Geochemistry of the Maastrichtian Rørdal Member, Jylland, Denmark: Ce anomaly as a palaeo-redox proxy

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The chemical composition of chalk and marl reflects the mixture of carbonate particles and clastic input deposited on the seabed together with growth of authigenic minerals and diagenesis. The Rørdal quarry in Jylland (Fig. 1) is known for its alternating chalk–marl succession (Surlyk *et al.* 2010) and the aim of this article is to investigate how this cyclicity is reflected in the geochemical signature of the sequence and test if this has implications for the interpretation of the depositional environment as well as the chemostratigraphy in the chalk.

The observed variation in the benthic fauna and the cyclic character of the chalk–marl succession may reflect an environmental response to orbital forcing. The benthic fauna shows higher species diversity and density in the chalk than the marl layers, suggesting more favourable living conditions in the former (Lauridsen & Surlyk 2008), whereas no differences in environmental stress between the two environments could be derived from a study of the trace fossils (Lauridsen *et al.* 2011).

The *c.* 10 m thick Rørdal Member was established as a lithostratigraphic unit by Surlyk *et al.* (2010) and recognised as an expression of a late Maastrichtian cooling event. X-ray diffraction (XRD) analysis indicates that the marly layers represent a relative increase in smectite clays and illite together with some quartz and analcime. The inorganic geochemical evolution in Maastrichtian chalk was investigated by Jørgensen (1986) who noted changes in Sr/Ca and Mn/Ca ratios towards the end of the Maastrichtian in the North Sea Central Graben, leading to the conclusion that geochemistry is a "conceivable tool in basin analysis in the lithologically rather monotonous chalk sequence" (p. 267). However, a systematic geochemical analysis of the chalk has never been undertaken and this work is an attempt to look into the potential of understanding the geology of the chalk by analysing a wide range of elements in chalk and marl.

Chemical variability related to clay content

Sixty-three samples from the Rørdal quarry were ground, digested in aqua regia and analysed for 66 elements using the Elan 6100 Quadrupole ICP-MS at the Geological Survey of Denmark and Greenland (GEUS). The data reduction was based on TotalQuant software with emphasis on the trace element analysis. The analytical procedure follows Larsen *et al.* (2009).

The cyclicity and the alternation between chalk and marl are easily recognised in the geochemical profile (Fig. 2) with an increase in the concentration of major and minor elements such as Al, Si, Fe, Mg and K in the marly layers caused by the presence of clay. The eight peaks in Fig. 2 can be correlated to the eight peaks in the marly layers of the Rørdal Member which can be identified in the gamma log in a nearby well (Surlyk *et al.* 2010). The gamma-radiation in the well log can be explained by the increased content of K in the marl (Fig. 2A). Iron is the element after Al with the highest increase in concentration in the marly layers indicating that the clay minerals are rich in Fe. Magnesium also shows an increase in the marly layers (Fig. 2A), and the combined clay minerals in the marl – which according to Surlyk *et al.* (2010) consist of smectite and illite – must be rich in Fe, K and Mg. The content of Al, Fe and K is about three times higher in the marl than in the chalk.
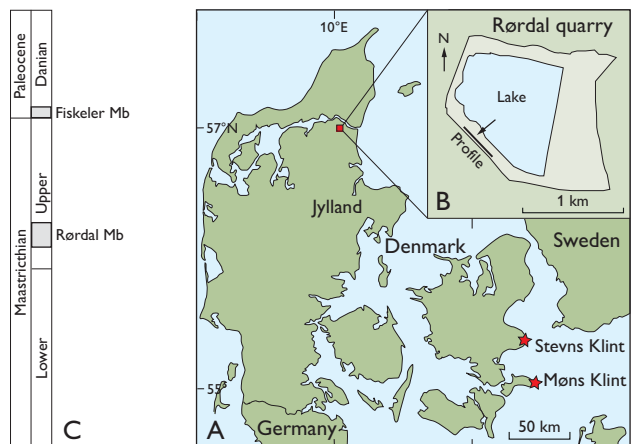

