Methanogenesis during Shu’aiba diagenesis: examples from Al Shaheen Field, Block 5, offshore Qatar

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ABSTRACT

Evidence has been found for the involvement of bacterial methanogenic processes in the diagenesis of late Early Aptian Shu’aiba Formation sedimentary rocks from Block 5, offshore Qatar. This is in the form of δ13C values significantly higher than the presumed late Early Aptian marine signal. High δ13C values were recorded in early-formed inclusion-rich calcite that represents neomorphosed aragonite/marine cement (+6.6‰) and the latest precipitated blocky non-ferroan calcite cement (+8.9‰). Oxygen-isotope data suggest that the later methanogenic episode occurred during burial. In bulk rock samples from another well, δ13C values of +6.5 to +11.5‰ were determined from a 10 ft thick zone located 4 ft below the top of the Shu’aiba. In other wells for which data were available the equivalent interval of the Shu’aiba was characterised by expected marine δ13C values. Finally, δ13C values up to +9.1‰ were recorded in a localised area of dolomite replacement immediately beneath the Top Shu’aiba surface, which can be dated to after the onset of Nahr Umr Formation deposition. These are the first reported examples of methanogenic reactions affecting the Shu’aiba Formation and provide new insight into the diagenesis of this formation, which is often assumed to be dominated by meteoric processes. The evidence presented for the resetting of the carbon-isotope composition of the bulk rock has implications for the application of carbon-isotope stratigraphy to the Shu’aiba Formation.

INTRODUCTION

Several hundred bulk rock δ13C/δ18O data have been published for the Shu’aiba of Oman and the U.A.E. (Moshier, 1989; Budd, 1989; Vahrenkamp, 1996; van Buchem et al., 2002; Immenhauser et al., 2004; Sattler et al., 2005 and others). Carbon values mostly fall in the range +1‰ to +5.5‰ and generally have been interpreted as being close to equilibrium with Aptian seawater (Vahrenkamp, 1996; Boote and Mou, 2003), with the spread in values being attributed mainly to secular variation in the carbon isotopic composition of seawater. It is relevant here that (1) not all biogenic components precipitate in equilibrium with seawater, with deviations of several per mil from ambient conditions being common place, (2) syn-depositional diagenesis in marine-derived pore waters can result in significant changes in isotopic composition of at least some grain types, dependant on original mineralogy and extent of disequilibrium (Patterson and Walter, 1994) and (3) the δ13C values of marine pore waters reflect an admixture of the marine signal and oxidised organic carbon, although in bulk terms the latter is typically insignificant in the open systems that characterise the bioturbated upper part of the sediment column. Therefore, syn-sedimentary marine diagenesis is a time of isotopic homogenisation and it is a slightly modified marine signal that is carried into the subsurface. Oxygen values vary from -9‰ to -3‰; higher figures having been interpreted as being close to equilibrium with Aptian seawater, while lower figures have been variously interpreted as due to alteration in meteoric water in the near-surface (Budd, 1989; Immenhauser et al., 1999; Cantrell et al., 2004; Sattler et al., 2005) or modified marine water during burial (Moshier, 1989). As with carbon values, not all biogenic grains form in oxygen-isotope equilibrium with seawater and original oxygen-isotope values are subject to minor modification during syn-sedimentary marine diagenesis.

These interpretations have been reinforced by some δ13C/δ18O data from separated components (bivalve shells, micrite matrix, cements, etc.) that imply that carbon is recycled during diagenesis, hence largely remains invariant (the premise upon which carbon isotope stratigraphy is based), whereas oxygen values are subject to change.
Bulk rock and separate component δ\(^{13}\)C/δ\(^{18}\)O analyses are reported here from the Shu’aiba of Block 5, offshore Qatar. These represent a subset of results generated from a number of studies that were undertaken to investigate the diagenetic history of the Shu’aiba Formation in Block 5, in particular the timing of porosity generation and destruction. A significant proportion of these data show enrichment in \(^{13}\)C, well above that expected for carbonate in equilibrium with Early Aptian seawater. The only process that can explain such high values is bacterial methanogenesis (Irwin et al., 1977), which results in the production of CO\(_2\) with a highly positive δ\(^{13}\)C value. Irwin et al. (1977) suggested this should be \(~ +15\%\)\(_o\), but Budai et al. (2002) reported methanogenic calcite cements with δ\(^{13}\)C values up to \(+34\%\)\(_o\). The presence of high carbon values in Block 5 indicates that the diagenesis of organic matter played a significant role in the post-depositional history of Block 5 Shu’aiba sediments, apparently in contrast to Shu’aiba shelf areas in the U.A.E. and Oman.

Three examples of high δ\(^{13}\)C values, two based on bulk rock data and the other using data from individually separated cement phases, are presented here with brief descriptions. The discussion provides an overview of the three examples and concentrates on (1) timing of methanogenesis, (2) source of the heavy carbon, (3) reasons for the difference in diagenesis between Block 5 and the Shu’aiba shelf areas to the south and east of the Bab Basin and (4) implications for carbon isotope stratigraphy.

GEODETICAL SETTING

Block 5 is situated approximately 70 km to the north of the Qatar peninsula, in the Arabian Gulf (Figure 1). The Oligocene to Cretaceous stratigraphy is summarised on Figure 2. During the Early Aptian, Block 5 was located close to the equator, lying within a carbonate platform area close to the northwest margin of the intra-platform Bab Basin (Murris, 1980; Sharland et al., 2001), where \(~ 200\ ft\) of moderately deep to shallow water sediments accumulated, very similar in character to those deposited elsewhere on the Shu’aiba shelf (Alsharhan and Nairn,1994). The material described here is exclusively late Early Aptian in age. Widespread development of karst features in Block 5 supports Late Aptian subaerial exposure of the shelf area, in line with other Shu’aiba shelf areas to the south and east (Sharland et al., 2001; van Buchem et al., 2002).

Subsequent flooding led to deposition of the claystone dominated Nahr Umr Formation and the overlying carbonate dominated formations of the Wasia Group. In Block 5 the base of the Nahr Umr is iron-rich and contains widespread chamosite ooids, siderite and pyrite, together with thin intervals of locally glauconitic sands. The Wasia Group is terminated by an angular unconformity associated with Turonian regional exposure related to development of a peripheral bulge associated with ophiolite obduction along the eastern margin of the Arabian Plate (Murris, 1980; Robertson, 1987).

Deposition of the Late Cretaceous Aruma Group was followed by another period of exposure and erosion during the Paleocene. The youngest part of the section consists of Paleocene to Eocene carbonates topped by yet another erosion surface. Currently, Top Shu’aiba is at a depth of \(~3,100\ ft\) true vertical depth sub-sea (TVDSS).

The oils present in Block 5 were sourced from the Jurassic Hanifa Formation to the southeast of the Qatar peninsula (Guthrie et al., 2005). This had reached maturity by 65 Ma and the salt anticlines that allowed leakage of oil into the Cretaceous strata were already forming at this time (He and Berkman, 2003). Thus, accumulation of hydrocarbon and cessation of diagenesis in the Al Shaheen field occurred during the early Paleogene.

