Title: Silica diagenesis in Cenozoic mudstones of the North Viking Graben: physical properties and basin modelling

Running title: Silica diagenesis in the North Viking Graben

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Abstract:

Silica diagenesis can significantly change physical properties of the host strata and release large volumes of water. Predicting these changes and their timing is essential to understanding compaction, fluid flow and rock deformation in sedimentary basins. In this paper, the influence of silica diagenesis (opal-A/CT transformation) on physical properties is determined, the sediment volume affected by these changes is mapped, and a new technique to model silica diagenesis is introduced. A petrophysical analysis of sixteen exploration wells shows that the opal-A/CT transformation leads to a porosity reduction of c.20% (from 49-29%) in the Cenozoic mudstones of the North Viking Graben. Using three-dimensional seismic reflection data, it is shown that the c.50 m thick opal-A/CT transformation zone covers an area of >1500 km², equating to a minimum volume of 75 km³. The spatial and temporal evolution of opal-A/CT transformation is simulated using an innovative basin modelling approach, the results of which indicate that the transformation started around Middle-to-Late Eocene times and then migrated upwards until it gradually fossilised between the Miocene and present. These findings are important, as they help understanding how these sediments compact and when fluids are released by diagenesis.
1. INTRODUCTION

Silica diagenesis typically includes three minerals that undergo two dissolution-precipitation phase changes. First, amorphous silica (opal-A), which is mainly of biogenic origin, is dissolved in pore fluids and precipitates as cristobalite/tridymite lepispheres (opal-CT). Secondly, opal-CT dissolves and precipitates as micro-crystalline quartz (e.g. Kastner et al., 1977; Williams & Crerar, 1985; Williams et al., 1985; Hesse, 1988). The extent and rate of these two phase changes are primarily controlled by temperature and time (Williams et al., 1985), although other factors, such as pressure, pH (of the solvent), surface area (of the solute), host rock lithology and content of organic matter, may also be important (e.g. Kastner et al., 1977; Isaacs, 1982; Keller & Isaacs, 1985; Hesse, 1988; Hinman, 1990; Dove & Rimstidt, 1994; Hinman, 1998).

In addition to altering host strata composition, diagenesis can also reduce its porosity, which in turn leads to increases in p-wave velocity and bulk density (Isaacs, 1981; Tada & Iijima, 1983; Compton, 1991; Guerin & Goldberg, 1996; Chaika & Dvorkin, 2000; Kim et al., 2007; Spinelli et al., 2007; Ishii et al., 2011; Tsuji et al., 2011). These changes typically cause the embrittlement of fine-grained sedimentary rocks and can thereby influence the hydraulic fracturing potential of unconventional reservoirs (see review by Passey et al., 2010). These diagenetic changes in bulk density and p-wave velocity often produce distinct seismic reflections that can be observed and mapped over several hundreds to thousands of kilometres (Hein et al., 1978; Davies & Cartwright, 2002; Lee et al., 2003; Volpi et al., 2003; Meadows & Davies, 2007; Neagu et al., 2010b; Ireland et al., 2011). Mapping these reflections using 3-D seismic data revealed that silica diagenesis can influence fluid flow, overpressure and compaction, and may trigger submarine slope failures, sediment remobilisations and injections (Davies, 2005; Davies & Clark, 2006; Davies et al., 2006; Cartwright, 2007; Davies et al., 2008; Neagu et al., 2010a;
In this paper, mineralogical, borehole and 3-D seismic reflection data are combined to answer the following key questions: 1) what is the influence of the opal-A/CT transformation on the physical properties of fine-grained clastic successions?; 2) what is the sediment volume affected by the transformation?; 3) when did the transformation occur?; and 4) what controlled its evolution?

The first question is addressed by a detailed petrophysical analysis of sixteen exploration wells penetrating the Cenozoic mudstones in the North Viking Graben. This analysis allows us to determine that the host rock porosity is reduced by c.20% (from 49-29%) during opal-A/CT transformation. We discuss whether the porosity reduction is caused by pore space collapse or cementation, before presenting new porosity-depth functions describing compaction of mudstones undergoing silica diagenesis. These functions can be used to predict porosities based on a seismically-imaged opal-A/CT transformations in areas where well data is unavailable. Predicting porosity reductions can be crucial for constraining fluid flow, pore fluid pressure and compaction in sedimentary basins.

To answer the second question, we interpret five 3-D seismic reflection volumes that are tied to borehole data. Mapping the reflection associated with the opal-A/CT transformation highlights that the c.50 m thick transformation zone currently covers c.1500 km². These results are important, as large volumes of water can be released during opal-A/CT transformation, potentially leading to overpressure build-ups, slope failures, sediment remobilisations and injections, or hydraulic fracturing.

To address question 3 and 4, we simulate the evolution of the opal-A/CT transformation zone using basin modelling. Because basin modelling allows the calculation and tracking of subsurface temperatures and because the opal-A/CT transformation is primarily controlled by
temperature and time, it is possible to simulate the transformation. This novel approach involves several fundamental processes occurring in sedimentary basins, e.g. sedimentation, compaction and thermal conduction. Crucially, it is possible to model the opal-A/CT transformation as a temperature- and time-dependent reaction. Using this approach, the timing of formation, migration and fossilisation of the opal-A/CT transformation can be constrained.

2. GEOLOGICAL SETTING

The study area is located in the North Viking Graben, northern North Sea (Fig. 1a, b). The Viking Graben formed in the late Middle Jurassic-to-earliest Cretaceous in response to crustal extension (Fig. 1c). The main Late Jurassic rift phase was characterised by rapid subsidence and the formation of large-displacement normal faults that bounded graben and half-graben basins (Fig. 1c) (e.g. Badley et al., 1988; Yielding, 1990; Faerseth et al., 1997). At the beginning of the post-rift phase, in the Early Cretaceous, a change from fault- to thermally-controlled subsidence occurred (Joy, 1993; Brekke, 2000; Jordt et al., 2000; Kyrkjebø et al., 2001; Faleide et al., 2002). The post-rift period was tectonically quiet, although two major uplift phases occurred in the North Viking Graben: an early Palaeocene phase, which was related to rifting, magmatism and the break-up NE Atlantic (e.g. Nadin & Kusznir, 1995), and a Middle Miocene phase which was related to the reorganisation of the North Atlantic plate (e.g. Løseth et al., 2013).

The post-rift succession in the North Viking Graben is up to 5 km thick and dominated by marine mudstones of the Shetland, Rogaland and Hordaland Group. This study focuses on the biogenic opal A-rich mudstones of the Balder Formation and the Hordaland Group (Rundberg, 1989). It has be suggested that the Balder Formation marks the onset of deposition of siliceous sediments during Eocene times. During the Early Oligocene, a basinward-thinning (i.e.
westward-thinning) wedge was deposited along the NE margin of the northern North Sea, indicating a change in sediment source area from the Shetland Platform in the W to Fennoscandia in the E (Rundberg & Eidvin, 2005; Anell et al., 2012). This wedge consists of organic-rich mudstones (Rundberg & Eidvin, 2005). The Hordaland Group (and the Balder Formation) consists of mudstones with variable proportions of biogenic silica (diatoms, radiolarians and sponge spicules) and glauconite, and shows an upward increase in the proportion of silty sandstones and siltstones, suggesting it was deposited in a prograding delta (Rundberg, 1989; Rundberg & Eidvin, 2005). During the Early Miocene a mudstone-dominated succession was deposited, with the top of the unit being eroded due to regional intra-plate shortening and related uplift (Eidvin & Rundberg, 2001; Rundberg & Eidvin, 2005; Løseth et al., 2013). Eidvin and Rundberg (2001) estimate the erosional break to last from approximately 17-6 Ma in the northern North Sea and Løseth et al. (2013) estimate a net erosion of less than 100 m.

