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Sedimentology and diagenesis of the ankeritized basal Zechstein conglomerate in the Campine Basin (Bree borehole, NE Belgium)

M. De Craen & R. Swennen
Katholieke Universiteit Leuven, Fysico-chemische Geologie, Celestijnenlaan 200C, B-3001 Heverlee, Belgium

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Abstract

The transgressive basal Zechstein conglomerate penetrated by the Bree borehole (NE Belgium) is 3.15 m thick and has a polymict composition. Originally, clasts consisted predominantly of limestone, dolomite, sandstone and quartzite. Pervasive replacement by ankerite has affected the carbonate clasts, especially in the middle part of the conglomerate layer. Ankerite also forms a pore-filling cement. An origin from Fe-rich waters derived from the underlying Carboniferous clastics is indicated by the chemical and isotopic (depleted $\delta^{18}O$ and $\delta^{13}C$) characteristics of the ankerite. An evolution in fluid composition due to increasing water/rock interaction is reflected in chemical and isotope variations. The preferential precipitation of both replacive and pore-filling ankerite in the middle part of the conglomerate, reflects channeling of ankerite-bearing waters in this originally highly porous and permeable part.

Introduction

In Belgium, Permian sediments are only exposed in the Malmédy Graben which cross-cuts the Caledonian Stavelot Massif (Fig. 1). However, Zechstein (Late Permian) sediments are present in the subsurface of the Campine Basin. Within this basin, the Zechstein, which mainly consists of carbonate-rich shales, lies discordantly upon thick mudstones, sandstones and coal of the Westphalian C or D (total thickness: 2200 m, Delmer 1963). The Permian is overlain by thick Mesozoic and Cenozoic sediments. At the base of the Zechstein a transgressive conglomerate is often present. In most boreholes this conglomerate is a few centimetres thick (M. Dusar, pers. comm. 1990). However, in the Bree borehole it is 3.15 m thick. The conglomerate occurs at a depth between 1289.25 and 1292.40 m. The Permian sediments have a total thickness of 39 m. They are overlain by the Buntsandstein (448 m), Cretaceous (280 m) and Cenozoic (526 m) sediments (Dusar 1990).

The burial history of the Zechstein strata (Fig. 1) is characterized by rapid subsidence during Buntsandstein deposition, followed by more gradual subsidence during the Middle to Late Triassic and Early Jurassic. The Jurassic and part of the Triassic sediments have been uplifted and eroded during Jurassic and Cretaceous time (195 to 85 my). According to Tys (1980), originally about 560 m Buntsandstein, 85 m Muschelkalk, 86 m Keuper and 17 m Rhaetian could have been present. For the Lias an original thickness in the range of 0 to 600 m is estimated (V. Langenaeker, pers. comm. 1990). Thus, up to some 900 m of strata could have been eroded. After the uplift, the area underwent gradual subsidence.

Conglomerates in contrast to sandstones are a

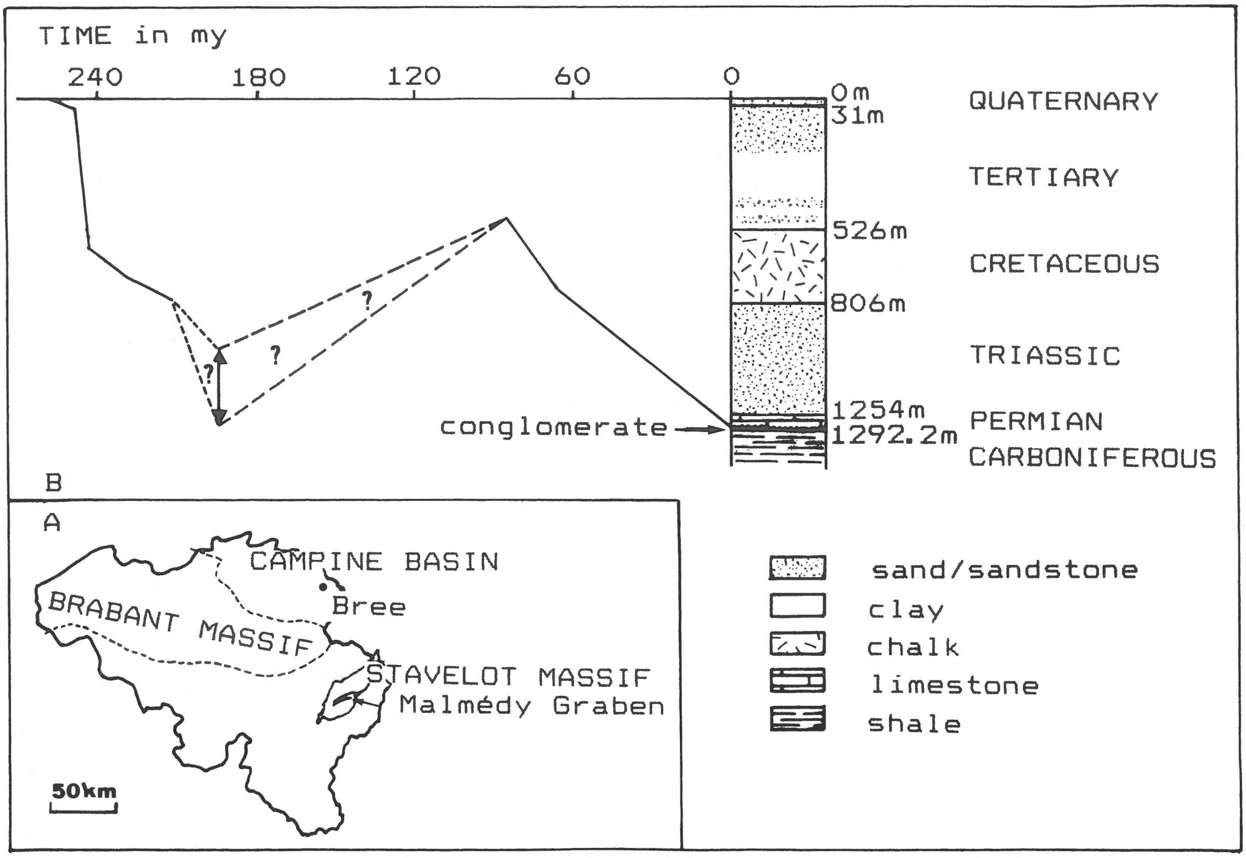


Fig. 1. A. Geographical position of the Bree borehole (KB 201: reference number of files at the Belgian Geological Survey); B. Stratigraphical profile and burial graph (not corrected for compaction) of the Bree borehole.

very suitable lithology for geochemical characterisation of diagenetic phases since most cements are more easily sampled in the amounts required for analysis. The purpose of this paper is to document the depositional and diagenetic history of the basal Zechstein conglomerate in the Bree borehole, and to propose a model to explain the pervasive ankeritization. The latter will be described in the context of the overall diagenetic evolution.

