

# Sulphate reduction associated with hardgrounds: Lithification afterburn!

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## Abstract

Negative excursions in  $\delta^{13}\text{C}$  profiles from platform carbonates that coincide with pyritised hardgrounds are commonly linked to subaerial exposure events, but we show here that they can also result from subsurface bacterially-mediated early cementation in addition to the precipitation of syndepositional marine cements. A non-soil-derived origin for  $\delta^{13}\text{C}$ -depleted micrites offers an alternative origin and bathymetric interpretation for these surfaces.

The Lower Cretaceous Lekhwair Formation platform carbonate successions from offshore Abu Dhabi contain abundant hardgrounds that are important for both regional correlation and control of subsurface flow. The micrite from these hardgrounds have average  $\delta^{13}\text{C}$  values of +0.7‰; 1.5‰ lower than non-hardground micrites that are similar to contemporary open ocean values. Hardground  $\delta^{13}\text{C}$  values are due to the addition of  $^{13}\text{C}$ -depleted carbonate, generated as a by-product of sulphate reduction, to the ‘normal’ marine calcite that caused hardground lithification. Pyritisation of the hardgrounds occurred before, during and after ‘normal’ calcite precipitation. The persistence of sulphate reduction after hardground lithification is shown by the presence of pyrite and low  $\delta^{13}\text{C}$  micrite in sediment up to a few mm above the hardgrounds.

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## 1. Introduction

The Early Cretaceous was an extreme greenhouse period;  $\text{CO}_2$  levels were estimated to be between 1.5 and 8 times above present day levels (Royer et al., 2001), and Aptian seawater had a Mg/Ca ratio of 1:1 (Dickson, 2002) to >3 (Steuber and Rauch, 2005) in contrast to modern seawater of ~5:1 and three times the  $\text{Ca}^{2+}$  concentration (Timofeeff et al., 2006). Vast areas of continent were flooded with shallow marine seas that produced extensive carbonate platforms, particularly throughout the Tethys Ocean. Such unusual global conditions produced not only distinctive depositional geometries in carbonate succes-

sions, but also early diagenetic phenomena such as abundant and widespread hardgrounds, i.e. syndepositional lithified seafloors (Wilson and Palmer, 1992).

The Lower Cretaceous carbonate deposits in the Middle East are among the most productive oil-bearing stratigraphic intervals in the world, and include the Thamama Group (Berriasian–Aptian) which outcrops in Oman and forms numerous giant subsurface hydrocarbon reservoirs in the United Arab Emirates (Alsharhan et al., 2000; Granier et al., 2003). In these strongly cyclic carbonates (van Buchem et al., 2002), hardgrounds and firmgrounds (omission surfaces) have been used as marker horizons for correlation (Immenhauser et al., 2000, 2004; Sattler et al., 2005) and act as boundaries for depositional units in the sequence stratigraphic hierarchy (Mitchum et al., 1977; Sarg, 1988; Handford and Loucks, 1993). As these cemented surfaces were likely barriers to fluid flow, understanding their origin is crucial for both correlation and characterising early subsurface flow architecture in these sequences.

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The lithification of modern hardgrounds is caused by the precipitation of marine cements that are coarsely crystalline and readily identified in grainstones, but in lime mudstones and wackestones they are often finely crystalline and cannot be distinguished from the matrix if cements are calcitic. The presence of cement in such rocks is implied from their associated boring and encrusting biota that require the sediment to be hard (cemented) before surface colonisation. Most bulk rock samples of modern calcitic hardgrounds have  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values that are close to those found in marine cements and both are equated with equilibrium precipitates from seawater (James and Choquette, 1990; Noé et al., 2006). Some hardgrounds, however, have lower reported  $\delta^{13}\text{C}$  values than micrites stratigraphically above or below (Immenhauser et al., 2000; Mutti and Bernoulli, 2003; Sattler et al., 2005). Marshall and Ashton (1980) proposed that hardgrounds may show heavier signatures due to the presence of marine cements; Swart and Melim (2000) showed negative excursions in hardgrounds and proposed sulphate reduction as a likely cause. Here, we use petrographic observations and stable-isotope-analyses to further investigate the processes responsible for the formation of hardgrounds in the Lekhwair Formation (Hauterivian–Barremian) of the Thamama Group from Abu Dhabi.