During the Pliocene and Pleistocene regional uplift of Fennoscandia resulted in a relatively rapid, volumetrically-significant influx of non-siliceous clastic material (Faleide et al., 2002) and deposition of a relatively thick (up to 600 m), clinoform-bearing succession along the eastern flank of the North Viking Graben (Anell et al., 2011; Ottesen et al., 2012).

3. DATA

3.1. 3-D SEISMIC DATA

We use five three-dimensional seismic reflection volumes that cover part of the eastern margin of the North Viking Graben (Fig. 1b). Three of these volumes (MN9201_R05, WESTERN3510, STNH98N) have a line spacing of 25 m and a vertical sampling of 4 ms, and two (NH0301, BPN9301) have a line spacing of 12.5 m and 2 ms vertical sampling. All surveys are time-migrated and zero-phase processed with SEG reverse polarity; i.e. an acoustic impedance
increase with depth is represented by a negative reflection event (blue or black), and a decrease in acoustic impedance with depth is represented by a positive reflection event (red or white). The P-wave velocity logs and check shots indicate that the average seismic velocity within and above the interval of interest is 2000±200 m/s, thus allowing vertical measurements made in milliseconds two-way time (ms TWT) to be directly converted to depth (m), as a first order approximation. In conjunction with the determined interval velocity, the dominant frequency for all the seismic datasets is c.50 Hz, suggesting that, in the interval of interest, the seismic data have a vertical resolution of c.10 m and a horizontal resolution of c.20 m.

3.2. WELL DATA

For this study, we use lithology, bottom-hole temperature, core and wireline data from sixteen exploration wells (Fig. 1b and Tab. 1). We checked the quality of all wireline logs using caliper and density correction logs (Rider & Kennedy, 2011). Lithology information is based on final well reports and cuttings descriptions provided by the Norwegian Petroleum Directorate (NPD, 2014). Bottom-hole temperatures and oven-dried porosity data, extracted over c.400 m of core, were also provided by the NPD (2014). We furthermore collected 50 washed drill-bit cuttings from exploration well 35/11-5 (depth: 1000-1500 m, sampling interval: 10 m) to determine the mineralogy of the studied succession, using X-ray diffraction (see below).

4. METHODS

4.1. X-RAY DIFFRACTION

To determine the mineralogy of the studied succession, we applied the quantitative X-ray diffraction method of Cressey and Schofield (1996) to cutting samples of exploration well 35/11-5. This method was chosen, because it allows a rapid and accurate quantification of the
mineralogy of clay-rich samples (Batchelder & Cressey, 1998). To do this, we measured unoriented powder samples of our cuttings, in addition to the mineralogical ‘standards’ held at the Natural History Museum. The quantity of a mineral in the cuttings was then determined by matching the diffraction pattern of the mineral and the whole sample. By repeating this procedure for all minerals and cuttings, we were able to determine the mineralogy of the cuttings (see Appendix) (Fig. 3). Batchelder and Cressey (1998) estimate the precision of this method to be ±3% in clay-bearing samples lacking an amorphous phase. Because amorphous opal produces a broad band rather than a sharp peak such as crystalline phases, the method of Cressey and Schofield (1996) is less certain in our case. Unfortunately, the uncertainty of this method when applied to amorphous phases has not been quantified. Conley (1998) however highlight that opal-A contents derived by X-ray diffraction (Eisma & Van der Gaast, 1971) typically exceed opal-A contents derived wet-chemical digestion techniques by >10%.

4.2. PETROPHYSICAL ANALYSIS

To determine the influence of silica diagenesis on physical properties of the host strata, we derived porosity logs from wireline data for all sixteen exploration wells. This was done by first calculating clay volume. Lithology information from well reports, together with neutron porosity and bulk density logs were used to calculate the clay volume (see Appendix). We then calculated five porosity logs based on bulk density, neutron porosity and sonic logs, and combinations of the neutron porosity/bulk density and neutron porosity/sonic logs (see Appendix). By comparing these porosity logs to oven-dried core porosities from the deeper reservoir section (in exploration wells 31/2-4 and 31/2-5), we found that porosity logs derived from the bulk density and clay volume logs matched the core porosities most accurately (average misfit <10%); these porosity
logs were therefore used for all subsequent analyses. Chaika (1998) notes that the assumption of
constant grain density is problematic, as mineral densities differ. However, the difference in
mineral density between opal (2.09 g/cm$^3$) and cristobalite/tridymite (c.2.30 g/cm$^3$) is only about
0.2 g/cm$^3$ (Duda & Rejl, 1990). Considering that opal-A and opal-CT constitute less than 30% of
these rocks (Fig. 3), the mineral density difference of 0.2 g/cm$^3$ would lead to a maximum grain
density difference of c.0.06 g/cm$^3$. Based on the employed porosity calculation, a maximum
grain density difference of c.0.06 g/cm$^3$ would produce maximum porosity differences of about
1%. This difference is an order of magnitude smaller than the observed porosity reduction of
20% associated with the opal-A/CT transformation.

4.3. SEISMIC-TO-WELL TIE

To ensure an accurate tie between well data (depth domain) and seismic data (time domain),
synthetic seismograms were calculated for each well (e.g. Fig. 3). For this purpose, we extracted
deterministic, zero-phase wavelets using the extended Roy White method (Walden & White,
1998). The synthetic seismogram for each well was then calculated by convolution of the
wavelet, that was extracted from the seismic traces surrounding the well path, with the
reflectivity log, that was derived from the bulk density and p-wave velocity logs. Establishing an
accurate tie between well and seismic data for all wells allowed key stratigraphic boundaries
(e.g. mid-Miocene unconformity and Eocene/Oligocene boundary), and the potential opal-A/CT
transformation zone (Zone 2), to be identified and mapped in seismic reflection data (Fig. 3).

4.4. SEISMIC INTERPRETATION

The seismic interpretation involved mapping the seismic reflections associated with the three
main stratigraphic boundaries (i.e. Top Eocene, Top Oligocene, mid-Miocene Unconformity),
beginning at the well locations (Fig. 3). By mapping these reflections away from the well locations and between seismic volumes, we were able to produce a series of regional maps of these key stratigraphic boundaries. Having established the main stratigraphic framework, we applied the same methodology to interpret the seismic reflection associated with the opal-A/CT transformation zone (Figs. 3, 4, 5 and 6a,b). This reflection required carefully mapping, as ‘diagenetic’ reflections are often discordant with stratigraphic horizons (Hammond & Gaither, 1983; Berndt et al., 2004; Ireland et al., 2011). We also generated a TWT-thickness map, which allow us to investigate spatial variations in thickness of the opal-A zone (Zone 1) (Figs. 6c).

4.5. BASIN MODELLING

We use basin modelling to explore the evolution of silica diagenesis in the North Viking Graben. Because basin modelling can be used to calculate subsurface temperatures through time and since silica diagenesis is primarily controlled by temperature and time, basin modelling can be used to simulate the opal-A/CT transformation. The accuracy of the temperature calculation depends on various boundary conditions that we tried to constrain as accurately as possible (see below).

