies sometimes separated by silty and sandy marls and siltstones. These sandstone bodies, with an individual thickness of up to 30 m, are composed of cosets of large-scale low- and high-angle cross-beds. Deposition occurred from south to southwestward and northwestward

prograding ebb-tidal delta lobes, transverse tidal bars, and lateral accretion along meandering ebb-tidal channels (Nio and Yang, 1983; Nio et al., in prep.). The different depositional units are separated by major abandonment surfaces, typified by burrowed bioclastic and matrix-rich wackestones or arenites. This indicates that sedimentation was strongly intermittent due to interruptions in the progradation of delta lobes and tidal bars and to the eventual total abandonment of the depositional area. The upper part of depositional lobes may have been cut and transformed into regular planar surfaces by wave-action.

METHODOLOGY

The texture, composition and diagenetic features of 193 samples from eight outcrops have been qualitatively determined by means of thin-section petrography. Clastic composition and diagenetic features were quantified by point counting.

The grain-size distributions of the siliciclastic components of 68 samples, separated from the sediment through hydrochloric acid treatment, were measured in duplicate using a Malvern 3600D laser particle sizer.

28 samples, each 30 mg, were analyzed for inversion temperatures and inversion reaction rates of detrital quartz by means of differential scanning calorimetry (DSC) with a DuPont DSC cell. The DSC curves of twenty samples were calibrated by repeated measurement of potassium sulphate (K_2SO_4), which has a known crystallographic inversion at a temperature of 583.5 °C (Smykatz-Kloss, 1974). The inversion temperatures, calculated as amplified initial reaction temperatures, were measured upon heating and cooling at a rate of 5 °C/min in a nitrogen atmosphere (3 ml N_2 per second).

Oriented glass-mounted preparations of the HAc insoluble residue less than 50 μm fraction of eight samples were analyzed for clay minerals by means of standard X-ray diffraction ((Cu-K_a radiation and a Ni-filter). The fraction smaller than 50 μm was used for analyses to obtain results representative for the whole matrix independently on variations induced through changes in hydrodynamic conditions and consequent absolute changes in grain-size (Towe, 1974).

EARLY DIAGENESIS: HARDGROUND FORMATION

During periods of low or no sedimentation, the sediments were modified. The intensity of modification is related to the length of the abandonment periods. Several processes changed the texture and composition of the sediment.

First non-biogenic processes were active; matrix, mainly consisting of carbonate, was introduced into the sediment through mechanical infiltration. Matrix infiltration resulted in the partial geopetal filling of pores and a bimodal

Figure 3: *Photomicrograph of a thin section of a sub-hardground. The sandstone has a clast-supported framework without compactional features. Mechanically infiltrated matrix occurs on top of and between clasts. Matrix infiltration was followed by an early diagenetic rim-cementation, which borders all carbonate matrix and carbonate clasts and sometimes also siliciclastic grains. A second generation of cement, consisting of sparry low-magnesian calcite, filled the residual pores. Carbonate clasts, matrix and rim-cement were replaced by low-magnesian calcite contemporaneous with this second cementation phase. In this sample the rim-cement has been replaced pseudomorphously by low-magnesian calcite. The arrow indicates the stratigraphic facing. The scale bar is 0.5 mm. Nicols are partly crossed.*

grain-size distribution of the sandstone. Matrix infiltration was a rapid process, which could only continue due to mixing of the sediment by burrowing, since it easily blocked the pore throats for further infiltration. Most probably, the matrix was introduced into the sands by pumping action of the tides, which had a range of about 4 m (Yang and Nio, 1985).

After matrix infiltration, a fauna populated the barren surface of the sands and burrowing was initiated. The surface was colonized by a partially infaunal association of benthonic foraminifers, echinoids and gastropods. This resulted in bioturbation of the sediment, and the production and accumulation of bioclasts. Through bioturbation, the preferred alignment of clasts parallel to lamination was disturbed, laminae were mixed, and carbonate matrix material

and bioclasts were mixed with the primary sediment. Matrix that has been introduced by bioturbation displays a irregular distribution, but where present completely fills the interstitial pores. Here, the framework of the sandstone commonly is matrix-supported, and the grain-size distribution of framework components is polymodal. Altogether, a siliciclastic sand was changed into a cemented matrix- and bioclast-rich arenite or wackestone, with poor sorting due to the cumulative effect of burrowing, matrix addition and introduction of (large) bioclasts (Molenaar et al., 1988).

Afterwards, a rim-cement precipitated around clasts, especially around carbonate clasts. This resulted in the formation of hardground-like layers. In the case that the sequence of processes is visible, rim-cementation appears a later process than matrix infiltration (Fig. 3).

Based on the extent of early modifications, a distinction is made between major abandonment surfaces (called hardgrounds) and minor abandonment surfaces (called sub-hardgrounds) (Molenaar et al., 1988). Sub-hardgrounds occur as individual layers or they constitute the lower parts of hardgrounds. They are an embryonic stage of hardground development, formed when the pauses in sedimentation were of relatively short duration. The (sub-)hardgrounds are at most 0.6 m thick, which is also the maximum thickness of the nodules.

Cementation in the Roda Sandstone Member occurred in two distinct phases. An early pre-burial phase, producing a marine aragonite rim-cement, occurred exclusively below abandonment surfaces (Molenaar et al., 1988). A late calcite cementation phase occurred during later burial. Apart from the near-surface location of the early cement, originated near or at the sediment-water interface, an inhomogeneous spatial distribution might be expected as well, because flow of interstitial water was restricted to the sediment-water interface and must have been influenced by slight lateral differences in sediment characteristics. Evidence for such fluid flow is given by the mechanically infiltrated matrix. Moreover, frequently insufficient time was available for complete cementation, since pauses in the sedimentation were of limited duration in the shallow-marine environment.

Rim-cement is commonly found in association with infiltrated matrix, which is only present below former abandonment surfaces. Moreover, compactional features are absent in sandstones with rim-cement. Both factors indicate that rim-cement must have precipitated at or very close to the sediment-water interface. Submarine erosion could have removed a soft sand layer on top of a concealed (partially) lithified incipient hardground layer. The top of some major hardgrounds have been truncated. However, erosional contacts between sub-hardgrounds and overlying sediments have not been observed.

In outcrop, the three main types of sandstone can be recognized based on differences in composition and in resistance to weathering. Major

hardgrounds appear as bioclast- and matrix-rich and well-lithified calcareous layers. Sub-hardgrounds as well as the nodules are also well-lithified and resistant against weathering, whereas the non-hardgrounds appear as friable and darker coloured layers. The latter have an greater amount of peloids and dark or opaque clasts.

LATER DIAGENESIS

In samples without the rim-cement stabilizing the framework, mechanical compaction reduced the porosity from approximately 38 % to about 21 %, as calculated from percentage of cement and matrix (Table 1). Mechanical compaction was effective in reducing the primary porosity because of a high percentage of ductile grains, such as peloids. Most of the porosity reduction was accomplished by plastic deformation of these soft grains between rigid framework components. A second generation of cement precipitated after compaction. It consists of blocky, more or less equidimensional low-magnesian calcite, ranging in crystal-size from 20 to 1000 μm. Larger crystal-sizes occur in non-hardgrounds, where the cement is sub-poikilotopic. The percentage of cement is inversely related to the degree of compaction except in case of hardgrounds with large amounts of matrix. Nodules contain a high percentage of calcite cement (30.9 % in nodules, as contrasted with 27.2 % in sub-hardgrounds and 17.0 % in the heavily compacted non-hardgrounds, Table 1).

CONSTITUENTS	NODULES	HOST ROCK		
		NON-HARDGROUNDS	SUB-HARDGROUNDS	HARDGROUNDS
MATRIX %	6.7 ± 5.2	3.8 ± 9.1	4.9 ± 4.7	24.5 ± 13.7
RIM - CEMENT %	6.7 ± 4.4	0.0	2.2 ± 1.5	1.0 ± 1.5
SPARITE CEMENT % (SEC. GENERATION OF CEMENT)	24.2 ± 7.5	17.0 ± 6.9	25.0 ± 6.8	11.6 ± 8.7
BIOCLASTS %	8.2 ± 3.4	5.5 ± 3.2	9.8 ± 1.8	16.1 ± 7.3
TOTAL CARBONATE CLASTS %	23.7 ± 5.5	23.9 ± 8.7	29.0 ± 11.0	26.3 ± 13.8
TOTAL CLASTS %	62.5 ± 4.1	79.2 ± 10.5	63.6 ± 17.8	62.8 ± 9.6
TOTAL CEMENT AND MATRIX %	37.5 ± 4.1	20.8 ± 10.5	29.0 ± 11.0	37.2 ± 9.7
NUMBER OF ANALYSES	34	48	13	21

Table 1: *Mean percentages and standard deviations of clastic components and diagenetic constituents obtained by pointcounting of 250 to 300 points per thin-section.*

At present, low-magnesian calcite is the only carbonate mineral present. Later diagenesis resulted in neomorphic replacement by low-magnesian calcite of all former aragonite and high-magnesian calcite in grains, matrix and rim-cement. Replacement of rim-cement was often pseudomorphous. The pervasive replacement destroyed all chemical and isotopic evidence about the primary and early diagenetic carbonate components. The stable carbon isotopic compositions of cement and total carbonate fractions are similar throughout the sandstone bodies (Table 2). Replacement and sparite cementation was a consequence of fresh water influx during erosional phases (chapter 6).

$\delta^{13}C$	NODULES	NON-NODULES
MEAN	-1.18 (-1.24*)	-1.51 (-1.38*)
RANGE	-0.59 – -1.54	-1.00 – -4.70
ST. DEV.	0.25	0.74
NUMBER	10	25

Table 2: *Stable carbon isotope compositions of nodules and non-nodules. Asterisks mark mean carbon isotope values without the two extreme values (-0.59 and -4.70, respectively). Differences are not statistically significant.*

FORM AND LOCATION OF NODULES

Nodules are a common feature in outcrops of the Roda Sandstone Member. They occur in all types of sandstone, but are especially frequent in the non-hardgrounds. Nearly all nodules display typical (sub-)hardground features such as infiltrated or burrowed matrix, rim-cement and the absence of compactional features. Rarely nodules, which solely occur in non-hardgrounds, do not show features indicative for early modifying processes associated with pauses in sedimentation. The main distinctive features are the percentage of rim-cement and the total amount of cement. Three kind of nodules can be distinguished (Table 3):

- Type I: nodules displaying hardground or sub-hardground characteristics occurring in hardground intervals (24.1 % of the sampled nodules),

- Type II: nodules displaying sub-hardgrounds characteristics, occurring in sub-hardground intervals (65.5 %), and

- Type III: nodules without matrix or rim-cement, occurring in non-hardgrounds (10.3 %). These nodules do not display signs of compaction in contrast to their surrounding rocks. Probably they did contain

rim-cement that has been replaced non-pseudomorphously by post-compactional second phase sparry-calcite cementation, leaving no further evidence for the presence of former rim-cement.

Zones of nodules are parallel to layering and abandonment surfaces. The nodules in sub-hardgrounds and non-hardgrounds display distinct outlines and have a flattened ovoidal or more irregular form, with their long axes, 10 up to 180 cm in length, parallel to the bedding. Most nodules in hardgrounds have an irregular form. They have diffuse outlines and grade into the surrounding host rocks. The pertinent intervals are better described as nodular layers. Because of their well-lithified nature, nodules are usually more resistant to weathering than the surrounding sandstones, especially nodules in sub-hardgrounds and non-hardgrounds. Nodules may lie detached on exposed and weathered surfaces,

TYPE	NODULES	HOST ROCK	NUMBER	%
I	□	□	5	17.2
I	△	□	2	6.9
II	△	△	1	3.4
II	□	○	4	13.8
II	△	○	14	48.3
III	○	○	3	10.3

Table 3: *The distribution of nodules in the various types of host rocks and the percentage of the total amount of sampled nodules. Squares denote hardgrounds; triangles: sub-hardgrounds; circles: non-hardgrounds. Note that nodules occurring in a non-hardground host rock represent the most abundant type.*

COMPOSITION OF NODULES AS COMPARED TO THAT OF THE SURROUNDING HOST ROCKS

Siliciclastics

The primary clastics of the Roda Sandstone Member are largely siliciclastic grains and minor extrabasinal dark grey carbonate fragments. Intrabasinal light coloured carbonate grains (i.e. bioclasts) are especially associated with abandonment surfaces. The main primary content of carbonate bioclasts is approximately 5.5 % (i.e. the content in non-hardgrounds). For a large part, they were introduced into the sediment postdepositionally, as

indicated by their relation with burrows and burrowed sediments. Relative amounts and ranges of variations of various major types of siliciclastic components are similar for nodules and host rocks (Fig. 4).