C- AND O-ISOTOPE COMPOSITION OF LATE EARLY APTIAN MARINE AND METEORIC WATER

The interpretation of the carbon- and oxygen-isotope compositions of any limestone or limestone component requires assumptions to be made regarding the expected isotopic compositions of carbonates precipitated in equilibrium with marine and meteoric waters present at the time of deposition.
Carbon-isotopes

Marine δ¹³C values varied substantially through the Aptian (Scholle and Arthur, 1980; Föllmi et al., 1994; Vahrenkamp, 1996; Menegatti et al., 1998; Weisssert et al., 1998; Jenkyns and Wilson 1999; van Buchem et al., 2002; Immenhauser et al., 2005). The late Early Aptian aged samples described here fall within the ‘Cismon Event’ of Weisssert et al. (1998), equivalent to unit C7 of Menegatti et al. (1998), and a preferred value of +5.0 to +5.5 for marine carbonate of this age is based on Shu’aiba bulk rock samples from Oman and the U.A.E. (Vahrenkamp, 1996). Despite Vahrenkamp’s (1996) Shu’aiba shelf data being consistently ~1‰ higher than the similarly aged pelagic Tethyan profile of Föllmi et al. (1994) and his Shu’aiba shelf data being consistently higher than data from nearby basinal wells, these samples show secular patterns that can be related to global changes in the carbon-isotopic composition of seawater and they represent the most comparable data to Block 5. 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value provides a conservative benchmark against which to judge the presence of methanogenesis-derived heavy carbon.

The $\delta^{13}C$ value of carbonate in equilibrium with meteoric water depends on the amount of $^{13}C$-depleted soil-gas CO$_2$ added to the water as it percolates through any soil zone that is developed on the exposure surface. Depletion of up to 8‰ has been captured in limestones immediately beneath an exposure surface (Beier, 1987), however, not all exposure surfaces have $^{13}C$-depleted zones (Allan and Mathews, 1982; Dickson and Saller, 1995 and 2006).

**Oxygen-isotopes**

Late Barremian-Aptian rudist calcite layers studied by Steuber et al. (2005) had average $\delta^{18}O$ values of -2.2 to -3.6‰, but showed seasonal variations in $\delta^{18}O$ of several per mil, except those from low original latitudes, which had small ranges in $\delta^{18}O$ values with no regular pattern. These average data are somewhat lower than the -0.5 to -1‰ suggested by Veizer et al. (1999) as typical of this time period, also based on shell calcite, but do fall in the 2σ bounds of the Veizer et al. (1999) dataset. Steuber et al. (2005) equated their results with a value of -0.66‰ VSMOW for the oxygen isotopic composition of seawater for that time period. The oxygen isotopic composition of Mesozoic seawater is generally estimated to be -1‰ lower than present day values (Shackleton and Kennet, 1975).

The difference between seawater and shell calcite $\delta^{18}O$ values reflects (1) temperature related fraction effects and (2) deviations from mean seawater composition due to the combined effects of evaporation, precipitation and freshwater influx from land areas. Whereas the Steuber et al. (2005) data mostly come from 17 to 25° N, Block 5 was situated close to the equator during the Aptian and may have experienced higher average temperatures, possibly resulting in slightly lower $\delta^{18}O$ values than those recorded at higher latitudes, although other factors such as increased evaporation could have pushed values in the opposite direction.

Preferred average values for shell calcite in the Shu’aliba Formation are based on the -0.66‰ VSMOW estimate for Tethyan seawater. This yields values for shell calcite of approximately -2

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**Figure 2:** Generalised stratigraphic column for offshore Qatar, based on Sharland et al. (2001).
and -3‰ at 21° and 25°C (mean sea surface temperature of Tethys during the Aptian (Steuber et al., 2005)), respectively, presuming equilibrium. Typically, bulk rock δ¹⁸O data are not quoted since they are widely believed to represent re-equilibrated values.

The present day global pattern of δ¹⁸O of precipitation is well known and average values show virtually no depletion compared to seawater at the equator, with increasing ¹⁸O-depletion toward the poles (Yurtsever, 1975; Bowen and Wilkinson, 2002). The present day average δ¹⁸O value for precipitation over the Arabian Gulf, currently at ~26° to 27° N, is less than 2‰ lighter than seawater (Yurtsever, 1975), meaning that the bulk δ¹⁸O of carbonates precipitated at the surface, in equilibrium with meteoric water, are indistinguishable from Recent marine carbonate, although serial sampling of sequential precipitates may well reveal more ¹⁸O-depleted values associated with shortlived periods of prolonged rainfall. Although Block 5 had an equatorial location during the Aptian, it is far from clear whether a uniformitarian approach can be applied. A different continental configuration and reduced or absent polar ice caps undoubtedly had an important influence on global climate patterns. Even so, given the low topography and marginal position during the Late Aptian it is hard to envisage average δ¹⁸O values for precipitation being substantially more depleted than at the present day, giving a preferred average Late Aptian value of no less than -2.66‰ SMOW. Assuming similar land surface and sea surface temperatures, this would have resulted in a minimum bulk rock δ¹⁸O of approximately -4 to -5‰ (calcite δ¹⁸O changes at a rate of approximately 1‰ per 4.5°C). More δ¹⁸O-depleted meteoric calcite, if it exists, is likely to be restricted to distinct zones within cements and speleothems.

METHODOLOGY

Different procedures were used for the analysis of the C and O isotopic compositions of bulk rock and separated component samples, as follows:

Example 1
Individual rock components (rudist bivalves, lime mud and individual cement zones) were identified and sampled from thin sections after staining (Dickson, 2003) and cathodoluminescence (C.L.) examination. Twenty to 200 µg of powder extracted from the thin sections using a steel needle, was placed directly into V-bottomed glass vials and dried in an oven at 50°C overnight. The vials were then sealed with a screw cap holding a septum and PCTFE washer to make a vacuum seal and the samples reacted with 100% orthophosphoric acid at 90°C using a Micromass Multicarb Sample Preparation System. The carbon dioxide produced was dried and transferred cryogenically into a VG PRISM mass spectrometer for isotopic analysis. The results were reported with reference to the international standard VPDB calibrated through the NBS19 standard (Coplen, 1995) and the precision was better than ±0.06‰ for ¹²C/¹³C and better than ±0.08‰ for ¹⁶O/¹⁸O.

Example 2
Bulk rock samples were taken from core and cuttings that were washed, crushed, sieved and ground using an agate mortar and pestle to produce several grams of fine powder. Bulk samples of 2 to 3 milligrams were placed into vials, sealed, flushed with helium and then reacted with 100% orthophosphoric acid at 70°C using an Analytical Precision Carbonate Acid Injection System. The resulting helium/carbon dioxide gas was analysed simultaneously for oxygen and carbon isotopes under continuous flow conditions using an Analytical Precision AP2003 mass-spectrometer. Results were reported to the international standard VPDB and the precision was better than 0.01‰.

