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Diagenesis of silica-rich mound-bedded chalk, the Coniacian Arnager Limestone, Denmark

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ABSTRACT

The Coniacian Arnager Limestone Formation is exposed on the Danish island of Bornholm in the Baltic Sea. It is composed of mound-bedded siliceous chalk, and X-ray diffraction and scanning electron microscopy indicate a content of 30–70% insoluble minerals, including authigenic opal-CT, quartz, clinoptilolite, feldspars, calcite, dolomite, and barite. Opal-CT and clinoptilolite are the most common and constitute 16–53% and 2–9%, respectively. The content of insoluble minerals varies laterally both within the mounds and in planar beds, and the opal-CT content varies by up to 10% vertically. The mounds consist of two microfacies, spiculitic wackestone and bioturbated spiculitic wackestone, containing 10–22% and 7–12% moulds after spicules, respectively.

Subsequent to deposition and shallow burial, dissolution of siliceous sponge spicules increased the silica activity of the pore water and initiated precipitation of opal-CT. The opal-CT formed at temperatures around 17 °C, the precipitation lowered the silica activity and the Si/Al ratio of the pore water, resulting in precipitation of clinoptilolite, feldspar and smectite. Calcite formed synchronously with the latest clinoptilolite. Minor amounts of quartz precipitated in pore water with low silica activity during maximum burial, probably to depths of 200–250 m. The dissolution of sponge spicules and decomposition of the sponge tissue also resulted in the release of Ba^{2+}, Sr^{2+}, Mg^{2+}, Ca^{2+} and CO_3^{2-}, facilitating precipitation of barite and dolomite. Precipitation of especially opal-CT reduced the porosity to an average of 40% and cemented the limestone. The study highlights the diagenetic pathways of bio-siliceous chalk and the effects on preservation of porosity and permeability.

1. Introduction

The diagenesis and depositional setting of siliceous chalk differ from that of the classical pelagic chalk of NW Europe. Precipitation of authigenic silicates is common and often reduces the porosity (Maliva and Dickson, 1992; Chaika and Dvorkin, 2000). However, formation of authigenic silicates may also result in lithification at shallow burial depths and hence preserve porosity during deeper burial (Aase et al., 2001), making it difficult to predict the effects of silica diagenesis on reservoir properties.

The diagenesis of sediments rich in biogenic silica includes precipitation of opal-CT, zeolites, feldspars and smectite, but opal-CT and zeolites are mostly preserved in shallow buried sediments, and rare to absent in more deeply buried successions (Berger and von Rad, 1972; Fabricius and Borre, 2007; Gingele and Schulz, 1993; Huggett et al., 2005; Karpoff et al., 2007; Kastner, 1981; williams et al., 1985). The silica activity and the Si/Al ratio of the pore water are the main controlling factors on diagenesis in silica-rich sediments (Berger and von Rad, 1972; Abercrombie et al., 1994; Wilkin and Barnes, 1998). The early silica diagenesis is characterized by minerals with high silica activity such as opal-CT, clinoptilolite and smectite, whereas precipitation of quartz dominates at lower silica activity and deeper burial (Abercrombie et al., 1994).

The mound-bedded siliceous chalk of the Coniacian Arnager Limestone Formation on Bornholm, Denmark has only been buried to shallow depths, probably 200–250 m and thus represents an unusual example of pre-Paleogene chalk where the early diagenetic paragenesis is preserved. The aim of this study is to identify sedimentary microfacies of the formation and to establish the diagenetic processes and their effects on porosity and permeability. The investigations are based on mapping and sampling of a mounded section in a coastal cliff at Arnager on the south coast of Bornholm. The data set allows estimates of the lateral and vertical variabilities in porosity and permeability on the metre to tens of metre scale, horizontally and decimetre to metre scale, vertically.