	NODULES	HOST ROCK
QUARTZ	68.3 ± 9.5	67.7 ± 8.5
LITHICS	6.2 ± 2.9	6.2 ± 3.5
FELDSPARS	25.5 ± 9.5	26.1 ± 8.6
NUMBER OF ANALYSES	13	54

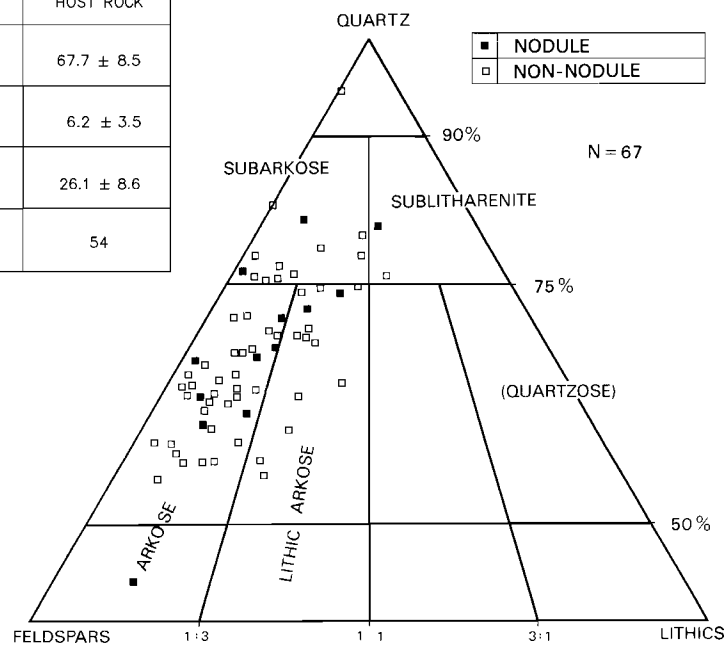


Figure 4: *The siliciclastic mineralogical compositions of nodules and host rocks. Percentages were obtained by pointcounting 300-400 points of 67 thin-sections.*
4A: *Diagram displaying compositions of nodules and host rocks with respect to primary siliciclastic grains in terms of percentages quartz (mono- and polycrystalline-quartz), lithics (mixed siliciclastic- carbonate clasts, extrabasinal carbonate clasts, siltstone and sandstone clasts, biotite, chlorite and chert grains) and feldspars. The triangular diagram is constructed according to the modified classification of Folk (1968).*
4B: *Mean and standard deviations of percentages quartz, lithics and feldspars of nodules and host rocks.*

Apart from standard petrography methods, the detrital quartz grains in nodules and host rocks were characterized by determining its thermal behaviour, i.e. by characterizing the low- to high-quartz inversion. The temperature of inversion as well as the inversion reaction rate were measured by differential scanning calorimetry (DSC). The behaviour during thermal treatment is typical for the various kinds of quartz (Smykatz-Kloss, 1970, 1971, 1974; Molenaar and

de Jong, 1987). Results are depicted in Figure 5, whereas the various measured thermal parameters are summarized in Table 4. The similarity of the inversion temperatures as well as the shape of the DSC curve and the inversion reaction rate, expressed by the onset reaction slope in Figure 5, suggest an identical clastic source for all quartz grains in all sandstones.

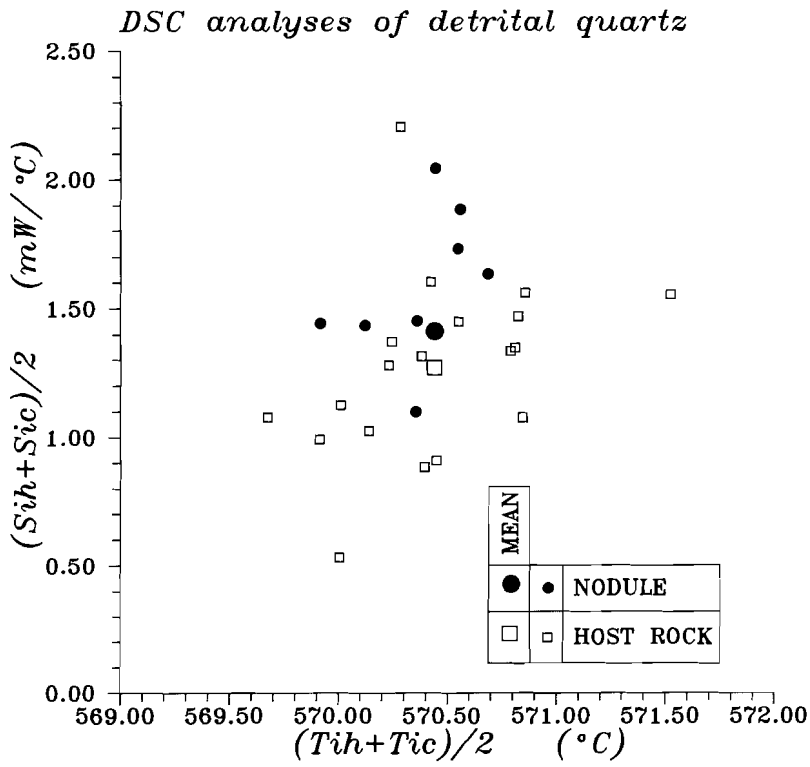


Figure 5: *The inversion temperatures of detrital quartz from nodules and host rocks are displayed against the reaction rates. Both parameters were measured up on heating by DSC. The inversion temperature gives an estimate of the equilibrium reaction temperature, whereas the reaction rate represents the form of the DSC curve. The reaction rate, which can be characterized by defining the onset slope of the curve, is independent of the amount of sample being analyzed (Molenaar and de Jong, 1987) and is expressed as mW/°C. There is no significant difference between the quartz in nodules and that in the host rocks.*

THERMAL PARAMETERS OF QUARTZ INVERSION	NODULES	HOST ROCK
Ti_H : TEMPERATURE OF QUARTZ INVERSION ON HEATING °C	570.38 ± 0.39	570.21 ± 0.60
Ti_C : TEMPERATURE OF QUARTZ INVERSION ON COOLING °C	570.50 ± 0.26	570.67 ± 0.32
ΔTi : $Ti_H - Ti_C$ °C	−0.12 ± 0.33	−0.44 ± 0.48
$\overline{Ti}$: $(Ti_H + Ti_C)/2$ °C	570.44 ± 0.29	570.44 ± 0.42
Si_H : INVERSION RATE ON HEATING mW/°C	1.492 ± 0.344	1.150 ± 0.360
Si_C : INVERSION RATE ON COOLING mW/°C	1.584 ± 0.272	1.380 ± 0.470
$\overline{Si}$: $(Si_H + Si_C)/2$ mW/°C	1.537 ± 0.299	1.270 ± 0.350
ΔSi : $Si_H - Si_C$ mW/°C	−0.090 ± 0.162	−0.220 ± 0.460
MEAN GRAIN-SIZE m	318 ± 93	311 ± 53
NUMBER OF ANALYSES	9	19

Table 4: *The mean values and standard deviations of various measured thermal parameters of nodules and host rocks are summarized. Both the inversion temperature and the rate of the inversion reaction are variable and dependent on the chemical conditions during growth of the quartz. The inversion of quartz grown in a distinct and narrow range of environmental conditions is a rapid reaction. To the contrary, quartz grown during a long period with changing conditions displays a broad range of inversion temperatures. Consequently, the inversion characteristics of detrital quartz are dependent on the kind of quartz and the amount of different types of quartz present.*

Bioclastics

Bioclasts are usually associated with burrows or are present in burrowed sediments. The total content of bioclasts increased during hardground formation (Table 5). The content of bioclasts in nodules and sub-hardgrounds is significantly higher (8.2 ± 3.4 and 9.8 ± 1.8 %, respectively) than in non-hardgrounds (5.5 ± 3.2 %). The content in hardgrounds is even higher (16.1 ± 7.3 %). This confirms the continuation of bioclast addition through bioturbation. In nodules, 38 % of the grains are carbonates, whereas in non-hardgrounds the relative percentages of carbonate grains accounts for 30 % only.

The assumed primary mineralogical composition of the bioclasts in the various types of sandstones and nodules is shown in Table 5. Gastropods and part of the bivalves are supposed to have been composed by aragonite; alveolinids, miliolinids and echinoids by high-magnesian calcite; and nummulitids, assilinids, discocyclinids and another part of the bivalves by low-magnesian calcite. The composition of bioclasts in nodules, non-hardgrounds and sub-hardgrounds is not significantly different. The faunal assemblage in nodules and non-hardgrounds is identical. Hardgrounds, to the contrary, contain more aragonite components (predominantly gastropods and bivalves) than the other types of sandstone. The fauna association changed with increasing time of non-deposition.

The amount of infiltrated and burrowed matrix

Percentages of matrix, i.e. non framework components smaller than 50 μm, are given in Table 1. The amounts of infiltrated and burrowed matrix in sub-hardgrounds and nodules are similar. In contrast, hardgrounds contain a significant greater percentage of matrix. Large amounts of matrix in the hardgrounds are consistent to the hypothesis that burrowing and matrix infiltration continued for a considerable amount of time here. On the contrary, nodules did not experience such intense bioturbation.

Primary grain-size distribution

In order to compare the primary grain-size distributions in the different diagenetic units of the Roda Sandstone Member it was necessary to restrict analyses to the fraction larger than 50 μm. Infiltrated and burrowed matrix, primary carbonate clasts, such as carbonate extraclasts and some of the bioclasts, and postdepositionally introduced grains, especially bioclasts, were removed by hydrochloric acid treatment. Results are summarized in Table 6. The fraction smaller than 10 μm, derived from matrix and peloids, which both contain some clayey material, consists of quartz, feldspars, smectite, illite and kaolinite (Fig. 6).

The general character of the siliciclastic grain-size population of nodules and host rocks is similar. Early cemented layers or nodules display a mean grain-size range similar to the surrounding rocks (Fig. 7A). Only the skewness and quartile deviations of siliciclastics in nodules and host rocks are statistically significantly different. However, a comparison of samples from the same section shows subtle differences in the characteristics of the grain-size distributions (Fig. 7B and 7C). The kurtosis, skewness and sorting coefficients indicate a slightly better sorted sand in the nodules than in the surrounding sandstones. Within nodules, the range of grain-sizes is narrower, i.e. the standard deviation is smaller, whereas the range is more symmetrically distributed around the mean. Moreover, often the mean grain-size of nodules is slightly larger (Fig. 7D).

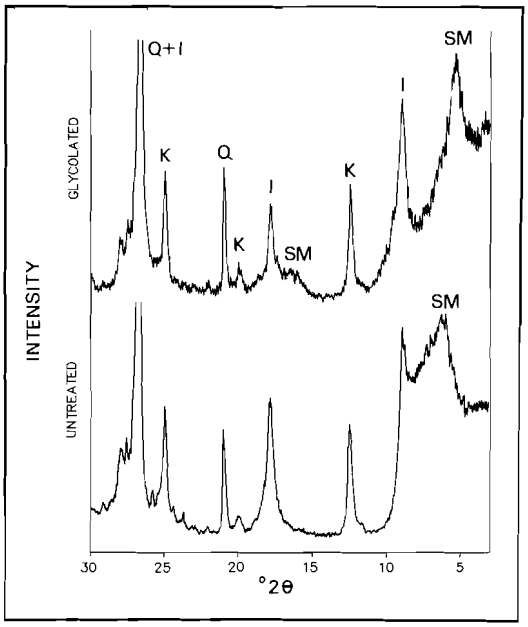
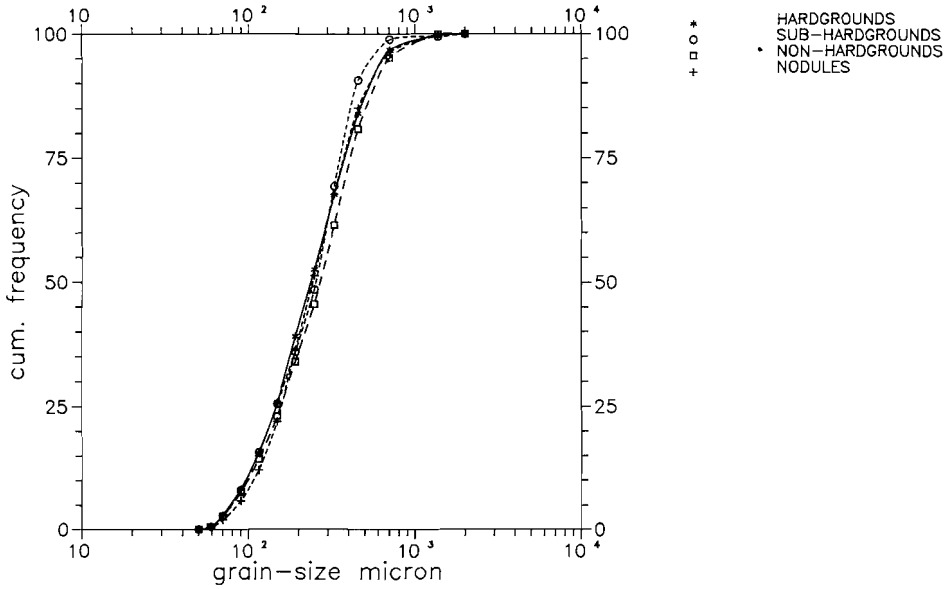