Fig. 1. **A**: Location of the Rørdal quarry, Stevns Klint and Møns Klint in Denmark. **B**: Map of the Rørdal quarry with the profile where the samples were collected. **C**: Stratigraphic section with Rørdal and Fiskeler members.
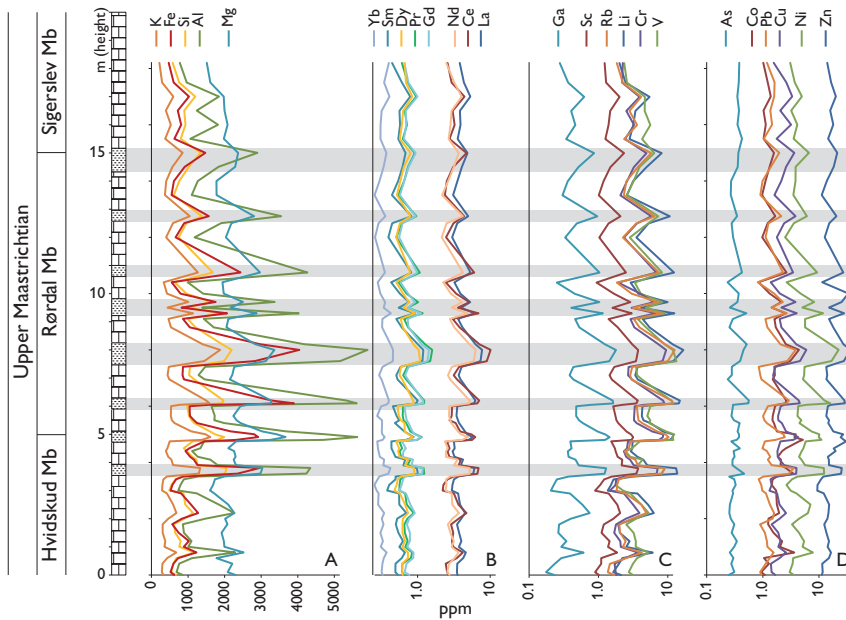
Fig. 2. Chemical profiles through the Rørdal Member including the uppermost part of the Hvidskud Member and the lowermost part of the Sigerslev Member. Marly layers are shown as grey shaded bands. **A**: Major and minor elements. **B**: REE; logarithmic scale. **C**: Lithophile trace elements; logarithmic scale. **D**: Chalcophile elements with Ni and Co; logarithmic scale. Stratigraphy from Surlyk *et al.* (2013).

The concentration of many trace elements, including the rare-earth elements (REE), is also elevated in the marly layers (Fig. 2B). If all REE were located in clay the increase would be three times higher, as is the case with Al, K and Fe, but the content of REE in the marl is 'only' 1.5 times higher than in the chalk. This suggests that although the REE concentration is higher in the clay than in the chalk a substantial fraction of the REEs is located in the carbonate component of both chalk and marl. Lanthanum and Nd follow parallel tracks (Fig. 2B), whereas Ce crosses both tracks with relatively high Ce in the marl. Light REE (La, Ce, Pr, Nd and Sm) are more abundant than heavy REE (Er, Tm, Yb and Lu) in the marl compared to the chalk, which can also be seen as higher La/Lu ratios (Figs 3E, 4).

Lithophile elements such as Th, Cs, Rb, Be, Cr, Sc and Li increase in concentrations in the marl (of which Rb and Li are shown in Figure 2C) and are *c.* 2.5 to 3 times higher in the marl than in the chalk, similar to the behaviour of Al and K. This suggests that these elements are almost entirely located in the clay. Chalcophile elements such as Pb, As, Zn and Cu (Fig. 2D) are *c.* 1.5 times higher in the marl than in the chalk similar to the REE mentioned above.

The content of most elements in the succession varies with the clay content. However, this is not the case for Nb, Zr, Mn and Ti (Fig. 3A). Mica and clay commonly contain some Ti, Zr and Nb, elements that also occur in mafic volcanic material. These elements are difficult to leach out of minerals and generally follow clay and mica in sedimentary environments. If the clay was clastic or volcanogenic one would expect that the content of elements such as Ti, Zr and Nb would be elevated in the marl. However, this is

not the case, suggesting that a fraction of the clay may be of authigenic origin.

Manganese is probably hosted in the carbonate and its concentration is relatively stable throughout the analysed section. There is a decrease in the Ba content in the Rørdal Member (Fig. 3B) relative to the underlying Hvidskud Member with the lowest contents in its middle part. There is an increase in Sr content in the overlying Sigerslev Member. Jørgensen (1986) observed a similar increase in the Sr content in chalk from the North Sea Basin and this may be regional.