Methods

After core-slabbing, calcite and Fe-rich phases were identified by staining with Alizarine-Red-S and potassium ferricyanide (Dickson 1966). This enabled us to distinguish different clast and cement types. After a detailed macroscopic description, about 60 thin sections were selected and examined using a petrographic microscope and cathodoluminescence (CL). Scanning electron microscopy (SEM) enabled us to further unravel the diagenetic history. The chemical composition of the cements and clasts was determined quantitatively by electron microprobe analysis. Dental drill techniques were used to carefully sample clasts and different cement generations for oxygen and carbon isotope analysis. Analyses were performed on CO_2 gas, after dissolution in anhydrous 100% orthophosphoric acid at 25° C. At this temperature ankerite only reacts very slowly. Consequently, almost all CO_2 collected within the first 24 hours of reaction originated from calcite or dolomite. For ankerite, dissolution occurred at a temperature of 100° C to make sure that the reaction was completed. All data have been corrected following procedures modified from Craig (1957). For fractionation during dissolution of dolomite and ankerite by phosphoric acid a correction value of respectively 1.01169 and 1.00901 (Rosenbaum & Sheppard 1986) was used. Both $\delta^{13}C$ and $\delta^{18}O$ are reported relative to the PDB international standard. Reproducibility, determined by replicate analysis, is better than ± 0.1‰ for oxygen and carbon at the 2σ level. The $\delta^{13}C$ and the corrected $\delta^{18}O$ values are given in Fig. 7 and Table 2.

Sedimentological characteristics

The conglomerate consists of well-rounded clasts, set in a fine-grained matrix (Fig. 9). In Fig. 2A, the relative abundance of clasts, matrix fines and cements is shown. On average, their respective abundances vary between 40–60%, 20–40% and 0–5%. The conglomerate is predominantly clast-supported (Fig. 9A). Near its top the matrix becomes gradually more important. In general, cements are not discernable macroscopically with the exception of the central interval where cements may comprise up to 15% by volume (Figs 9B, 9C). It is in this interval near 1290.95 m that a 4 cm-thick sandy layer is present (Fig. 9D). This sandy layer subdivides the conglomerate into two parts. Minus-cement porosity in this sandy intercalation was around 15%.

The size of the clasts ranges from 0.2 cm (smaller components have been classified as matrix) to larger than 6.3 cm (the drillcore diameter). Based on the clast-size variation (Fig. 2B), the conglomerate can be divided into two units which both consist of a lower coarsening-upward sequence and an upper fining-upward sequence. In between, the sandy layer occurs. The sorting of the conglomerate is highly variable, but generally poor. Most of the clasts are rounded to well-rounded; some are elongated. In some intervals, imbrication structures are present (Fig. 9C). This imbrication and the position conformably below marine strata, at the base of a transgressive system tract, probably indicate shoreline deposition. In such a setting, the presence of the sandy layer is most probably a local feature. This would explain its absence in other boreholes intersecting the Zechstein in the Campine Basin (M. Dusar, pers. comm. 1990).

The conglomerate is polymict. In Table 1, major and minor clast types are listed and tentative provenances are given. Sandstone, quartzite, limestone, dolomite and clasts consisting mineralogically of ankerite, are the most important clast types. Their respective abundances are given in Fig. 2C. The conglomerate can, from a lithological point of view, be subdivided into three units (Fig. 2D). Sandstone and quartzite clasts are present throughout. Their abundance varies between 5 and 80%. The central part of the conglomerate (unit 2) is characterized by the presence of clasts which mineralogically consist of ankerite. Their abundance generally varies around 60% but can grade up to 95%. It is within this central unit that limestone clasts are absent. In contrast, the 'ankerite' clasts are absent at the base (unit 1) and at the top (unit 3) of the conglomerate, where limestone is the most important clast type (often more than 50%). Dolomite clasts are present throughout. Their abundance is always below 40% and they are less abundant in the ankerite-rich unit.

The matrix of the conglomerate consists of particles smaller than 0.2 cm. Approximately 70% of the particles consists of subrounded to rounded quartz grains. These grains often possess an iron-oxide coating. The other 30% of the particles display a composition similar to that of the clasts.

Diagenesis

Successive stages of cementation have been differentiated, allowing subdivision of the conglomerate's diagenetic history into a pre-compactional and a late-diagenetic, post-compactional period (Fig. 3).

After sedimentation, a thin fringe of calcite cement precipitated around most of the clasts. This early-diagenetic, circumgranular, equant cement is zoned under CL (Figs 10A, 10B) and possesses a non-luminescent core (stage A) followed by a bright (stage B) and subsequently dull luminescent fringe (stage C). This type of evolution of luminescence characteristics has generally been related

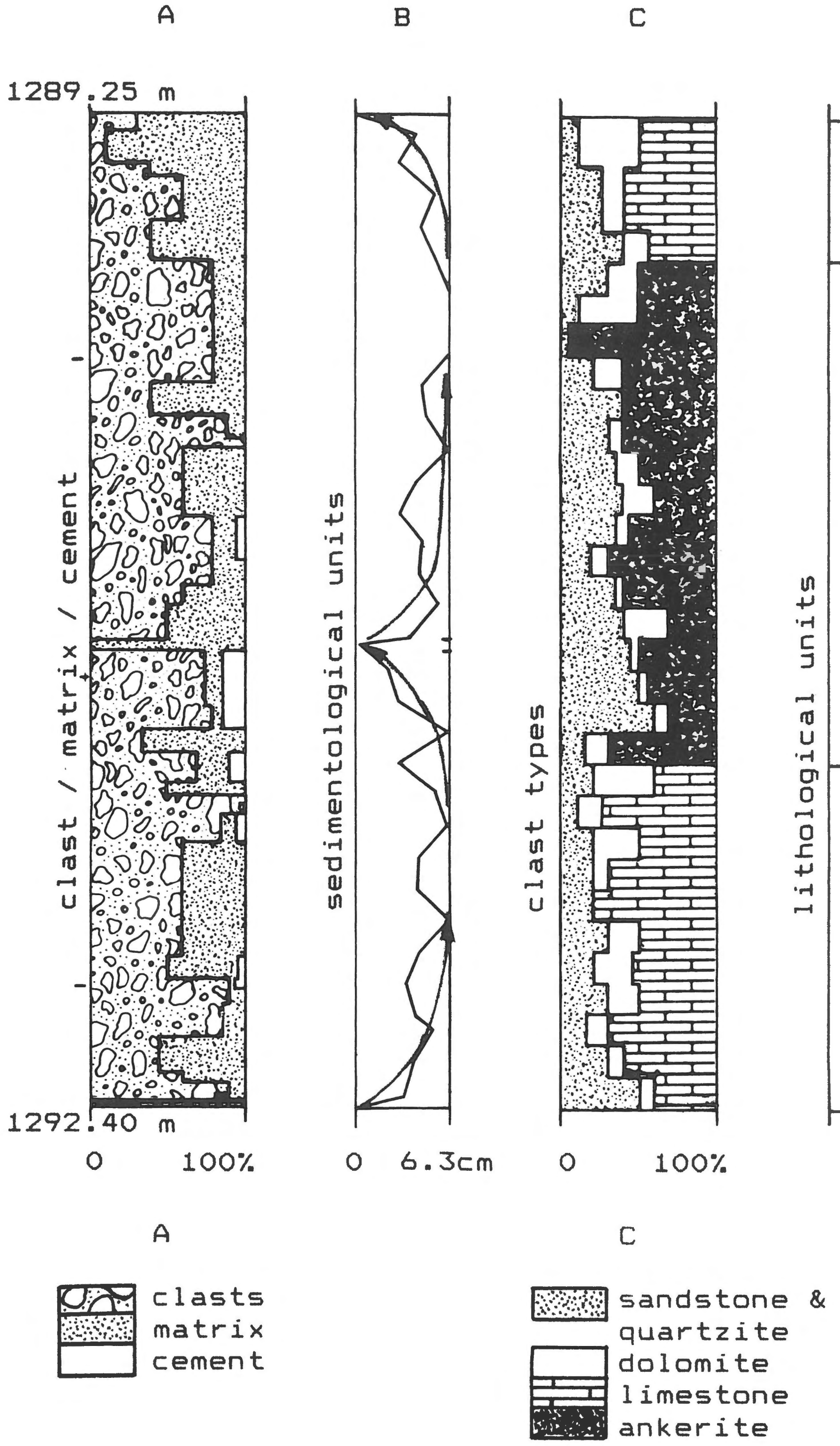


Fig. 2. General lithological characteristics of the basal Zechstein conglomerate in the Bree borehole. A. Clast/matrix/cement abundances of macroscopically discernable phases (in %); B. The maximal diameter of the clasts, measured within 10 cm intervals. The arrows indicate coarsening/fining upward sequences; C. Distribution of clast types (in %); D. Lithological subdivision based on the distribution of clast types.