2. Geological setting

During the Mesozoic the stable Baltic Shield was separated from the subsiding Danish Basin by the block-faulted NW–SE trending Tornquist Zone (Fig. 1) (Liboriussen et al., 1987). The island of Bornholm is a basement horst situated in the zone. During the Late Cretaceous, much of the horst became transgressed. The initial Early to

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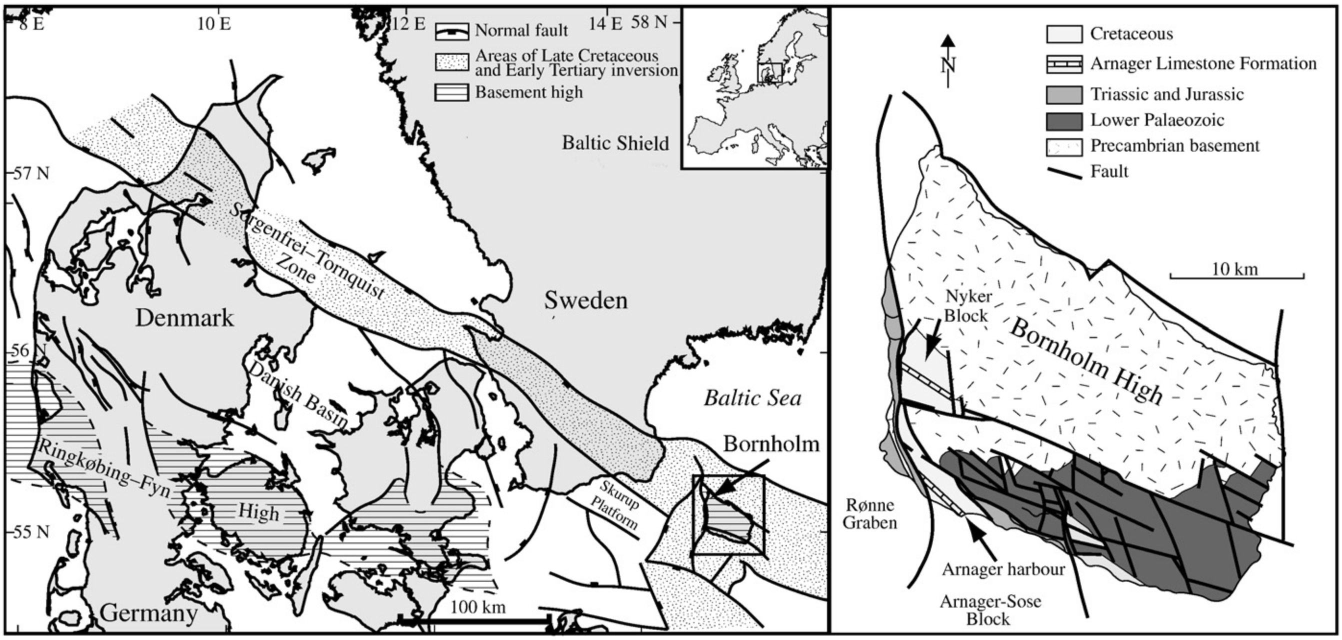

Fig. 1. Structural map of Denmark and southern Sweden and geological map of Bornholm. Modified after Liboriussen et al. (1987) and Gravesen et al. (1982).

Middle Cenomanian transgression led to deposition of the Arnager Greensand Formation in a shallow shelf environment (Christensen, 1985; Packer and Hart, 1994). The basal part of the overlying Coniacian Arnager Limestone Formation is a thin conglomerate composed of several generations of phosphatised and glauconitised pebbles reflecting alternating phases of deposition, non-deposition, erosion and mineralisation (Ravn, 1918). Deposition of the Arnager Limestone took place in an outer shelf setting (Packer and Hart, 1994).