Figure 6: *Typical example of clay mineral composition as determined with X-ray diffractometry (untreated and ethylene glycol saturated). Analyses included also difractometry after heating to 500 °C for eight hours. SM: smectite; K: kaolinite; I: discrete illite; Q: quartz. The same clay minerals occur in all studied samples (N=8), although the amounts are variable.*

DISCUSSION

The total amount of late cement in the Roda Sandstone Member was determined by the absence or presence and the amount of early stabilizing rim-cement below abandonment surfaces and thus by the amount of mechanical compaction and open pore space where late cement could precipitate. The increased percentage of calcite cement of nodules with respect to the surrounding sandstone and the resulting well-lithified nature is undoubtedly the main reason for their enhanced resistance against weathering. The origin of nodules, which contain distinctly higher amounts of rim-cement than the surrounding host rocks, is thus linked to the process of rim-cementation during pauses in the sedimentation. Local differences in the factors controlling this rim- cementation caused differences in the amount and timing of rim-cementation. Variations in one or more particular sedimentary parameters were responsible for a "spot-like" initiation of and differences in the intensity of the various hardground forming processes, although these processes were always bounds to planar abandonment surfaces. Parameters which might have controlled the beginning of rim-cementation are texture, mineralogical

A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NON-HARDGROUNDS
NODULES

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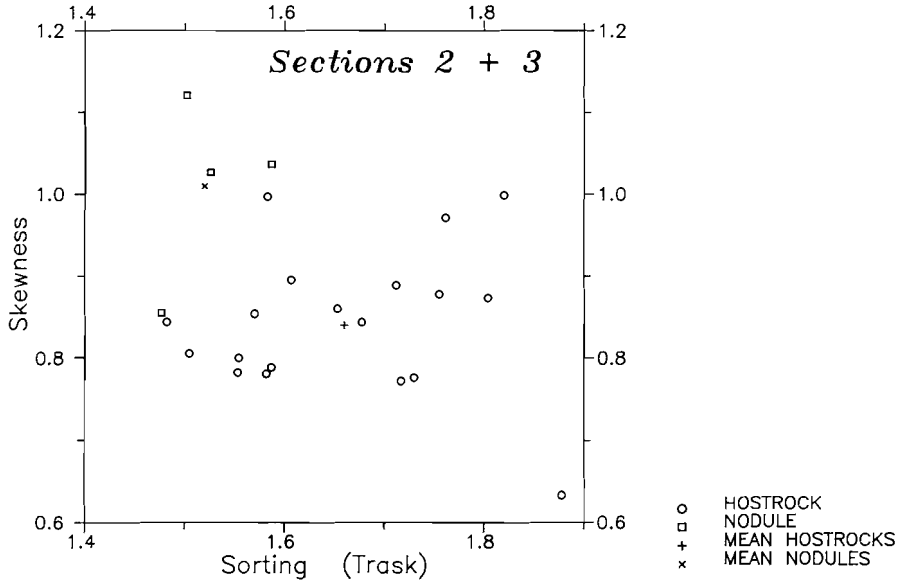
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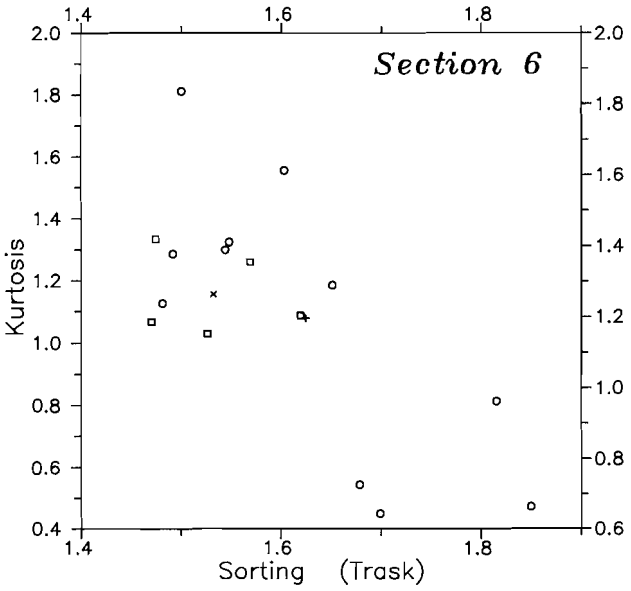
MEAN NODULES

C


Section 6
Kurtosis
Sorting (Trask)
1.4
1.6
1.8
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4

D

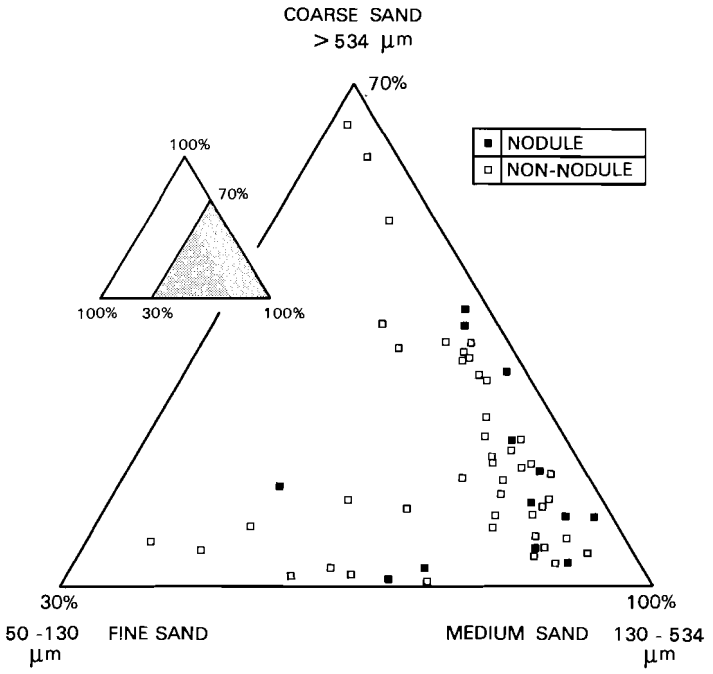

COARSE SAND
> 534 µm
70%
100%
70%
100%
30%
100%
NODULE
NON-NODULE
30%
100%
50 -130 µm
FINE SAND
MEDIUM SAND
130 - 534 µm

Figure 7: *Grain-size properties of nodules and host rocks as measured with a laser particle sizer. The fraction larger than 50 μm of 61 samples was used, in order to exclude postdepositional modifications induced by the addition of matrix and variations in the content of peloids and other micritic grains. Grain-size parameters have been calculated in μm.*

7A: *Mean cumulative frequencies of the grain-size distributions of hostrocks, subdivided into hardgrounds (N=13), sub-hardgrounds (N=4) and non-hardgrounds (N=31), and nodules (N=13) are plotted against grain-size in micron. The similarity of all frequency distributions suggests one common siliciclastic source during deposition of the various types of sandstone. Systematic differences related to postdepositional alteration of the sand below abandonment surfaces are not evident.*

7B: *Sorting coefficients (Trask, 1930) are plotted against skewness (Trask, 1930) for samples of section 2 and 3 (selected as being representative). Nodules have a slightly better sorting and a more positive skewness.*

7C: *Sorting coefficients (Trask, 1930) are plotted against Kurtosis (Folk and Ward, 1957) for samples of section 6. Nodules seem to have a more uniform grain-size distribution than the directly surrounding host rocks.*

7D: *Grain-size distributions of siliciclastics in nodules and host rocks are expressed as percentages of silt to very fine sand (50-130 μm), fine to medium sand (130-534 μm) and coarse sand (>534 μm) fractions. There is no significant distinction between nodules and host rocks.*

Figure 8: *Nodules occur in a horizon which is parallel to the coset boundaries. The individual nodules are lensoid and parallel to the mega cross-bedding. The hammer measures 33 cm.*

composition, permeability and porosity, degree of bioturbation and matrix content. One or a combination of these parameters must have controlled the initiation and eventual degree of early rim-cementation, and thereby the total amount of compaction and cementation. Differences in composition and/or texture may be primary, related to depositional processes, or, more likely, secondary, and due to early postdepositional modifying processes. Several possibilities will be discussed.

Differences in primary clastic composition

Local variations in hydrodynamic conditions cause differences in grain-size and grain-size distribution as well as variations in the mineralogical composition of sands. The availability of clastic grains in the various size-fractions and their specific grain-density consequently determine the composition of the sediment as a result of changes in the hydrodynamic conditions during deposition and grain (or mineral) sorting during transport.

The uniformity of the siliciclastic grain composition throughout the Roda Sandstone Member excludes large variations in the primary source with respect to spatial differences in primary composition of nodules and host rocks.

Primary grain-size distribution

Slight variations in the porosity and permeability, caused by differences of the grain-size distribution, are a possible explanation for local variations in the amount of early rim-cement. Permeability controlled the flow of pore water, and thus the cementing agents, through the sandstone. Both porosity and permeability are dependent on sorting and mean grain-size. Porosity is maximal in medium sand, and increases with increasing sorting. Permeability increases with the degree of sorting and increasing median grain-size (Beard and Weyl, 1973; Fig. 3 of Leeder and Park, 1986). Local or regular variations in grain-size and grain-size distributions might have generated zones with a maximum permeability, through which a preferential flow of interstitial water would have occurred. In such a case, early cementation would have been initiated in zones with a high porosity and permeability.

The sand in nodules is slightly better sorted and often slightly coarser than in the surrounding sandstone. Therefore, the nodules may represent points where a relatively high primary porosity and permeability could have favored rim-cementation if other boundary conditions were suitable. Burrowing and matrix infiltration lasted for a longer time in the host rocks. The worse sorting and smaller grain-size in the host rocks could be due to the prolongation of the addition of fine-grained material and especially the homogenizing effect of sediment bioturbation. The addition of fine-grained material to the sediments surrounding the nodules would have inhibited precipitation of rim-cement. However, there is no consistent trend in sorting and grain-size from

	ARAGONITE BIOCLASTS %	HIGH–MAGNESIAN CALCITE BIOCLASTS %	LOW–MAGNESIAN CALCITE BIOCLASTS %	NUMBER OF ANALYSES
NODULES	7.1 ± 6.9	53.6 ± 20.0	39.3 ± 18.7	21
HARDGROUNDS	29.7 ± 23.3	46.5 ± 23.8	23.8 ± 3.7	5
SUB–HARDGROUNDS	6.8 ± 6.5	69.6 ± 5.8	23.7 ± 6.0	5
NON–HARDGROUNDS	5.7 ± 10.5	67.6 ± 19.4	26.7 ± 15.6	19

Table 5: *Variations in the total amount of bioclasts and in the inferred original mineralogical composition of bioclasts subdivided into aragonite (gastropods and part of the bivalves), high-magnesian calcite (alveolinids, miliolinids and echinoids), and low-magnesian calcite (nummulitids, assilinids, discocyclinids and part of the bivalves). Mean values and standard deviations were calculated for a 100 % bioclasts composition. Percentages were obtained by pointcounting of 250 to 300 points per thin-section.*

GRAIN–SIZE PARAMETERS	NODULES	HOST ROCK	FORMULA AND REFERENCE	
SORTING COEFFICIENT	1.542 ± 0.083	1.693 ± 0.364	$\sqrt{(P75/P25)}$	TRASK (1930)
QUARTILE DEVIATION	127.2 ± 47.3	155.1 ± 69.5	(P75–P25)/2	KRUMBEIN & PETTIJOHN (1938)
QUARTILE COEFFICIENT	0.178 ± 0.126	0.124 ± 0.091	(P25–2*P50+P75)/(P75–P25)	
SKEWNESS	0.974 ± 0.101	0.843 ± 0.125	$(P25*P75)/P50^2$	TRASK (1930)
SKEWNESS	0.274 ± 0.134	0.231 ± 0.114	(P16+P84–2*P50)/(2*(P84–P16))+ (P5+P95–2*P50)/(2*(P75–P25))	(1957) FOLK & WARD
KURTOSIS	1.228 ± 0.266	1.151 ± 0.406	(P95–P5)/(2.44*(P75–P25))	FOLK & WARD (1957)
MEDIAN	288.7 ± 98.4	305.0 ± 118.6	P50	TRASK (1930)
NUMBER OF ANALYSES	13	48		

Table 6: *Results of grain-size measurements by a laser particle sizer. Grain-size distribution parameters of nodules and host rocks are characterized by mean values and standard deviations.*

non-hardgrounds to nodules and eventually to hardgrounds. The absence of a trend suggests that the differences in grain-size distributions between nodules and surrounding rocks are a primary property.

