Palaeogeography, Palaeoclimatology, Palaeoecology 468 (2017) 216–227

Contents lists available at ScienceDirect

Palaeogeography, Palaeoclimatology, Palaeoecology

journal homepage: www.elsevier.com/locate/palaeo

Biostratigraphy and carbon and nitrogen geochemistry of the SPICE event in Cambrian low-grade metamorphic black shale, Southern Norway

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ARTICLE INFO

Article history:
Received 7 September 2016
Received in revised form 30 November 2016
Accepted 4 December 2016
Available online 18 December 2016

Keywords:
Furongian
Alum shale
Oceanic anoxic event
Trilobites
Rock-Eval
HHXRF

ABSTRACT

We present new chemo- and biostratigraphical data from 90 m of Alum Shale Formation stratigraphy from the middle Cambrian (Series 3) to the lowermost Ordovician (Tremadocian) at Krekling, southern Norway. The alum shale was deposited during a transgression covering parts of the Baltic craton, and contains up to 13.5 wt.% total organic carbon (TOC) increasing up section through the Furongian. Pyrolysis confirms that the alum shale is affected by low grade metamorphism, either from a nearby pluton or during deep burial, where the remaining organic matter has lost most of the hydrocarbon productivity (S2 = 0–0.9 mgHc/g rock) compared to equivalent formations in Sweden (TOC = 8–22 wt.%; S2 = 20–80). Still, the carbon isotopic trend ($\delta^{13}C_{org}$) shows that the positive carbon isotope excursion known as the SPICE event (Furongian) is preserved and that the carbon isotopes did not fractionate significantly while undergoing metamorphism. The $\delta^{13}C_{org}$ increases steadily from the base of the section, from −30.8‰ to a maximum of −27.3‰, likely due to increasing atmospheric oxygen concentrations and cyanobacteria productivity. The heaviest values are recorded in an interval with abundant pyrrhotite nodules, suggesting that the organic productivity led to euxinic conditions, as shown from several other SPICE-sections worldwide. The evolution of bulk rock nitrogen isotopes ($\delta^{15}N$) shows positive correlations with $\delta^{13}C_{org}$ and TOC, with an increase from −2 to +1.5‰. Before the onset of the SPICE, negative $\delta^{15}N$ values indicate that atmospheric nitrogen was fixed in the shallow ocean. During the transition from low to high TOC shale at about 18 m in the section, both the nitrogen content and the $\delta^{15}N$ increase, but the $\delta^{15}N$ is not high enough to imply water mass nitrogen reduction (denitrification) as a dominant process. Instead we suggest that the Krekling section was affected by sediment denitrification during SPICE, a process resulting in a ca. 1.5‰ post-depositional increase in $\delta^{15}N$. At the same time, in the upper parts of the water column, atmospheric nitrogen was still fixed by cyanobacteria. We conclude that the Cambrian ocean transgressed the Baltic craton and inhibited deep water upwelling, leaving geochemical signals characteristic of other greenhouse climates spanning the Phanerozoic.

1. Introduction

The Cambrian occupies a pivotal position in the evolution of the geobiosphere. Still, the Cambrian paleoclimate, paleogeography, paleoceanography and ocean chemistry and their relation to the Cambrian Explosion and extinction pulses, are not yet well understood (Babcock et al., 2015). Recent geochemical work has emphasized the importance of major carbon isotope excursions and associated marine anoxic events for unravelling the middle to upper Cambrian Earth System evolution (e.g. Gill et al., 2011; Saltzman et al., 2011). The globally correlated Drumian carbon isotope excursion (DICE) and Steptoean positive carbon isotope excursion (SPICE) (Saltzman et al., 2000; Zhu et al., 2006) have been identified in Baltoscandia previously, in Scania in southernmost Sweden (Ahlberg et al., 2009; Lehnert et al., 2013) (Figs. 1—3). The SPICE interval in Baltoscandia is characterized by high organic carbon and sulphur concentrations, a positive $\delta^{34}S$ excursion, and elevated levels of elements immobile during anoxic and euxinic conditions, such as Mo, Ni, U, and V (Buchardt et al., 1997; Gill et al., 2011). The enhanced carbon burial has been interpreted as due to an increased availability of nutrients and resulted in fractionation of carbon isotopes with a progressive ^{13}C–enrichment in the organic matter (cf. Kump and Arthur, 1999; Saltzman et al., 2011).