Basin modelling can be divided into four steps: 1) input, 2) definition of boundary conditions, 3) simulation and 4) calibration (Hantschel & Kauerauf, 2009). The input data are specific to the area and stratigraphic interval of interest and include: 1) basin geometry, 2) stratigraphy and 3) lithology (Fig. 7). To define the basin geometry, we depth-converted an east-west trending seismic section passing through exploration wells 35/10-1 and 35/11-5, the latter being the well for which detailed mineralogical data is available (Fig. 3). The underlying velocity model was based on well tops of each lithostratigraphic group, and linear velocity-depth
functions that were derived from checkshot data for each of these groups. We also added the formation ages and lithologies from the NPD (2014) to the basin model (Fig. 7).

The second step comprised the definition of boundary conditions: 1) palaeo water depth, 2) palaeo seafloor temperature and 3) heat flow history (Fig. 8a). We used palaeo water depths presented by Kyrkjebø et al. (2001) (Fig. 8a) and palaeo seafloor temperatures derived from oxygen isotope ratios of Jensen and Buchardt (1987) and Anderson et al. (1994) (Fig. 8a). The heat flow history was based on a reconstruction by Lucazeau and Le Douaran (1984) (Fig. 8a). This heat flow history reflects the initial Triassic and secondary Late Jurassic rift episodes, as well as the far-field effect of the opening of the North Atlantic during the Palaeogene.

The third step comprises the simulation of: 1) deposition and erosion 2) pressure and compaction and 3) temperature. Deposition was simulated by adding layers at the model surface. The thickness of a newly deposited layer was calculated via porosity controlled backstripping. During erosion layers were removed on the upper surface. We assumed mid-Miocene erosion occurred for 11 Myr, between 6-17 Ma, as suggested by a detailed biostratigraphic analysis by Eidvin and Rundberg (2001), and resulted in net erosion of approximately 70 m (<100 m), as highlighted by the measurement of erosional escarpments by Løseth et al. (2013). The pressure calculation was based on the overburden weight caused by sedimentation and compaction. The final step of the simulation was the calculation of the subsurface temperature based on heat conduction, convection as well as heat generation from radioactive decay. For the theoretical background of these processes and their implementations, we refer the reader to Hantschel and Kauerauf (2009).

The final step of the basin modelling was the calibration. The model was calibrated by matching the modelled and measured present day temperatures at the bottom-hole of exploration
wells 35/10-1 and 35/11-5 (Fig. 8b,c). Assuming they have been allowed to re-equilibrate, bottom-hole temperatures are well-constrained and are therefore suitable to calibrate basin models (Hantschel & Kauerauf, 2009). For the calibration, the heat flow of Lucazeau and Le Douaran (1984) was increased by a constant 13 mW/m², which reflects the fact that Lucazeau and Le Douaran (1984) derive surface heat flow, whereas our basin model requires heat flow to be added at its base, simulating heat addition from the asthenosphere into the lithosphere. Our study also differs from Lucazeau and Le Douaran (1984) in that we use a more realistic range of thermal conductivities for the crustal lithologies (1.8 Wm⁻¹K⁻¹ for shale, 3.2 Wm⁻¹K⁻¹ for sandstone and 2.4 Wm⁻¹K⁻¹ for granite) instead of a single value (3 Wm⁻¹K⁻¹).

4.6. MODELLING OF THE OPAL-A/CT TRANSFORMATION

The opal-A/CT transformation involves a series of chemical reactions that are controlled by multiple factors; the slowest of these reactions typically controls the overall transformation rate (e.g. Lasaga & Kirkpatrick, 1981; Heaney, 1994; Giles, 1997). In the case of the opal-A/CT transformation, experimental data demonstrate that it is the rate of opal-A dissolution that controls the overall transformation rate (Williams et al., 1985; Hinman, 1998). It is therefore assumed that opal-A dissolution kinetics can be utilised to model the opal-A/CT transformation. Furthermore, experimental data indicate that the opal-A dissolution rate is primarily time-temperature dependent (e.g. Kastner et al., 1977; Kastner & Gieskes, 1983; Keller & Isaacs, 1985; Williams et al., 1985; Dove & Rimstidt, 1994). Thus, as a first order approximation, we here model the opal-A/CT transformation as a time-temperature dependent reaction. The validity of this approach is critically discussed in section 6.2.

To model the opal-A/CT transformation dependent on time and temperature, the transformation rate can be described by Arrhenius’ law (1889):
\[ k = A \cdot \exp\left(-\frac{E}{RT}\right) \]  

1. Transformation rate  
2. Activation energy  
3. Frequency factor  
4. Gas constant (8.314 J K\(^{-1}\) mol\(^{-1}\))  
5. Temperature  

The key parameters in this equation are the frequency factor, which is the frequency at which molecules react, and the activation energy, the threshold energy to initiate reaction. For opal-A dissolution, these parameters (A=22 kcal/mol and E=7.18 \cdot 10^{13} \text{ Ma}^{-1}) were experimentally derived and summarised by Icenhower and Dove (2000). Because the rate of opal-A dissolution seems to control the opal-A/CT transformation rate (see above), frequency factor and threshold energy can be utilised to model the transformation. These parameters seem to produce realistic results, as predicted transformation temperatures (Fig. 8d) are in the range of previously documented transformation temperatures of the opal-A/CT transformation (Fig. 8e). This approach is furthermore validated by the match between the modelled and observed opal-A/CT transformation ratios in exploration well 35/11-5 (Fig. 8f).

5. RESULTS

5.1. PRESENT STRUCTURE OF SILICA ZONES

In this section, we describe the wireline and seismic characteristics of the key silica zones (1-3) and combine them with mineralogical and lithological data to highlight physical property changes and determine the affected sediment volume. The Balder Formation and Hordaland
Group consist of marine mudstones with minor sandstones. Zones 1 and 3 consist of opal-A and opal-CT-rich mudstones, respectively, whereas Zone 2 hosts the opal-A/CT transformation. We describe these zones in stratigraphically-descending order (i.e. youngest zone first) because this, as we will describe below, more closely follows the diagenetic stages experienced by Zones 1-3. It is furthermore worth noting that: 1) all property changes are described in absolute terms (e.g. a porosity change from 50 to 40% is described as a 10% porosity reduction).

### 5.1.1. ZONE 1

Zone 1 thickens westwards from 280 to 450 m and comprises sediments of Late Oligocene to Early Miocene age (Figs. 4, 5, 6c). The top of Zone 1 corresponds to a continuous, parallel, high-amplitude, positive seismic reflection located 300-700 meters below the present seafloor (900-1050 ms TWT) and which broadly coincides with the mid-Miocene Unconformity (Figs. 4, 5, 6a). In Zone 1, the bulk density (1.81±0.07 g/cm$^3$), p-wave velocity (1.95±0.06 km/s) and porosity (49±5%) are more or less constant, even though minor (±10%) high frequency variations (<5 m) are observed (Fig. 2). On seismic data, Zone 1 is characterised by continuous, parallel, medium-to-high amplitude reflections (Figs. 2-5).

Rundberg (1989) and Thyberg et al. (1999) documented the presence of diatoms, radiolarians and sponge spicules (opal-A) in Early Miocene-to-Late Oligocene sediments of the North Viking Graben using X-ray diffraction and scanning electron microscopy (i.e. our Zone 1). We were able to confirm the presence of opal-A in Zone 1 using X-ray diffraction data from well 35/11-5 (Fig. 3). The top of Zone 1 (the mid-Miocene Unconformity) is commonly associated with the end of siliceous sedimentation in the North Sea (Rundberg, 1989; Rundberg & Eidvin, 2005) and the bottom of Zone 1 marks the onset of opal-A to opal-CT transformation (see below:...
Zone 2). Because opal-A is the dominant silica mineral in this zone, we will refer to Zone 1 as the opal-A zone. This zone represents the earliest stage of the silica diagenetic sequence (opal-A/ opal-CT/quartz), in which no transformation has occurred.