Primary bioclastic composition

When the slight differences in the siliciclastic grain-size distributions between nodules and host rocks are the effect of depositional processes, then these differences could have been associated with slight variations in the content of extrabasinal and primary intrabasinal carbonate grains. The specific weight of carbonate is higher than the most of the siliciclastics present. Carbonate grains should therefore behave differently during transport and sedimentation. Most carbonate clasts in the Roda Sandstone Member consist of skeletons with large internal voids. In this case, a larger bioclast will have a similar grain-density and fall velocity as a smaller quartz or feldspar clast. An effect could be that carbonate grains were concentrated in specific locations and/or levels of the sedimentary sequence. There they could have preferentially induced nucleation of cement without any substantial secondary enrichment of bioclasts during pauses in sedimentation. Such primary hydraulic accumulations of bioclasts in clusters or layers can cause localized or differential carbonate cementation (e.g., Chafetz, 1979; Kantorowicz et al., 1987; McBride, 1988). Although these differences can not be totally excluded, they do not seem to be very likely considering the results depicted in Figure 7D. The triangular diagram (Fig. 7D) displays the fractions very fine sand, fine and middle sand, and coarse sands of nodules and host rocks. In general, there is no significant distinction between nodules and host rocks.

Depositional environment and variations in permeability

Primary differences in permeability in the Roda Sandstone Member can have been caused by the sedimentary depositional structures and sequences. Different sites on the large transverse or longitudinal bars were dominated by characteristic hydrodynamic conditions. According to these conditions, different sites have different grain-size distributions. Fore example, toe-sets of giant foresets contain sediment which has accumulated by suspension fall out as well as coarser grains associated with the avalanching the foresets. As a result, the permeability should be slightly less in toe-sets than higher in the same sets, where only traction transported grains accumulated. In the top part, individual foresets have a greater height because of a shallower depth (Nio and Yang, 1983) and consequently higher flow rates caused deposition of coarser-grained sand. Where preserved, the upper parts of large bed forms should be more suitable for the development of early cement. These persistent porosity and permeability trends in the depositional sequences probably constrained the flow of interstitial water during pauses in sedimentation and limited rim-cementation to the uppermost superficial parts of the sandstone bodies. Such a dependency between early cementation and primary textures has been demonstrated by a

study of James (1985).

In some cases nodules are arranged in horizons at the top of the sets, whereas the long axes of individual nodules are aligned according to large scale foresets (Fig. 8). The form of a nodule thus may be determined by directional differences in permeability as was also demonstrated by Pirrie (1987). A directional anisotropy can be a consequence of layering, lamination, preferred orientation of elongate or platy clasts. An elongate oblate form has been observed in sub-hardground nodules, where part of the primary clast-orientations parallel to the cross-bedding have been preserved. Nodules with hardground characteristics do not show any regular form. This probably is a consequence of intensive bioturbation that disturbed the primary clast orientation and lamination completely and/or of the irregular nature of the burrowed zone.

Variations in the content of organic material

Organic material might locally have accumulated due to depositional processes and/or biological activity, such as suspension feeding activity. Degradation of organic material can cause increased CO_2 concentrations (Berner, 1981). Biological reactions, which use organic matter for their metabolism, are important pH modifying agents. It is, however, questionable if, under normal marine conditions and concentrations of organic matter, dissolution or precipitation of $CaCO_3$ can be induced. According to studies of Kocurko (1986), precipitation of early cement may possibly occur due to oxidation of organic matter. Anaerobic methane oxidation may cause localized carbonate precipitation (Raiswell, 1987). Usually, the latter process is accompanied in the marine environment by the authigenesis of pyrite due to sulphate reduction (Berner, 1981; Raiswell, 1987). Pyrite has not been observed in the Roda Sandstone Member, suggesting oxidizing conditions.

If any carbon derived from fractionated organic material is incorporated into a carbonate cement, than this cement should have a light carbon isotopic composition. Carbon isotopic compositions of cement and total carbonate fraction of host rocks and nodules are not significantly different in the Roda Sandstone Member (Table 2). However, present isotope compositions are not a good measure of primary composition because of the almost total replacement of primary and early diagenetic carbonate components by a later diagenetic low-magnesian calcite. The replacement was pervasive and probably destroyed any evidence of initial anomalous carbon isotope composition.

Local variations in the amount of postdepositionally introduced bioclasts

Apart from the availability of time needed for early rim-cementation, a second restricting condition, already mentioned, is the presence of suitable nuclei for precipitation of cement. If nuclei are absent, the degree of

supersaturation needed is too high for most natural environments. Most of the carbonate clasts in the Roda Sandstone Member were introduced into the sand during pauses in sedimentation. The content of postdepositionally introduced carbonate clasts probably is approximately proportional to the time of non-deposition. Carbonate clasts were predominantly produced within the basin, or upon the pertinent abandonment surfaces. The main difference in the composition of various types of sandstones was caused by the postdepositional change in composition due to the introduction of bioclasts by burrowing. These carbonate bioclasts and also micritic intrabasinal carbonate clasts, such as peloids and aggregate clasts, were preferentially used as nucleation sites during early rim-cementation. Siliciclastic grains were also covered with rim-cement only in case that rim-cementation was very intense and the percentage of rim-cement is high. Probably this occurred when the pause in sedimentation was relatively long. As the content of bioclasts increased in proportion to time of non-deposition, nuclei for rim-cementation became more abundant. A locally enhanced bioclast content probably induced an increase in the degree of rim-cementation.

On the other hand, processes which retard or inhibit active cementation, such as reducing conditions and the consequent preservation of cement-inhibiting organic coatings on carbonate clasts, could also be important.

Apart from the duration of non-deposition, the amount of introduced carbonate clasts is dependent on the environmental factors which determine the development of an epi- and infauna association. Also the fauna association, and thus the mineralogy of the bioclastic components, may change depending on the environmental conditions. The mineralogy, aragonite or high-magnesian calcite, determines the suitability of bioclast for nucleation purposes. Bioclasts can also act as nucleation sites for precipitation of the second cement generation. Moreover, an increased content of aragonite induced local supersaturation with respect to calcite during introduction of meteoric water and subsequent dissolution of aragonite. Replacement and second phase cementation is likely to have started on places with a high content of aragonite. Both the presence of more nuclei and a consequent local higher supersaturation explain the smaller crystal sizes of sparry calcite cement in sub-hardgrounds and hardgrounds as compared with non-hardgrounds.

Differences in the amount of matrix

Matrix blocks the connections between pores and thus decreases the permeability. The permeability is inversely proportional to the amount of matrix. The presence of infiltrated or burrowed matrix should thus increase the time needed for the development of rim-cement, since matrix infiltration was an earlier process than rim-cementation. On the other hand, since the matrix consisted primarily of carbonate micrite, it also amplified the suitability for rim-cementation by enlarging the availability of precipitation nuclei and therefore created preferential sites of rim-cementation. The increased amount of

matrix in hardgrounds (24.5 ± 13.7 %; N=21) apparently did not inhibit rim-cementation. Therefore, the lower permeability was compensated for by the larger amount of nuclei.

ORIGIN OF THE NODULES

Nearly all nodules in the Roda Sandstone Member are affiliated with abandonment surfaces and the penecontemporaneous processes which were active below them (Table 3). These processes converted the sediment below abandonment surfaces into hardgrounds. Nodules resulted from relatively high amounts of rim-cement that prevented compaction, and, as a consequence, the large total amount of second generation calcite cement. Nodules were thus initiated during very early diagenesis. Initial primary differences in the sediment have been accentuated during later diagenesis, by relatively less compaction and greater secondary cementation than the host rocks, and during recent weathering.

Beginning stage of hardground formation: Cementation began at separate sites, representing possible future nodules, depending on the availability of suitable nucleation sites for precipitation and on local differences in porosity and permeability. The latter governed the flushing of the sediment with water and thus regulated the supply of chemicals for rim-cementation. Nodules contain rim-cement, and some contain infiltrated matrix. Matrix-infiltration and rim-cementation were earlier processes than massive bioturbation. After a short phase of matrix-infiltration, rim-cementation began and blocked the pores for further infiltration, which continued in the surrounding sediments. Subsequently, the barren surface became inhabited by a fauna that burrowed the surface layer, especially adjacent to nodules.

Intermediate stage: When a pause in sedimentation prolonged, individual nodules aggraded into continuous layers. Layers developed through continuing rim-cementation and burrowing. The layers contain rim-cement and have a slightly increased content of bioclasts and infiltrated matrix. This is the sub-hardground stage. Nodules may still remain as discrete entities within these layers.

Final stage: Continuing bioturbation totally disrupted the original texture and structure of the sediment, which became increasingly enriched in bioclasts and matrix. Where cementation was locally abundant, this resulted in nodular laterally continuous hardgrounds. These places could withstand burrowing organisms and pores were obstructed for further matrix infiltration. The differentiation between nodules and host sandstone is at a climax.

Present situation: The intensity of deformation of non-hardgrounds and (sub-)hardgrounds is different. The framework of the latter was at most slightly elastically deformed. To the contrary, deformation of the non-hardgrounds was accomplished by plastic deformation (squeezing) of the

ductile clasts, like carbonate intraclasts, also during burial. The second phase of cementation was completed first in the nodules, slightly later followed by cementation of the surrounding (sub-)hardgrounds and non-hardgrounds, respectively. This resulted in differences in the amount of plastic and elastic deformation. As a result of recent decompaction, dilation cracks developed between the different types of sandstone. The various parameters determining the kind and amount of deformation during burial compaction vary only little and laterally gradual within any given horizon of the sandstone bodies. At a certain point, critical with respect to elastic behaviour, dilatation cracks developed along planes separating well-lithified (sub-)hardgrounds intervals and compacted non-hardgrounds. The sharp boundaries of nodules and layers are accentuated by recent weathering, since dilatation cracks are preferential infiltration paths for meteoric water. The rounded forms of nodules are due to enhanced weathering along intersections between abandonment parallel and perpendicular cracks.

Furthermore, differential behaviour during weathering is also caused by slight differences in the crystal-size of the second generation of cement. In (sub-)hardgrounds and nodules the cement has a smaller crystal size and form a firm interlocking lithifying agent. In the non-hardgrounds however, the sub-poikilotopic cement is not very coherent. In addition, present day contact with meteoric water causes renewed swelling of the smectite clay.

SUMMARY

Nodular features originated through slight differences in sorting of the sediments and the presence of more carbonate nuclei. Subtle variations in the timing and degree of early rim-cementation caused differences in the amount of mechanical compaction and, therefore, in the amount of post-compactional sparry calcite cement. Present visibility of the nodules is caused by the variable susceptibility to present-day weathering.

ACKNOWLEDGEMENTS

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CHAPTER 6

CALCITE CEMENTATION IN SHALLOW MARINE EOCENE SANDSTONES AND CONSTRAINTS OF EARLY DIAGENESIS.

N. MOLENAAR

ABSTRACT

The Lower Eocene shallow-marine Roda Sandstone Member forms part of the Paleogene fill of the Tremp-Graus Basin in the southern Spanish Pyrenees. It is composed of mixed siliciclastic-carbonate sandstones that were severely modified in composition and texture shortly after deposition during pauses in sedimentation. Moreover, part of the sand was lithified by an early marine rim-cement. This early diagenetic cement stabilized the sandstone framework, and counteracted mechanical compaction. Where early cement was absent, mechanical compaction severely reduced the primary porosity during a first burial phase. Ductile grains were squeezed between rigid grains, obstructing pore connections. This caused the development of distinct porosity patterns in the sandstone bodies. After the first burial phase, two major phases of uplift and erosion resulted in the truncation of the Roda Sandstone Member in the northern part of the area studied. After the erosional phases, the sandstones were buried again. Recharge of the sandstone bodies with fresh water caused replacement of aragonite and high-magnesian calcite by low-magnesian calcite. Simultaneously, a second generation of sparry calcite cement was precipitated. Replacement and cementation were completed first in the most porous and permeable levels represented by those parts of the sandstone that contained the early cement. The compacted intervals were cemented later or cementation was completed later.

INTRODUCTION

Carbonate cementation is an important porosity reducing process in sandstones, but also can act as a porosity preserving agent. As this process becomes better understood, the prediction of reservoir properties becomes easier.

The shallow-marine Lower Eocene (Ypresian) Roda Formation in the Isábena Valley (Figs. 1 and 2) belongs to the Paleogene fill of the Tremp-Graus Basin (Mey et al., 1968; Schaub, 1973; Nijman & Nio, 1975; Jimenez, 1988), one of the southern Pyrenean foreland segments. The lithostratigraphy of the Tremp-Graus Basin is shown in Figure 2. The Roda Sandstone Member, forming the lower member of the Roda Formation, was examined in order to define

controls of porosity-permeability properties resulting from early diagenetic modification or later diagenesis. The Roda Sandstone Member consists of several vertically-stacked sandstone bodies with maximum individual thicknesses of about 30 m. These sandstone bodies, with a mixed siliciclastic-carbonate composition, are interbedded with silty marls.

