## Interpretational challenges related to studies of chalk particle surfaces in scanning and transmission electron microscopy

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Scanning and transmission electron microscopy (SEM and TEM) are capable of characterising the morphology and structure of sub-micron size substances attached to chalk particle surfaces. Some characteristics, however, may originate from sample preparation or reflect interaction between sample and the electron beam. Misinterpretation of surface features may lead to wrong conclusions regarding grain surface properties and cementation level and thus to erroneous characterisation of hydrocarbon reservoirs with respect to e.g. wettability, mechanical strength and maximum burial depth. In SEM, conductive coatings may mask surface details or generate artificial ornamentations, and carbon adhesive discs may cause the chalk surface to be covered with a thin carbon film. Electron beam acceleration voltage controls the degree of detail revealed by the electron beam, but in SEM a high electron beam acceleration voltage may provoke bending or curling of ultrathin particles. Recent organic filaments may be confused with clay flakes, and authigenic non-carbonate minerals may have formed in the pore fluid and settled during fluid removal. In TEM, the high acceleration voltage may cause beam damage to calcite and transform the outermost atomic layers into Ca oxide. Thin graphite membranes observed by TEM may be contamination from the carbon film supporting the sample, and overlapping chalk particles in samples formed by drying of a suspension may give the impression of being cemented together. In TEM residual adhesive from the ion-milling process can be confused with cementation features.

*Keywords*: Scanning electron microscopy, transmission electron microscopy, chalk, surface coating, surface ornamentation, image interpretation.

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Oil recovery from chalk reservoirs in the North Sea is governed by the low permeability of the chalk matrix where significant amounts of oil are retained within the micrometre- or nanometre-sized pores. Oil recovery is further controlled by the properties of the particle surface in terms of its affinity towards various pore fluids. The chalk surface may vary from completely oil-wet over mixed-wet to completely water-wet depending on factors such as type of pore fluid and its affinity towards calcite or e.g. clay minerals covering the calcite surface. Further, the surface area available for wetting may be controlled by the amount, type and distribution of clay and silica minerals (Røgen & Fabricius 2002) and by the degree of diagenesis, which in turn is controlled by maximum burial depth and timing of oil invasion (Hjuler & Fabricius 2009). In order to improve recovery efficiency, various improved oil recovery (IOR) and enhanced oil recovery (EOR) techniques are being tested and employed. In this context, understanding the properties of chalk particle surfaces is crucial and reliable characterisations are necessary.

Chalk is a granular material which seems rather homogenous to the naked eye, but on closer scrutiny visual traces of e.g. bioturbation, hardgrounds and diagenetic alterations are revealed. Microscopically, the heterogeneous appearance of chalk is further increased. Microfossils, remains of larger fossils and clasts of non-carbonates are unevenly distributed in a matrix of partly or completely disintegrated nannofossils, mainly coccoliths (Fabricius 2007). Diagenetic alterations are seen as recrystallised calcite particles, calcite-cemented fossil cavities and fractures, moulds after siliceous fossils, authigenic silica and clay, as well as stylolites transecting the chalk matrix.

Research into reservoir chalk properties addresses the interaction between chalk particles and pore fluids in order to understand and control how mechanical and chemical mechanisms affect reservoir stiffness and strength (Risnes & Flaageng 1999; Heggheim et al. 2005; Katika et al. 2015; Generosi et al. 2017; Nermoen et al. 2018) as well as oil recovery (Austad & Standnes 2003; Strand et al. 2007; Katika et al. 2018). The relation between the calcite surface and other non-carbonate minerals or other substances plays a central role in this discussion, and it is thus of interest to reveal any presence of ultrathin organic films or clay coatings covering the calcite surface.

Several petrographic investigation techniques have been employed to improve our understanding of chalk behaviour including scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (e.g. Hjuler & Fabricius 2009) and atomic force microscopy (AFM) (e.g. Generosi et al. 2017), as well as various spectroscopy techniques including energy dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy. This article focuses on SEM and TEM.

SEM and TEM investigations of chalk performed at high magnifications present the microscopist with numerous interpretational challenges. Contamination from various sources must be identified and excluded from interpretation. Sample interaction with the electron beam may alter the sample morphologically and structurally. Removal of pore fluids may cause suspended material to settle at the surface of particles, thus changing the spatial distribution of pore space constituents. Similarly, pore fluid removal may force

#### Table 1. Sample localities

dissolved ions to combine, precipitate and settle on the particle surfaces. The application of a conductive surface coating, e.g. gold, may mask surface details and in addition generate secondary ornamentation.