Example 3
Powders from different rock components (dolomite, calcite cement, bivalves and lime mud) were collected from polished core samples by drilling. This is a relatively crude means of sampling and some contamination of one component with another is likely. The powders were reacted with 100% orthophosphoric acid at 50°C. For samples predominantly consisting of dolomite, evolved gas was vented after one hour, in order to exclude that coming from any calcite contaminants, and the reaction vessels were then resealed. Data were reported against the PDB standard. Duplicate samples were run in order to determine reproducibility and indicated an accuracy better than 0.1 to 0.2‰ for both carbon and oxygen.
EXAMPLE 1
Sample description

A four-inch diameter core was cut in horizontal Well A, an estimated 11.5 ft TVD below the Top Shu’aiba surface. The core consisted of orbitolinid wackestones, with three discrete bouquets of the robust shelled rudist Glossomyophorus costatus. A low energy, protected, shelf top depositional environment was inferred. Integrated transmitted light and C.L. petrography revealed that all of the rudist bouquets had the same long and complex diagenetic history, which could be divided into pre-, syn- and post- Late Aptian Shu’aiba subaerial exposure events (Figure 3). Four stages of cementation were recognised (Table 1 and Figure 4).

The pre-subaerial exposure diagenetic history was complex and the relative timing of events often ambiguous. Important pre-subaerial exposure diagenetic processes included (1) inclusion-rich calcite formation as a result of rudist aragonite shell neomorphism and cement precipitation (Stage 1 cement), (2) precipitation of minor amounts of both ferroan and non-ferroan sparry calcite cement, often intimately associated with inclusion-rich calcite, and including cementation of peloidal internal sediment, (3) dissolution episodes affecting both rudist aragonite and inclusion-rich calcite and (4) widespread pyrite formation (Figure 4a). The common occurrence of ferroan calcite, either as cement or neomorphic calcite, and the presence of early pyrite suggest that anoxic conditions were established soon after deposition.

The moulds formed by the dissolution of rudist aragonite shell layers fall into two groups. In a minority of cases mouldic porosity formation was juxtaposed with areas of aragonite neomorphism in the same shell. Such areas of mouldic porosity contain inclusion-rich Stage 1 cements. This aragonite dissolution event was ascribed to the pre-subaerial exposure diagenetic history of the sediments and presumed to have taken place in modified marine pore waters (Patterson and Walter, 1994; Melim et al., 2002). However, the majority of moulds formed by the dissolution of rudist aragonite shell layers show no association with aragonite neomorphism and the cements they contain are Stage 2 or later. This suggests not only a later dissolution event, but also one that was more efficient at removing the dissolved carbonate. On the basis of independent evidence in support of subaerial exposure at the end of Shu’aiba deposition, the bulk of aragonite dissolution is interpreted as meteoric. However, there remains uncertainty concerning the relative importance of marine versus meteoric dissolution of aragonite. What is certain is that aragonite bioclast dissolution was completed prior to deposition of the overlying Nahr Umr Formation. This is confirmed by the infiltration of Nahr Umr sediments into biomoulds in nearby wells, to a depth of 88 ft into the Shu’aiba.

Figure 3: Paragenetic sequence for the cored interval of Well B.
Stage 2 cements could be interpreted as meteoric on the basis of their largely non-luminescent C.L. character, but such a C.L. character is not unique to this setting (Meyers, 1991). Consequently, it is unresolved whether Stage 2 cements are syn- or post-subaerial exposure in age. They do, however, pre-date compaction related fractures that developed in the rudist bouquets after Shu’aiba burial. Stages 3 and 4 cements clearly post-date this fracturing event (Figure 4a). The C.L. characters of the various cements are illustrated in Figure 5 and summarised in Table 1.

Unlike the rudist bouquets, the surrounding wackestones were poorly cemented, with common mouldic porosity. Early formed pyrite is again widespread. Minor pre-fracture non-ferroan calcite is present that is possibly coeval with Stage 2 cement. Post-fracture ferroan calcite (Stage 3 cement) is notably absent and rare compactive fractures remain largely open. Rare blocky non-ferroan calcite is present and may correlate with either Stage 2 or 4 cements.

Carbon and oxygen-isotope analysis of depositional components and sequential cement extracts was undertaken on two samples, 1 inch apart, from the central rudist bouquets. The cement extracts analysed from Sample A1 come from the same rudist cavity, while those from Sample A2 were taken from two different cavities.

### Results

The results of the C- and O-isotope analyses are listed in Table 2 and illustrated in Figure 6. Sequential calcite cement data show a large and systematic variation of δ¹³C and δ¹⁸O values, first to lower and then to higher values. Two samples of Stage 1 cement show modest enrichment in ¹³C (δ¹³C = +6.6 and +6.1‰) compared to the δ¹³C values of rudist calcite layers (mean +3.6‰, n=3) and micrite matrix (mean +4.9‰, n=2). Stage 4 cement records a progressive change in isotopic composition (δ¹³C of ~ +1.5‰ to +8.9‰), with the youngest Stage 4 cement displaying considerable enrichment in ¹³C above marine values. This is mirrored by an increase in δ¹⁸O from ~ -8.3‰ to -5.3‰.

### Interpretation

Both Stage 1 and Stage 4 cements show evidence for the addition of heavy carbon, indicating two episodes of methanogenesis were captured in the cements present in the rudist bouquets.

**Methanogenic episode 1**

Carbon-isotope values only slightly in excess of expected marine values, as defined above, indicate that Stage 1 cement includes only a small methanogenesis-derived component. Stage 1 cement consists
predominantly of inclusion-rich calcite which has been interpreted as a product of marine diagenesis pre-dating Late Aptian subaerial exposure, based on petrographic relationships. However, the mean δ18O value of the two Stage 1 samples showing 13C enrichment is -4.3‰, while another sample of Stage 1 calcite (δ13C = +5.1‰) has a δ18O value of -6.6‰. These δ18O values are too low to be normal late Early Aptian marine values and near or outside the limit thought likely for meteoric values (see above). Consequently, the low δ18O values are attributed either to addition of light oxygen resulting from sulphate reduction (Sass et al., 1991) or re-equilibration during shallow burial at temperatures slightly greater than those at the surface. In support of the former, samples A1 and A2 contain frambooidal and polyhedral pyrite crystals intimately associated with Stage 1 cements.

**Methanogenic episode 2**

The δ13C values of +9‰ that typify the later part of Stage 4 precipitation indicate a considerable enrichment in 13C above marine values, consistent with a substantial contribution of carbon from a methanogenic source, the proportion being greater than that present in Stage 1 cement. The progressive increase in δ13C through Stage 4 precipitation is attributed to the increasing significance of methanogenesis over time.