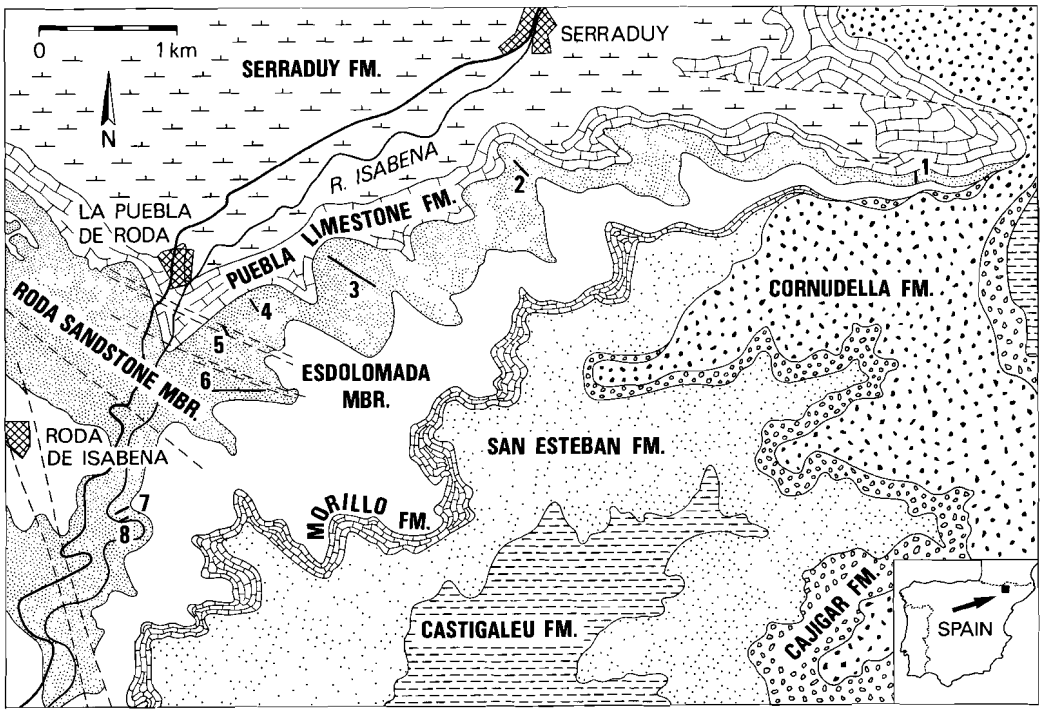


Figure 1: *Geological sketch map of the northern part of the Isábena valley, southern Pyrenees, Spain. Numbers refer to sample locations. A core was drilled near location 6. The map location is shown on the inset.*

METHODS

A total of 131 samples were taken from eight outcrops and one short core of the two major sandstone bodies of the Roda Sandstone Member (Fig. 1). These were thin sectioned and stained for ferroan carbonate according to the method described by Dickson (1966).

Carbonate and clay mineralogy were determined by means of powder X-ray diffractometry (XRD, using Cu-K_α). Contents of Ca, Mg, Sr, Mn and Fe

in sparite cement and grains in 18 samples were verified by electron microprobe (energy dispersive and wave length dispersive X-ray analyses) analyses on polished thin sections.

Sparry calcite cement from 14 samples and the bulk carbonate fraction of 19 samples were analyzed for stable oxygen and carbon isotope compositions. Carbon dioxide, liberated from 4 to 12 mg samples by reaction in vacuo with 100 % H_3PO_4 for 4 hours at 25 °C, was analyzed on a Micromass 602C constant ratio mass spectrometer.

The grain-size distributions of the siliciclastic components of several samples, separated with hydrochloric acid, were measured using a Malvern 3600D laser particle sizer.

The effective porosity of 28 samples was determined. After determination of sample volume and weight, samples were saturated with carbon tetrachloride (CCl_4) and weighted again. This gives the weight and thus the percentage of interconnected pores.

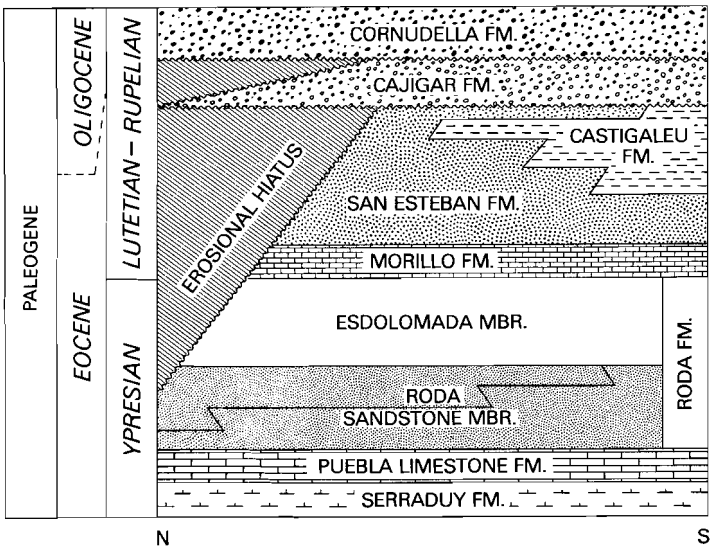


Figure 2: *Schematic lithostratigraphy of the Tremp-Graus Basin in the Isábena Valley along a north-south section. Erosional surfaces and hiatuses are indicated (after Mey et al.; 1968; Schaub, 1973; Nijman & Nio (1975)). Used symbols are the same as those of Figure 1.*

DEPOSITIONAL ENVIRONMENT AND STRATIGRAPHY

The basal part of the Roda Sandstone Member is composed of silty and sandy shale with several thin intercalations of sandy limestone. The upper part, attaining a thickness of approximately 40-65 m, consists of several major, medium- to coarse-grained sandstone bodies separated by sandy to silty marls and siltstones. The sandstone bodies were deposited as part of estuarine tidal-delta complexes on a shallow shelf (Yang & Nio, 1985). Rich and diverse fossil associations attest to a normal salinity and oxygen concentration. On the inner shelf, deposition was dominated by the migration of large tranverse tidal bars. The preserved sedimentary structures are well-defined cosets of very large and extensive low-angle cross-beds with set heights of up to 4 m, and cosets of megaripple cross-beds with set heights of 0.2 to 1.0 m. Progradation of transverse sand bars due to ebb-tidal currents in an estuarine mouth area produced very large sets of high-angle cross-bedding with set heights up to 10 m. A part of the sedimentation occurred through lateral migration of meandering estuarine channels. This resulted in deposits characterized by fining-upward sequences consisting of cosets of tabular mega-cross-bedding at its base, with complete tidal bundle sequences preserved (Nio et al., 1983; Yang & Nio, 1985) and tidal delta lobes.

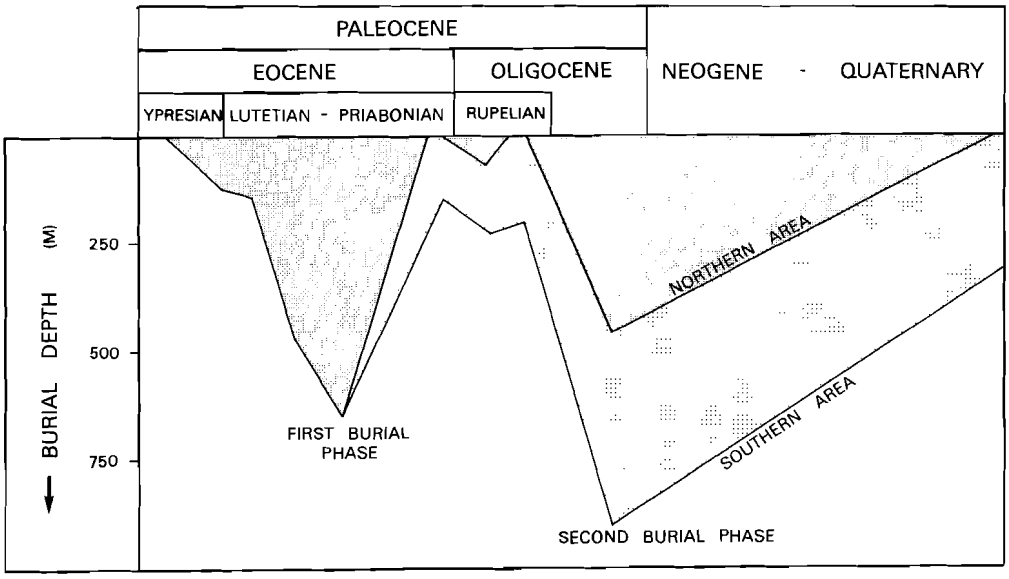


Figure 3: *Graph showing the burial history of the Roda Sandstone Member.*

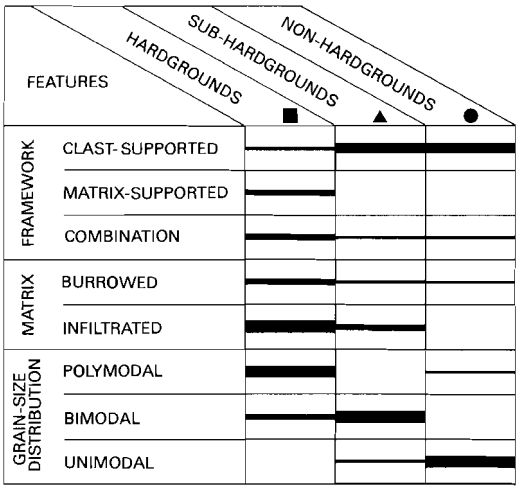


Figure 4: *Summary of characteristic fabric features of hardgrounds, sub-hardgrounds and non-hardgrounds. The thickness of a bar is proportional to the importance of the process or feature. A quantification of various constituents is given in Table 1.*

EARLY MODIFICATION

The progradation of transverse sand bars and tidal delta lobes was not always continuous and frequently it ceased for a variable lenght of time. During periods of low or absent sedimentation, the sediments of the top part of a depositional unit and even the slopes of large fore-sets were modified to a degree, proportionally increasing with the length of abandonment time. Several processes, whih have been desribed by Molenaar et al. (1988) were active, which changed the texture and composition of the sediment. Summarizing the various processes active during pauses in sedimentation:

- an increase in the matrix content through bioturbation and mechanical infiltration;
- the disturbance of the primary texture through bioturbation;
- an increase in the content of carbonate bioclasts through infaunal activity;
- a general decrease of sorting due to the accumulated effect of burrowing, increase in matrix content, and addition of (large) bioclasts;
- the stabilization of the framework through rim-cementation.

Altogether, half of the siliciclastic sand was changed into a matrix and bioclasts-rich sandstone, or even into a mixed siliciclastic-carbonate rock during early diagenesis.

A tripartite subdivision of the sandstones was made, reflecting differences in the duration of pauses in the sedimentation (Table 1 and Fig. 4)

% CONSTITUENTS	HARDGROUNDS	SUB-HARDGROUNDS	NON-HARDGROUNDS
BIOCLASTS	20.7 ± 13.9	8.3 ± 3.8	4.5 ± 3.9
TOTAL CARBONATE CLASTS	25.6 ± 13.1	25.3 ± 8.0	23.8 ± 8.6
TOTAL SILICICLASTICS	5.7 ± 3.6	38.8 ± 5.8	55.3 ± 11.9
TOTAL CLASTS	61.8 ± 9.6	62.8 ± 10.5	79.1 ± 10.3
MATRIX	24.4 ± 13.3	6.1 ± 5.1	3.8 ± 9.0
RIM-CEMENT	1.1 ± 1.4	5.3 ± 4.2	0.0
SECOND GENERATION CEMENT	12.6 ± 8.7	24.5 ± 7.3	17.1 ± 6.8
TOTAL CEMENT AND MATRIX	38.2 ± 9.7	35.9 ± 5.9	20.9 ± 10.3
NUMBER OF ANALYSES	25	42	49

Table 1: *Quantification of characteristic features of hardgrounds, sub-hardgrounds and non-hardgrounds. Percentages are based on data obtained by thin section point counting.*

(Molenaar et al., 1988). A distinction was made between hardgrounds and sub-hardgrounds as opposed to non-hardgrounds. Hardgrounds are the modified parts below major abandonment surfaces where the period of non-deposition was relatively long ad processe were intense. Sub-hardgrounds represent relatively short periods of non-deposition, and are therefore regarded as incipient hardgrounds. The lower part of major hardgrounds may have the same appearance. Hardgrounds and sub-hardgrounds were lithified by a rim-cement during the pauses in sedimentation. Whenever sedimentation was more or less continuous, the sandstones were not modified and are referred to as non-hardgrounds. An interpretation is depicted in a profile through a complete hardground in Figure 6. The tripartition is manifested in outcrop morphology and weathering patterns of the sandstones. In outcrops, hardgrounds and sub-hardgrounds appear as well-lithified and weathering resistant horizons, whereas non-hardgrounds are friable and easily weathering.