to increasingly reducing pore water conditions (Franks et al. 1982; Grover & Read 1963; Barnaby & Rimstidt 1989). In some places this fringing cement is detached from the clasts and subsequently broken up (Fig. 10C) indicating its pre-compactional origin. The irregular outline of the bright and the outermost dull luminescent stages B and C indicates that dissolution occurred after these stages.

The next diagenetic period is characterized by ankerite cementation and ankerite replacement of clasts and earlier cements. The late-diagenetic origin of the ankerite is attested by the fact that these cements have not been affected by compaction. Ankerite cement precipitated in the pores between the clasts. In the central part of the conglomerate, most pre-compactional calcite cement was replaced by ankerite. In this interval, several ankeritized clasts occur, while limestone clasts are absent and dolomite clasts less common than in the intervals above and below. Ankerite replaced both limestone and dolomite clasts as deduced from the presence of limestone or dolomite relicts in the ankeritized clasts. There is a very sharp transition from conglomerate dominated by limestone and dolomite clasts to conglomerate dominated by ankeritized clasts within a distance of 5 cm (Fig. 2), both at the top and the bottom of unit 2. Often a central cavity occurs within the ankeritized clasts. This cavity probably relates to a decrease in volume during replacement of calcite by ankerite (Boles 1978). These central cavities are often lined or filled with a white ankerite cement. Thus three types of ankerite have been recognized (Fig. 4): ankerite as a replacement of other carbonate clasts or cements (RA), ankerite cement between the matrix components of the conglomerate (MAC) and ankerite cement in the central cavities of the ankeritized clasts (CAC). In contrast to the two whitish ankerite cements, most of the ankeritized clasts

Table 1. Clast types occurring in the basal Zechstein conglomerate of the Bree borehole with suggestion of most likely age and provenance area (1. Thorez & Dreesen 1988; 2. F. Geukens, pers. comm.; 3. Peeters et al. 1991; 4. Muchez & Viaene 1991)

lithology	major characteristics	age/possible provenance
major constituents:		
sandstones	quartzarenite >99.5% quartz	?
	sublitharenite to lithic subarkose detritals: quartz > carbonate clasts > feldspar > dolomite	Famennian/Dinant Basin (1)
	subarkose (psammite) detritals: quartz > feldspar > mica	Famennian/Ardennes (1)
quartzites	quartzarenite quartz detritals characterized by undulous extinction and sutured contacts	Caledonian Massifs (2)
dolomites	idiotopic-S-texture (2 types)	Dinantian/SE of the Brabant Massif Campine Basin (3, 4)
	spherical texture	?
limestones	bioclastic wackestone	Visean–Devonian/Dinant & Campine Basin (3, 4)
	peloidal packstone	Visean/Dinant & Campine Basin (3, 4)
	oolitic packstone	Visean/Campine Basin (3, 4)
	mudstones	Visean/Dinant & Campine Basin (3, 4)
	breccia	Visean/Dinant & Campine Basin (3, 4)
ankerites	undulous extinction; saddle-shaped texture	diagenetic in origin
minor constituents:		
red shales	<5 mm, elongated	Rotliegendes/?
cherts	sometimes with euhedral dolomite crystals	Dinantian/Campine Basin or SE of the Brabant Massif (3, 4)

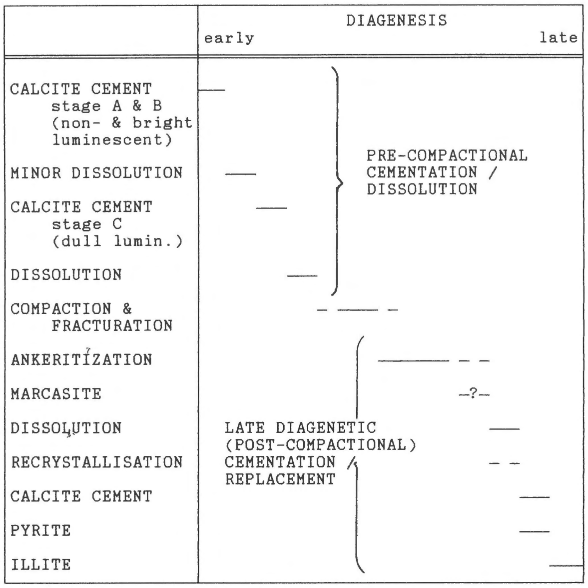


Fig. 3. Diagenetic history of the basal Zechstein conglomerate of the Bree borehole.

have a grey hue. This colour is caused by clay and organic matter between the ankerite crystals. These impurities are not present in the ankerite cements. From a petrographic point of view, there is no other difference between the replacive and non-replacive ankerites. All types of ankerite possess an undulous exctinction and are saddle-shaped. This saddle-shaped texture is better developed towards the cavities. There exists an optical continuity between ankerite crystals of replacive origin and those of the cements in the matrix (Fig. 10D). The origin and emplacement of these different ankerite phases are discussed below.

Within many of the ankeritized clasts, needle-shaped marcasite crystals occur (Figs 9D, 10E). They 'float' within the ankerite. After the ankeritization, the ankerite cement in the matrix of the conglomerate together with the marcasite needles in the clasts was partially to completely dissolved. Recrystallisation of limestone clasts and calcite cements possibly took place at the same time.

The next diagenetic event was the precipitation of a zoned, bright luminescent calcite cement, occurring in association with pyrite. As shown in Fig. 10E this calcite phase locally fills up marcasite molds.

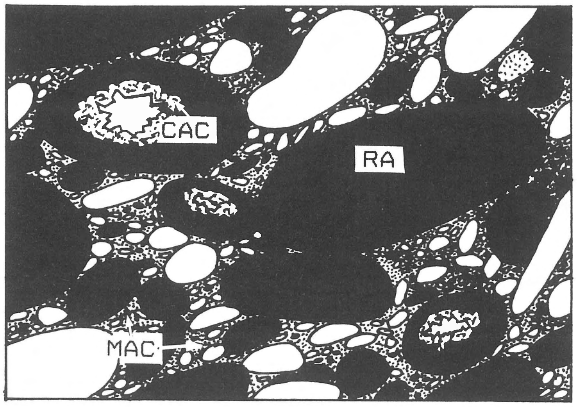


Fig. 4. Drawing of a typical sample from the ankeritized interval of the basal Zechstein conglomerate in the Bree borehole with indication of the three different types of ankerite: replacive ankerite (RA), clast infill ankerite cement (CAC) and ankerite cement in the conglomerate matrix (MAC).