Nitrogen geochemistry is an important tool to understand marine redox conditions, organic productivity, and oceanographic changes (cf. Kikumoto et al., 2014; Saltzman, 2005; Morel and Price, 2003; Algeo et al., 2008), but has so far not been explored in detail for the SPICE event. During the Cambrian, the oceans are thought to have been dominated by nitrogen-limited organic productivity that may have changed

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http://dx.doi.org/10.1016/j.palaeo.2016.12.016

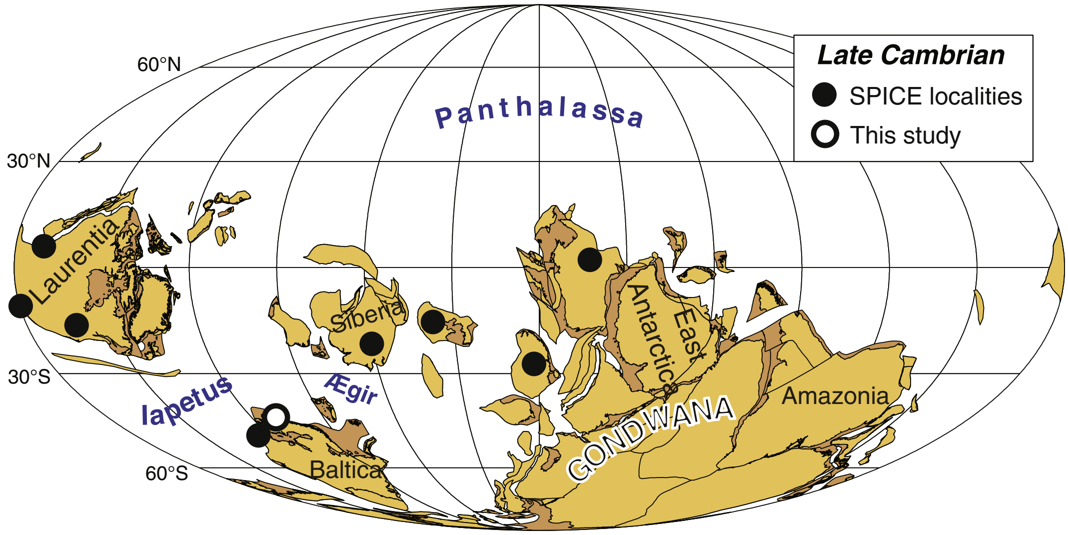

Fig. 1. Global plate reconstruction of the late Cambrian (ca 490–500 Ma), modified from Torsvik and Cocks (2016). SPICE localities are taken from the compilation of Gill et al. (2011).

to becoming phosphorous-limited during the SPICE-event (Saltzman, 2005). Nitrogen may get extracted from the atmosphere by cyanobacteria that reduce N_2 to NH_4^+, a process called fixation. Fixation results in deposition of marine nitrogen-bearing organic matter with $\delta^{15}N$ values (usually in the −3 to +1‰ range) close to the atmospheric value (0‰) and may be associated with negative $\delta^{15}N$ isotope excursions in the sedimentary record (cf. Heofs, 2004). Trace metal availability (Fe, Mo, V) has an important role in the nitrogen cycle as nitrogen fixation depends on microbial metalloenzymes (Falkowski, 1997; Morel and Price, 2003), where Fe and Mo-bearing enzymes are the most efficient transformers. In contrast to fixation, denitrification is a process that involves microbial reduction of already dissolved nitrogen (nitrate and nitrite). Denitrification ultimately produces N_2 which then can be removed from the ocean and transferred back to the atmosphere and thus complete the nitrogen cycle (e.g., Falkowski, 1997). Denitrification is associated with a large positive $\delta^{15}N$ shift in organic matter in the water column and sediments, and recent results suggest that denitrification is a characteristic of oceanographic changes and enhanced upwelling during icehouse conditions rather than oceanic anoxia (e.g., Algeo et al., 2008; Algeo et al., 2014; Wang et al., 2015).