SANDSTONE PETROLOGY

The composition of extrabasinal clastics, mainly comprising siliciclastics, is constant for all sandstone samples of the Roda Sandstone Member (Table 2) (Molenaar et al., 1987). The mean sandstone composition falls within the (quartzose) subarkose field (Folk, 1968). Minor amounts of coarse crystalline carbonate rock fragments and mixed siliciclastic-carbonate silt grains are present. They are probably of extrabasinal origin because of their texture and

rigid behaviour during compaction. Some of the samples can be classified more accurately as sandy peloidal-bioclastic packstones to wackestones. Marked differences in the various sandstones are only manifested by changes in the percentages of bioclasts, which were admixed during pauses in sedimentation. Most of the bioclasts were originally composed of high-magnesian calcite (e.g., echinoids and test of porcellaneous imperforate foraminifers such as alveolinids and miliolinids) or aragonite (e.g., gastropods). Other carbonate clasts are peloids and aggregate grains (according to Flügel, 1982). The latter are grapestones, i.e. faecal pellets cemented at the sediment-water interface. Considering their ductile behaviour during compaction, these grains must have an intrabasinal origin.

	HARDGROUNDS	SUB-HARDGROUNDS	NON-HARDGROUNDS
QUARTZ	65.9 ± 7.5	69.6 ± 7.6	67.8 ± 8.6
LITHICS	5.0 ± 3.7	9.3 ± 1.9	6.0 ± 3.5
FELDSPARS	29.2 ± 6.4	21.1 ± 8.6	26.1 ± 8.3
NUMBER OF ANALYSES	18	10	26

Table 2: *Mean content and standard deviations of Quartz, Lithics and Feldspars of the various types of sandstone.*

Besides as grains, carbonate occurs as matrix, which is mainly composed of lime mud with a low content of clay minerals (± 3 % illite, smectite and kaolinite). Matrix probably originated from bio-erosion of skeletal material or degradation of skeletons after death and decomposition of the organic binding material or from destruction of peloids through bioturbation.

BURIAL HISTORY

The burial history of the Roda Sandstone Member has been reconstructed and is depicted in Figure 3. During the Paleogene, sedimentation in the Tremp-Graus Basin was strongly influenced by tectonic activity (Ori & Friend, 1984), especially along the northern margin of the basin. Deposition of the Roda Formation was followed by a long period of stable basin conditions with deposition of carbonate, i.e. the Morillo Limestone Formation. Afterwards, tectonic activity resulted in the rapid accumulation of a thick fan-delta complex of the San Esteban and Castigaleu Formations along the northern margin of the Tremp-Graus basin. As a result, the Roda Sandstone Member was buried rapidly to a maximum depth of 650 m. During the late Middle Eocene, tilting and uplifting of the northern margin of the Tremp-Graus Basin resulted in partial erosion of the San Esteban Formation and ultimately of the Roda Sandstone

Member in the northeastern part of the Isábena Valley (Fig. 1 and 2). This period of tectonic activity is marked by a major unconformity represented by an angular discordance. Alluvial fan deposits of the Cajigar Formation overly the unconformity. A second unconformity due to a subsequent period of tectonic activity triggered the formation of large proximal alluvial fan complexes of the Cornudella Formation. The Roda Sandstone Member attained burial depths during the second phase of burial of at least 450 m. in the north and at maximum 900 m. in the south of the area studied.

During the two erosional phases, infiltration of fresh water into the Roda Sandstone Member was possible, with a recharge area situated at the unconformities in the northern part of the study area near section 1 (Fig. 1).

COMPACTION

The rim-cement in hardgrounds and sub-hardgrounds stabilized the framework and counteracted mechanical compaction. To the contrary, non-hardgrounds were compacted severely. Here, compaction was highly effective in reducing the primary porosity from an original percentage of ± 37 to 21 % by ductile grain deformation. Ductile clasts, in particular peloids and aggregate grains, were squeezed into the interstitial pores between rigid framework components (Fig. 5d). Feldspar grains that were intensely replaced by illite and kaolinite also behaved as ductile grains.

POST-COMPACTIONAL DIAGENESIS

Calcite sparite cementation

A second generation of cement filled residual pores, brittle fractures in siliciclastic grains and ruptures in exfoliated biotite grains indicating that it was precipitated after burial compaction. The cement consists of sparry low-magnesian calcite as supported by electron microprobe analyses (Table 3). The sparry calcite cement of (sub-)hardgrounds and non-hardgrounds has minor differences. In most of the (sub-)hardgrounds it is more or less equant-shaped or slightly drusy, with crystals measuring 20 to 200 μm. In the non-hardgrounds single crystals of the second cement almost encompass the individual framework components, displaying a sub-poikilotopic habit with crystal diameters of up to ± 1000 μm. No cathodeluminescence zonation was observed in visible light within the sparite cement.

The southern area suffered a deeper burial during the second burial phase than during the first phase. Despite of this, no significant difference exists between the amount of compaction in the northern and southern area. This indicates that the sparry calcite cement had already stabilized the non-hardgrounds during the second burial phase before the maximum burial depth of the first burial phase was exceeded.

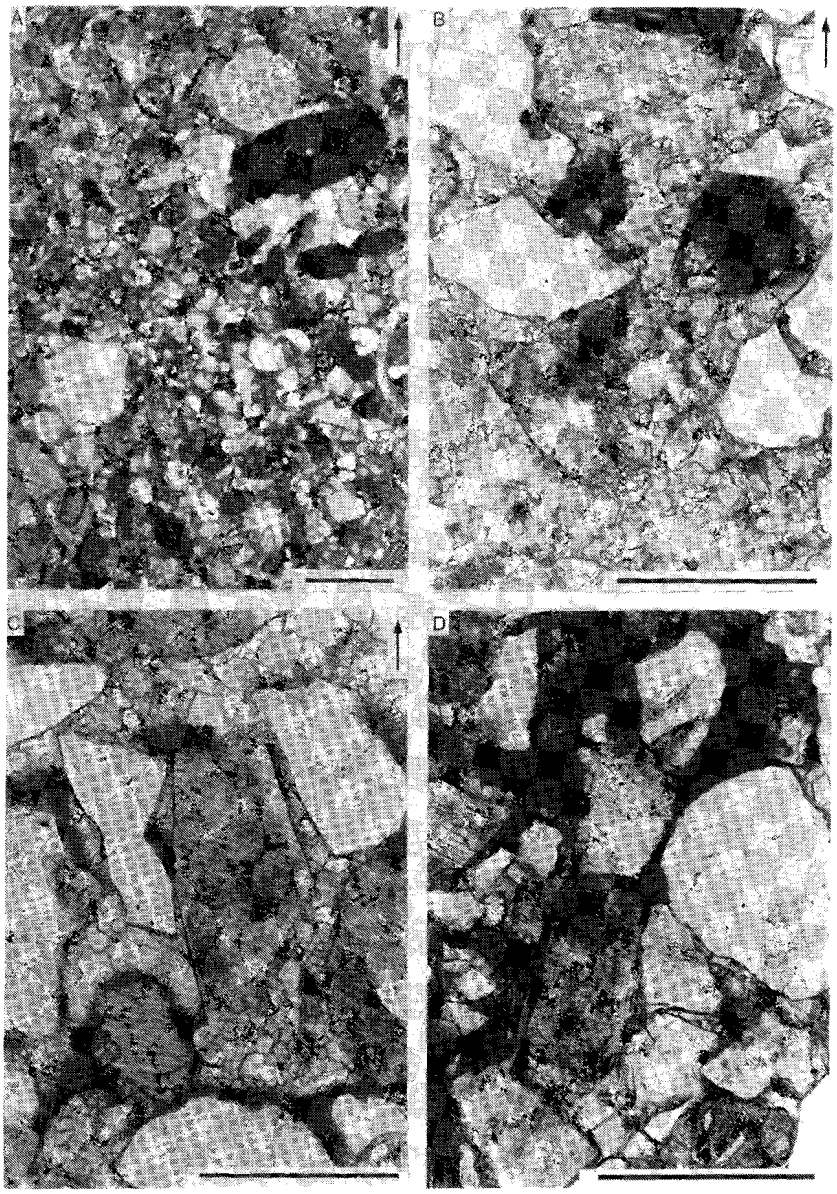


Figure 5: *Photomicrographs of thin sections showing the typical differences between hardgrounds, sub-hardgrounds and non-hardgrounds.* **5A**: *Hardground with abundant matrix and bioclasts, a polymodal grain-size distribution and a partially matrix-supported framework resulting from intense burrowing. The micrite has largely been replaced by microsparry calcite during neomorphism.*

Burrowing destroyed most of the primary texture. Large bioclasts, such as the alveolinid test, served as umbrellas to the infiltration of matrix, resulting in shelter structures. Locally the pores are completely filled with matrix. This was introduced into the sediment by infiltration as well as by burrowing. Plane-polarized light. Scale bar is 1 mm. The arrow indicates the stratigraphic facing. **5B***: A sub-hardground with little infiltrated matrix, some pre-compactional rim-cement, a second equant-shaped low-magnesian calcite cement and no signs of compaction. Matrix infiltration predated the precipitation of rim-cement, since the latter coats the matrix. The original mineralogy of the rim-cement was aragonite, as indicated by the crystal forms. It has been pseudomorphously replaced by low-magnesian calcite. Plane-polarized light. Scale bar is 0.5 mm. The arrow indicates the stratigraphic facing.* **5C***: A sub-hardground showing infiltrated matrix, which accumulated geopetally on top of clasts and blocks pore-connections. Plane-polarized light. Scale bar is 0.5 mm. The arrow indicates the stratigraphic facing.* **5D***: Non-hardground showing compactional features such as concavo-convex contacts between rigid and ductile clasts and kinked biotite flakes. Note the deformation of ductile micrite that obstruct pore connections, reducing the permeability. Plane-polarized light. Scale bar is 0.5 mm.*

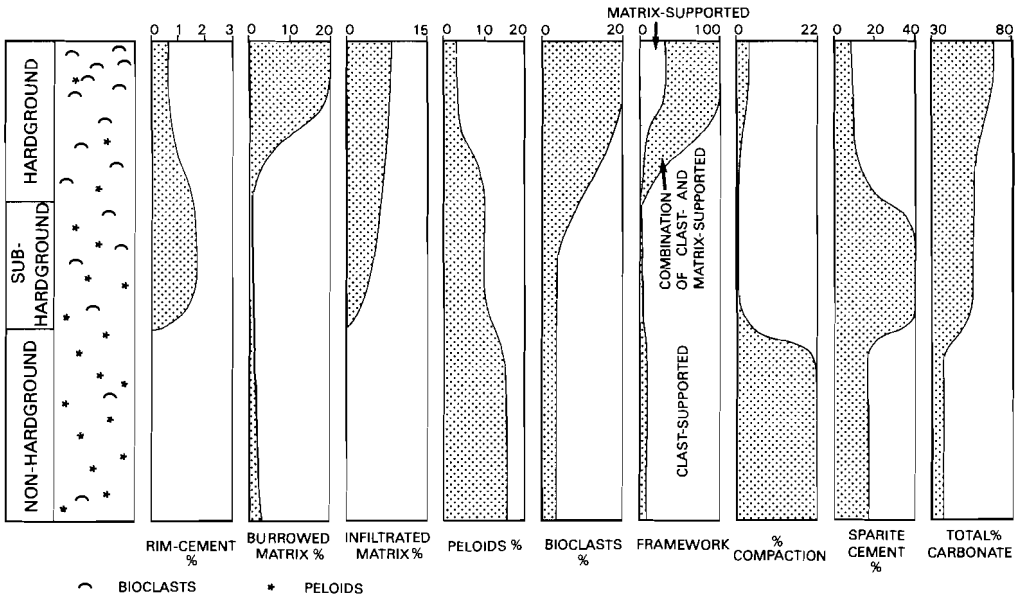


Figure 6*: Schematic profiles displaying variations of several parameters below a hardground surface though a hardground, sub-hardground and non-hardground. Profiles are based on mean values obtained by point-counting and AAS data (i.e. carbonate content).*

Replacement

Low-magnesian calcite is the only carbonate mineral present, as indicated by microprobe analyses (Table 3) and XRD. X-ray diffractograms show but one sharp low-magnesian calcite reflection at a d-value between 3.0250 and 3.0266 Å. On average, the calcite contains 3.05 ± 0.19 mole % $MgCO^3$ (ranging from 3.35 to 2.82 %; N=9). Occasionally a small shoulder is present, attesting to an inconspicuous amount of intermediate-magnesian calcite.