The latest diagenetic event was the precipitation of fibrous to flaky illite which often bridges the pores.

Geochemistry

Conglomerate matrix

Early-diagenetic fringing calcite cement
As described above, the early-diagenetic, fringing calcite cement is zoned. The three petrographically distinct calcite zones can also be characterised by their chemical composition, as established by electron microprobe analysis (Fig. 5). The non-luminescent stage A has very low Fe and Mn contents, varying between the detection limit and 0.54% for Fe and values close to the detection limit for Mn. In the bright luminescent stage B, the Fe content varies between 0.27 and 1.64% but the Mn content is very high: 2.26 to 2.76%. In comparison with stage B, the dull luminescent stage C calcite shows an increase in Fe (1.39–2.70%) and a decrease in Mn content (0.80–1.40%). The observed petrographic and chemical variations are consistent with a change of the fluid from oxic to reducing conditions (Barnaby & Rimstidt 1989).

The stable isotope signature of early diagenetic

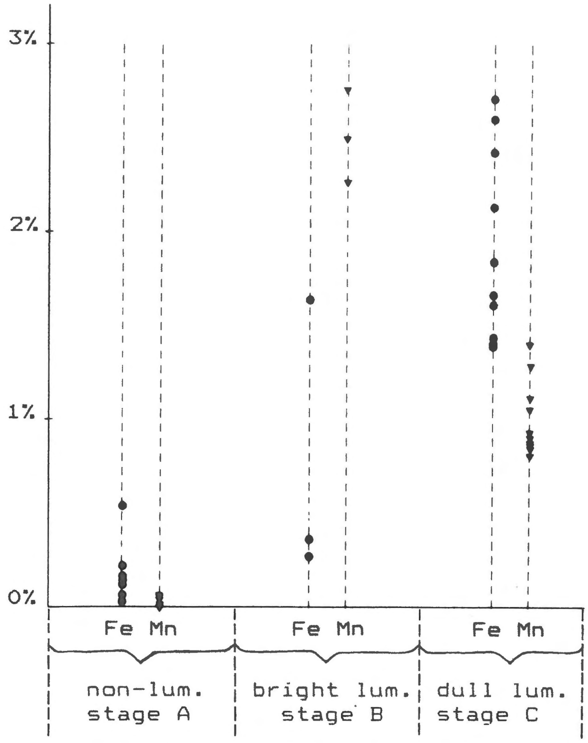


Fig. 5. Fe and Mn contents of the different stages of the early-diagenetic fringing calcite cement.

phases, such as the fringing calcites, should be compared with the original composition of Zechstein marine water. This initial composition serves as a baseline against which diagenetic re-equilibration has to be evaluated. According to Popp et al. (1986), calcite in equilibrium with Zechstein marine water would have $\delta^{13}C$ values of + 2.5 to + 5.8‰ and $\delta^{18}O$ values of + 0.5 to + 2.0‰. As it was not possible to sample the individual cement stages separately, stable isotope analyses were performed on the entire pre-compactional cement phase. The low $\delta^{13}C$ value of − 5.65‰ of this phase as compared to a Zechstein marine source water indicates the presence of a CO_2-depleted source. Possible depleted sources are soil gas derived from anaerobic bacterial oxidation of organic carbon, or CO_2 produced during bacterial sulphate reduction. In the latter case, the sulphate source would be of marine origin. The depleted $\delta^{18}O$ value of − 4.38‰ in combination with an early, pre-compactional origin indicates precipitation from an ^{18}O-depleted fluid. This may reflect influence of meteoric water.

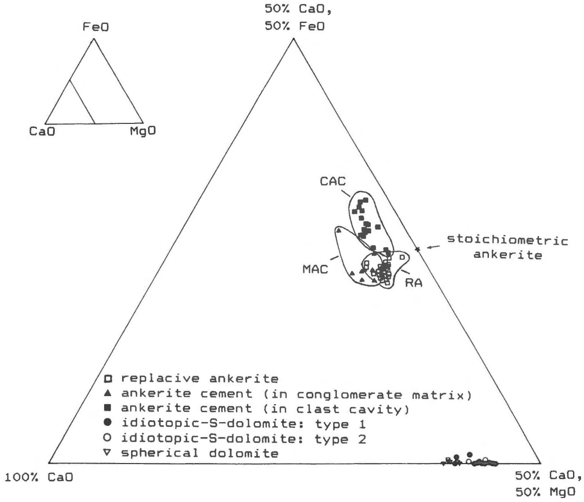


Fig. 6. Chemical composition of the different ankerite and dolomite types as determined by microprobe analysis.

Late-diagenetic ankerite cement

Mean ankerite cement composition in the conglomerate matrix is $Ca_{0.56}$ $(Fe_{0.22}, Mg_{0.21}, Mn_{0.01})$ $(CO_3)_2$ (Fig. 6). These values are within the range of reported ankerite cements (Boles & Franks 1979; Kantorowicz 1985). The $\delta^{13}C$ values range from − 0.26 to − 1.16‰ and $\delta^{18}O$ values from − 7.52 to − 10.94‰. There is no systematic variation in chemical or isotopic composition throughout the conglomerate. The low $\delta^{18}O$ values reflect the late-diagenetic burial origin of this ankerite cement, because such depleted $\delta^{18}O$ values are compatible with a derivation from hot fluids. A discussion on the origin of this cement phase is presented in the ankeritization model.

Late-diagenetic bright luminescent calcite cement

The late-diagenetic, bright luminescent calcite cement possesses a relatively high Fe content (around 9100 ppm) and a low Mn content (around 2500 ppm). However, most of the Fe present during the corresponding diagenetic stage, was preferentially incorporated in the pyrite, which is often associated with this cement. The bright luminescent calcite phases have a wide range of $\delta^{13}C$ and $\delta^{18}O$

