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Marine sedimentation of nano-quartz forming flint in North Sea Danian chalk

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ABSTRACT

A new theory for formation of flint in the North Sea Danian Ekofisk Formation chalk has been formulated, according to which the flint formed by sedimentation of nano-size α-quartz particles. These α-quartz particles have crystallized in the sea from silicon supplied from dissolution of radiolarians. In the present work this model has been tested by sedimentological and mineralogical investigation of sedimentary features in chalk containing silica. Methods applied are X-ray diffraction (XRD), atomic force microscopy (AFM), scanning electron microscopy (SEM) and thermal analysis (DTA-EGA). In the Ekofisk Formation, silica was present in flint, in quartz beds, and as quartz particles dispersed in the chalk. The quartz in the flint, in the quartz intervals and the quartz particles in the chalk are one and the same kind of quartz. It is composed of 0.1–0.3 μm spheres of α-quartz having perfect three-dimensional order but with slightly larger cell dimensions compared to standard α-quartz. The quartz in the flint, in the quartz horizons and dispersed in the chalk must accordingly have formed by one and the same mechanism, which is crystallization in the water phase prior to sedimentation. It is proposed that the difference in proportion of calcite in the flint and the quartz horizons on one side and the chalk with quartz particles on the other is due to different degrees of dissolution of the pelagic skeletal debris of coccolithophorids in the seawater during sedimentation. This variation is attributed to differences in concentration of CO_2 in the seawater, and the high amounts of CO_2 dissolving the calcite during sedimentation of the pure quartz are proposed to come from volcanic activity. This implies that the quartz-rich horizons (consisting of dispersed quartz, quartz horizons, or flint) are regional features and may as such be present as regional sheets in the pelagic Danian Ekofisk chalk reservoir.

1. Introduction

Current theories for silica diagenesis in chalk assume that flint has formed through synsedimentary and post-depositional dissolution of Si-containing organisms (primarily silica-sponges) in the chalk followed by migration of the silicon and precipitation/recrystalization of silica associated with replacement of chalk under special favourable chemical conditions. During burial, dissolution–precipitation has been assumed to transform the silica gel and opal-CT to α-quartz (Holmes, 1965; Bromley and Ekdale, 1986; Clayton, 1986; Zijlstra, 1987; Madsen and Stemmerik, 2010). Investigation of flint has largely been carried out on chalk outcrops located marginally in the chalk sea basin where a large number of flint bands are present. In the central part of the North Sea flint beds are less frequent in the Chalk Group.

Investigations of the silica phases have predominantly been carried out by standard petrographic methods, such as X-ray diffraction (XRD) for phase identification and scanning electron microscopy (SEM) for imaging. However, Micheelsen (1966) investigated the structure of a sample of dark flint from Stevns, Denmark, by XRD, optical microscopy, thermal and chemical analysis and infrared spectroscopy. It was tentatively concluded that this sample consisted of 2–30 μm grains composed of plates of α-quartz. We have for our studies applied nano-technological methods such as atomic force microscopy (AFM) and detailed XRD using diffraction peak modelling to describe in detail the silica phases of the dispersed particles in the white chalk and of the flint (Jakobsen et al., 2000; Lindgreen et al., 2010, 2011).

Microcrystalline α-quartz particles are present in the white chalk in variable amounts (Maliva and Dickson, 1992; Lindgreen et al., 2010). Maliva and Dickson (1992) found 80–100% quartz in the insoluble residues from the Ekofisk Formation in the Eldfisk Field and suggested that the main source for quartz formation was Si from dissolution of radiolarians. Recent studies on the chalk in Danish Chalk Fields proved the presence and pre-dominance of α-quartz as nano-particles in the insoluble residue. In the Ekofisk Fm. the α-quartz content of the total rock ranges from a few percentages to locally 100% (Lindgreen et al., 2010). In the Rigs-1 well in the

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South Arne Field a 10 cm thick bed characterized by 100% nano-silica has been described (Jakobsen et al., 2000). The bed was different from the usual flint beds in that it visually resembled chalk and has been described as a tight chalk with low porosity and permeability. The silica particles did not show evidence of severe recrystallization or any replacement of the chalk and was therefore interpreted to have formed by sedimentation.

It was demonstrated that the nano-size α-quartz in the flint and the nano-quartz dispersed in the chalk matrix had identical cell parameters which deviated significantly from those of standard quartz (Lindgreen et al., 2011). The similarity in silica phase and identical cell parameters in the nano-quartz indicated the same mechanism of formation. The origin of the sediment was proposed to be silica particles formed by crystallization in the free-water phase from silicon released from the opal-A of radiolarians (Lindgreen et al., 2010). Crystallization and flocculation of quartz at the silicon concentration range of the marine environment has been described by Williams and Crerar (1985). The variation in the nano-quartz content in the Ekofisk Formation has been explained to be due to fluctuations in the level of CO_2 in the marine environment, which controls the dissolution of carbonate particles (Lindgreen et al., 2011).