However, aragonite and high-magnesian calcite originally were present. Aragonite occurred as bioclasts and possibly as rim-cement, whereas high-magnesian calcite composed several kinds of bioclasts. All former aragonite and high-magnesian calcite components were replaced by microsparite- or sparite-sized low-magnesian calcite during diagenesis. Apart from meta-stable carbonate components in bioclasts and rim-cement, also all precursor micritic carbonate in matrix and carbonate clasts were replaced by microsparite-sized low-magnesian calcite with equant-shaped but variable sized crystals. In recent shallow-marine carbonate environments, intrabasinal non-skeletal grains such as peloids and aggregate grains are commonly composed of aragonite (Milliman, 1974). Rim-cement was sometimes replaced pseudomorphously, but replacement by sparite-sized calcite also occurs. Replacement was pervasive throughout all kinds of sandstone. At least 90% of the carbonate components does not display primary textures anymore, and is replaced. The remaining 10% consists of porcellaneous large benthonic foraminifer tests, primary consisting of low-magnesian calcite, and some mollusk shells, both displaying their original texture. This either indicates a pseudomorphous replacement or the preservation of their original stable mineralogical composition. Furthermore some extrabasinal clasts probably survived transport because of a stable low-magnesian calcite composition.

The replacement calcite usually merges into the sparry calcite cement. In case of sparite-sized calcite replaced clasts, inclusion patterns form the only indication of the former presence of these clasts. The absence of collapse structures and the merging character of replacement and cement indicate a contemporaneous diagenetic event.

Plagioclase may be replaced by calcite that is optically continuous with the sparry calcite cement. Quartz, as well as feldspars, may show a slight replacement at its margins by sub-poikilotopic sparry calcite cement in non-hardgrounds. Biotite grains display a variable degree of replacement by chlorite. Where the replacement is almost complete, chlorite is intergrown with sparry calcite cement at the borders of the former biotite grains. This attests to the simultaneity of the pertinent diagenetic reactions.

POROSITY

A primary interparticle porosity of approximately 38 % can be deduced

from the amounts of cement and matrix in non-compacted sandstones with clast-supported frameworks. The modification of texture and composition below the abandonment surfaces resulted in a decrease of primary porosity in the affected parts of the sandstone (Table 4). The porosity was reduced by the introduction of matrix and rim-cement and eventually by a decrease in sorting through burrowing. This caused the development of distinct zones with a decreased porosity. Thus, after the early modification, the hardgrounds, and to a lesser extent the sub-hardgrounds, constituted intervals of low porosity. The resulting porosity patterns were accentuated and inversed by compaction during the first burial. After burial compaction, the porosity of non-hardgrounds was considerably reduced due to the plastic deformation of ductile grains in contrast to the stable (sub-)hardgrounds. At this time, the sub-hardgrounds were the most porous and probably also the most permeable zones in the system. Before the second phase of calcite cementation, i.e. after the first burial, several zones of distinct porosity were present in the sandstone bodies. In order of decreasing porosity (Table 4) these were: sub-hardgrounds, hardgrounds and non-hardgrounds. Obviously, this distinct zonation could control post-compactional processes that were dependent on the supply of material from external sources.

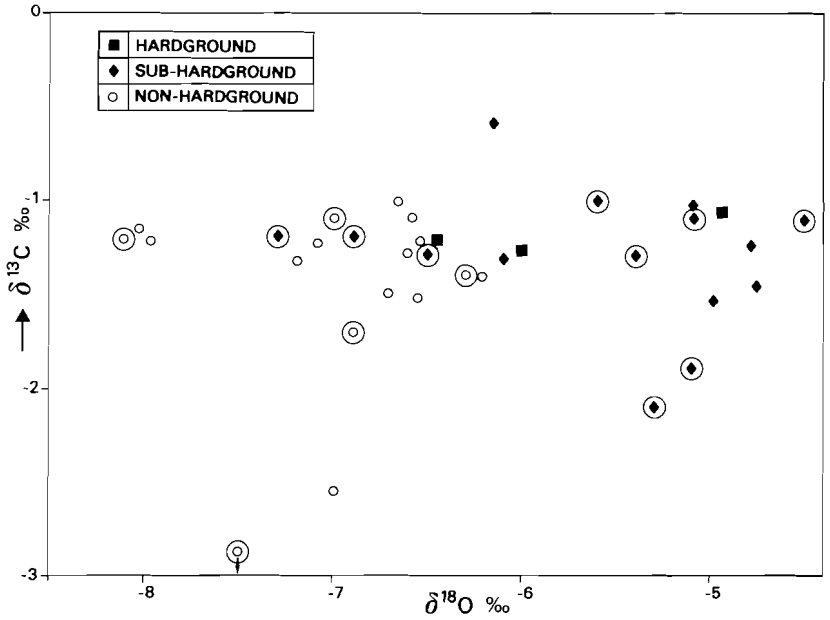
TIMING / KIND OF SANDSTONE	UP ON DEPOSITION	AFTER PRE-BURIAL MODIFICATION	AFTER FIRST BURIAL COMPACTION	PRESENT
HARDGROUNDS □	38	13	12	2.8
SUB-HARDGROUNDS △	38	27	24	3.2
NON-HARDGROUNDS ○	38	34	17	5.1
	POROSITY %			EFFECTIVE POROSITY %

Table 4: *Measured effective porosity and inferred porosity during various stages in the diagenesis. Inferred porosity percentages are based on percentages cement and matrix obtained by point counting.*

STABLE ISOTOPIC COMPOSITION

Oxygen isotopes

In order to reconstruct cementation conditions, the oxygen and carbon



SAMPLE LOCATION	$\delta^{18}O$ SUB-HARDGROUNDS	$\delta^{18}O$ NON-HARDGROUNDS
1	-6.03 (1)	-7.01 (1)
2	-5.67 ± 0.48 (4)	-6.75 ± 0.43 (5)
3	-5.72 ± 0.72 (4)	-6.84 ± 0.34 (5)
4		-8.00 ± 0.03 (2)
6	-5.48 ± 0.71 (6)	-7.38 ± 0.72 (2)
7	-5.52 ± 1.27 (3)	-6.63 ± 0.08 (2)

Figure 7: *Stable oxygen and carbon isotopes.* **7A**: *Diagram of the oxygen and carbon isotope composition of (sub-)hardgrounds and non-hardgrounds relative to the PDB standard. Encircled data represent measurements of separated sparry calcite cement, whereas others were obtained from bulk carbonate samples. Note that, although the differences between (sub-)hardgrounds and non-hardgrounds is significant, both groups are not distinctly separated.* **7B**: *Mean oxygen isotope composition of (sub-)hardgrounds and hardgrounds in each sample location. Numbers refer to sample locations as indicated on the map of Figure 1. No significant lateral trend is present, although the maximum burial depth reached during the second burial phase was higher in the southern study area.*

isotope composition of the cement of several samples as well as several bulk carbonate fractions have been determined. The delta ^{18}O and ^{13}C values are depicted in Figure 7A in per mil deviation from the PDB standard. The similarity of the isotopic compositions of bulk carbonate and sparry cement indicates that indeed very little primary unaltered carbonate is present. However, differences exist in oxygen isotope composition of (sub-)hardgrounds (mean δ ^{18}O is -5.6 ± 0.8, ranging from -7.3 to -4.5) and non-hardgrounds (mean δ ^{18}O is -7.0 ± 0.6, ranging from -8.1 to -6.2). The δ ^{18}O composition of the diagenetic carbonate in sub-hardgrounds is significantly heavier than that of non-hardgrounds.

Light oxygen is preferentially incorporated into precipitating carbonate minerals. This fractionation of oxygen isotopes between water and $CaCO_3$ is strongly temperature dependent, resulting in a progressive lighter oxygen composition for carbonate precipitated at higher temperatures. The measured oxygen isotope composition of the carbonate fraction reflects the temperature during its diagenetic introduction and the isotopic composition of the water involved in its precipitation. However, the composition of this water was also a function of the isotope composition of the replaced carbonate components. During dissolution of meta-stable carbonates oxygen isotopes with a marine signature were mixed with the interstitial water. The oxygen isotope composition of the primary carbonate is estimated to range between -2 per mil for the foraminiferal carbonate and 0 per mil for carbonate matrix and peloids (Milliman, 1974). The foraminiferal carbonate has a slightly lighter oxygen isotope composition than the equilibrium composition due to biogenic fractionation. Thus, the interstitial water was probably modified by fractionation between precipitating carbonate cement and replacement and the water, and through addition of isotopes derived from dissolution of primary carbonates.

Assuming a geothermal gradient of approximately 25 °C/km and a mean surface temperature of ± 10 °C, the maximum temperature reached during the second burial phase was about 21 to 33 °C for the northern and southern area, respectively. The approximate possible conditions for diagenetic carbonate precipitation during the second burial phase are depicted in Figure 8, where equilibrium calcite δ ^{18}O values are plotted against the temperature and the oxygen isotope composition of the water out of which the calcite precipitated. For this purpose, the fractionation equation of Friedman and O'Neil (1977) with a CO_2-H_2O fractionation of 1.0412 according to Anderson and Arthur (1983) has been used.

Considering the maximum temperatures possible during the second burial phase (Fig. 8), the oxygen isotope compositions can only be explained if the diagenetic carbonate was precipitated from interstitial water with a light ^{18}O composition, which is characteristic of fresh water. This is in accordance with the supposed influx of fresh water from the north during erosion.

No lateral trend from the entrance point of the fresh water in the north towards the south can be detected for oxygen isotope composition of the

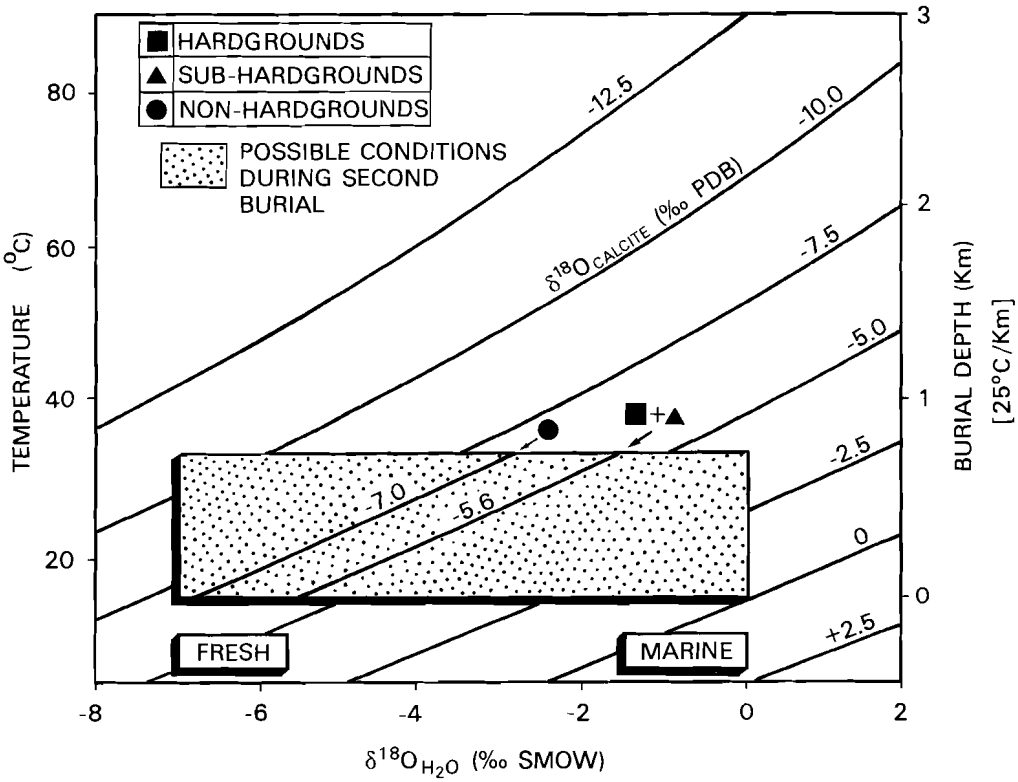


Figure 8: *Equilibrium oxygen isotope composition of calcite for various temperatures and oxygen isotope compositions of water. Possible conditions in terms of temperature and kind of water as calculated from the measured oxygen isotopes using the fractionation curve* $1000*ln\ \alpha_{(calcite-water)} = 2.78*10^{(6)}*T^{(-2)} - 3.39$ *(Friedman & O'Neil, 1977 using a* CO_2-H_2O *fractionation of 1.0412);* $\alpha = (1000+\delta^{18}O_{mineral})/(1000+\delta^{18}O_{water})$; the temperature T in the formula is denoted in °K. *The stippled area indicates an approximation of the possible conditions during the second burial phase, i.e. during neomorphic replacement and precipitation of sparry calcite cement.*

carbonate (Fig. 7B). The isotope composition of the carbonate remained laterally identical for both (sub-)hardgrounds and non-hardgrounds, despite of the continuous modification of interstitial water through fractionation and addition of primary carbonate. This point to the large amounts of water indeed being necessary for precipitation and an external source of the carbonate.