Stage 4 cement consists of non-ferroan calcite that post-dates compaction related fracturing, indicating precipitation after substantial burial. This is supported by the δ18O data, which are lower than the 13C-enriched Stage 1 cement, consistent with precipitation at higher temperature. There is no evidence to support addition of light oxygen derived from bacterially mediate sulphate reduction reaction, consistent with a burial origin.
The progressive decrease in δ\(^{18}\)O of ~3‰ through Stage 4 cements can be explained by (a) a decrease in temperature through time and/or (b) addition of water enriched in \(^{18}\)O compared to the formation water present at the start of Stage 4 precipitation. With respect to option (a), two prominent unconformities are present in the stratigraphic record that may be relevant in this respect. This is considered further in the Discussion section as it is believed to be the most likely option, although not without problems. Option (b) is less likely because the principal sources of 'heavy' water are either evolved water that has been involved in silicate mineral reactions (Lawrence, 1989) or younger marine or meteoric water of an age when the δ\(^{18}\)O of seawater and/or precipitation was greater than in the late Early Aptian. The Nahr Umr is the most prominent siliciclastic formation in the stratigraphic column and overlies the Shu’aiba, however, the low iron content of Stage 4 cement suggests that the iron-rich Nahr Umr Formation did not play a role in its origin. Veizer et al. (1999) suggest that seawater δ\(^{18}\)O has been heavier than in the Aptian only since the Eocene, but there is much scatter in their data. At this time hydrocarbons are expected to have been present in Block 5, hence Stage 4 cements were already formed.

**EXAMPLE 2**

**Sample description**

Well B is a deviated well situated ~3,250 ft distant from the core described in Example 1. The upper half of the Shu’aiba was cored, while cuttings were obtained from the lower half. The core was composed dominantly of *Lithocodium/Bacinella* floatstones and bindstones with frequent wackestones in the lower part and rudist-coral floatstones at the very top (Figure 7). Calcite bulk rock samples were analysed from the entire Shu’aiba interval; thin sections, at ~1ft intervals from the core, were used to confirm facies and mineralogy. The sampling interval was ½ ft at the core top increasing to 2 ft at the base, with a 20 ft interval for the cuttings (all intervals TVD).
Additionally, Sample B from 2 ft TVD below Top Shu’aiba, was taken apart and analysed for various depositional and diagenetic components.

**Results**

The δ¹³C and δ¹⁸O sections for Well B are illustrated in Figure 7. The δ¹³C section in all but the upper 46 ft is similar to that reported by Vahrenkamp (1996) from Oman/U.A.E. and other profiles from Block 5, except for an isolated value of +8.6‰. The lower part of the cored interval is approximately 1‰ lower than our preferred local marine carbonate value for the late Early Aptian, but this is well within the natural scatter reported between various outcrop and well sections and is not considered significant. Above this the δ¹³C profile from Well B shows a shift to higher values of approximately 1.5‰, being similar to or slightly above that expected. Additionally, within this interval there is a 10 ft thick zone with extremely heavy δ¹³C values (maximum +11.6‰), referred to below as the heavy carbon zone (HCZ). A well 11.2 km to the northwest of Well B contains similar facies and is thought to be time equivalent, but over the upper half of the Shu'aiba the δ¹³C profile displays constant marine values. Carbon-isotope profiles from other Block 5 wells developed in different facies and for which the chronostratigraphic correlation with Well B is unclear also show largely constant and marine δ¹³C values over the upper half of the Shu’aiba.

The δ¹⁸O profile from Well B generally follows a similar trend to δ¹³C, except over the HCZ, where there is a small shift to lower values. The δ¹⁸O values from Well B are variably similar to or lower than those expected for late Early Aptian aged marine carbonate.

**Table 2**

Carbon- and oxygen-isotope composition of separated depositional and diagenetic components from rudists bouquets, Well A.

| Cement Stage | Description                                           | δ¹³C (%)PDB | δ¹⁸O (%)PDB |
|--------------|-------------------------------------------------------|-------------|-------------|
|              |                                                       | Sample A1   |             |
| -            | Compacted micrite                                     | 5.78        | -4.53       |
| -            | Rudist calcite layer, non-luminescent                  | 3.67        | -3.44       |
| 1            | Inclusion-rich neomorphic calcite/cement with patchy C.L. | 6.63        | -4.28       |
| 1            | Inclusion-rich neomorphic calcite/cement with patchy C.L. | 5.10        | -6.63       |
| 2            | Non-ferroan inclusion-poor cement                      | 5.02        | -2.90       |
| 3            | Sequential Stage 3 ferroan calcite cement              | 1.93        | -7.25       |
| 4            | Sequential Stage 4 non-ferroan calcite cement          | 2.35        | -8.23       |
|              |                                                       | 4.09        | -7.76       |
|              |                                                       | 8.43        | -5.59       |
|              |                                                       | Sample A2   |             |
| n/a          | Rudist calcite layer, non-luminescent                  | 3.67        | -4.09       |
|              | Rudist calcite layer, non-luminescent                  | 3.58        | -3.95       |
|              | Compacted peloidal micrite                             | 4.39        | -4.24       |
|              | Uncompacted peloidal micrite with Stage 1 cement       | 4.09        | -4.41       |
| 1            | Non-ferroan calcite on top of internal sediment, patchy C.L. | 6.11        | -4.39       |
| 3            | Sequential Stage 3 ferroan calcite cement              | 3.90        | -6.76       |
|              |                                                       | 3.21        | -7.00       |
| 4            | Sequential Stage 4 non-ferroan calcite cement          | 1.54        | -8.32       |
|              |                                                       | 3.71        | -8.12       |
|              |                                                       | 3.90        | -7.97       |
|              |                                                       | 6.42        | -7.41       |
|              |                                                       | 8.85        | -5.28       |
Figure 6: C- and O-isotopic composition of separated cement stages and depositional components from the central rudist bouquet in Well B, compared to the expected composition of late Early Aptian aged marine carbonates.

Figure 7: C- and O-isotopic composition of bulk rock samples from Well A, together with spectral gamma, TOC and facies data.
Uranium (from spectral gamma) and TOC data are shown adjacent to the isotope data on Figure 7. Both datasets indicate that the Shu’aiba organic content in Well B is very low (TOC generally < 0.5%). The uranium data suggests higher organic content at the base of the Nahr Umr Shale, but uranium is not exclusively linked with organic matter and, in the absence of direct measurements, the organic content of the basal Nahr Umr sediments is uncertain.

All depositional and diagenetic components from Sample B showed relatively high δ¹³C values (Table 3). The blocky calcite cements separated from Sample B are similar to the Stage 4 cements from Example 1 in that they are (a) non-ferroan, (b) post-date compactive fracturing and (c) similar in C.L. character.

**Interpretation**

Shu’aiba bulk rock δ¹⁸O values from Well B are at most 2‰ depleted compared to calcite precipitated in equilibrium with Early Aptian aged seawater. Given that the slight ¹⁸O-depletion appears unrelated to any exposure surface, the same explanation provided for Example 1 applies.