The aim of this study was to investigate the bio- and chemostratigraphy of the Cambrian in Krekling, Øvre Eiker, Norway (Figs. 1—3). In particular, we aimed at establishing a carbon and nitrogen isotope dataset that can be used to correlate the Krekling section to other sections after correcting for possible metamorphic effects, and finally to understand geochemical cycles in the Cambrian ocean.

2. Geology of the Krekling area

The traditional middle to upper Cambrian (provisional Cambrian Series 3 and Furongian) is represented over large areas of Baltoscandia by the Alum Shale Formation (reviewed by Andersson et al., 1985; Nielsen and Schovsbo, 2007), with shelf deposits reaching a thickness of 90—100 m in Norway. Most of the available outcrops in Norway are confined to the Oslo Graben, which is a Carboniferous to Permian rift structure extending about 200 km from the Skien—Langesund area in the south to the Mjøsa district in the north (e.g., Sundvoll and Larsen, 1994; Nakrem and Rasmussen in Calner et al., 2013). The Cambrian succession in Norway was described in classical contributions by Kjerulf and Dahll (1857) and Brøgger (1875, 1879, 1882). Major and trace element geochemistry of a selection of samples from the Alum Shale Formation were presented by Bjørlykke (1974) in his work on the geochemistry of Cambrian to Silurian sedimentary rocks in the Oslo Graben, but no systematic studies from specific localities are available and high resolution chemostratigraphy, including carbon isotopes, has never been reported.

The Alum Shale Formation in the Oslo Region and the offshore areas to the south was thermally affected during basin subsidence in the Devonian. In the latest Permian, rapid burial resulted in top basement levels reaching 9 km depth in Skagerrak (based on the Felicia-1A borehole) and the organic matter passed through the gas window and beyond (Pedersen et al., 2007). Within the Oslo Graben, the alum shales were affected by heat released during volcanism and magmatism in the 305—260 Ma period, resulting in high grade contact metamorphism near plutons and low grade metamorphism further away (Jamtveit et al., 1997; Svensen and Jamtveit, 1998).

The studied sections are situated between Krekling and Stavlum in the Øvre Eiker area, Southern Norway (Fig. 3), at the western boundary of the Oslo Graben where the Cambrian succession rests unconformably on Precambrian crystalline basement. In this area, a ca. 2.5-m-thick, basal interval of conglomerate, sand, silt and shale marks a regional transgression of early Cambrian age (Høyberget and Bruton, 2008). These beds are overlain by middle Cambrian (Cambrian Series 3) shales of the Alum Shale Formation, deposited in a shallow to deep marine shelf environment at about 40° south along the northern margin of the Baltic craton (Figs. 1 and 2).

In contrast to most other heavily tectonized Cambrian localities in Norway, Krekling is situated in the foreland of the Caledonide orogeny and the bedding is mainly sub-horizontal, with a gentle southeast dip. There is, however, a major reverse fault about 1.8 km to the east of the locality (Fig. 3). During the Oslo Graben rifting phase, the Eikeren peralkaline granite (Ekerite) pluton was emplaced in the area with the contact situated ca. 3.5 km to the east. The shale in contact with the granite experienced high temperature metamorphism and recrystallization (Jamtveit et al., 1997), but the heating may also have affected the study area, resulting in low grade contact metamorphism in addition to pre-existing metamorphism.

Stratigraphic work on the Cambrian of the Krekling area started with the classical contribution by Brøgger (1879), describing the middle Cambrian (Series 3) succession and biostratigraphy in great detail. A number of sections were illustrated, but few of them covering the entire Alum Shale Formation. The upper Cambrian (Furongian) succession was briefly described by Brøgger (1882). In 1946, several cores were drilled throughout the entire Alum Shale Formation in the Krekling area. Unpublished biostratigraphical work on these cores by Gunnar Henningsmoen is kept at the Natural History Museum in Oslo, and the