The Arnager Limestone, 12–20 m thick, is characterized by mounded bedding possibly caused by growth of sponges thickets and baffling of sediment (Noe-Nygaard and Surlyk, 1985). Siliceous sponges are very common and comprise mainly Hexactinellida and rarely Demospongiae (Brückner and Janussen, 2005; Brückner, 2006). The remainder of the macrofauna is dominated by inoceramid bivalves (Tröger and Christensen, 1991), whereas other macrofaunal elements, including bivalves, brachiopods, belemnites (Christensen and Schulz, 1997) and ammonites (Kennedy and Christensen, 1991) are very rare. The limestone is composed of 34–76% insoluble minerals, primarily opal-CT, which formed during diagenesis (Noe-Nygaard and Surlyk, 1985; Mogensen, 1994). Flint nodules incorporating siliceous sponges are rare (Ravn, 1918).

Syn-depositional volcanism occurred in southern Sweden, northern Germany and Poland (Norin, 1933, 1934; Dorn and Bräutigam, 1959; Printzlau and Larsen, 1972; Solokowski, 1976; Seibert and Vortisch, 1979). On the Arnager Block the Arnager Limestone Formation is overlain by about 150 m of Santonian Bavnodde Greensand (Ravn, 1921; Christensen, 1985, Jensen and Hamann, 1988) and possibly additional younger Cretaceous sediments, indicating minimum burial depth of the Arnager Limestone of 200–250 m. Increased tectonic activity during Late Cretaceous and Paleogene times caused inversion and uplift of the Arnager Block and erosion of the overlying sediments (Graversen, 2004).

3. Materials and methods

The Arnager Limestone is exposed in a 200 m long coastal cliff profile west of Arnager harbour (Fig. 1). Mound structures were mapped and 56 samples were taken along the profile. Point counting was carried out on 20 thin sections to quantify the content. The insoluble residue analysis was based on samples crushed in a porcelain mortar until it passed a 2 mm sieve and calcite was removed using a buffered acetic acid at pH 4.5 to avoid dissolution of non-calcite minerals. X-ray diffraction (XRD) of the insoluble residue was carried out on randomly oriented specimens using a Philips 1050 goniometer with Cu-Kα radiation. Quantification of the minerals was made by the Rietveld method using the software Topas 3.

SEM analyses were carried out on small samples of limestone which were coated with gold in vacuum at 25 kV and 20 mA for 2–3 min using a SEM Coating Unit E5000. Photography and qualitative chemical analysis were made on a PHILIPS XL 40 SEM equipped with a ThermoNoran energy dispersive X-ray detection system (EDX). Backscatter images of carbon-coated polished thin sections were taken at 50× and 1500× magnifications at five places, 6 mm apart and perpendicular to bedding. Quantification of large pores (φ_{large}, $>20\ \mu m$) and small pores (φ_{small}, $<5\ \mu m$) was based on the backscatter images using the free software UTHSCSA Image tool version 3.0, following the method of Røgen et al. (2001). Average φ_{large} and φ_{small} values from the image analyses were corrected by multiplying their relative contribution with the measured porosity.

Porosity and gas permeability were measured in the core laboratory at the Geological Survey of Denmark and Greenland (GEUS). The porosity was determined by using a Helium porosimeter on clean and dried plugs of known dimensions oriented parallel to bedding and by subtracting grain volume from the measured bulk volume. Boyle's Law was employed to determine the grain volume. The gas permeability was measured on a steady state instrument with confining pressure of 400 psi and by flowing nitrogen gas through plugs at differential pressures between 0 and 1 bar.

4. Sedimentology

The base of the Arnager Limestone Formation is exposed in the eastern part of the coastal cliff west of Arnager harbour (Fig. 3). The formation dips 5° to the W, thus exposing stratigraphically younger limestone going from the east to west along the cliff.

Noe-Nygaard and Surlyk (1985) demonstrated that the strongly jointed limestone in wet condition reveals markedly mounded bedding (Fig. 2). In the basal part of the formation, the mounds or hummocks are 20–30 m long and around 1 m high (Fig. 3). They are asymmetric with the eastern slope generally dipping 10–12° and the western slope dipping 6–8°. The crests of successive beds in some