The bulk δ¹³C values are close to equilibrium with Early Aptian seawater except for the HCZ where substantial addition of ¹³C-enriched carbon occurred. The 1.5‰ shift in values that occurs 46 feet below the top of the Shu’aiba in Well B may also reflect minor addition of heavy carbon through the remainder of the upper part of the section.

The δ¹³C values from isolated portions of two rudist calcite layers separated from Sample B were +4.2‰ and +6.2‰. Both shells showed evidence of alteration, manifested by cathodoluminescence. In contrast, δ¹³C values of isolated portions of non-luminescent (?unaltered) rudist calcite layers from Block 5 are typically ~ +3.6‰ (Table 2), suggesting that the rudist calcite from Sample B had incorporated heavy carbon, either during skeletogenesis or, more likely, afterwards. Other available data for Shu’aiba shell calcite ranges from +2.9‰ to +5.0‰ (Moshier, 1989; Alsharhan et al., 2000), although some of these are probably altered because their δ¹⁸O values range from -7.0‰ to -4.3‰. For rudist specimens originally from mid-latitudes, some variability in oxygen-isotopic composition between samples of the type described above is to be expected, because of intra-shell isotope variations related to annual temperature variations, but such variability was small at the low latitudes where the Shu’aiba Formation was deposited (Steuber, 1999). In fact, the δ¹³C values of all separated components (depositional and diagenetic) from Sample B were relatively high, indicating that the δ¹³C value of +6.0‰ from the closest bulk rock sample was unlikely to be due to the presence of only one component with an unusually high δ¹³C value.

The bulk rock oxygen-isotope data from the HCZ confirm that the unusually high δ¹³C values are not due to the inclusion of calcite cement with a strong methanogenic signature in the samples. The average δ¹⁸O value of the depositional components in Sample B (-3.2‰, n=3) is the same as

**Table 3**

| Component                                  | δ¹³C (%PDB) | δ¹⁸O (%PDB) |
|--------------------------------------------|------------|------------|
| Micrite matrix                             | 6.71       | -3.23      |
| Shell (altered, dense)                     | 6.16       | -3.41      |
| Shell (altered, fibrous)                   | 4.20       | -3.84      |
| Rounded calcite crystals in clay matrix (non-ferroan) | 5.72       | -6.67      |
| Rounded calcite crystals in clay matrix (non-ferroan) | 6.38       | -6.89      |
| Rounded calcite crystals in clay matrix (non-ferroan) | 6.85       | -6.44      |
| Blocky calcite cement (non-ferroan)        | 8.18       | -5.73      |
| Blocky calcite cement (non-ferroan)        | 7.85       | -5.98      |
| Nearest bulk rock sample (0.2 ft TVD lower)| 6.04       | -3.33      |
the average of the bulk rock samples from the HCZ (-3.2‰, n=10), indicating that negligible calcite cement (average -5.9‰, n=2) is present in the HCZ samples and that the bulk δ\textsuperscript{13}C values of these samples is dominated by the depositional components.

Uranium and TOC data (Figure 7) provide no evidence for enhanced levels of organic matter, the fuel for methanogenesis, in the HCZ. Also, the development of the HCZ does not appear to be facies related.

**EXAMPLE 3**

**Sample description**

The closely spaced vertical wells C, D and E are situated 9 to 13 km from Well B. In wells C and E, four inch cores were recovered from the uppermost 11 and 43 ft of the Shu’aiba, respectively. In well D similarly sized core was recovered from 8 to 41 ft below the top of the Shu’aiba. The cores consisted mainly of mudstones and wackestones, with minor interbedded marls. The cored intervals showed substantial replacement by dolomite (up to 100%), which generally decreased downward, although there was some lithological control, with limestone intervals often being more affected than marls. Wells C, D and E are the only wells in which extensive dolomitisation of Shu’aiba limestones has been recognised in Block 5.

Three types of dolomite have been identified:

**Type 1**: Ferroan dolomite with crystals 30–40 µm in size (Figure 8a) occur replacing marls in Wells D and E. This is often associated with pyrite, although the age relationship is unclear.

**Type 2**: Dolomite crystals replacing limestone lithologies generally are 125–150 µm in size, but range up to 400 µm in Well C. They often have an inclusion-rich core that is brown in colour (Figure 8b). Alternating ferroan and non-ferroan zones are common, although locally the dolomite appears either uniformly one or the other. There is often common associated pyrite and marcasite, although the age relationship between the iron sulphides and dolomite is unclear. The time relationship between dolomitisation and calcite fracture fills within areas of dolomite is ambiguous. Locally in Well C intercrystalline porosity exists between dolomite rhombs that do not entirely interlock, suggesting that undolomitised limestone has been dissolved (Type 2A). Type 2A dolomite is largely non-ferroan.

**Type 3**: Inclusion-poor dolomite, often with ferroan zones, occurs filling or lining vugs in Type 2 dolomite. Some vugs have a calcite cement fill (Figure 8c), similar to that seen in fractures. Where Type 3 dolomite lines open pore space it clearly represents cement and where patches of such dolomite occur they are presumed to be fully cemented vugs. However, where dolomite lines vugs with a calcite cement fill, it is unclear if the dolomite is cement, pre-dating the calcite, or a replacement product that post-dates the calcite (Figure 8c). In Well C quartz grains that filtered down into the formation during deposition of the Nahr Umr Formation occurred tightly encased in Type 3 dolomite (Figure 8d), indicating that dolomite formation post-dated at least the initial stage of Nahr Umr Formation deposition.

**Results**

The δ\textsuperscript{13}C and δ\textsuperscript{18}O results are listed in Table 4. These data are also plotted, together with the trend lines delineating the evolution in isotopic composition of calcite cements from Well A, on Figure 9.

The dolomite data have a δ\textsuperscript{13}C range of ~5‰, with all but one sample being higher than expected for equilibrium with late Early Aptian seawater. In Well C there is an overall decrease in dolomite δ\textsuperscript{13}C values with increasing distance below the Shu’aiba top. However, no such relationship is seen in Wells D and E, where extremely heavy dolomite is present further below Top Shu’aiba than in Well C. There is no significant isotopic difference between Type 1 and Type 2/3 dolomites in Wells D and E.

Micrite samples have δ\textsuperscript{13}C values that are similar to or slightly greater than those expected for a late Early Aptian marine calcite. The higher than expected δ\textsuperscript{13}C values of some micrite samples possibly
reflect contamination by dolomite, since thin sections examination revealed that minor amounts of scattered dolomite rhombs were commonly present in the matrix and the sampling method could not exclude these. One sample of shell calcite has a $\delta^{13}C$ value in the marine range. Calcite cement samples fall within the lower half of the range captured in the Well A cements. Micrite samples have a mean $\delta^{18}O$ value of $-4.0\%_o$ ($n = 16; \sigma = 0.4$) which is slightly higher than shell calcite ($-5.05\%_o$). As with the $\delta^{18}O$ values for depositional components reported in Examples 1 and 2, the $\delta^{18}O$ values are lower than expected for carbonates in equilibrium with late Early Aptian seawater. Calcite cements have $\delta^{18}O$ values similar to or lower than the micrite samples, but fall within the range determined for cements in Well A.