The significant lighter ^{18}O composition of the diagenetic carbonate in

non-hardgrounds can be explained as a consequence of slight but consistent differences in the conditions during diagenesis: a change either in the reaction temperature, or in the composition of the interstitial water.

Carbon isotopes

The mean carbon composition is -1.42 ± 0.66 pro mil (-4.70 to -0.59). In contrast to oxygen, carbon isotope composition is only slightly modified by temperature fractionation and thus is merely determined by the composition of the water out of which the calcite was precipitated. Temperature fractionation induces only a shift of +0.04 per mil for each degree increase in temperature (Emrich, Ehhalt & Vogel, 1970). The uniformity in carbon isotope composition of all but one sample indicates that the source of carbon for diagenetic carbonate was the same throughout the sandstone bodies.

Dissolved HCO_3^- in water of normal to slightly alkaline water, which is in isotopic equilibrium with the atmospheric CO^{2-}, has a $\delta\ ^{13}C$ of about 0 to +1 per mil (Mook, Bommerson & Staverman, 1974). Calcite precipitated from water that is in isotopic equilibrium with the atmosphere (the largest carbon reservoir) should also have a delta ^{13}C of about 0 to +1 per mil. Fresh waters may show negative carbon isotope compositions because of addition of organic carbon derived from soils and plant material. During bacterial oxidation and abiotic degradation of organic matter carbon dioxide is produced with approximately the same light carbon isotope composition as the organic matter from which it is derived (Irwin, Curtis & Coleman, 1977).

The carbon isotope composition reflects a supply of carbon by pore water that was partly equilibrated with atmospheric carbon dioxide. The slightly negative composition of the diagenetic carbonate may have resulted from a small modification of entering water by the addition of carbon derived from the dissolution of replaced primary marine carbonates, or it may indicate fresh water with slight amounts of organic carbon. Internal sources of biogenic carbon, such as carbon dioxide derived from oxidized organic matter, were either homogeneously dispersed or not present.

CHEMICAL COMPOSITION OF THE CARBONATE FRACTION

Mean values and ranges of Ca, Mg, Sr, Mn and Fe contents of sparite cement, infiltrated matrix, peloids and porcellaneous foraminifer tests of sub-hardgrounds and non-hardgrounds determined by electron microprobe analyses are given in Table 3. Low-magnesian calcite is the only carbonate mineral present. All former aragonite and high- magnesian calcite components, such as matrix, peloids and porcellaneous foraminifer tests were replaced by low-magnesian calcite. Contents display a quite large range, although this range is not consistent with respect to type of sandstone or spatial occurrence. Differences between sub-hardgrounds and non-hardgrounds are not significant,

ELEMENT	SUB-HARDGROUNDS	NON-HARDGROUNDS
Ca %	38.96 ± 0.36 (48)	39.12 ± 0.34 (34)
Mg %	0.39 ± 0.16 (48)	0.32 ± 0.16 (34)
Sr %	0.23 ± 0.12 (16)	0.26 ± 0.14 (12)
Mn %	0.14 ± 0.08 (20)	0.12 ± 0.06 (19)
Fe %	0.59 ± 0.26 (44)	0.50 ± 0.21 (30)
NUMBER OF ANALYSES	10 SAMPLES 48 POINTS	8 SAMPLES 34 POINTS

Table 3: *Electron microprobe results. Mean values and ranges of Ca, Mg, Sr, Mn and Fe contents of sparry calcite cement, porcellaneous foraminifer tests, peloids and infiltrated matrix in sub-hardgrounds and non-hardgrounds. Rim-cement crystals were too small for accurate measurements. Element values are recalculated to 100 % carbonate. The differences between sub-hardgrounds and non-hardgrounds are non-significant (within 5 % limits), as is evidenced by student-t tests. The number of analyzed points is displayed between brackets.*

possibly with exception of the iron contents. The chemical similarity of all carbonate components, replacement or cement, confirms the contemporaneity of replacement and sparite cementation during one single diagenetic event. The water involved was generally identical for all parts of the sandstone bodies, as is indicated by the absence of lateral changes in the chemical composition of the carbonate.

The Mg, Sr, Mn and Fe content of carbonate is governed by the concentration or activity ratio of the various coprecipitating elements relative to that of calcium in the water. The interdependence of the molar concentration ratio in the water and in the precipitating carbonate during equilibrium inorganic precipitation is given by the distribution coefficient (e.g., Veizer, 1983). This relation is more or less modified during biogenic precipitation. Biogenic fractionation with respect to element concentrations may result in higher contents of Mg and Sr than could be expected for normal equilibrium co-precipitation in marine water.

A general decrease in elements as Mg and Sr is to be expected during diagenetic replacement of primary marine carbonates, whereas the content of Mn and Fe usually increases (e.g., Veizer, 1983). In the Roda Sandstone Member all meta-stable carbonates, aragonite with high Sr content and high-magnesian calcite with low Sr and high Mg content, were replaced by low-magnesian calcite. Primary aragonite contains higher amounts of Sr, up to 9000 ppm for inorganic equilibrium aragonite (Veizer, 1983), irrespective of the origin.

Aragonite has a high receptivity to co-precipitation of Sr in its crystal lattice, expressed by a distribution coefficient of approximately 1 (Kinsman, 1969; Kitano, Kanamori & Oomori, 1971). During replacement of aragonite by calcite Sr is excluded from the mineral phases and enriched in the interstitial water. The distribution coefficient of Sr of calcite is lower than unity, with reported values ranging from 0.055 (Katz, et al., 1972) to 0.14 (Holland et al., 1964; Kinsman, 1969). As a consequence, the replacement of aragonite by calcite results in a severe loss of Sr out of the mineral phase.

The solubility of Fe and Mn, and thus the possibility to coprecipitate in a carbonate, are largely dependent on their oxidation state and thus on the Eh of the water. Anoxic conditions permit high concentrations of reduced Mn^{2+} and Fe^{2+} dissolved from particulate fines in the interstitial water available for co-precipitation, whereas oxidized water contains virtually no Fe^{2+} and Mn^{2+} in solution. The eventual content of these cations in calcite is thus merely determined by the Eh of the interstitial water. Moreover, fractionation during precipitation results in the preferential incorporation of Fe and Mn in the carbonate minerals. Values of 1 (Richter & Füchtbauer, 1978; Füchtbauer, 1980) or up to 20 (Veizer, 1974) are given in the literature for the distribution coefficient of Fe, whereas that of Mn is approximately 15 (Pingitore, 1978). Both Fe and Mn will therefore be enriched in calcite relative to the water out of which the calcite precipitates.

The low Mg and Sr and intermediate high Fe and Mn contents are characteristic for an inorganic diagenetic calcite. The contents of Sr indicate that the diagenetic calcite has been precipitated from water with a relatively high Sr/Ca concentration ratio, more or less half that of mean ocean water. The low Mg contents, however, point to fresh water. Fe and Mn contents indicate moderately reducing conditions, which is also attested by the partial replacement of biotite grains by chlorite. Part of the Fe present in the calcite could have been derived from the biotite.

The element contents of the carbonate are a function both of the composition of the interstitial water and of the primary carbonate. During dissolution of the primary meta-stable marine carbonates (at least part of it consisted of aragonite and high-magnesian calcites) the interstitial fresh water was modified. A further modification was consequented by fractionation between water and diagenetic calcite during precipitation of the latter. The Sr/Ca and Mg/Ca ratios of biogenically and chemically marine precipitated carbonate are usually pronouncedly higher than of fresh water carbonates. As a consequence, the composition of any fresh interstitial water will be modified through the dissolution of pre-existing carbonates because of the mentioned differences. Modification should not have a large impact if precipitation occurs from a large water reservoir. Deviations in elemental concentrations were caused by local variations in content and composition of primary marine carbonates with increased Sr and Mg contents, differences in the pore volume and variations in the rate of flow of interstitial water as dependent on permeability. This also accounts for the range in measured carbonate compositions.

Modification should be more effective when the system was locally relatively closed, i.e. if the flow of interstitial water was slow. A similar effect would be reached if the reactions were instantaneous and thus the time that elapsed between dissolution and (re-)precipitation was relatively short. The instantaneous dissolution of unstable primary carbonates and (re-)precipitation of diagenetic calcite as microsparite, pseudosparite and cement is attested to by the absence of framework collapse structures. It is also indicated by the common pseudomorphous replacement of aragonite rim-cement by low-magnesian calcite.

The Sr concentrations have been modified through dissolution of pre-existing carbonate causing high Sr/Ca ratios more or less similar to mean ocean water. Contrary to Sr concentrations, those of Mg were only slightly increased with respect to a fresh water precipitate. This suggests that aragonite was the main component of the peloids, rim-cement and matrix. For marine aragonite contains high amounts of Sr and very low amounts of Mg irrespective of biogenic of inorganic origin. High-magnesian calcite was probably restricted to tests of porcellaneous foraminifers and echinoid skeletons.

CONSTRAINTS OF EARLY MODIFICATION ON LATER DIAGENESIS

Large amounts of sparry calcite cement are present. Some of this cement could have been generated through the volume increase due to the replacement of aragonite by calcite, which is theoretically 8% (Bathurst, 1971). Assuming the hypothetical case that all primary carbonate was aragonite a total replacement can account for maximal 32.5% of the sparite cement in hardgrounds, 4.0% in sub-hardgrounds and 9.9% in non-hardgrounds (Table 5). Obviously, a large part of the sparite cement is thus derived from an external source. Therefore, a large volume of water supersaturated with respect to calcite was necessary to provide the solutes for precipitation of the second generation of cement.

Recharge of the system with fresh water most likely started in the most permeable zones of the sandstones. At the time of the second cementation phase a distinct porosity zonation existed in the sandstone bodies associated with early modifications during pauses in sedimentation and subsequent burial compaction. The decrease in sorting and the increase in matrix content caused a reduction of porosity and of permeability. The presence of rim-cement governed the development of highly compacted horizons within the sandstone bodies with strongly reduced porosity. The obstruction of pores in the latter horizons by squeezed ductile clasts reduced the permeability. A relationship between the zones and sparite cementation seems logical. Flow of interstitial water, carrying the solutes for the second cementation phase, preferentially should take place in the most permeable parts of the sandstone. Flow of fresh water into the sandstones would have been established at first and highest flow rates in the non-hardgrounds, gradually shifting to the non-hardgrounds with increasing burial compaction and decreasing flow rates.

HARDGROUND	SUB-HARDGROUND	NON-HARDGROUND	
59.3	55.3	36.5	TOTAL % CARBONATE
47.6	18.2	20.4	% CARBONATE PRESENT BEFORE SPARITE CEMENTATION
11.7	37.1	16.1	% SPARITE CEMENT
3.8	1.5	1.6	MAXIMUM % VOLUME INCREASE DUE TO ARAGONITE REPLACEMENT
32.5	4.0	9.9	MAX. RELATIVE % OF CEMENT DUE TO VOLUME INCREASE
7.9	35.6	14.5	MINIMUM % OF CEMENT SUPPLIED FROM EXTERNAL SOURCES

Table 5: *Calculated maximum increase in volume of carbonate due to the replacement of aragonite by calcite, with indication of the minimum amounts of calcite which had to be supplied from external sources.*

The chemical composition of carbonate indicates no differences between (sub-)hardgrounds and hardgrounds, which is in accordance with the supposed amounts of carbonate supplied from outside the sandstone bodies. This eliminates a changing composition in terms of mixing of marine and fresh water as a cause for the distinction in oxygen isotope composition of (sub-)hardgrounds and non-hardgrounds. A slightly higher temperature in non-hardgrounds during precipitation of diagenetic carbonate is thus probably the cause of the oxygen isotope difference. The isotope data thus confirm lower temperatures during sparry calcite cementation in (sub-)hardgrounds. The difference in isotope values is in accordance with the porosity and permeability patterns during the second cementation phase.

The crystal-size of the sparry calcite cement is generally smaller in sub-hardgrounds than in non-hardgrounds. This points either to a higher supersaturation in sub-hardgrounds and, as a consequence, a higher nucleation rate, or to the presence of more nucleation sites in sub-hardgrounds. The latter contained more carbonate in bioclasts, matrix and rim-cement than non-hardgrounds. In sub-hardgrounds the cementation rate was higher and cementation was completed sooner. Probably cementation commenced at approximately the same time in all parts of the sandstone complexes or slightly earlier in the most porous parts. However, its completion took variable lengths of time with steadily increasing burial depths, and hence increasing lighter oxygen isotope compositions. The measured isotope values merely reflect a range of temperatures during cementation. The non-hardgrounds represent the last parts of the system that were cemented or where cementation was completed at the highest temperatures.

The spatial distribution and intensity of early diagenetic modification governed the onset and duration of replacement and bulk cementation in the

Roda Sandstone Member. Depositional processes, such as the rate and continuity of sedimentation, constrained the course of diagenesis.

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