Although the above mentioned sources of error cannot always be identified or described satisfactorily, it is important to be aware of their existence during investigation and interpretation in high magnification studies. This study presents a number of cases where morphological information (SEM) and structural information stored in diffraction patterns (TEM) is prone to misinterpretation. For a fundamental introduction to electron microscopy, see e.g. Goodhew et al. (2001). For in-depth information on the SEM and TEM techniques, respectively, see e.g. Goldstein et al. (2003) and Williams & Carter (2009).

### Methods

#### Sample material

The chalk samples used in this study were collected from outcrops in various countries in the North Sea area and sampled from well cores from the Central Graben in the North Sea; a single Greensand sample was included. More sample information is presented in Table 1.

#### SEM investigations

Small pieces of chalk were placed on a carbon adhesive disc mounted on an aluminium stub and coated with gold or gold-palladium by an Emitech K550 sputter coater. The sample chamber was evacuated and filled with argon at a pressure of 10<sup>-1</sup> mbar, and the coating applied with a current of 17 mA. Coating was applied

Onshore location	Locality	Outcrop	Age
France	Hardivillers	Hardivillers quarry	Late Santonian
Germany	Lägerdorf	Schinkel	Santonian-Campanian
		Heidestrasse	Campanian
		Saturn	Campanian-Maastrichtian
Denmark	Stevns	Sigerslev quarry	Maastrichtian
	Ellidshøj	Ellidshøj quarry	Maastrichtian
	Vokslev	Vokslev quarry	Maastrichtian
	Aalborg	Rørdal quarry	Maastrichtian
	Taasinge	Quarry at Bjerreby	Palaeogene*
Offshore location	Field	Depth	Age
North Sea, Central Graben	Ekofisk	3200–3600 m	Maastrichtian
North Sea, Central Graben	Valhall	3200–3300 m	Maastrichtian

Onshore data from Hjuler & Fabricius (2009). Offshore data from Røgen *et al.* (1999). \*Greensand



**Fig. 1.** Aluminium stub mounted with a double-sided carbon adhesive disc. Chalk pieces and dust distributed on the surface may sink partly or completely into the carbon substrate. Carbon from the disc may migrate onto and cover chalk particles with thin, barely visible films.

to the samples for 30 seconds or 2 minutes at a sputter rate of 18 nm/min, resulting in estimated thicknesses of 9 and 36 nm, respectively. Investigations were carried out in high vacuum mode in a Zeiss Supra 35VP field emission microscope using the secondary electron (SE) detector for imaging and the energy dispersive spectrometer (EDS) for mineral identification.

### **TEM** investigations

TEM investigations were carried out in a Jeol JEM-200CX and a Jeol 2000FX transmission electron microscope, both equipped with an EDS detector and operated at 200 kV. Two types of samples were prepared:

**Suspension samples.** Gently crushed chalk was suspended in ethanol and a droplet of the mixture pipetted onto a carbon film supported by a copper grid, leaving a fine layer of chalk dust behind after drying. This preparation technique allows the study of isolated particles and provides diffraction data with minimum interference from neighbouring particles.

**Ion-milled samples.** A slice of chalk was impregnated with epoxy, ground into a thin section and polished,

then impregnated with a soluble adhesive and ionmilled. Subsequently, the adhesive was removed. The objective of using this technique was to study the contact points between calcite particles. One disadvantage of this method is the risk of altering the structure of the sample surface as the sample integrity may be affected during the ion-milling process.

### Interpreting SEM images of chalk

## Artificial surface coatings produced by carbon adhesive

Apart from adhesive qualities, the carbon adhesive disc conducts electricity and may prevent or reduce charging problems. However, chalk particles and small aggregates may sink into the carbon disc and become completely buried (Fig. 1). From the carbon disc, carbon may climb partly embedded particles and small aggregates, covering their surfaces and smudging surface details (Figs 1, 2A). Carbon may also spread to the lower parts of larger chalk aggregates, covering particle surfaces with a thin film (Figs 1, 2B). The film gradually thins toward the upper parts



**Fig. 2.** Carbon spreading from the carbon disc. A: Chalk particles completely or partly embedded in carbon of a carbon adhesive disc; towards the right the presence and effect of carbon is harder to estimate. Chalk from Vokslev, Denmark. B: Ultrathin carbon film visible at the contact points between calcite particles (arrows). Chalk from Lägerdorf, Germany.