5.1.2. ZONE 2

Zone 2 occurs between Zone 1 (above) from Zone 3 (below) and is located 680-975 meters below the present day seafloor (Fig. 6b). Zone 2 is c.50 m thick and is defined by an overall downward increase in bulk density of 0.24±0.08 g/cm$^3$ (from 1.81±0.07 to 2.05±0.08 g/cm$^3$) and p-wave velocity increase of 0.20±0.05 km/s (from 1.95±0.06 to 2.15±0.05 km/s), and a porosity reduction of 20±5% (from 49±5 to 29±4%) (Fig. 2). The continuous, high amplitude, negative seismic reflection that corresponds to Zone 2 coincides with the top of the Lower Oligocene succession in the eastern part of the study area (Fig. 4). In the western part, Zone 2 cross-cuts the several stratigraphic reflections and correlates to a sharp change in seismic facies from continuous, parallel, medium-to-high amplitude reflections in Zone 1 (above) to discontinuous, sub-parallel to chaotic, low amplitude reflections in Zone 3 (below) (Fig. 4).

X-ray diffraction data, more specifically the downward decreasing proportion of opal A and an increasing proportion of opal-CT, indicate that Zone 2 corresponds to the opal-A/CT transformation zone (Fig. 3), which is the volume of rock hosting the most recent transformation. The spatial and temporal evolution of the opal-A/CT transformation is discussed later.

5.1.3. ZONE 3

Zone 3 thickens westwards from 50 to 350 m, comprises Early Oligocene sediments and is buried 680-1200 meters below the present seafloor (Figs. 2-5). Zone 3 lies beneath Zone 2. In
Zone 3, the bulk density (2.05±0.08 g/cm$^3$), p-wave velocity (2.15±0.05 km/s), and porosity (29±4%) are consistent, and show only high frequency (<10 m), moderate magnitude (±30%) variations (Fig. 2). Low porosity values correlate to high density and p-wave velocity values, and vice versa. On seismic data, Zone 3 is characterised by discontinuous, sub-parallel to chaotic, low amplitude reflections (Figs. 4, 5).

Our X-ray diffraction results, as well as those presented by Rundberg (1989) indicate that opal-CT is present in Early Oligocene sediments of the North Viking Graben (i.e. our Zone 3). Zone 3 is overlain by an interval that hosts the opal-A/CT transformation (i.e. Zone 2). Zone 3 therefore represents the opal-CT-rich sediments that have undergone opal-A/CT transformation. For these reason, Zone 3 is termed opal-CT zone. It is worth noting that c. 10% opal-A are present in sediments below the opal-CT zone (Fig. 2).

5.2. DISTRIBUTION OF THE OPAL-A/CT TRANSFORMATION

In this section, we describe the basin modelling results, which provide insights into the spatial and temporal evolution of the opal-A/CT transformation in the North Viking Graben. To describe the evolution of the transformation, we use transformation ratios of 0.1, 0.5 and 0.9 which correspond to 10, 50 and 90% of opal-A being transformed to opal-CT (Fig. 8d).

Transformation ratios of 0.1 were first reached during the middle Eocene (44 Ma) (Fig. 9a). A transformation ratio of 0.5 was first reached during the Late Eocene (c.35-38 Ma) (Fig. 9b). In both cases, these transformation ratios occurred in the lowest part of the Balder Formation (Fig. 9a,b).

These transformation ratios subsequently moved upwards, during the Eocene to Miocene through most of the Balder Formation and the lower part of the Hordaland Group (Fig. 9). To
quantify this movement, we extracted the distance between base of the Balder Formation and the transformation ratios through time, i.e. the cumulative distance (Fig. 10a-c). This distance increases with time and is generally higher in the west compared to the east. We also derived the rate (i.e. distance per time) of transformation ratio advancement, showing that it systematically decreases with time and reaches values around zero between the Miocene and present (Fig. 10d-f).

6. DISCUSSION

6.1. POROSITY OF SILICEOUS MUDSTONES

In this section, we discuss the influence of silica diagenesis on the porosity of Cenozoic mudstones in the North Viking Graben. In general, the porosity of mudstones is primarily controlled by mechanical compaction during shallow burial (<500 m) and chemical compaction during deeper burial (>500 m; e.g. Velde, 1996; Bjørlykke, 1999). Whereas mechanical compaction typically causes a near-continuous porosity reduction, chemical compaction often leads to abrupt porosity reductions. Silica diagenesis, for example, can cause abrupt porosity reductions in highly-siliceous sedimentary rocks (e.g. Isaacs, 1981; Tada & Iijima, 1983). We use an extensive well-database and detailed petrophysical analysis of wireline data to analyse, and ultimately predict, the influence of silica diagenesis on the porosity of Cenozoic mudstones in the North Viking Graben.

6.1.1. OPAL-A ZONE

The opal-A zone describes the sediment volume in which opal-A is the main silica mineral. The average porosity of the opal-A zone is c. 49%, which is relatively low in comparison to previous
studies of siliceous sediments/rocks (Tab. 2). This difference is explained by a lower depositional opal-A content in the Hordaland Group of the North Viking Graben (<30%; Fig. 3) (Rundberg, 1989) than that encountered in other siliceous mudstones (up to 90%; e.g. Isaacs, 1981; Tada & Iijima, 1983). Since biogenic opal-A is highly porous, high opal-A contents cause high porosities (Compton, 1991). A relatively low opal-A content in mudstones furthermore translates into a relatively high clay content. The higher the clay content is, the lower the preserved porosity, as clays compact more than opal-A during shallow burial (e.g. Compton, 1991; Chaika & Dvorkin, 2000).