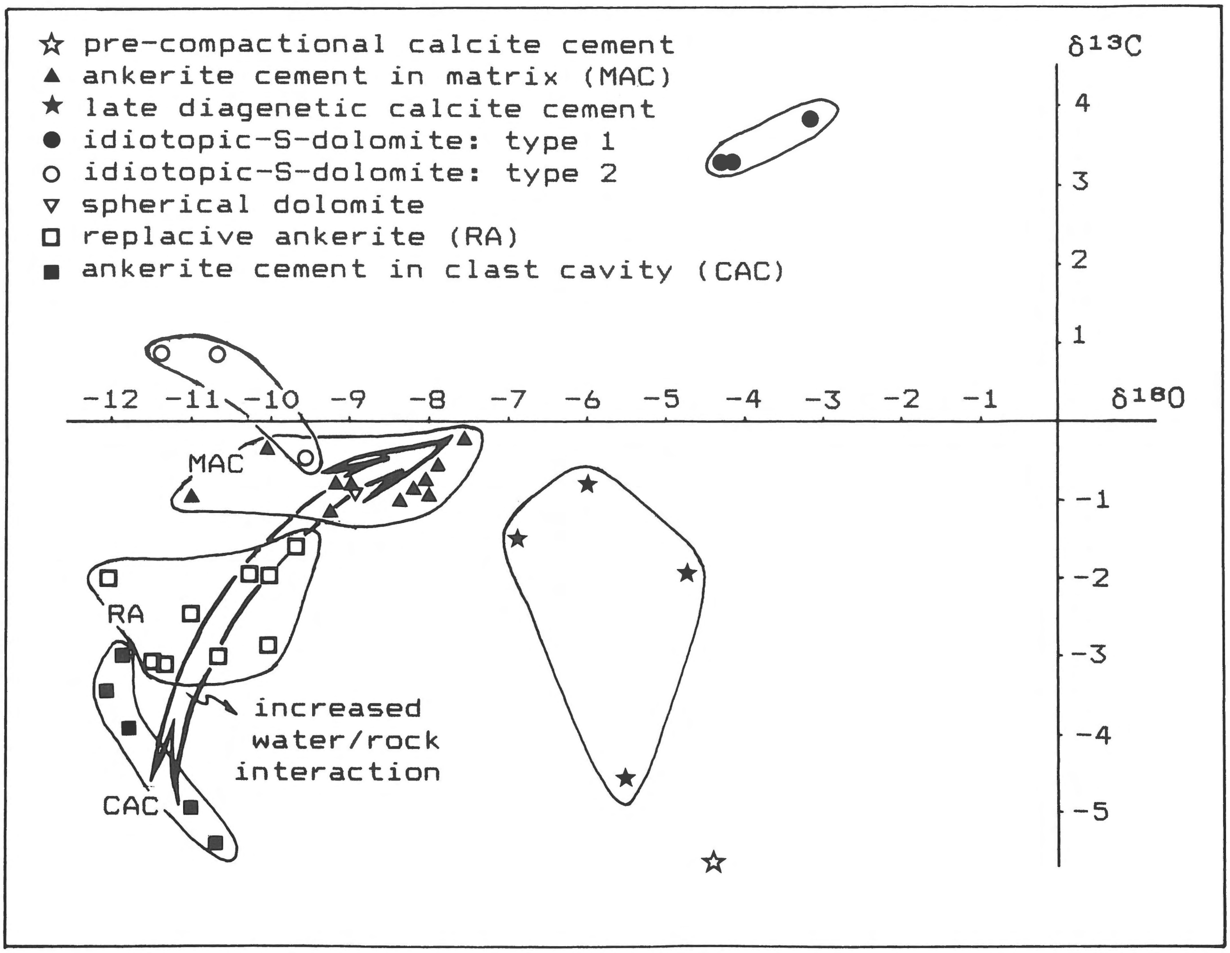


Fig. 7. $\delta^{18}O$–$\delta^{13}C$ isotopic composition of cements and clasts.

values (Fig. 7), mainly due to the fact that it was impossible to sample this phase separately. A variable proportion of the sometimes partly recrystallised, early-diagenetic fringing calcite cement was nearly always present and thus included in the analyses. The $\delta^{13}C$ values range from −0.70 to −4.56‰. These negative $\delta^{13}C$ values may reflect the contribution of depleted CO_2 from the fringing pre-compactional calcite. However, the presence of another depleted CO_2 source, such as CO_2 formed by thermal reduction of sulphate is a likely alternative. The $\delta^{18}O$ values range from −4.70 to −6.85‰. These less negative values of $\delta^{18}O$ in comparison to $\delta^{18}O$ values of the ankerite cement may indicate that this calcite cement precipitated at lower temperatures, or from less depleted solutions. Alternatively, the $\delta^{18}O$ values of this cement reflect equilibrium with the maximal burial temperature. If this assumption is correct, $\delta^{18}O_{smow}$ values of the fluid would range from +1.4 to +3.3‰.

Conglomerate clasts

Dolomite clasts

Based on the petrographical characteristics and the chemical (Fig. 6) and stable isotope composition (Table 2 and Fig. 7), at least three dolomite types can be differentiated.

The first type consists entirely of zoned dolomite crystals (Fig. 10F) and is an idiotopic-subhedral-dolomite. The Ca/Mg ratio which grades from crystal centre to crystal edge from 55/45 to 59/41, reflects its non-stoichiometric composition. It possesses positive $\delta^{13}C$ values varying around +3.40‰, while $\delta^{18}O$ values vary between −3.12 and −4.18‰. These values fall within the range of Dinantian dolomites recognized in the Campine Basin (Muchez & Viaene 1991) and Dinant-Namur Basin (Peeters et al. 1991). The $\delta^{13}C$ values most likely reflect inheritance from the dolomitized host lithology, while the $\delta^{18}O$ values could reflect shallow burial dolomitization by mixed meteoric/marine fluids, or dolomite recrystallisation by meteoric solutions (Gao & Land 1991).

The second type is also an idiotopic-subhedral-dolomite. It occurs as individual clasts in units 1 and

Table 2. Stable isotope values of $\delta^{13}C$ and $\delta^{18}O$ in ‰. $\delta^{18}O$ values have been corrected for fractionation by phosphoric acid dissolution (see methods)

		$\delta^{13}C_{PDB}$	$\delta^{18}O_{PDB}$
Cements	pre-compactional calcite	−5.6	−4.4
	ankerite cement (in matrix conglomerate) MAC	−0.6	−7.9
		−1.0	−8.0
		−0.7	−8.0
		−0.9	−8.2
		−0.3	−7.5
		−0.8	−9.1
		−1.0	−8.3
		−1.2	−9.2
		−0.8	−8.9
		−0.4	−10.1
		−1.0	−10.9
	ankerite cement (in clast cavity) CAC	−3.0	−11.8
		−2.8	−9.7
		−5.4	−10.7
		−5.0	−10.8
		−3.4	−12.0
		−3.9	−11.8
	late-diagenetic bright luminescent calcite	−4.6	−5.4
		−1.9	−4.7
		−0.7	−6.0
		−1.5	−6.8
	idiotopic-S-dolomite type 1	+3.4	−4.2
		+3.4	−4.1
		+3.8	−3.1
	idiotopic-S-dolomite type 2	+0.9	−11.3
		−0.5	−9.5
		+0.9	−10.6
Clasts	spherical dolomite	−0.9	−8.9
	replacive ankerite RA	−3.1	−10.6
		−2.0	−10.0
		−2.9	−10.0
		−1.6	−9.6
		−2.4	−11.0
		−2.0	−10.2
		−2.0	−12.0
		−3.1	−11.3
		−3.1	−11.4