## 2. Geological setting

The eastern Arabian Peninsula was a stable carbonate platform from the Late Permian to the Late Cretaceous (Early Turonian), a period of some 170 Myr (Murris, 1980). In the offshore areas of Abu Dhabi, the Thamama Group formed an extensive and broad low-energy ramp (Murris, 1980) that incorporated the Habshan, Lekhwair, Kharaib, Hawar, and Shu'aiba Formations (Fig. 1). All these divisions were defined from subsurface data and can be correlated throughout the whole of the southeastern Arabian Gulf oil province using bounding sequence stratigraphic surfaces (van Buchem et al., 2002). Deposition of the Hauterivian–Barremian Lekhwair Formation is highly cyclic, which is reflected in the recognition of multiple stacked major reservoirs each separated by low porosity, cemented, or 'dense' horizons.

Cretaceous	Time (Ma)		Thamama Group	
	115 –	Aptian		Shu'aiba Fm.
	120 –	121 –		Hawar Mbr.
		Barremian		Kharaib Fm.
	125 –	127 –		Lekhwair Fm.
		Hauterivian		
	130 –	132 –		
		Valanginian		Habshan Fm.
	135 –	136 –		
		Berriasian		
	140 –			

Fig. 1. Early–Middle Cretaceous stratigraphy (of the Thamama Group in U.A.E. modified from Immenhauser et al., 2004).

An idealised 'Lekhwair' cycle commences with shale of variable thickness ( $\sim 0.1$ – $1$  m), followed by 4–15 m of marly, wavy-bedded wackestone–packstones with shell-rich and *Choffatella* accumulations, compacted burrow systems, and thin shaley beds. The top of this unit is dominated by *Thalassinoides* burrows that are sharply defined and filled with coarse sediment that includes scattered green minerals, presumably glauconite. This section is interpreted as commencing in a deep, low energy, open marine environment that shallows upward into a condensed section capped by a firmground.

The marly unit is succeeded by 5–20 m of packstone–grainstone with an *in situ* benthos; commonly *Lithocodium*–*Bacinella* crusts pass upwards into rudist-rich horizons, most rudists appear to be minimally transported. This unit is interpreted to have formed under subtidal, open marine conditions.

The packstone–grainstone unit is usually succeeded by 2–15 m of *Thalassinoides* dominated marls stained with hematite that marks a return to the burrowed lithology at the top of the shaley-marl unit.

The top of the cycles is marked by prominent hardgrounds from 1–10 cm thick that formed on the firmgrounds, with marked *Gastrochaenolites* (some with *in situ* *Lithophaga*) and *Trypanites* borings (Fig. 2A). No encrusting biota was recognised in core. Many of the hardgrounds are mineralised and can be coloured either black/golden with pyrite (Fig. 2A) or red with hematite. They are invariably overlain by the shales and marls of the next cycle, indicating a return to deeper, more open waters. By analogy with modern hardgrounds (Shinn, 1969), the hardgrounds are inferred to have formed during periods of sediment starvation. This second condensed section of firmground and hardground is interpreted as being the deepening-upward part of the cycle ending in a sequence boundary.

## 3. Methods

Core slabs and thin sections were examined from the hardgrounds, and from sediment above and below by normal light, using stains and cathodoluminescence microscopy. Powders were extracted for isotope analysis from core slabs or thin sections using a tungsten-steel needle under the binocular microscope with in-built transmitted or reflected fibre optic light source.

Carbon and oxygen isotope analyses were performed using a Micromass Multicarb separation system connected to either (1) a VG SIRA or (2) a VG Prism II stable-isotope ratio mass spectrometer. Each sample was accompanied by 10 reference carbonate and 2 'control' samples. The results are reported as deviations from the international standard VPDB (‰). Precision was measured as better than 0.06‰ for  $\delta^{13}\text{C}$ , and as better than 0.08‰ for  $\delta^{18}\text{O}$ .

## 4. Results

The hardground shown on Fig. 2A has prominent burrows that now extend  $\sim 5$  cm below the hardground surface; the distance may have been greater to the original sediment/water interface before reduction in sediment thickness by bioturbation

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