6.1.2. OPAL-A/CT TRANSFORMATION ZONE

The opal-A/CT transformation zone describes the c.50 m thick sediment volume in which both opal-A and opal-CT occur. The proportion of both silica minerals typically changes as a result of the depth-dependent transformation of opal-A into opal-CT (e.g. Hein, 1978; Isaacs, 1982; Ireland, 2011). At the top of the opal-A/CT transformation zone, the opal-A content is highest, while opal-CT is absent. With increasing depth, the opal-A content decreases and the opal-CT content increases. At the base of the transformation zone, opal-A is absent and the opal-CT content is highest. Previous studies show that the transformation of opal-A to opal-CT reduces host rock porosities (Tab. 2). The average porosity reduction due to the opal-A/CT transformation is for example 21% in the Monterey Formation, California, USA and 19% in the Early Pliocene/Miocene succession, northern Japan (Hokkaido Basins). A comparable porosity reduction of 20% (from 49-29%) associated with the opal-A/CT transformation is observed in the North Viking Graben. We also note that the porosity reduction is consistent with the observed bulk density and P-wave velocity increases associated with the transformation.
Considering the much lower silica content of these sediments (<30%; Rundberg, 1989), compared to the example from the USA (up to 90% from Isaacs, 1982) and Japan (up to 90% from Tada & Iijima, 1983), it might be surprising that the porosity reductions are comparable. This is interpreted as evidence that the porosity reduction during opal-A/CT transformation might be independent of host rock silica content. The independence of the porosity reduction may be explained by pore fluid solubility. For example, at a given time, the amount of opal-A dissolved in the pore fluid will be limited by its solubility; therefore the extent of rock matrix collapse and porosity reduction may also be limited. Based on the independence of the porosity reduction, it is suggested that the same process, outlined by previous studies (see below), also led to the porosity reduction during the opal-A/CT transformation in the North Viking Graben (e.g. Isaacs, 1981 and Tada and Iijima, 1983). This process starts with porosity preservation due to highly-porous, rigid opal-A during early burial. Once the opal-A bearing mudstones reach sufficient temperatures, opal-A starts to dissolve in the pore fluid. The dissolution of opal-A reduces the strength of the matrix until it collapsed under the lithostatic pressure. The matrix collapse reduced the porosity abruptly; resulting in a relatively thin opal-A/CT transformation zone (c. 50 m). Subsequent precipitation of opal-CT cement can further decrease the porosity of the host strata. Because very little is known about the relative timing between opal-A dissolution and opal-CT precipitation, it is hard to separate the impact of 1) matrix collapse due to opal-A dissolution and 2) cementation due to the impact of opal-CT precipitation on the porosity of the host strata. It is worth noting that in highly siliceous sediments, the opal-A/CT transformation can occur close to the seafloor (e.g. Bohrmann et al., 1992; Bohrmann et al., 1994). In these cases, silica diagenesis predates mechanical compaction of the host rock. In less siliceous sediments as documented in this study, the opal-A/CT transformation typically occurs between
burial depths of 500-1000 m. A compilation of porosity-depth curves shows that mudstones lose between 30-60% porosity in the first 1000 m of burial (see Figure 10.32 of Giles, 1997). In these cases, silica diagenesis affects the host rock properties after they have been mechanically compacted. It is interesting to note the opal-A/CT transformation reduces the host rock porosity despite previous mechanical compaction.

6.1.3. OPAL-CT ZONE

The opal-CT zone describes the sediment volume in which opal-CT is the main silica mineral. The average porosity of the opal-CT zone is c.29%, which is again relatively low in comparison to previous studies (Tab. 2). This difference is also explained by the lower depositional opal-A content and enhanced mechanical compaction of the clay fraction of these sediments (see above). We also observe high frequency (<10 m) variations in porosity, density and p-wave velocity values in the opal-CT zone. Lower porosity values correlate to high density and p-wave velocity values, and vice versa (Fig. 2). These variations are most likely induced by depositional variations in opal-A content. In siliceous mudstones, the stratigraphic variability of biogenic silica is typically quite high (e.g. Isaacs, 1984). These compositional variations induce porosity variations. High biogenic opal-A contents correlate to high porosities, as opal-A forms highly-porous structures (e.g. Compton, 1991). Previous studies (Isaacs, 1981; Tada & Iijima, 1983; Compton, 1991) together with the presented results highlight a weak correlation between silica content and the amount of porosity reduction during opal-A/CT transformation. Assuming opal-A content is the primary control on host rock porosity and that the opal-A/CT transformation does not depend on the opal-A content, high porosity values would correspond to highly siliceous layers and, conversely, low porosity values would correspond to less siliceous layers, both before and after diagenesis.
6.1.4. Porosity-Depth Functions

Porosity-depth functions describing the compaction of mudstones are typically negative-exponential functions of the burial depth. The effective vertical stress (and therefore the burial depth) is assumed to be the main driving force behind mechanical compaction. Silica diagenesis, on the other hand, is primarily controlled by temperature and time, hence occurs abruptly when the host strata reach sufficient temperatures. Previous studies highlight the abrupt porosity reductions in highly-siliceous rocks during diagenesis (Tab. 2). Because comparable porosity reductions also occur in less-siliceous mudstones (see above), it can be inferred that the porosity reduction during opal-A/CT transformation is at least to a certain degree independent of the silica content of the host strata (see above). Based on these observations, we introduce a series of porosity-depth functions accounting for the diagenetic porosity reduction of siliceous mudstones (see Appendix). Note that these functions would not be appropriate for mudstones undergoing smectite-to-illite transformation. The input parameters for these functions are the diagenetic porosity loss (Δф), and the top (d₁) and bottom (d₂) of the opal-A/CT transformation zone. These new porosity-depth functions follow negative exponential porosity-depth functions with an additional term for the diagenetic porosity loss in the transformation zone; these functions also describe the porosity above, below and within the opal-A/CT transformation zone (see Appendix). These functions approximate the measured porosities more accurately than conventional exponential porosity-depth function (Fig. 8a). By changing the input parameters, these porosity-depth functions can be adapted to describe the diagenetic porosity reductions offshore Norway (e.g. Meadows & Davies, 2009), Japan (e.g. Tada & Iijima, 1983) and California (e.g. Isaacs, 1981). Using conventional porosity-depth functions to estimate the porosity of diagenetically-altered rocks can lead to significant overestimations (Fig. 8b).
therefore suggest that our new porosity-depth functions is used to estimate the porosity of
diagenetically-altered mudstones during hydrocarbon exploration, in situations when the kinetics
of diagenetic reactions and chemical compaction models are difficult to constrain (Schneider et
al. (1996).

6.2. PRESERVATION OF OPAL-A

In this section, we discuss the preservation of opal-A below the present opal-A/CT
transformation zone. Considering that X-ray diffraction can overestimate opal-A contents by
>10% (Conley, 1998), the observation of c.10% opal-A below the transformation could be
interpreted as a measurement artefact. Previous studies however document that opal-A is
preserved down to 1500 m depth in the northern North Sea (Thyberg et al., 1999) suggesting that
the observation of opal-A below the transformation is a real phenomenon. This interpretation
challenges our assumption that the transformation was primarily time-temperature dependant
(see section 4.6) and we thus need to consider which other parameters may play a role. The
presence of opal-A below the transformation zone suggests that opal-A was not fully dissolved in
these rocks, which may be explained by various factors. For example, Thyberg et al. (1999)
suggest that the preservation of opal-A depends on the silica-producing biota; i.e. biosiliceous
material of sponge spicules and radiolarians being more resistant to dissolution than that of
diatoms; a hypothesis that could be tested by optical- and scanning electron microscopy in the
future. Williams et al. (1985) argue that the preservation of opal-A depends on the surface area;
i.e. the higher the surface area, the higher the solubility. Opal-A preservation can also be
enhanced by the formation of detrital surface coatings (e.g. Rickert et al., 2002; Michalopoulos
& Aller, 2004). Although these controls may have been active, they cannot be assessed with the
available data. Furthermore, we suggest that the persistence of opal-A below the transformation zone is not at odds with the time-temperature dependency of opal-A dissolution. Assuming that the amount of opal-A that is dissolved depends on the time the host rocks were subject to certain temperatures (see section 4.6), the persistence of opal-A beneath the transformation zone may be a result of the host rock not being subject to sufficient temperatures for a sufficient period of time. The times and temperatures required to complete opal-A dissolution depend on the initial opal-A content; i.e. the more opal-A is present, the longer it takes to fully dissolve it. Opal-A could, for example, fully dissolve in rocks with low initial opal-A contents, whereas it may still be present in rocks that have been subject to exactly the same temperatures and for the same time because they had higher initial contents. The persistence of opal-A may also be explained by supersaturation of the pore fluids. Supersaturation of the pore fluids with respect to opal-A and opal-CT might be achieved by opal-A dissolution. If fluid migration is limited and opal-CT precipitation slow, the pore fluids may remain supersaturated (with respect to opal-A) and further opal-A dissolution would be inhibited. In these ways, the preservation of opal-A below the transformation zone can thus be explained by the time-temperature dependency of opal-A dissolution.