The dolomite $\delta^{18}O$ data show a small scatter about a mean value of $-2.2\%_o$ ($n = 19; \sigma = 0.38$); an offset of $+2\%_o$ with respect to the associated micrite.

**Interpretation**

The fact that dolomitisation is localised in the area of Wells C, D and E suggests that, although the dolomite varies in character somewhat, nevertheless, all of the dolomite occurrences are genetically related. This is supported by their similarity in isotopic composition, especially with respect to $\delta^{18}O$, which is sensitive to temperature.
Dolomites with δ¹³C up to +11.6‰ have been described by Teal et al. (2000) forming in Holocene sediments in northern Belize, in the shallow marine diagenesis zone. However, growth of the dolomite described here around quartz grains that infiltrated into Well C from the top of the Shu’aiba during deposition of the sandy basal part of the Nahr Umr Formation, indicates that the dolomite is not syn-sedimentary in origin, but post-dated at least the earlier stages of Nahr Umr Formation deposition.

Table 4
Carbon- and oxygen-isotope composition of separated depositional and diagenetic components, Wells C, D and E.

| Well | Below Top Shu’aiba (ft) | Sample Type     | δ¹³C (% PDB) | δ¹⁸O (% PDB) |
|------|-------------------------|-----------------|--------------|--------------|
| C    | 0.9                     | Dolomite (2a)   | 9.11         | -2.41        |
|      | 1.0                     | Dolomite (2a)   | 9.06         | -2.50        |
|      | 1.1                     | Dolomite (2a)   | 8.87         | -2.12        |
|      | 1.3                     | Calcite Cement  | 3.26         | -5.05        |
|      | 1.3                     | Dolomite (2a)   | 9.27         | -2.04        |
|      | 1.6                     | Dolomite (2a)   | 5.97         | -1.94        |
|      | 1.6                     | Dolomite (2a)   | 6.20         | -1.87        |
|      | 1.8                     | Dolomite (2a)   | 6.32         | -1.76        |
|      | 3.3                     | Dolomite (2a)   | 5.44         | -2.38        |
|      | 3.8                     | Dolomite (2a)   | 5.49         | -2.31        |
|      | 5.3                     | Dolomite (2a)   | 5.76         | -2.03        |
|      | 6.8                     | Lime Mdst       | 5.52         | -2.97        |
|      | 7.8                     | Dolomite (2)    | 4.51         | -1.32        |
|      | 7.8                     | Calcite Cement  | 4.02         | -5.53        |
|      | 9.05                    | Lime Wkst       | 5.46         | -3.91        |
|      | 19.3                    | Dolomite (1)    | 8.01         | -2.28        |
|      | 19.3                    | Calcite Shell   | 4.90         | -5.05        |
|      | 21.0                    | Lime Wkst       | 5.36         | -4.77        |
|      | 23.0                    | Lime Wkst       | 5.23         | -4.41        |
|      | 23.0                    | Calcite Cement  | 5.19         | -3.80        |
|      | 23.5                    | Lime Mdst       | 4.80         | -4.21        |
|      | 26.0                    | Dolomite (1)    | 7.05         | -2.26        |
|      | 35.0                    | Lime Wkst       | 5.45         | -4.15        |
|      | 35.0                    | Calcite Cement  | 4.96         | -6.44        |
| D    | 0.0                     | Marl            | 2.96         | -4.29        |
|      | 0.9                     | Marl            | 5.16         | -4.37        |
|      | 3.3                     | Marl            | 4.49         | -4.71        |
|      | 10.0                    | Dolomite (1)    | 7.01         | -2.19        |
|      | 10.8                    | Dolomite (1)    | 7.31         | -1.67        |
|      | 11.0                    | Dolomite (2)    | 8.25         | -2.71        |
|      | 11.1                    | Dolomite (2)    | 7.61         | -3.00        |
|      | 11.2                    | Dolomite (2)    | 8.57         | 2.20         |
|      | 12.0                    | Lime Wkst       | 5.71         | -4.34        |
|      | 13.0                    | Lime Wkst       | 5.79         | -4.16        |
|      | 15.0                    | Lime Wkst       | 6.10         | -3.67        |
|      | 16.0                    | Lime Wkst       | 6.02         | -3.86        |
|      | 16.0                    | Dolomite (2)    | 7.57         | -2.20        |
|      | 18.0                    | Lime Wkst       | 6.08         | -3.65        |
|      | 21.0                    | Lime Mdst       | 5.47         | -4.18        |
|      | 21.0                    | Calcite Cement  | 3.72         | -7.10        |
|      | 23.0                    | Lime Wkst       | 5.49         | -4.16        |
|      | 27.5                    | Lime Mdst       | 5.48         | -4.01        |
|      | 34.5                    | Lime Wkst       | 5.42         | -4.14        |
|      | 34.5                    | Calcite Cement  | 3.49         | -7.65        |
|      | 38.0                    | Lime Wkst       | 5.29         | -4.04        |
The presence of common Fe and Mg bearing minerals (glaucocite, chamosite, siderite, dolomite and pyrite) in the basal part of the Nahr Umr Formation makes it the most likely source of Mg and Fe for dolomitisation, which is supported by the downward decrease in dolomite. Methanogenic CO\(_2\) was supplied either from the Nahr Umr or from the Shu’iba itself. This is considered further in the Discussion section. The character of the basal part of the Nahr Umr Formation is consistent throughout Block 5. If the Nahr Umr Formation was the source of the dolomitising fluids, any satisfactory explanation of the dolomitisation process must explain the restricted occurrence of dolomite. In this respect it is noteworthy that no relationship has been found between faulting and dolomitisation.

The cause of the alternation of ferroan and non-ferroan zones commonly seen in the dolomites, especially in Well C, is unlikely to be due to alternation of anoxic and oxic conditions, given that there is strong evidence that dolomitisation occurred during shallow burial and methanogenesis is an anaerobic process. It is possible that it reflects periods of exhaustion of the iron supply.

A 3‰ fractionation with respect to oxygen has been proposed between coexisting calcite and dolomite (Land, 1980; McKenzie, 1981; Vasconcelos et al. 2005). The observed ~2‰ offset between the dolomite and micrite data reported here, suggests either that the dolomite is in equilibrium with rock matrix, which itself has been interpreted to have recrystallised during burial (Example 2), or was precipitated at an only slightly greater temperature.

**DISCUSSION**

**Number and timing of methanogenic events**

Example 1 provides evidence of two discrete episodes of methanogenesis. Petrographic data strongly suggest that the earlier episode occurred prior to substantial burial, probably under shallow marine burial conditions, although the \(\delta^{18}O\) data are ambiguous in this respect. Both the petrographic and \(\delta^{18}O\) data suggest that the later methanogenic episode, associated with the precipitation of Stage 4 cements, occurred after substantial burial. Although the exact oxygen-isotope composition of the parent pore fluid of Stage 4 cement is unknown, substituting the preferred value for Early Aptian seawater of -0.66‰ VSMOW yields a depth estimate of 2,784 ft, assuming the present geothermal gradient of 35°C/km and a surface temperature of 25°C (Craig, 1965). This is not unreasonable, being less than the present burial depth of 3,100 ft TVDSS.