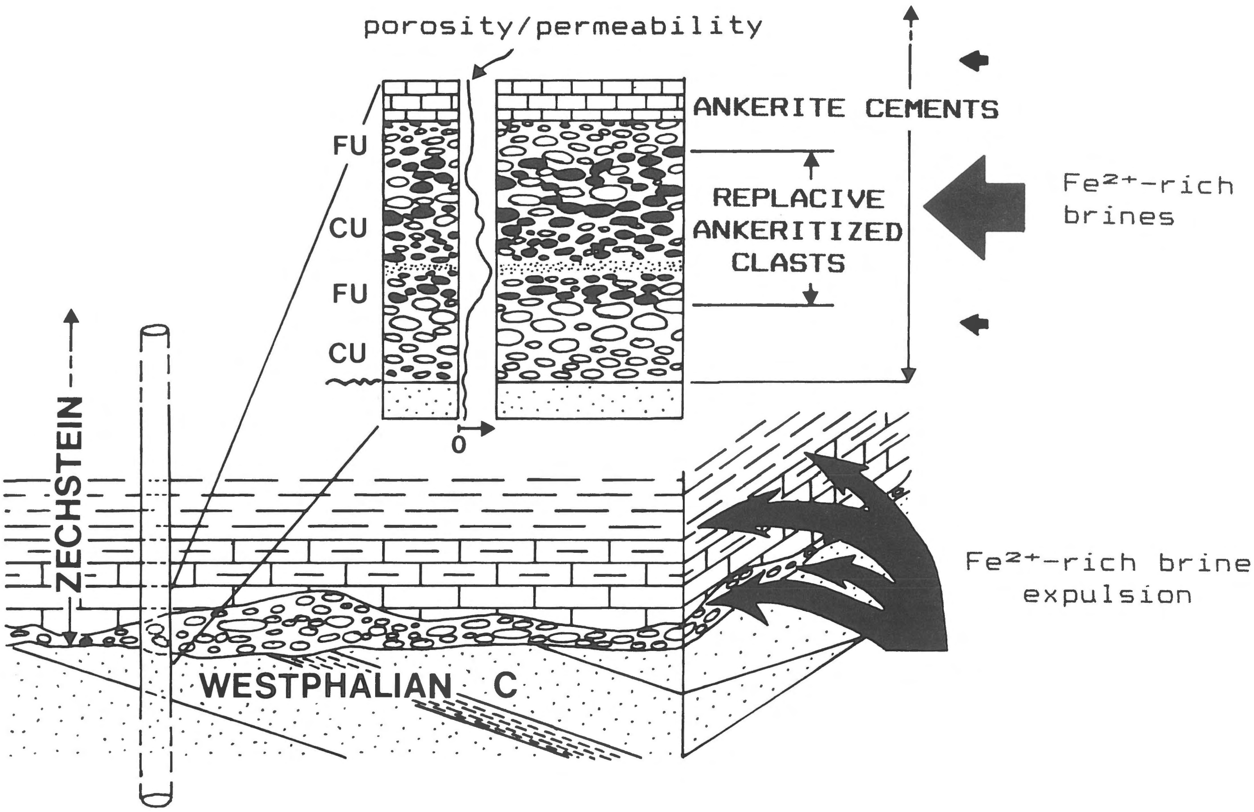


Fig. 8. Proposed ankeritization model where Fe-rich solutions were channelled along the originally more porous and permeable unit 2. They caused a pervasive replacement by ankerite of calcite cements and limestone and dolomite clasts. The interval where ankeritized clasts are present, thus represents an ankeritization front. CU: coarsening upward, FU: fining upward sequence.

3, and as relict phases within the ankeritized unit 2 (Fig. 10G). In the latter, only the red luminescent crystal core remains. The Ca/Mg ratio varies around 57/43. This non-stoichiometric aspect could explain why this second dolomite type is often nearly entirely replaced by ankerite within the central interval. Its $\delta^{13}C$ values range from -0.47 to $+0.86$‰ and reflect major inheritance of the host carbonate phase. However, a minor contribution from a depleted CO_2 source seems likely. As reflected by the highly depleted $\delta^{18}O$ values, which range from -9.53 to -11.34‰, dolomitization or recrystallisation occurred either from highly depleted solutions, or at elevated temperatures.

The third type was found in a single clast containing a dolomite relict phase with 'spherical' crystal outlines (Fig. 10H). The crystals are zoned under CL. From centre to edge the Ca/Mg ratio changes from 58/42 to 60/40; these crystals are clearly non-stoichiometric and the least stable of all dolomite types. The $\delta^{13}C$ value is -0.90‰. This slightly negative value suggests that the composition was buffered by interaction of the fluids with the dolomitised limestone. However, a minor contribution of a depleted CO_2 source was also present. The $\delta^{18}O$ value is -8.86‰. This value falls within the field of $\delta^{18}O$ values of the second idiotopic-subhedral-dolomite variety. The negative value thus could indicate dolomitization or recrystallisation from highly depleted solutions, or at elevated temperatures.

Ankeritized clasts

The 'replacive' ankeritized clasts (RA) possess a rather uniform chemical composition (Fig. 6), with as mean formula: $Ca_{0.55}$ $(Fe_{0.21}, Mg_{0.23}, Mn_{0.01})$ $(CO_3)_2$. The chemical composition of the ankerite cement (CAC), however, changes systematically. A clear