To summarise, there are many possible explanations for the preservation of opal-A below the opal-A/CT transformation zone, five of which are presented above. Unfortunately, the validity of these explanations cannot be assessed with the available data. It therefore remains unclear what led to the persistence of opal-A below the transformation zone. Because of this uncertainty, the persistence of opal-A cannot be used to identify the controls on the opal-A/CT transformation in the North Viking Graben. In accordance with numerous experimental studies (e.g. Mizutani, 1967; Kastner et al., 1977; Kastner & Gieskes, 1983; Williams et al., 1985;
Duffy, 1993; Dove & Rimstidt, 1994) we assume that the opal-A/CT transformation is, as a first-order approximation, time-temperature dependent. In future, it might be possible to determine the factor(s) controlling opal-A preservation and to describe their influence on the opal-A/CT transformation using different kinetics.

6.3. EVOLUTION OF THE OPAL-A/CT TRANSFORMATION ZONE

The evolution of the opal-A/CT transformation has been previously divided into three stages: 1) formation, 2) migration, 3) fossilisation (Davies & Cartwright, 2002). This division is adapted to discuss the timing, location and controls on the opal-A/CT transformation in the North Viking Graben, northern North Sea.

6.3.1. FORMATION

The formation of the opal-A/CT transformation zone has been previously described as the point when a minimum transformation temperature has been reached (Davies & Cartwright, 2002). This definition makes sense, if it is assumed that the transformation starts at a well-defined temperature. If the opal-A/CT transformation rate is calculated, ‘the start of transformation’ must be refined. According to Arrhenius’ (1889) equation, the transformation rate is low at low temperatures (Fig. 8e). We therefore suggest defining the ‘start of the opal-A/CT transformation’ as the first time a specific transformation ratio (of opal-A to opal-CT) has been reached. We suggest 0.1 and 0.5 as upper and lower boundaries for this ratio, respectively (Fig. 8d). If we define the ‘start of transformation’ as the first time a transformation ratio of 0.1 is reached, then basin modelling indicates that the opal-A/CT transformation started in the middle Eocene in the lower part of the Balder Fm (c.44 Ma) (Figs. 9a, 12a). A transformation ratio of 0.5 has been
reached in the Late Eocene (c.35-38 Ma) (Figs. 9b, 12a). For any other transformation ratio between 0.1 and 0.5, the ‘start of transformation’ can be estimated using Figure 10a-c.

The opal-A/CT transformation zone was formed in the lowest part of the Balder Formation (Fig. 9a,b), the unit documenting the onset of siliceous deposition in the North Viking Graben (Rundberg, 1989). It can be inferred that burial of the Balder Formation resulted in increasing sediment temperatures, that led to progressively higher transformation rates (e.g. Fig. 8d) and the formation the opal-A/CT transformation zone (Figs. 9a,b, 12a).

The formation of the opal-A/CT transformation occurred in a period of: 1) broadly constant sedimentation, 2) broadly constant heat flow, 3) an overall decrease in water depth and 4) relatively high seafloor temperatures (Fig. 10). Especially striking is the correlation between the middle Eocene seafloor temperature maximum, documented by oxygen isotope studies from the North Sea (Buchardt, 1978; Jensen & Buchardt, 1987; Anderson et al., 1994), and the formation of the opal-A/CT transformation zone (Fig. 10). This correlation may indicate that the temperature maximum controls the timing of opal-A/CT transformation zone formation.

6.3.2. MIGRATION

The migration of the opal-A/CT transformation can be defined as formation (see above) in strata overlying the initial transformation zone. The migration is therefore an upward movement of the transformation relative to the host strata. The basin modelling results suggest that migration directly followed formation of the transformation zone (Fig. 10). The opal-A/CT transformation zone migrated through most of the Balder Formation and the lower part of Hordaland Group (Figs. 9, 12b). Migration distance and rate systematically increases from east to west (Fig. 10a-f), most likely as a result of more rapid burial due to a westward increase in sediment thickness and
accumulation rate (Fig. 9). The migration rate was furthermore highest during formation and then systematically decreased until present day (Fig. 10e-f). According to our results, negligible migration of the opal-A/CT transformation zone occurred in the last 5 Myrs (Fig. 10). Although high sedimentation rates increased burial depth and compaction of underlying sediments, the coeval lowering of surface temperatures during the Pliocene and Pleistocene resulted in no significant temperature increase at the A/CT transformation zone and thus no further upward migration. As such, the migration rate follows the general trend of seafloor temperature (Fig. 10d-i). This seems plausible, as seafloor temperature should intuitively be positively correlated to opal-A/CT transformation zone migration.

6.3.3. FOSSILISATION

The fossilisation of the opal-A/CT transformation zone has been previously described as the ‘arrest of upward migration’ (Davies & Cartwright, 2002). In here, fossilisation is defined as the point when the migration rate becomes zero despite the presence of opal-A in the overlying strata. According to this definition, the opal-A/CT transformation probably started to fossilise in early Miocene time in the North Viking Graben (Figs. 10d-f, 12c). The basin modelling results furthermore suggest that fossilisation occurred earlier in the east than in the west (Figs. 10d-f, 12c) presumably due to a westward increase in sediment thickness (Fig. 9). In general, the opal-A/CT transformation zone appears to have been fossilised close to its current position in the Hordaland Group (Fig. 9d-f). It seems that fossilisation of the opal-A/CT transformation zone seems to mark the end of a general decrease in migration rate (Figs. 10d-f, 12c).

7. CONCLUSIONS
Using mineralogical and wireline data, we were able to identify and quantify the change in physical properties due to silica diagenesis. The porosity of the Cenozoic mudstones in the North Viking Graben is reduced by an average of 20% due to the opal-A/CT transformation. In accordance with previous work, we suggest that these changes were caused by matrix collapse and cementation during silica diagenesis. The microscopic processes linking silica diagenesis to these porosity reductions are however not well-understood yet and require further research.

The physical properties changes caused by the opal-A/CT transformation produce a mappable seismic reflection. By mapping the reflection on three-dimensional seismic reflection data, we were able to show that the opal-A/CT transformation affected a c.50 m thick zone covering an area of >1500 km². Keeping in mind that significant amounts of water are released and that the host rock porosity is reduced during silica diagenesis, overpressure may build up, possibly leading to sediment failure and remobilisation.

Basin modelling can be used to calculate subsurface temperatures through time and simulate the time-temperature dependent opal-A/CT transformation using fundamental physical and chemical principles. The basin modelling results indicate that the opal-A/CT transformation started around Middle-to-Late Eocene times and then migrated upwards until it fossilised between the Miocene and present.

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9. CONFLICT OF INTEREST

Co-author Christopher Jackson is an Associate Editor of Basin Research.

10. REFERENCES


**11. APPENDIX**

**11.1. X-RAY DIFFRACTION**

To determine the mineralogy of the studied rocks, we applied the quantitative X-ray diffraction method of CRESSEY and SCHOFIELD (1996). We measured unoriented powder samples of the cuttings of exploration well 35/11-5 and standards of the Natural History Museum using an Enraf-Nonius PDS 120 diffractometer with a curved position-sensitive detector configured in vertical geometry with a 2θ detection range of 0-120°. CuKα₁ radiation was selected using a
germanium 111 monochromator. We used tube-operating conditions of 45 kV and 45 mA and slits to restrict the beam to 0.24×5.0 mm (horizontally/vertically) and chose an acquisition time of 30 min per sample. The 2Θ linearization was conducted using a least-spare cubic spline function.