100 nm

**Fig. 3.** Film growth during sputter coating. Initially, atoms settle on the sample surface forming tiny islands (A), which grow as more atoms arrive (B), then coalesce (C) to finally produce a conductive coating (D).

of the aggregate where it may disappear or become unobservable. The carbon artefacts should not be mistaken for original organic coatings, clay or any other natural coating. The observation that carbon is capable of climbing and covering calcite particles and aggregates indicates a strong carbon affinity towards calcite. Whenever carbon coatings may cause interpretational difficulties it is advisable to avoid studying single particles or parts of aggregates in direct contact with or close to the carbon disc.

## Masking of surface detail by conductive coatings

Chalk is composed of electrically non-conductive calcite, and as an uncoated chalk sample is bombarded with electrons it builds up charge that interferes with the incident electron beam, causing flares and sample drift. In order to avoid these unwanted side effects, chalk samples should be kept small and excess electrons should be guided away by a thin coating of a conductive material such as carbon, gold or gold-palladium. For most chalk investigations the conductivity of carbon is insufficient and the more conductive metal coatings are preferred. Thus, carbon coatings will not be discussed further here.

A sputter coater is commonly used to apply a 10–40 nm thick layer of metal to the chalk sample. The mode of operation involves the initial release of atoms from a coating source; released atoms are directed towards the sample where they bind to the sample surface and each other, forming tiny 'islands' (Fig. 3A). As more atoms arrive, these islands grow laterally (Fig. 3B) and finally coalesce (Fig. 3C) to produce a continuous film on top of the sample surface (Fig. 3D) (Goldstein et al. 2003). A 40 nm thick coating is acceptable for standard investigations of chalk at relatively low magnifications. At high magnification, examination demands a much thinner coating to avoid masking of delicate details (e.g. Folk & Lynch 2001; Henriksen et al. 2004). A thinner coating causes increased risk of charging, but we find that a 10 nm thick layer is a reasonable compromise as charging is small and masking effects are limited. This is illustrated by high magnification images of the delicate blades of opal-CT lepispheres (Fig. 4). A 36 nm thick gold coating increases the blade thickness and gives them a robust appearance, and fine structural details remain hidden below the coating or may be confused with topographical features of the thicker coating (Fig. 4A). With a 10 nm thick coating, a more correct representation of the thinness and fragility of the blades is produced and the tiny crystals



**Fig. 4.** Masking and distortion of details caused by coating thickness. A: Blades of opal-CT lepisphere covered with c. 36 nm of gold which more than doubles the blade thickness. B: Reducing coating thickness to c. 10 nm reveals blade delicacy and the tiny blade-building crystals. Chalk from Aalborg (A) and Ellidshøj (B), Denmark.

building each lepisphere blade are revealed (Fig. 4B).

The chemisorbed water film covering the surface of chalk grains, often referred to as the irreducible water layer, is estimated to be c. 5 nm thick (Larsen & Fabricius 2004) and thus 2–8 times thinner than the 10–40 nm thick coating. This implies that original topographical features may be masked by the coating and thus that the surface area defining the amount of chemisorbed water may be significantly changed, most likely reduced as the coating tends to smooth the surface topography. Therefore, attempts to assess surface area and the amount of chemisorbed water should be approached with caution.

## Artificial surface textures created by conductive coatings

The complex interaction between sample and sputter coater settings may result in coatings which at high magnifications display ornamentations. At small coating thicknesses (10 nm) ornamentations are hardly visible (Fig. 5A), but thicker coatings of 40 nm or more may display significant ornamentations such as reticulate crack-like patterns (Fig. 5B) or grainy surfaces (Fig. 5C). At high magnification, the single grains/drops of the coating material become clearly visible and may dominate the ornamentation of the sample surface (Fig. 5D).