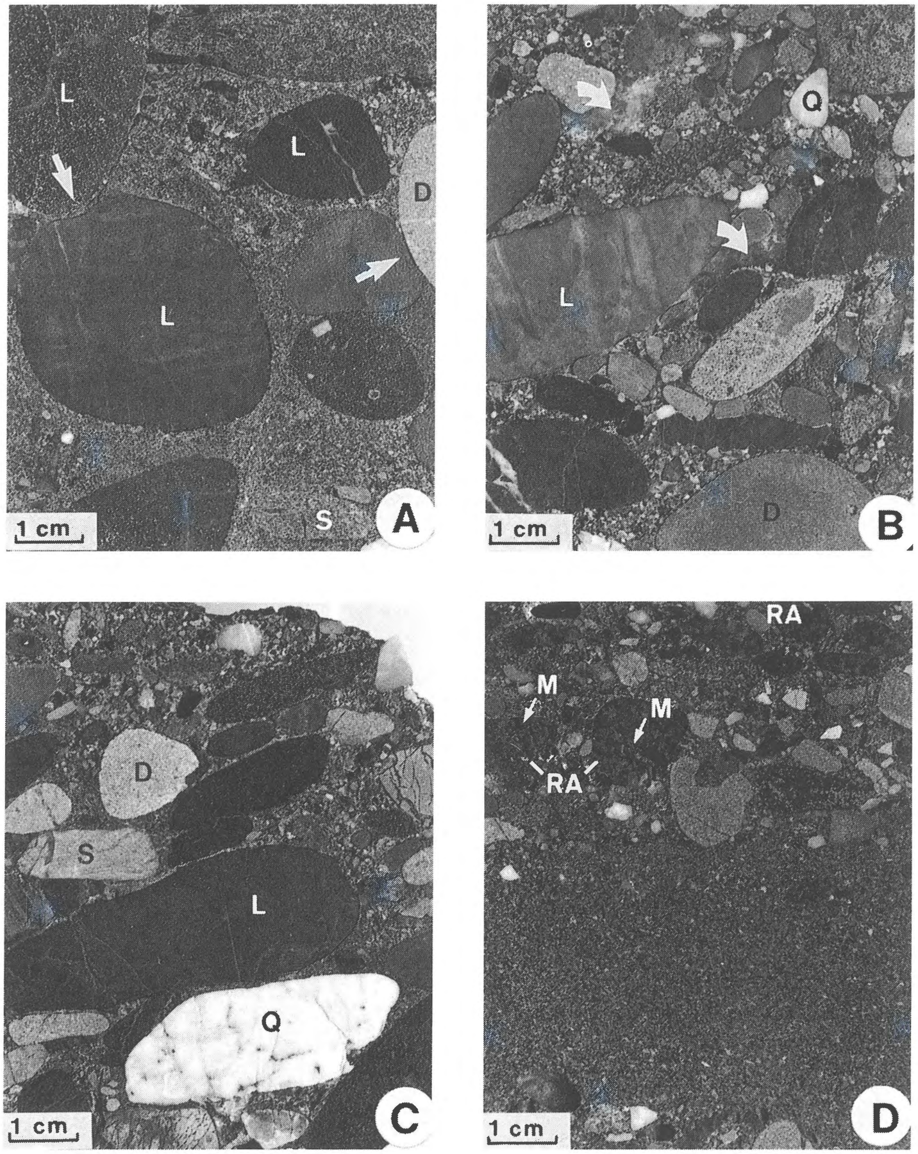
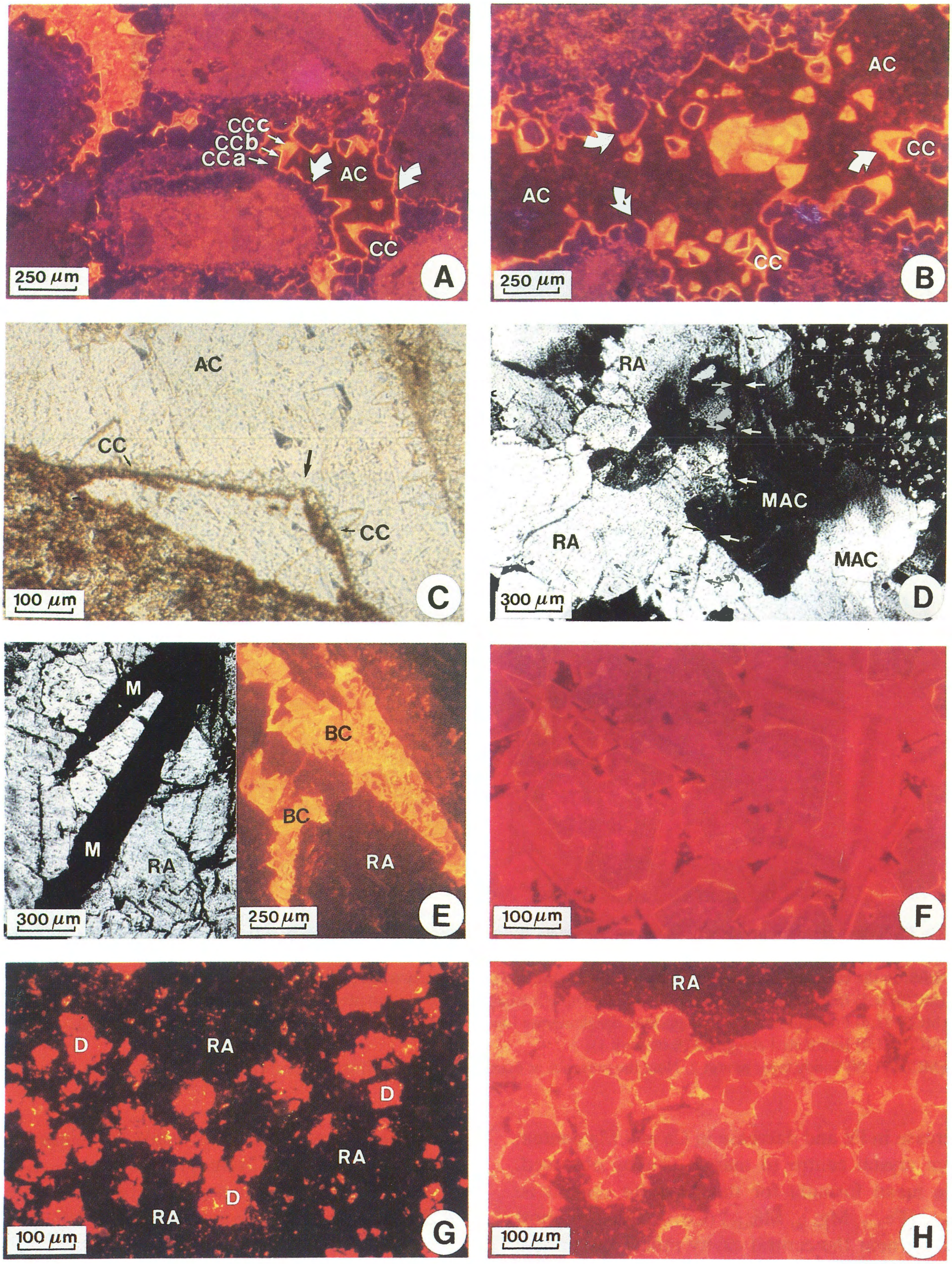


Fig. 9. Overview of different parts of the basal Zechstein conglomerate of the Bree borehole (macroscopic view). The polymict conglomerate consists mainly of limestone (L), dolomite (D), sandstone (S) and quartzite (Q) clasts set in a matrix of mainly sand-sized particles. In the central part of the conglomerate, limestone and dolomite clasts are progressively replaced by ankerite.
A. (MC/B/31:1) Interval of unit 1 where the conglomerate is locally matrix-supported. Compaction deformed the clasts (see arrows).
B. (MC/B/31:6) Predominantly clast-supported conglomerate (unit 1). Note the presence of macroscopic cements (arrows).
C. (MC/B/31:4) Imbricated elongated clasts (unit 1).
D. (MC/B/31:19) Sandy layer in unit 2. Note the presence of marcasite needles (M) in the ankeritized clasts (RA).

increase in Fe and decrease in Ca and Mg content from crystal centre to margin can be observed. The mean formula for this ankerite cement is: $Ca_{0.54}$ $(Fe_{0.27}, Mg_{0.18}, Mn_{0.01})$ $(Co_3)_2$. The outermost margin near the central cavity reflects an Fe-rich dolomite composition. The ‘replacive’ ankerite possesses negative $\delta^{13}C$ values ranging rrom − 1.60 to − 3.12‰ and $\delta^{18}O$ values ranging from − 9.65 to − 12.02‰. The ankerite cement (CAC) has $\delta^{13}C$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values ranging from − 2.84 to − 5.40‰ and $\delta^{18}O$ values ranging from − 9.75 to − 12.04‰.

Model of ankeritization

The post-compactional nature of the ankerite phases and the depleted $\delta^{18}O$ values indicate that ankeritization and ankerite cementation occurred late in the diagenetic history, a feature in common with ankerite occurrences reported in the literature. According to Boles (1978), Boles & Franks (1979), Curtis (1985), Gawthorpe (1987) and Taylor (1990) ankeritization is often associated with late-diagenetic clay-mineral transformations, more specifically the transformation from smectite to illite. The smectite/illite conversion starts at temperatures as low as 50° C (Lahan 1980) to 125° C (Boles & Franks 1979). Water and cations as Fe^{2+} and Mg^{2+} are released during this transformation and can react under favourable conditions with other phases to form ankerite. The conglomerate at present occurs at its maximum burial depth (1292 m) which corresponds to an estimated temperature of maximum 60° C. That is where this process could have taken place. But whether it would be efficient at such low temperature is difficult to establish. However, it is more likely that the ankeritizing Fe-rich fluids were sourced from underlying thick clay-rich formations e.g. from Upper Carboniferous shales (Muchez et al. 1991) where the smectite-illite conversion occurred at more elevated temperatures. Ascending Fe-rich fluids preferentially followed the most permeable central part of the conglomerate aquifer. It is within this central interval that ankerite cements are macroscopically visible (Fig. 2A). The Fe-rich solutions which were focussed into this interval (Fig. 8) caused pervasive replacement of limestone and dolomite clasts by ankerite (RA) and ankerite cementation of the matrix (MAC).

Despite the fact that it is not possible to differentiate the three ankerite phases (RA, CAC & MAC) from a petrographical point of view, their chemical composition differs (Fig. 6). The RA plots closest to stoichiometric ankerite, while the MAC is enriched in Ca; the CAC has the highest Fe content. As can be seen in the isotope crossplot (Fig. 7), the three ankerite phases plot within different $\delta^{18}O$–$\delta^{13}C$ areas. The 'matrix' ankerite cement (MAC) possesses the least depleted $\delta^{13}C$ and $\delta^{18}O$ values, while the $\delta^{18}O$ values of the 'replacive' ankerite (RA) and the 'clast infill' cement (CAC) phases are similar and most depleted.