Ce anomaly as a proxy for redox potential

The REE commonly occur as cations with a valency of three and the different REE have similar geochemical behaviour in the sedimentary environment. However, one of the elements, Ce, can also occur as Ce^{4+} with a very low solubility in marine environments as compared to Ce^{3+}. Where no fractionation of Ce relative to the other REE has occurred, the distribution would be seen as a straight line on Fig. 3D. To quantify the fractionation of Ce, the term Ce anomaly (Ce/Ce*) has been introduced; Ce is the measured cerium concentration and Ce* is what the Ce content would have been without fractionation, based on the contents of La and Nd. The Ce anomaly is calculated: $Ce/Ce* = 3Ce^N/(2La^N + Nd^N)$ where REE^N is the measured concentration normalised relative to chondrite (Boynton 1984). In this paper a Ce anomaly is referred to as negative when Ce is depleted relative to the other REE and as positive if Ce is enriched relative to the other REE. In

Fig. 3. Chemical profiles in the Rørdal Member. Same stratigraphy as Fig. 1. Marly layers are shown as grey shaded bands. **A**: Nb, Zr, Rb, Mn and Ti; logarithmic scale. **B**: Ba. **C**: Sr. **D**: Ce anomaly. **E**: La/Lu ratio; logarithmic scale.
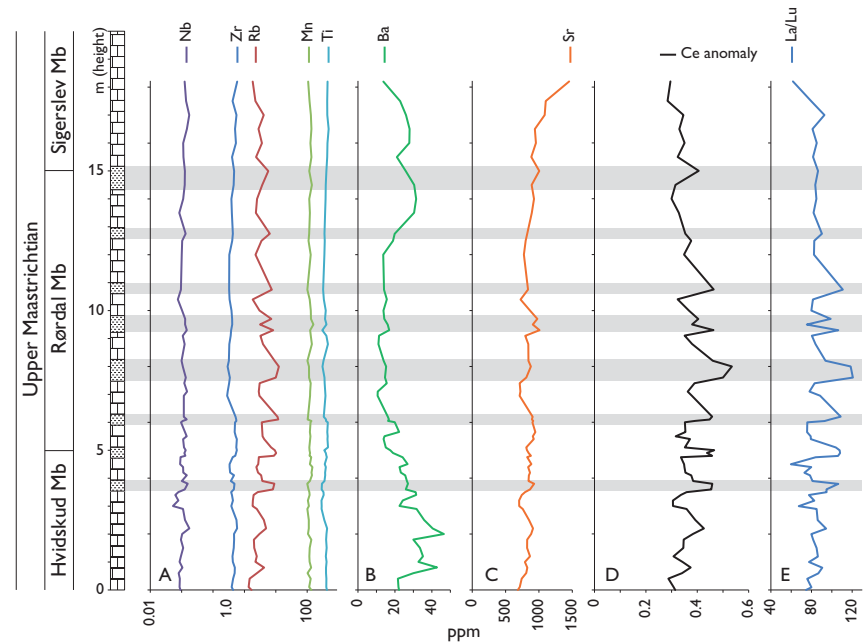
the modern marine environment, a negative Ce anomaly is indicative of oxic conditions (German & Elderfield 1990) which, in turn, is caused by the low solubility of Ce^{4+} and low availability of Ce. This feature offers the possibility to look into variations in the redox conditions during deposition of the chalk (Jeans *et al.* 2015). In Fig. 4 it can be seen that there is a negative Ce anomaly both in the chalk and in the marl in the Rørdal quarry as well as in the chalk and the fish-clay at Stevns. There is also a negative Eu anomaly which is probably caused by the source of the REE being slightly depleted in Eu (Frei & Frei 2002). The negative Ce anomaly in the chalk at Stevns is more pronounced than in the chalk at Rørdal (Fig. 4) suggesting that the environment during deposition of the chalk at Stevns was more oxic than at Rørdal. The chalk at Stevns has a higher stratigraphic position (in the Sigerslev Member) and the change in the Ce anomaly with time could suggest that the oxygen availability in the chalk sea increased with time during the late Maastrichtian. Alternatively, this could suggest that the chalk at Stevns was deposited in a shallower sea.