The \(\delta^{18}O\) values through the HCZ presented in Example 2 are higher than those of the Stage 1 methanogenic cements from Example 1, suggesting that this zone is also of early origin, although whether it is coeval with the Stage 1 cements is unresolved. It clearly represents a separate episode of
methanogenesis to that recorded in the blocky calcite cements from Sample B. These are interpreted to be equivalent to Stage 4 cement from Example 1 due to similarity in carbon- and oxygen-isotope, petrographic and C.L. character.

Petrographic observations indicate that the dolomites described in Example 3 formed after initiation of Nahr Umr Formation deposition. The most likely source of magnesium and iron required for dolomitisation was the Nahr Umr Formation, consigning dolomitisation to an episode of Nahr Umr Formation dewatering during burial. The fact that the δ¹⁸O data suggest that the dolomites are close to equilibrium with the limestone matrix supports dolomite formation at fairly shallow burial depth and indicates that it is unlikely to be associated with the precipitation of Stage 4 cement (Example 1), a conclusion further supported by the exclusively non-ferroan character of the latter.

Understanding of the absolute timing of the methanogenic event recorded in Stage 4 cements is intimately linked to understanding of the 3.3‰ increase in δ¹⁸O values that occurred through Stage 4 cement precipitation. It was suggested above that the most likely explanation was precipitation during a cooling episode. Although there are other means of causing temperature reduction, it is notable that there are two conspicuous unconformities above the Shu'aiba that may have contributed to this trend, the Turonian unconformity being the most likely candidate. This is an attractive hypothesis because it provides a mechanism for reinvigorating the hydrological system, providing a source of carbonate for Stage 4 cement and stimulating methanogenesis (Budai et al., 2002). In this respect regional interpretations suggest that to the northeast of Block 5 the unconformity cuts down possibly as far as the Nahr Umr, perhaps providing an access point for meteoric fluids. However, there are problems associated with the amount of section that has to be lost to effect a 3.3‰ increase in δ¹⁸O, if this is its sole cause (estimated at ~1,500 ft assuming a present day geothermal gradient and that temperature equilibrium was achieved (Craig, 1965)). Although Robertson (1987) and Patton and O’Connor (1988) suggest Turonian erosion in the northern Emirates of 800 ft and 1,970 ft, respectively, which is in the required range, Block 5 in a different situation and the loss of section in Block 5 at this time is poorly constrained. Only 250 ft can be confirmed by Block 5 data, although the loss is likely to be at least twice this.

A fuller understanding of the timing of burial methanogenic events recorded in Block 5 requires a more detailed evaluation of the burial history of the block and the nature and distribution of cements in the Cretaceous strata above the Shu’aiba. No fluid inclusions suitable for analysis were found in the Stage 4 cements.

**Source of heavy carbon**

The present day organic content of the Shu’aiba in the studied wells is very low, although it was undoubtedly higher at the time of deposition. The methanogenic episode captured in Stage 1 cement in Well A most likely occurred within the Shu’aiba itself, sourced by organic matter associated with the rudist bouquets in which the cements formed. The source of the organic matter that sourced the methanogenic episodes responsible for the HCZ, the heavy dolomites and the Stage 4 cements remains enigmatic.

Yose et al. (2004) illustrated the complex mosaic of shallow water environments that existed on the Shu’aiba shelf, which had varying propensities to accumulate organic material. In this setting any methanogenic diagenesis that occurred would be localised, restricted to the more organic-rich facies, perhaps extending into immediately adjacent areas. Thus, the presence of the HCZ in Well B may reflect proximity to a localised accumulation of organic-rich sediment.

This is also a possible explanation for the limited distribution of the dolomite. Teal et al. (2000) demonstrated that methanogenesis could promote dolomitisation and a local accumulation of organic matter that acted as a focus for methanogenesis during shallow burial could explain the limited occurrence of dolomites. However, spectral gamma data provide no evidence of unusually high concentrations of organic matter in the upper part of the Shu’aiba in Wells C, D and E and there is no apparent difference between the facies present in dolomitised and equivalent undolomitised intervals.
The basal part of the Nahr Umr Formation is an alternative source of ‘heavy’ carbon, in addition to Mg and Fe, for the dolomites. No TOC data are available, but uranium spectral gamma data (Figure 7) suggest that more organic matter may be present than in the Shu’aiba Formation. Uranium data from the basal Nahr Umr of Wells C, D and E are similar to Well B. That the Nahr Umr acted as a source of ‘heavy’ carbon is supported by a rapid decrease in dolomite $\delta^{13}C$ with increasing distance below the top of the Shu’aiba in Well C, a trend that is supported by the two dolomite samples from Well D. However, no such trend is evident in Well E. Also against the basal Nahr Umr as a source of ‘heavy’ carbon is the fact that the limited amount of Nahr Umr carbon-isotope data that is available from Block 5 shows no support for methanogenic diagenesis. The limited occurrence of dolomite and the lack of correlation between dolomitisation and fault juxtapositions of Shu’aiba against Nahr Umr also counts against the Nahr Umr as a source of ‘heavy’ carbon.

Blocky cements with similar carbon- and oxygen-isotope compositions and C.L. characteristics to Stage 4 cements described from Well A are widespread in the Shu’aiba Formation in the northeast of Block 5, their similarity in characteristics suggesting a close generic relationship. Their distribution illustrates that methanogenic CO$_2$ was probably widely available when Stage 4 cements were precipitated. Given the very low TOC evident in Well B and the burial origin of Stage 4 cements, import of ‘heavy’ carbon into the Shu’aiba of Block 5, either laterally or vertically is the most likely explanation. In addition to the sources already mentioned, higher stratigraphic intervals with enhanced organic carbon content, such as the basal Mauddud, could play a role.

Although there is convincing evidence that these cements precipitated during burial, there is uncertainty with regards to their absolute age; an association with the Turonian unconformity has been suggested above. Notably, Hendry (1993) associated cements with similar C.L. characteristics to those of Stage 4 cement to late stage meteoric recharge in the subsurface. If the Stage 4 cements are of a similar origin it provides a possible explanation for their carbon-isotope composition. Periods of enhanced meteoric recharge have led to late stage bacterial methanogenesis in the Antrim Shale, with the precipitation of strongly methanogenic calcite cement (Budai et al., 2002). A similar mechanism could explain Stage 4 cement. It is proposed that addition of freshwater reactivated methanogenesis in organic-rich formations, the products of which were imported into the Shu’aiba.