The latter phase possesses the lowest $\delta^{13}C$ values. These differences could point to ankerite replacement and cementation by different fluids, thus at different times. However, we prefer to in-

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Fig. 10. A. to E: Overview of diagenetic phases within the basal Zechstein conglomerate in the Bree borehole.

A. & B. Cathodoluminescence photomicrograph (MC/B/43:16&19) illustrating pre-compactional circumgranular calcite cement (CC) precipitated around the clasts. The calcite is characterized by a non-luminescent core (stage CCa), surrounded by a bright (stage CCb; presently partly dissolved) and a dull luminescent fringe (stage CCc). The irregular outline of the outermost dull luminescent zone shows that dissolution (see arrows) has affected these calcites. A late-diagenetic ankerite cement (AC) precipitated in the remaining matrix pores.

C. Photomicrograph (MC/B/62:13) showing that due to compaction the pre-compactional, fringing calcite cement (CC) is peeled off the clasts and subsequently broken (arrows). After compaction, an ankerite cement (AC) precipitated within the pores.

D. Photomicrograph (MC/B/64:19) of an ankeritized clast (RA) occurring next to matrix ankerite cement (MAC). Notice the optical continuity (arrows) between both ankerite phases.

E. Left: Photomicrograph (MC/B/64:18) of marcasite needles (M) occurring in an ankeritized clast (RA); right: cathodoluminescence photomicrograph (MC/B/43:4) of zoned, bright luminescent calcite cement (BC) occurring in marcasite crystal molds.

F. to H. Overview of the different dolomite types.

F. Cathodoluminescence photomicrograph (MC/B/43:14) of an idiotopic-subhedral-dolomite (first type). This dolomite is totally composed of zoned dolomite crystals.

G. Cathodoluminescence photomicrograph (RS 1562) of an idiotopic-subhedral-dolomite (second type). This dolomite (D) is present as a relict phase in an ankeritized clast (RA).

H. Cathodoluminescence photomicrograph (MC/B/43:22) of dolomite with 'spherical' crystal shape, present as a relict phase in an ankeritized clast (RA).

terpret these data in the light of one major ankeritization episode, characterized by evolving fluids. According to the proposed ankeritization model by which Fe-rich solutions were channelled along the most porous and permeable central part of the conglomerate, matrix cementation (MAC) would have occurred after clast replacement by ankerite (RA). Otherwise pores would have been occluded and porosity and permeability of the central interval would have been dramatically reduced. In that situation it would have been very difficult to explain why replacement only occurred in the central part of the conglomerate. Ankerite cementation within the clasts (CAC) could only have occurred after cavity development, thus after ankerite replacement took place. Whether both cement phases (CAC and MAC) developed simultaneously or not, can not be inferred from petrographical observations alone.

According to their $\delta^{18}O$ values, the RA and the CAC phases formed from fluids at similar temperature or of similar isotopic composition. $\delta^{13}C$ values of the CAC (-2.84 to -5.40‰) point towards involvement of isotopically light carbon. The currently favoured mechanism for producing bicarbonate depleted in ^{13}C in the deep burial realm is thermal maturation of organic matter. This process produces very light bicarbonate with $\delta^{13}C$ values varying between -10 to -25‰ (Irwin et al. 1977). The absence of large amounts of organic matter in the Zechstein and its relatively shallow maximum burial depth as well as the proximity of thick Westphalian organic-rich mudstones under the Zechstein make these mudstones the most likely source of the isotopically light carbon. The carbon isotopic composition of the CAC, however, is too enriched in ^{13}C to have originated solely from bicarbonates derived by thermal maturation of organic matter. Its $\delta^{13}C$ values reflect a mixing of the depleted organic carbon with isotopically heavy carbon. The latter may have been derived from fluids within the Zechstein sequence, or from the dissolution, equilibration and reprecipitation of in-situ carbonate components, such as the limestone and dolomite clasts. The less depleted $\delta^{13}C$ value for the RA phase in comparison to the CAC phase points towards an increased contribution of isotopically heavy carbon. The CAC $\delta^{18}O$–$\delta^{13}C$ signature thus possibly reflects a precipitate which is more in equilibrium with the parental ascending Fe-rich fluids than is the case for the RA. This would also explain why the CAC are most enriched in Fe. After replacement, the MAC precipitated from ascending fluids which, according to the less depleted isotope values and increased Ca content of the MAC, evolved due to increased water/rock interaction or decreased temperature (equilibration with host rocks). Both processes would explain the less depleted $\delta^{18}O$ signature. The $\delta^{13}C$ values point toward increased input of isotopically heavy carbon, most likely of inorganic origin. The slightly higher Ca values of this cement in comparison with both other ankerite phases support this interpretation.

A more detailed isotope geochemical interpretation however, is only possible if $^{87}Sr/^{86}Sr$ data and fluid inclusion data become available (research in progress).

Conclusions

The following conclusions can be drawn:

1. The basal Zechstein conglomerate of the Bree borehole is polymict and consisted originally mainly of limestone, dolomite, sandstone, and quartzite clasts. The limestone and dolomite clasts are locally ankeritized. The conglomerate occurs at the base of a transgressive marine sequence. It most likely formed in a shoreline environment.
2. Based on sedimentological criteria, the conglomerate (3.15 m thick) can be divided into two units. These are separated by a thin sandy layer. Both consist of a lower coarsening-upward sequence and an upper fining-upward sequence.
3. The diagenetic history of the conglomerate is complex. It started with the development of a circumgranular, equant, zoned calcite cement. Its pre-compactional origin and its $\delta^{18}O$ and $\delta^{13}C$ values suggest that this cement has a meteoric phreatic origin. After compaction and dissolution, ankeritization was the most important diagenetic process. Ankerite is present as a cement all through the conglomerate. In the mid-

dle part of the conglomerate (unit 2), ankerite replaces limestone clasts, some types of dolomite clasts as well as early-formed calcite cements. Its post-compactional origin and depleted $\delta^{18}O$–$\delta^{13}C$ signature indicate that this cement formed during burial. A late-stage, zoned, bright luminescent calcite cement associated with pyrite and also of burial origin, formes the latest diagenetic product.

4. To explain the distribution of the ankeritized clasts, a model invoking the focussed flow of Fe-rich solutions in the originally more porous and permeable middle part of the conglomerate is proposed. This model is consistent with the fact that this central part contains more cements than the lower and upper units 1 and 3.
5. As a result of the diagenetic overprinting, three lithological units can be recognized. This contrasts with the two units differentiated on sedimentological criteria.
6. $\delta^{13}C$–$\delta^{18}O$ values of the three different ankerite phases (replacive as well as cementing) indicate that ankeritization was complex. Fe-rich ascending fluids most likely originated from organic-rich Upper Carboniferous mudstones. The low $\delta^{13}C$ values of the replacive ankerite and the ankerite cements (CAC) reflect mixing with diagenetic carbon derived from late-stage thermal maturation of organic matter of organic-rich Westphalian mudstones and CO_2 most likely derived from the replaced carbonate phases. Increased water/rock interaction explains the least depleted $\delta^{13}C$ values of the ankerite cement in the matrix, while this interaction or a reduced temperature of the ascending fluids explains the less depleted $\delta^{18}O$ values. Variation in chemical composition of these phases reflects gross compactional changes due to evolving water/rock interaction.

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