For the mineral quantification, we first determined the ratio between the intensity of each mineral and the intensity of the whole sample. We did this by fitting the diffraction pattern of each mineral to the diffraction pattern of the whole sample (see supplementary Figure). In technical terms, we minimised the absolute difference between the diffraction pattern of the whole sample and the sum of the diffraction patterns of each mineral by scaling their diffraction patterns using a generalised reduced gradient algorithm. This algorithm is suitable for non-linear optimisation problems because it is an “efficient and reliable way to solve small to moderate size non-linear programming problems” (Lasdon et al., 1978). Because this algorithm is most effective at finding local minima, we manually fitted the sum of the diffraction patterns of each mineral to the diffraction pattern of the whole sample by varying the intensity ratios prior to the optimisation. We fitted the following previously identified minerals (angles are given in 2Θ): 1) opal-A: diffuse band c.10-40°, 2) opal-CT: double peaks at c.20 and 21.5°, 3) quartz: peak at c.26.6°, 4) illite-smectite: asymmetric diffuse band c.3-9°, 5) illite: peaks at c.9, 18 and 26°, 6) kaolinite: peaks at c.12 and 25°, 7) calcite: peak at c.29°, 8) pyrite: peak at c.33°, 9) barite: peak at c.42.8°, 10) sylvite: peak at c.28.3° and 11) halite: peak at c.31.7°. After initial fitting, we ran the general reduced gradient algorithm to find a minimum for the difference between the diffraction pattern of the whole sample and the sum of the diffraction patterns of each mineral. We then calculated the required absorption coefficients (see supplementary Table) and
determined the content of each mineral in the sample as described by Batchelder and Cressey (1998).

11.2. PETROPHYSICAL ANALYSIS

11.2.1. CLAY VOLUME

We calculated the clay volume from the neutron porosity and bulk density logs using a standard method described by Rider and Kennedy (2011). First, we defined three end-member points (i.e. clay point, fluid point and matrix point) on the neutron porosity/bulk density cross-plot. Based on the distance to these end-member points, we calculated the clay volumes of each data point. Because the definition of these end-member points is crucial to the precision of the method, we used lithology information from well reports (NPD, 2014) in addition to our data cloud to define the end-member points for each well. The clay point had typically values around 0.6 (neutron porosity) and 2.2 g/cm$^3$ (bulk density). We also assumed the pore fluid to be pore water, i.e. the fluid point had values of 1 (neutron porosity and bulk density) and the matrix to consist of clays, i.e. the matrix point to had values of 0 (neutron porosity) and 2.2 g/cm$^3$ (bulk density). Based on these parameters, we calculated the clay volume for each data point as the relative distance between end-member points:

$$V_{clay} = \frac{(\rho_F - \rho_M) \cdot (n - n_M) - (\rho - \rho_M) \cdot (n_F - n_M)}{(\rho_F - \rho_M) \cdot (n_C - n_M) - (\rho_C - \rho_M) \cdot (n_F - n_M)}$$

\(V_{clay}\) – Clay volume
\(\rho\) – Bulk density of data points
\(\rho_C\) – Bulk density of clay point (c.2.2 g/cm$^3$)
934 $\rho_F$ – Bulk density of fluid point (1 g/cm$^3$)
935 $\rho_M$ – Bulk density of matrix point (c.2.2 g/cm$^3$)
936 $n$ – Neutron porosity of data points
937 $n_C$ – Neutron porosity of clay point (0.6)
938 $n_F$ – Neutron porosity of fluid point (1)
939 $n_M$ – Neutron porosity of matrix point (0)

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941 11.2.2. POROSITY

942 We calculated porosity logs for all wells from clay volume and bulk density logs using the following equation:

$$\phi = \frac{\rho_M - \rho - V_{clay} \cdot (\rho_M - \rho_C)}{\rho_M - \rho_F}$$  \hspace{1cm} (9)

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946 $\phi$ – (Effective) porosity
947 $\rho_M$ – Matrix density (2.2 g/cm$^3$)
948 $\rho$ – Input bulk density log
949 $V_{clay}$ – Clay volume (calculated earlier)
950 $\rho_C$ – Wet clay density (2.3 g/cm$^3$)
951 $\rho_F$ – Filtrate density (1 g/cm$^3$)

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953 11.2.3. POROSITY-DEPTH FUNCTIONS
We defined a series of porosity-depth functions for diagenetically altered mudstones. These functions generally follow conventional, negative exponential porosity-depth functions for mudstones with an additional component for the porosity loss across a transformation zone:

$$\phi^* = \phi - \phi_d$$  \hspace{1cm} (12)

- $\phi^*$ - New porosity-depth function
- $\phi$ - Conventional porosity-depth function
- $\phi_d$ - Diagenetic component

Above the silica transformation zone (opal-A/CT or opal-CT/Q), the diagenetic component ($\phi_d$) is zero and the new porosity-depth function is equivalent to the conventional one:

$$\phi^*(d) = \phi(d) = \phi_0 \cdot e^{-c \cdot d}$$  \hspace{1cm} (13)

- $\phi_0$ - Initial porosity (during deposition at surface)
- $d$ - Burial depth
- $c$ - Porosity coefficient

In the transformation zone, the diagenetic component increases linear with depth. The gradient of the increases depends on the diagenetic porosity loss across the transformation zone as well as the top and bottom of the zone:

$$\phi_d(d) = \frac{\Delta\phi}{d_2 - d_1} \cdot (d - d_1)$$  \hspace{1cm} (14)

- $\Delta\phi$ - Diagenetic porosity loss across the transformation zone
- $d_1$ - Top of transformation zone
- $d_2$ - Bottom of the transformation zone

Below the transformation zone, the diagenetic component is zero and the new porosity-depth function follows a conventional, negative exponential porosity-depth function with a modified initial porosity:
\[
\phi_0 = \frac{\phi^*(d_2)}{e^{-cd_2}}
\]  \hspace{1cm} (15)

\(\phi_0\) - Modified initial porosity

\(\phi^*\) - Porosity at the bottom of the transformation zone

\(c\) - Porosity coefficient

12. TABLES

**Tab. 1:** Well table (AC-Average sonic travel time, AIMP-acoustic Impedance, BHT-bottom hole temperature, CALI-calliper, DEN-bulk density, DRHO-density correction, DT-interval transit time, DTS-shear wave slowness, GR-gamma ray, HEL_POR-helium porosity, NEU/ NPHI-neutron porosity, RD/RDEP-deep resistivity, RHOB-bulk density, RM/ROMED-medium resistivity, RMIC/RSH-micro resistivity, SP-spontaneous Potential, VELC-compressional velocity, VSH-shale volume) XRD-X-ray diffraction data.

**Tab. 2:** Average porosities and porosity reductions (in \%) in opal-A, opal-A/CT and opal-CT zone from the Monterey Formation, California, USA (Isaacs, 1981; Compton, 1991; Chaika & Dvorkin, 2000); Early Pliocene/ Miocene succession of the Hokkaido basins, northern Japan (Tada & Iijima, 1983; Kim et al., 2007; Sanada et al., 2009) and the Hordaland Group, North Viking Graben, North Sea (this study)

13. FIGURE LEGENDS

**Fig. 1:** a) Simplified map of the North Viking Graben, offshore Norway, highlighting the major faults, the Horda and East Shetland Platform (modified after Holgate et al., 2013), the inserted
regional map shows previous studies of silica diagenesis in the VB: Vøring Basin (e.g. Davies & Cartwright, 2002), GR: Gjallar Ridge (e.g. Ireland et al., 2011), SHB: Faeroe-Shetland Basin (e.g. Davies, 2005) and the MB: Møre Basin (e.g. Neagu et al., 2010b). b) Basemap showing the surface well locations and 3-D seismic surveys used in this study, c) Geoseismic section illustrating the major faults and stratigraphic units and d) Simplified stratigraphic column for the North Viking Graben. Location of the basemap (Fig. 1b) and geoseismic section (Fig. 1c) is illustrated in Fig. 1a. The well section (Fig. 2), the well correlation (Fig. 3), seismic lines (Fig. 4 and 5), maps (Fig. 6 and 7) and basin modelling section (Fig. 8) are shown on Fig. 1b.