### Affinity between coating and sample

Whereas carbon has high affinity to the calcite surface (Fig. 2), the opposite is observed for metal coating (Fig. 6). In this extreme case, the gold atoms probably aggregated before settling due to insufficient vacuum in the sputter coater and failed to spread out on the calcite surface. The reason for this difference is that calcite is a covalently and ionically bonded mineral (Skinner et al. 1994) with a monolayer of hydrolysed water so strongly chemisorbed to the surface that it is preserved even in ultra-high vacuum (Stipp 1999). Gold and gold-palladium are noble metals that cannot bond to the water layer, whereas graphite coal has the possibility to share electrons covalently. Gold and



**Fig. 5.** Surface textures produced by coatings. A: Barely visible, 10 nm thick gold-palladium film; sample details smaller than 50 nm are clearly visible. Chalk from Valhall field, North Sea. B: Approximately 36 nm thick film with a pronounced crackled appearance; sample details smaller than 50 nm are hard to discern from the coating. Chalk from Aalborg, Denmark. C: coating 36 nm thick, showing grainy texture. Chalk from Stevns, Denmark. D: 20–30 nm-sized opal-CT crystallites covered with gold grains less than 5 nm in diameter. Greensand from Taasinge, Denmark.

gold-palladium coatings with crack-like appearance were accordingly also observed at surfaces of other water-wet minerals such as quartz, opal-CT, clinoptilolite, various clays and apatite.

That metal coatings may not be strongly attached to the surface of the investigated minerals was observed on several occasions during EDS spot analysis at high



**Fig. 6.** Gold coating concentrated in isolated droplets due to a malfunctioning sputter coater; charging is not prevented. Chalk from Lägerdorf, Germany.



**Fig. 7.** Electron bombardment during EDS analysis has locally removed the gold–palladium coating from the surface of a quartz particle (arrow). Chalk from the Ekofisk field, North Sea.

magnification (Fig. 7). The continuous electron bombardment of a restricted area over time has removed the coating from the sample surface.

### Acceleration voltage and surface detail

The acceleration voltage determines the energy of beam electrons and is thus a major control of electron capability to penetrate into the sample. At high acceleration voltages (15–30 kV) the beam electrons penetrate beneath the sample surface to produce electron signals mostly carrying information of the sample interior (Goldstein et al. 2003) (Fig. 8). Thus relatively few of the secondary electrons are generated at or near the surface and little surface information is obtained, so that surface ornamentation is weakly depicted in the final SEM image (Figs 9A and C). By reducing the acceleration voltage to 5 kV or less the penetration depth of the beam electrons is confined to near-surface regions (Fig. 8C). Accordingly, the resulting electron signal will carry surface related information from which a SEM image rich in surface detail is provided (Figs 9B and D). Enhancing surface detail also increases the relative contribution from surface coatings.

One negative consequence of lowering the acceleration voltage is reduced production of secondary electrons per time unit (signal) and thus reduced image quality. One way to overcome this problem is to reduce scan speed. Unfortunately, this action also increases the possibility of charging effects and sample drift. Charging may be avoided without loss of image quality by producing an average image from a number of identical high speed scans; this method, however, is time-consuming and may prove useless due to beam drift, especially at high magnifications.

### Electron-induced sample alteration

Tiny substances within chalk may be morphologically modified during interaction with the electron beam. Among such substances are clay flakes extending for less than 1  $\mu$ m and attaining thicknesses below 50 nm (including coating). Clay flakes often protrude into the pore space and are likely to bend when hit by the focused electron beam at high magnification. The clay mineral illite frequently occurs as filaments which will curl into spirals when hit by electrons (Fig. 10). The sample sensitivity to electron beam interaction may be reduced by lowering the acceleration voltage.

## Sample contamination by recent organic material

Characteristic thin filaments (hyphae of fungi?) are





Low acceleration voltage Small interaction volume **Fig. 8.** Electron–sample interaction. A: Interaction depth and volumes of various SEM signals. Penetration depth of secondary electrons is limited but may be controlled by adjusting the acceleration voltage. B: High acceleration voltage: significant electron penetration depth and limited surface information. C: Low acceleration voltage: shallow electron penetration and increased surface information.

frequently observed in outcrop chalk. These recent, cobweb- or spaghetti-like occurrences may cover large areas or volumes (Fig. 11A) and presumably develop within chalk fractures in situ or at chalk surfaces during sample preparation. The filaments are easily discernible from calcite and non-carbonate particles, however, the filament terminations may form flattened attachments on the surfaces of chalk particles which resemble clay flakes (Fig. 11B).