**Why is Block 5 different?**

The question arises as to why methanogenic associated diagenesis of the Shu’aiba has only been observed in Block 5. Is it because methanogenic reactions were restricted in their occurrence, or is it that they were more widespread, but haven’t been recognised?

Of particular relevance to the latter scenario are the methods employed for separation of cement samples. Example 1 is the first published Shu’aiba example presenting data from sequential cement stages from within a single pore. If the full cement sequence had been sampled *en-mass*, then the methanogenic signals that are evident in the Stage 1 and late Stage 4 cements would undoubtedly have been hidden, since they represent a minor proportion of the total volume of cement. The isotopic composition for the bulked sample would have been in the region of $\delta^{13}C = +4\%_o$ and $\delta^{18}O = -6\%_o$, i.e. in the middle of the range for previously published data. In the majority of previously published studies virtually no information was provided regarding the methods used to separate cement samples or what petrographic and C.L. variability the cement samples encompassed. Certain authors discriminated between earlier and later cements based on the nature of the pores they occurred in. For instance, the restriction of certain cement stages to fractures allows some discrimination between different cementation episodes (Budd, 1989; Sattler et al., 2005). It is concluded that one reason why heavy carbon cements have not been recognised before, if they are indeed present, may simply be because sampling methods were too crude.

The same criticism cannot be levelled against bulk rock samples and the Well B $\delta^{13}C$ data are the first such Shu’aiba data to be published that show a strong methanogenic signal. Although there is good evidence to suggest early resetting of the carbon-isotope system, the fact that (a) the HCZ in Well A is unusual even for Block 5 and (b) it does not have an unusually high organic content, makes it difficult
to address the problem as to why such zones have not been recognised elsewhere. If the development of the HCZ and the dolomites described here were due to proximity to a local accumulation of organic-rich facies, then similar zones should be expected elsewhere in similar depositional settings.

At least some of the methanogenic events affecting the Block 5 Shu‘aiba sediments post-dated Shu‘aiba deposition, so part of the explanation as to why methanogenesis has been recognised here, but not in areas further southeast, possibly relates to differences in post-Shu‘aiba geological history. In particular, (a) Block 5 was in a relatively proximal position during deposition of the Nahr Umr Formation, compared to the U.A.E. and Oman, and the sands and iron-rich sediments that comprise the base of the Nahr Umr Formation in the Qatar area disappear eastward and (b) regional differences in burial history may be important, especially the vertical extent of Turonian erosion.

**Implications for carbon-isotope stratigraphy**

Vahrenkamp (1996) noted that the range of δ¹³C of Shu‘aiba carbonates (+0.5 to +7‰) was generally wider than that for the pelagic signature from the Tethys ocean (+1.4 to +4.5‰) and that most Shu‘aiba shelf profiles were enriched in ¹³C by up to +2.5‰ compared to the intra-shelf basin signature. One of a number of explanations put forward was that diagenesis could play a role. Methanogenic reactions may be significant in this respect. In particular, Vahrenkamp’s Well A4 from Field ‘A’, U.A.E showed a bulge in δ¹³C values from the more normal +5.5‰ up to values approaching +7‰. In light of the data from Block 5, this result could be due to methanogenesis.

Bulk rock carbon isotope stratigraphy has proved to be a useful means of correlating Cretaceous sections. However, the HCZ in Well B highlights that it is possible to completely overprint the original marine carbon-isotope signal of a limestone and reinforces the message that bulk rock data should be treated with care when using carbon-isotope profiles for stratigraphic correlation. Although incorporation of substantial amounts of methanogenic CO₂ produces a strong and characteristic carbon-isotope signal, in situations where the supply of methanogenic CO₂ was limited, much smaller amplitude fluctuations in bulk rock δ¹³C values, on the scale of those observed in the secular signal, could result. This could lead to incorrect correlations.

The possible occurrence of ¹³C-enriched cements highlights the importance of excluding cement from bulk rock samples as far as is possible. Although such cements have not unduly affected the results presented here due to careful sampling, under certain circumstances the addition of relatively small amounts of cements with very heavy carbon values could have a disproportionately large effect on bulk rock δ¹³C values and could result in a spurious carbon-isotope signal. This emphasises the importance of having a thorough and detailed understanding of the carbon-isotope characteristics of the various rock components before undertaking bulk rock carbon-isotope profiling. It cannot be assumed on the basis of very low organic carbon contents that methanogenic reactions have not played a role in Shu‘aiba diagenesis and will not influence bulk rock composition.

**CONCLUSIONS**

The three examples presented here provide evidence that bacterial methanogenic processes have repeatedly influenced the diagenesis of Shu‘aiba sediments in Block 5 and provide an insight into the importance of the subsequent geological history of the region on Shu‘aiba diagenesis. The HCZ in Well B and the ¹³C-enriched dolomites in Wells C, D and E are apparently unique and further work is required to fully understand their origin, particularly as they are also unusual within Block 5. Methanogenic cements have not been recorded from the Shu‘aiba before, but their widespread occurrence within Block 5 means it is highly likely that they extend beyond its limits. The main conclusions are:

- A minimum of three methanogenic events occurred during Shu‘aiba diagenesis. The earliest was syn-sedimentary, while the later two occurred during burial. It is tentatively suggested that Stage 4 cements and their equivalents were precipitated during a period of uplift, most likely during the Turonian, but more data are required to confirm this.
Early diagenetic methanogenesis was fuelled by organic matter buried with the sediment, but the methanogenic reactions influencing burial diagenesis occurred either in a laterally equivalent organic-rich facies or outside of the Shu’aiba.

It is possible to re-equilibrate the original carbon-isotope content of the bulk rock with methanogenic CO$_2$, although the circumstances under which this can happen appear highly restricted in space.

The addition of small amounts of methanogenic CO$_2$ to Shu’aiba sediments, either by re-equilibration of the depositional component or by the addition of heavy carbon cement, has the potential to produce fluctuations in bulk rock $\delta^{13}$C profiles with amplitudes similar to secular marine signal. In situations where bulk rock analysis gives rise to inconsistent $\delta^{13}$C profiles or unreasonable correlations a thorough investigation of the carbon-isotope composition of all rock components is recommended.

The results presented here reinforce the conclusions of other studies that the main period of Shu’aiba porosity production extended up to and included the Late Aptian Shu’aiba subaerial exposure event, whereas porosity destruction as a result of cementation took place almost exclusively during burial.

ACKNOWLEDGEMENTS

The authors would like to thank Qatar Petroleum and Maersk Oil Qatar AS for permission to publish this paper. The constructive comments of Troels Albrechtsen and Torben Krarup are much appreciated, as are those of the reviewers. The stable isotope analysis of samples from Examples 1 and 2 was done in the Godwin Laboratories, Cambridge; those for Example 3 were done at the University of Texas. The Example 3 samples were initially investigated in conjunction with Peter Scholle. The final design and drafting of graphics by Gulf PetroLink is appreciated.

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Manuscript received February 19, 2006
Revised July 6, 2006
Accepted July 7, 2006
Press version proofread by authors December 4, 2006