The Ce concentration at Rørdal changes with lithology and stratigraphic position in the section (Fig. 3D); it is lower in the chalk than in the marl, indicating that the environment was more oxic in the chalk than in the marl. The REE (including Ce) are located in the carbonate component as well as in the clay as mentioned above. Accordingly, the Ce anomaly reflects the combined effect of the composition of the seawater where the coccoliths and where the clay were formed. Surlyk *et al.* (2010) suggested that the clay in the Rørdal Member is derived from volcanic eruptions. Such clay, derived from alteration of volcanic glass, is

likely to have an overall resemblance to the REE distribution in the source. However, the transformation from glass to clay in the marine environment could be the cause of the negative Ce anomaly found in the marl. The fish-clay at Stevns also has this negative Ce anomaly which is indicative of formation of clay in a marine environment (Kastner *et al.* 1984; Frei & Frei 2002). The question is then whether the clay was (trans)formed from volcanic glass in the free water masses or in the seabed. The seabed is likely to have been less oxic than the free water mass, and formation of the clay in the seabed would explain the difference in the redox potential compared to the chalk formed in the free water mass. Finally, the composition of the clay minerals could have been modfied during diagenesis in the presence of organic material affecting the Ce anomaly.
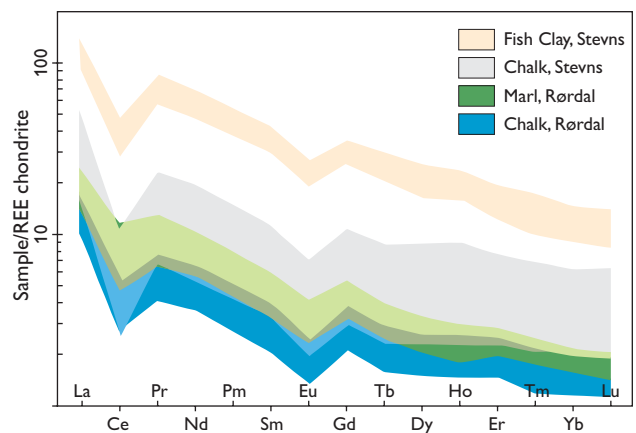

Fig. 4. Chondrite-normalised REE distribution patterns for the Rørdal samples compared with REE data from Stevns Klint (Frei & Frei 2002).

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Summary and outlook

The chemical composition of the chalk–marl sequence at Rørdal in Jylland reflects the varying proportions of carbonate and clay. The content of major and minor elements such as Si, Al, Fe and K is proportional to the clay content, with a threefold increase in the marly layers relative to the chalk layers. It is suggested that these elements are located in clay minerals together with lithophile trace elements such as Li, Ga, Rb, Cs and Th which likewise increase threefold in the clay relative to the chalk. Other elements such as Pb, As, Zn and Cu and the REE are found in *c.* 1.5 times higher concentrations in the marl, and these elements are located both in the clay and the carbonate component of the succession. The clay has a light REE enrichment compared to the chalk.

Formation of the clay as authigenic minerals may explain why large ion lithophile elements such as Zr and Nb, as well as Ti, are not incorporated in the clay. The content of Ba in the Rørdal Member is low relative to the under- and overlying strata, and the deposition of Ba could be tested as a chemo-stratigraphic marker and environmental proxy.

The REE distribution shows a negative Ce anomaly both in the chalk and in the marl, suggesting that the environment was oxic throughout the deposition, and as the Ce anomaly is more pronounced in the chalk, the environment was more oxic where the carbonate was formed than in the clay. This observation matches the observation that there is higher species diversity and density in the chalk than in the marl (Lauridsen & Surlyk 2008). If the clay and the carbonate were formed in the same water mass, the observed alternating redox level would be indicative of changing conditions in the sea. However, if the main part of the clay was formed in the seabed as authigenic minerals or was affected by diagenesis, then the alternating redox levels indicated by the Ce anomaly reflects changes in redox conditions at or in the seabed. The Ce anomaly in chalk from Stevns is larger than in chalk from Rørdal, suggesting that the environment was more oxic in the chalk sea towards the end of the Maastrichtian. These differences could be related to changes in temperature over time. A recent study by Thibault *et al.* (2016) suggests a global cooling with superimposed cool/warm fluctuations in the last 8 Ma of the Maastrichtian including e.g. the Rørdal and Sigerslev Members. It is suggested that the Ce anomaly can be used as a palaeo-redox indicator or proxy to compare environments across chalk basins. In this context it is interesting to analyse both carbonate and clay components from the marl.

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