## Suspended or appended growth of authigenic non-carbonates

During diagenesis, some non-carbonate minerals such as kaolinite and opal-CT grow in the pore water, but as pore water is removed during sample preparation, these minerals will settle on calcite particles. Thus, SEM images do not necessarily reflect the original position of non-carbonate minerals relative to chalk



**Fig. 9.** The effect of high and low acceleration voltages. The amount of surface details is significantly increased when the acceleration voltage is reduced from 10 kV (A, C) to 2 kV (B, D). A and B: Chalk from Lägerdorf, Germany; C and D: Chalk from Hardivillers, France.

particles. The diagenetic fabric of chalk may reveal whether or not a mineral occupies its original position.



**Fig. 10.** Tiny filaments at the rim of a clay flake curl in response to the electron beam. Chalk from the Ekofisk field, North Sea.

During recrystallisation and cementation of chalk, the expanding surfaces (overgrowths) of calcite particles may grow around and embed another mineral attached to the surface (Fig. 12A); or the non-carbonate mineral may grow around a calcite particle (Fig. 12B). In these cases it is evident that the minerals occupy their original positions. Where clay flakes are positioned on top of calcite particles, it cannot be decided whether their position is original or whether they settled from suspension during sample preparation (Fig. 12C).

## Mineral precipitation during evaporation of pore water

If chalk samples are not cleaned for salt and hydrocarbons before SEM investigation, various salts and possibly clay flakes few nanometres thick will precipitate during drying of the sample (Fig. 13).



Fig. 11. Contamination by recent organic material. A: A web of organic filaments spans a crevice in chalk. Chalk from Aalborg, Denmark. B: Flattened filament terminations (arrows) form thin attachments similar to clay flakes. Chalk from Stevns, Denmark.



**Fig. 12.** Growth of non-carbonate minerals in chalk. A: Appended growth: opal-CT lepisphere partly embedded in overgrown calcite crystal. B: Appended growth: opal-CT lepisphere once growing around a now disappeared coccolith, as witnessed by the impression left. C: Appended or suspended growth (?): clay flakes positioned on top of chalk particles A: Chalk from Lägerdorf, Germany; B and C: Chalk from Aalborg, Denmark.



**Fig. 13.** Halite crystals presumably precipitated from brine in the pore space. Chalk from the Ekofisk field, North Sea.

## Interpreting TEM images of chalk

## Destruction of the atomic structure of calcite

In order to perform analytical studies in the TEM, beam electrons are accelerated to energies high enough to allow sample transmittance. However, high electron energy also produces the undesirable side effect of beam damage, by which the atomic arrangements of the sample are altered irreversibly either by displacement of atoms (knock-on damage) or by breakage of chemical bonds (radiolysis) (Williams & Carter 2009). An electron beam fixed in one spot for some time may cause the atomic structure to change from crystalline into amorphous, a process directly observable in the TEM as the diffraction pattern becomes more diffuse. Different materials respond differently to the impact of electrons and display varying degrees of susceptibility to beam damage. Beam damage probably always occurs to some degree, but may not be noticeable.

## Formation of new mineral coatings on calcite

Based on TEM investigations of Cretaceous and Palaeogene chalk, Bürki et al. (1982) and Glasser & Smith (1986) reported siliceous coatings covering the surfaces of coccoliths and proposed that these coatings were formed from an organic membrane produced by the living organism. Attempting to observe these reported coatings in situ on fossil coccoliths should be done with beam damage in mind. Beam damage may be restricted to the sample surface, causing displacement of surface atoms and possibly altering surface chemistry (Williams & Carter 2009). This may explain observations in this work of ultrathin polycrystalline coatings covering the surface of calcite particles (Fig. 14A). The coating is evidenced by barely visible diffraction rings superposed onto the diffraction pattern of the calcite crystal (Fig. 14B). By calibrating these

 Table 2. Interplanar spacings (d) of observed surface coatings of calcite and CaO

Observed coatings <i>d</i> spacing (Å)	CaO <i>d</i> spacing (Å)	CaO Relative intensity (X-ray?)	hkl
2.8	2.7799	38	111
2.4	2.4075	100	002
1.7	1.7024	59	022
	1.4518	16	113
1.4	1.3900	18	222
	1.2038	8	004
	1.1046	7	133

Diffraction data for CaO based on information from Figuet et al. (1999).



**Fig. 14.** Beam damage. A: Bright field image of particle identified as calcite based on its diffraction patterns. B: Diffraction pattern representing the  $[\overline{1} \ \overline{76}]$  projection of the calcite particle with superposed diffraction rings belonging to polycrystalline CaO. Chalk from Aalborg, Denmark.

diffraction rings towards the interplanar spacing in a calcite diffraction pattern of known crystallographic orientation, the coating was identified as CaO (lime) (Table 2). Presumably, the surface layers of calcite were chemically altered into polycrystalline CaO during interaction with the electron beam.