In the present work, intervals including the lowermost Danian and the K/T boundary in a number of wells in the Danish North Sea fields have been investigated in order to test the new theory for the formation of flint formulated by Lindgreen et al. (2011). We demonstrate that the nano-quartz is an important constituent in the chalk and that lithologies described as chalk hardgrounds actually may be deposits dominated by nano-quartz. The regional nature of the flint/nano-quartz horizons and especially the presence of the thick horizons at the K/T boundary are discussed.

2. Samples

The cored sections in the well SA-1 in the South Arne Field, the Sif-1 and Nana-1 in the Halfdan Field, and the well N-22 in the Gorm Field have been investigated with focus on the silica rich intervals, see Table 1 (for location see Fig. 1).

Core samples were taken from white chalk, from flint horizons and from hardened horizons, some of which have been described as hardgrounds (Fig. 2 and Table 1). Core photos of the examined chalk intervals are shown in Figure 3. In lithological heterogeneous intervals a dense and selective sampling using a 0.5 cm Ø drill bit was carried out.

Special focus has been on the K/T boundary and the lowermost Ekofisk Fm. A correlation of the Danian and uppermost part of the Maastrichtian section in the examined wells is shown in Figure 2. Log porosity and overall lithology and hydrocarbon saturation are shown together with indication of the depth.

3. Methods

3.1. Removal of calcite

The large amounts of calcite in chalk must be removed by dissolution procedures prior to mineralogical investigation of the non-calcite minerals. This procedure was applied to the large samples, whereas the 0.5 cm Ø samples were investigated by XRD and differential thermal analysis (see below). The chalk samples were crushed to pass a 4 mm sieve. The samples were then added 200 ml of distilled water, and the calcium carbonate was removed by stepwise addition of acetic acid while keeping the pH of the solution at pH 4.5–5. The supernatant was removed by centrifugation. The residue was air-dried and the weight determined for determination of proportion of non-calcite in the samples. XRD showed that the samples investigated here consisted of nano-quartz together with calcite and that the residues consisted of quartz. Accordingly, the content of quartz was calculated as the proportion of the residue (* in Table 1).

Table 1
Quartz content in the samples (For location of samples, see Fig. 3).

Well, depth	Sample	Lithology	% Quartz
Sif-1, 2065.13–2065.31 m	S-1	Chalk	12*
	S-2	Chalk above flint	42*
	S-3	Flint	100*
	S-4	Chalk below flint	14*
Sif-1, 2071.06–2071.35 m	S-5	Chalk	29*
	S-6	Dark chalk	66*
	S-7	Chalk	24*
	S-8	Dark chalk	43*
Sif-1, 2088.23–2088.50 m	S-9	Flint	96*
	S-10	Chalk above flint	27**
	S-11	Chalk below burrow	52**
	S-12	Burrow below flint	87**
Nana, 2134.80 m	N-1	Hardground	31**
	N-2	Hardground	46**
Nana, 2135.85 m	N-3		100*
N22, 2155.50–2155.71 m	G-1	Chalk above hardground	6*
	G-2	Hardground (1)	81*
	G-3	Chalk below hardground	99*
	G-4	Burrow	36**
	G-5	Burrow	37**
	G-6	Chalk	88**
	G-7	White chalk	93**
	G-8	Bluish chalk	99**
	G-9	White chalk	96**
	G-10	White chalk	31**
SA-1, 3344.15 m		Chalk	35*

*Determined as residue after calcite removal; **determined as non-calcite proportion of sample by thermal analysis.

This buffered dissolution of calcite was applied in order to avoid corrosion or dissolution of the fine-grained non-calcite minerals, such as the clay minerals and nano-quartz.

3.2. X-ray diffraction

The mineral phases in the samples were identified and the structure of the quartz investigated by XRD. The XRD patterns have been modelled to determine the cell dimensions and size of coherent scattering domains (CSDs) of the quartz (Lindgreen et al., 2011). XRD patterns were obtained using CoKα radiation with

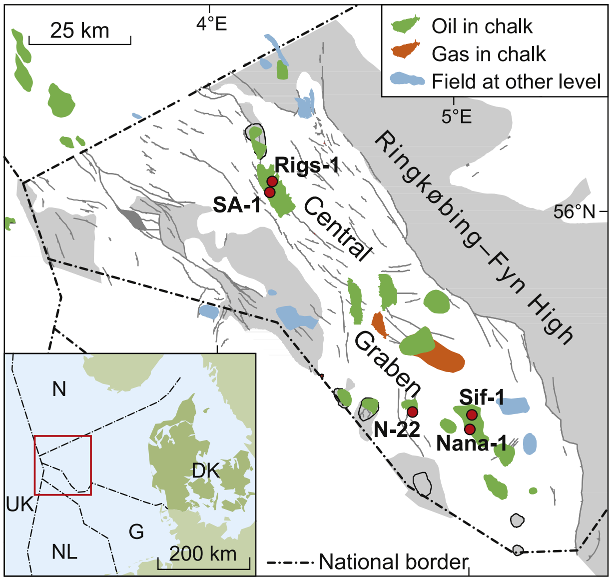

Figure 1. Location of wells in the North Sea.