**Fig. 2:** Well- and seismic section (N-S) through exploration wells a) 35/8-2, 35/11-6, 35/11-2, 35/10-1, 35/11-5, b) 31/2-8, 31/2-9, 31/2-14, 31/2-7, 31/2-4, and c) 31/2-12, 31/2-11, 31/2-10, 31/2-13 S, 31/2-5, 31/5-3 showing the bulk density logs (left), p-wave velocity (left, dotted) and porosity logs (right), the silica zones (Zones 1-3). Note changes of the wireline logs and seismic reflections across the opal-A/CT transformation zone (Zone 2).

**Fig. 3:** Well correlation chart of exploration well 35/11-5 showing a) interpreted silica zones, b) X-ray diffraction data, c) bulk density, d) p-wave velocity, e) reflection coefficient, f) synthetic seismic trace and g) seismic reflection data (synthetic and real). Note the p-wave velocity increase with depth in the opal-A/CT transformation zone and the tie to the accompanied seismic reflection of negative polarity (black). The vertical section is part of the Hordaland Group.

**Fig. 4:** a) Seismic line in dip direction and b) Geoseismic section in dip direction with opal-A, opal-CT and quartz zones as well as opal-A/CT and opal-CT/Q transformation zones, litho- and
chronostratigraphy and polygonal fault system (PFS). Note the westward-dipping, sometimes discordant reflections associated with the opal-A/CT and opal-CT/Q transformation zone.

**Fig. 5:** a) Seismic line in strike direction and b) Geoseismic section in strike direction with opal-A, opal-CT and quartz zones as well as opal-A/CT and opal-CT/Q transformation zones, litho- and chronostratigraphy and the polygonal fault system (PFS). Note the sometimes discordant reflections associated with the opal-A/CT and opal-CT/Q transformation zone.

**Fig. 6:** Time structure map of: a) the mid-Miocene unconformity, i.e. Top of Zone 1, b) opal-A/CT transformation zone, i.e. Zone 2 and c) Isochron map of the opal-A zone (Zone 1). Note the similarities between the time structure maps of the mid-Miocene unconformity (a) and the opal-A/CT transformation zone (b).

**Fig. 7:** Geoseismic section (through exploration wells 35/10-1 and 35/11-5) used to define the geometry, stratigraphy and lithology of all basin models.

**Fig. 8:** a) Boundary conditions used for basin modelling including seafloor temperature (from Jensen & Buchardt, 1987; Anderson *et al.*, 1994), heat flow (after Lucazeau & Le Douaran, 1984) and water depth (from Kyrkjebø *et al.*, 2001). b) Calibration of basin model using bottom hole temperature of exploration well 35/10-1. c) Calibration of basin model using bottom hole temperature of exploration well 35/11-5. d) Kinetic data from Icenhower and Dove (2000) used to model the opal-A/CT transformation. e) Phase diagram for silica diagenesis (from Keller & Isaacs, 1985; Behl, 2011). f) Comparison of transformation ratio observed in exploration well 35/11-5 (see Fig. 3) and predicted using kinetic data from Icenhower and Dove (2000).
**Fig. 9:** Basin modelling results for the a) Middle Eocene (44 Ma), b) Late Eocene (35 Ma), c) Late Oligocene (25 Ma), d) Middle Miocene (15 Ma), e) Pliocene (5 Ma) and present day. Note: 1) the formation of the opal-A/CT transformation zone (a-b), 2) the migration of the zone (a-f) and 3) the decrease in migration (e-f).

**Fig. 10:** Key parameters extracted from basin modelling results. Cumulative migration distance (between various transformation ratios and the base of the Balder Formation) in the a) west (Fig. 7: distance: 0 km), b) middle (Fig. 7: distance: 17.5 km) and c) east (Fig. 7: distance: 35 km). Migration rate (derived from cumulative migration distance) in in the a) west (Fig. 7: distance: 0 km), b) middle (Fig. 7: distance: 17.5 km) and c) east (Fig. 7: distance: 35 km). g-i) Boundary conditions used for basin modelling including seafloor temperature (from Jensen & Buchardt, 1987; Anderson et al., 1994), heat flow (after Lucazeau & Le Douaran, 1984) and water depth (from Kyrkjebø et al., 2001).

**Fig. 11:** a) Porosity-depth trend for exploration well 35/10-1 (grey points) interpolated by conventional (black dotted) and newly defined porosity-depth functions (red), b) Series of conventional (black dotted) and newly defined porosity-depth functions (red). Note abrupt porosity reductions at depth of the opal-A/CT transformation zone and the difference between the conventional (black dotted) and newly defined (red) porosity-depth functions.

**Fig. 12:** Evolutionary model showing: a) the formation, b) migration, and c) fossilisation of the opal-A/CT transformation zone in the North Viking Graben.
14. SUPPORTING INFORMATION LEGENDS

Supplementary Fig. 13: Example of X-ray diffractogram

Supplementary Fig. 14: a) Current amount of opal-A in cuttings samples of exploration well 35/11-5, b) Hypothetical amount of opal-A dissolved, and c) Hypothetical amount of opal-A prior to dissolution.

Supplementary Tab. 3: Mass absorption coefficients (μ/ρ) for various minerals.
a) Seismic line in strike direction

b) Geoseismic section in strike direction
a) Boundary condition (basin modelling)

Seafloor temperature
Heat flow
Water depth

Age [Ma]

b) Calibration

Well 35/10-1

Heat flow [mW/m²]

Temperature [°C]

Temperature [°C]

BHT

Depth [m]

c) Calibration

Well 35/11-5

BHT

Depth [m]

d) Kinetics (opal-A/CT transformation)

Frequency factor: 7.18E+13 Ma⁻¹
Activation energy: 22 kcal/mol

Transformation ratio

Temperature [°C]

0 10 20 30 40 50 60 70 80 90 100

Transformation ratio

Temperature [°C]

heat rate: 1°C/My
heat rate: 2°C/My
heat rate: 3°C/My

after Icenhower and Dove (2000)

e) Phase diagram

Opal-A
Opal-CT
Quartz

Temperature [°C]

Relative opal-A content [weight %]

Transformation ratio

f) Validation

Well 35/11-5

Observed
Modelled (Fig. 9e)

Depth [m]
Evolution of the opal-A/CT transformation in the North Viking Graben

a) Middle Eocene (44 Ma)

b) Late Eocene (35 Ma)

c) Late Oligocene (25 Ma)

d) Middle Miocene (15 Ma)

e) Pliocene (5 Ma)

f) Present day
a) Formation of opal-A/CT transformation zone (Middle-Late Eocene)

b) Migration of opal-A/CT transformation zone (Eocene-Miocene)

c) Fossilisation of opal-A/CT transformation zone (Miocene- Present day)
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<th>Wireline data</th>
<th>Others</th>
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**Table 3:** Mass absorption coefficients (μ/ρ) for various minerals.