The well-defined diffraction rings prove the CaO layer to be polycrystalline rather than amorphous, and diffuse higher-intensity areas on the rings indicate a minor degree of preferential orientation. To

observe these diffraction rings, long exposure time is needed and thus the rings are easily overlooked. Consequently, estimating the prevalence of this type of beam damage is difficult.

#### Carbon contamination

The siliceous coatings described by Bürki et al. (1982) and Glasser & Smith (1986) are depicted as ultrathin, low contrast membranes often reflecting the structure



**Fig. 15.** Graphite particles. A and C: Bright field images showing membrane-like structures. B and D: Diffraction patterns of A and C showing relatively well-defined diffraction rings indicating polycrystallinity; interplanar spacings (*d*) are indicated. E: Bright field image of graphite viewed along the [001] projection. F: Diffraction pattern of E, polycrystallinity is clearly visible. In order to better observe details in the bright field images, the contrast has been significantly increased. A–F: Chalk from Aalborg, Denmark.

of coccoliths (Glasser & Smith 1986, figs 11.2, 11.4a). In the present study, similar membrane-like structures were frequently observed scattered on TEM carbon films. These membranes are ultrathin, probably just a few nanometres, and irregularly shaped with sizes ranging from less than 100 nm to more than 5  $\mu$ m (Fig. 15A and C). Size and shape of the membranes are difficult to determine due to their crumpled appearance, and none of the observed examples reflect coccolith morphology. The membranes produce fairly well-defined diffraction rings suggesting the coatings to be polycrystalline rather than amorphous (Fig. 15B and D). The diffraction planes with a d spacing of 3.6 Å and 1.8 Å, respectively, normally show some degree of preferential orientation (Fig. 15B and D). Initially, we thought that these membranes were siliceous coatings as described by Bürki et al. (1982) and Glasser & Smith (1986). The interplanar spacing of diffraction planes observed in Fig. 15B and D, however, did not correspond to those of silica. Ultimately the membranes were found to consist of graphite, as evidenced from comparison of observed diffraction data with graphite diffraction data (Table 3). It is thus possible that the membranes of this study and the coatings of Bürki et al. (1982) and Glasser & Smith (1986) are separate phenomena.

Occasionally more crystallographically mature versions of membranes are found (Fig. 15E) with diffraction patterns corresponding to the [001] projection of graphite (Fig. 15F). Possibly, this graphite originates from the carbon film supporting the chalk sample.

#### Apparent cohesion between calcite particles

In order to understand and describe the mechanical strength of chalk, the cementation features related to particle contacts were investigated in TEM, but interpretation of contact points between calcite particles should be approached cautiously. Fig. 16A shows two calcite particles from a suspension sample; the particles are apparently grown together along a line bounded by meniscus-like cement (Fig. 16B). These

Table 3. Interplanar spacings (d) of observed mem	branes	and
graphite		

3.3         3.3553         100.0         002           2.1319         3.5         100	
2.1319 3.5 100	
2.0 2.0318 16.7 101	
1.7994 3.0 102	
1.7 1.6777 5.4 004	
1.5433 4.5 103	
1.3184 0.7 104	
1.2 1.2309 5.0 110	
1.1556 7.3 112	
1.1358 1.0 105	
1.1184 0.7 006	
1.1 1.0659 0.1 200	
1.0527 1.0 201	
1.0159 0.3 202	
0.9924 4.1 114	
0.9904 2.0 106	
0.9623 0.8 203	
0.8997 0.2 204	
0.8743 0.4 107	
0.8388 0.3 008	
0.8347 0.6 205	
0.8277 2.7 116	
0.8 0.8058 0.3 210	
0.8000 1.5 211	
0.7835 0.5 212	

Diffraction data for graphite are cited from Howe et al. (2003).

observations fit well with the dissolution-precipitation theory presented by Heggheim *et al.* (2005) and discussed further by Strand *et al.* (2007).

However, during tilting of the stage it became clear that this cementation phenomenon was an optical illusion created by one particle partly covering another (Fig. 17A). As coverage was increased during tilting of the stage, the apparent line of coalescence grew longer and the meniscus-like cement was pushed outwards



**Fig. 16.** Apparent cohesion. A: Two calcite particles apparently in contact with each other. B: Close-up of the contact area. The particles seem to have grown together along a line flanked with meniscus-like cement.



**Fig. 17.** Apparent cohesion. The upper row of drawings represents lateral views of the particles; the lower row shows the particles as observed in the microscope, i.e. from above. A: Slight overlap, the particles seem to have grown together. B: Tilting the sample +30 increases the overlap; the particles seem intimately intergrown. C: Tilting the sample –30 decreases the overlap; the particles appear to be loosely connected.

(Fig. 17B). Reversing the tilt angle reduced the contact area between the two particles correspondingly (Fig. 17C), and ultimately it became probable that what we saw was two separate particles settled next to each other during sample preparation.

By tilting the stage it may be possible to visually separate two calcite particles apparently in contact. However, revealing truly intergrown calcite particles visually poses significant difficulties; irregularly shaped interfingering particles may not have been



**Fig. 18.** Ion-milled chalk sample. The meniscus-like structure situated between two calcite particles may be interpreted as cementation but is more likely constituted by residual adhesive from the thinning process or carbon from the conductive carbon film.

in contact originally but this fact may remain hidden during stage tilting as the particles will seem to be in contact visually at all times.

### Residual adhesive in ion-milled samples

Highly porous and weakly consolidated chalk is a challenging material when it comes to preparing samples of limited thickness, e.g. ion-milled samples. Thinning of such chalk by ion-milling requires stabilisation of the chalk structure by saturating the pore space with a soluble adhesive. After finishing the thinning process, the slice of chalk is cleaned by adding a solvent removing the adhesive. However, traces of adhesive will probably always be left behind, and to avoid charging, a thin carbon film is applied to the chalk sample. This can lead to a false interpretation of two calcite particles being cemented together (Fig. 18).

# Consequences of misinterpretations

Erroneous characterisation of particle surface chemistry may result in wrong assessment of wettability and how wettability may be modified to increase oil recovery. Thus, correct detection of coatings and other substances a few nanometres thick attached to particle surfaces, and determining the extent of such matters, are important tasks in attempts to increase oil recovery. This study has pointed out several cases where sample preparation and instrument settings of SEM and TEM are responsible for creating, hiding, altering or preventing identification of structures related to chalk particle surfaces and particle contacts.

### Artificial surface coatings

**SEM.** Carbon from the carbon adhesive disc may spread to and cover calcite particles with a uniform, few nanometres thick coating (Figs 1–2) that should not be confused with any original organic coatings and seen as an indicator of oil wettability. Conductive metal coatings applied to the chalk particle surface may change the appearance of the surface texture depending on type and thickness of the coating (Figs 3–5).

**TEM.** Ultrathin graphite membranes (Fig. 15), possibly originating from the sample holder, should not be mistaken for organic coatings originally covering the particles with the implication this would have for chalk surface properties.

## Artificial surface substances and appearances

**SEM.** Electron-induced sample alteration may have implications for illite filaments, which will curl into tiny spirals when hit by electrons (Fig. 10). As illite commonly is associated with smectite in mixed-layer structures (e.g. Lindgreen *et al.* 2002), the erroneous conclusion may be drawn that the curling phenomenon is due to smectite loosing water and transforming into illite. This, however, requires that a sufficient amount of potassium ions is available for the illite structure from the pore fluid, which necessarily has to be water as oil is incapable of transporting ions. The transformation from smectite to illite is used as an indicator of maximum burial depth, and wrong determination of the smectite–illite transition may lead to wrong assessments of maximum burial depth.

Recent organic filaments in chalk (Fig. 11) are easily identified, but the clay-like flattened terminations of the filaments may deceive as they often cover large parts of the chalk particle surfaces and thus give the impression that clay plays a major role in the particle surface–pore fluid interaction.

Whether authigenic non-carbonates, typically clays or submicron-sized quartz, were originally suspended in the pore fluid or attached to or covering the chalk particle surface is difficult to affirm. If the non-carbonates originally stuck to the particle surfaces, they would determine the interaction between particle and pore fluid. In order to investigate original positions of non-carbonates in chalk, a cryo (freezing) SEM should be employed. Original pore fluids must remain in place during and after sampling and sample preparation. In the frozen sample, suspended constituents remain suspended and fixed in the pore fluid and may be observed in situ. Normally, chalk is cleaned for salt and drilling mud before it is subjected to various analyses. However, sometimes evaporating pore water leaves some salt behind in the chalk, which may affect the outcome of e.g. X-ray diffraction analysis (XRD) and conventional core analysis (porosity and permeability).

**TEM.** Beam damage (Fig. 14, Table 2) may not only change the mineralogy of the particle surface layers, but possibly also the particle properties. This may have an effect on wettability.

### Hidden surfaces

**SEM.** The thin carbon coatings derived from the carbon adhesive disc (Figs 1–2), and also the applied conductive metal coatings (Figs 3–6), may mask the true nature of the particle surfaces, depending on the type and thickness of the coating. Important information regarding surface mineralogy may remain undetected and result in erroneous characterisation of the surface properties of the particle.

## Undetected substances adhering to the particle surface

**SEM.** The effect of high acceleration voltage is loss of surface detail (Fig. 9A, C) and thus loss of information on ultrathin substances adhering to the particle surface, as seen in Fig. 9B, D. That ultrathin flakes adhering to calcite may be clay was proposed by Skovbjerg *et al.* (2012), who also demonstrated intermediate wettability of the flakes. This finding suggests that barely detectable clay particles may play a major wettability-controlling role and thus emphasises the importance of careful analysis of particle surfaces. However, it still remains unresolved whether these flakes before removal of the pore fluids were adhering to the particle surface or were suspended in the pore fluids.

## Apparent contact cement between chalk particles

**SEM.** When conductive metal coatings are applied to chalk in thicknesses of 40 nm or more, submicronsized details become blurred and indistinct and attain a false robustness (Fig. 5). The contact cementation between chalk particles may appear more well-developed than it really is, which may lead to overestimation of chalk consolidation and mechanical strength.

**TEM.** The visual challenges related to identification of particle contacts in TEM (Figs 16–17) as well as identification of residual adhesive (Fig. 18) may result in overestimation of the degree of cementation between particles and the mechanical strength of the chalk.

### Conclusions

SEM and TEM investigation of chalk at high magnification provides detailed information on the morphology, size and mineralogy of chalk particles, and structural features including cementation and spatial distribution of non-carbonate minerals can be visualised. However, the ability to resolve fine details also exposes morphological and structural changes caused by sample preparation and interaction between sample and electron beam. Misinterpretation of features as described in this study may lead to inaccurate characterisation of the surfaces of chalk particles and untenable conclusions with regard to their properties. As a possible consequence, wettability, mechanical strength and maximum burial depth of a chalk reservoir may be evaluated wrongly.

For SEM investigations of chalk, microscopists are encouraged to pay attention to the following phenomena.

- 1. Conductive coatings may produce artificial surface textures and artificial ornaments, which may mask genuine surface details. To minimise these effects, coating application time should be kept at a minimum.
- 2. Chalk particles and small chalk aggregates mounted on carbon adhesive discs may submerge into the carbon substrate, or their surfaces may be covered by an ultrathin film of creeping carbon.
- 3. Acceleration voltage determines the probing depth of the electron beam and thus the amount of observable detail. By lowering the acceleration voltage, an apparently smooth surface may reveal significant ornamentation.
- 4. High-energy electrons hitting delicate particles may cause the particle shape to change. For example, submicron-sized thin clay flakes tend to bend or curl when hit by electrons.
- 5. Flattened terminations of organic filaments attached to calcite particle surfaces mimic clay flakes.
- 6. Authigenic non-carbonate minerals attached to the calcite surface may have resided suspended in pore fluids and settled when the fluids were removed during sampling or sample preparation.
- 7. Removal of pore fluids by drying may cause suspended ions to concentrate and precipitate. The occurrence of salt crystals indicates the original presence of brine.

During TEM investigations of chalk, attention should be paid to the following phenomena:

- 1. The high acceleration voltage necessary to transmit electrons through calcite particles may damage the crystal structure and cause gradual amorphisation. A thin CaO coating is interpreted as a mineralogical change from CaCO<sub>3</sub> to CaO (lime) caused by beam damage restricted to the calcite surface.
- 2. Ultrathin membranes sharing similarities with siliceous coatings described in earlier literature may be graphite, possibly derived from the carbon film supporting the chalk sample.
- 3. Calcite particles overlapping each other in suspension samples may seem to be cemented together but may in fact be separate particles settled next to each other during sample preparation.
- 4. Residual adhesive from the ion milling process or applied conductive carbon film should not be confused with cementation.

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