Introduction

The Slottsmøya Member, Agardhfjellet Fm., Svalbard (Dypvik et al. 1991a, 1991b) is a black to grey shale, 70-100 m thick, with subordinate silty, sideritic beds and occasional carbonate concretions. The depositional environment was fully marine. Based on foraminiferal and ammonite biostratigraphy (Nagy & Basov 1998; Wierzbowski et al. 2011) the member corresponds approximately to the Volgian and Ryazanian Stages, highly condensed in the upper part and with a probable hiatus in the Upper Volgian. The Slottsmøya Member therefore spans the Jurassic-Cretaceous boundary, and may contain evidence for the Mjølnir meteorite impact event close to the Volgian-Ryazanian boundary in the Barents Sea (Dypvik et al. 1996). The member is also notable because of its fossil-rich methane seep carbonates (Hammer et al. 2011) and the extremely abundant remains of marine reptiles (Hurum et al., this volume).

Our current work on the paleontology and hydrocarbon migration history of the Slottsmøya Member (Hurum et al., this volume) requires high stratigraphic resolution. The variable lithology and thickness of this member, combined with overthrusts and slumping (Dypvik et al. 1991a), complicate the use of lithostratigraphic markers. Ammonites are concentrated in only a few horizons, usually with poor preservation (Nagy & Basov 1998). Foraminiferal biostratigraphy has been successful, but gives limited vertical resolution (Nagy & Basov 1998). These difficulties provide the impetus to attempt chemostratigraphic methods, with markers that have the potential to provide at least intra- and ideally interbasinal correlation.

Carbon isotope curves are generally difficult to interpret in terms of environment, but can be highly useful for correlation (e.g., Jenkyns et al. 2002). Such correlation is often based on carbonate carbon ($\delta^{13}C_{\text{carb}}$). However, carbonates and calcified fossils are less common in the High Boreal Mesozoic successions, and usually do not provide sufficient stratigraphic resolution. For example, the resolution in Ditchfield’s (1997) $\delta^{13}C_{\text{carb}}$ data from Svalbard is only to member level, each member corresponding to several stages. The Agardhfjellet Fm. does include some scattered carbonate concretions and carbonate-cemented silts of diverse mineralogies (sideritic, dolomitic, ankeritic; Dypvik 1978; Krajewski 2004). However, their $\delta^{13}C_{\text{carb}}$ values show a strong diagenetic overprint, with much lighter values than expected for a clean marine signal. Krajewski (2004) reported $\delta^{13}C_{\text{carb}}$ in the range -14 to -2‰ VPDB in the Ingebrigtsenbukta Member in southern Spitsbergen. Hammer et al. (2011) found authigenic carbonates reaching -43‰ VPDB in the Slottsmøya Member. We will here present additional data from a collection of concretions and carbonate-cemented beds, confirming that carbonate isotopes are unsuitable for stratigraphic purposes in this member.
samples were analyzed for stable isotopes (δ13C and δ18O) at the Institute for Geosciences, University of Bergen. Powdered samples were analysed on Finnigan MAT 251 and MAT 253 mass spectrometers coupled to automated Kiel devices. The data are reported on the VPDB scale calibrated with NBS-19. The long-term analytical precision of both systems as defined by the external reproducibility of carbonate standards (>8 mg) over periods of weeks to months exceeds 0.05‰ and 0.1‰ for δ13C and δ18O, respectively.

Galfetti et al. (2007) collected shale samples from the Lower Triassic Vikinghøgda Formation at Dicksonfjellet on the northern shore of Isfjorden in Spitsbergen, approximately 20 km from the Jurassic sections described here. Their δ13Corg curve reproduced the global Smithian-Spathian carbon isotope excursion (usually recorded from δ13Ccarb), indicating that the organic carbon isotope record in the Triassic of Spitsbergen is not strongly overprinted either by weathering or by the regional-scale, Cretaceous sill intrusions into the Triassic sections. These results give some confidence in our results obtained by similar sampling in the Jurassic. Based on Rock-Eval analyses, the kerogen in the Slottsmøya Member is generally of the intermediate type II according to Dypvik et al. (1991b). This indicates reducing conditions, contributing to the preservation of the carbon isotope record (e.g. Hayes et al. 1999).

Material and methods

Carbonates were collected from scattered beds and concretions throughout the Slottsmøya Member at Knorringfjellet in the Sassenfjorden area, central Spitsbergen (Fig. 1). Dolomites were mainly collected from around 0 m in the section (Fig. 2), whilst siderites were mainly collected from between 27 and 40 m. Selected carbonate samples were analyzed for stable isotopes (δ13C and δ18O) at the Institute for Geosciences, University of Bergen. Powdered samples were analysed on Finnigan MAT 251 and MAT 253 mass spectrometers coupled to automated Kiel devices. The data are reported on the VPDB scale calibrated with NBS-19. The long-term analytical precision of both systems as defined by the external reproducibility of carbonate standards (>8 mg) over periods of weeks to months exceeds 0.05‰ and 0.1‰ for δ13C and δ18O, respectively.

Bulk shale was collected from two sections situated c. 500 m apart at Janusfjellet, and one section c. 10 km to the southeast at Knorringfjellet. At both localities, the sections were sampled from the upper sandy beds in the Oppdalssåta Member (Dypvik et al. 1991a) up to a level just below the Myklegardfjellet Bed marking the top of the Slottsmøya Member (Fig. 2). One additional sample was taken from the basal part of the Rurikfjellet Fm. at Janusfjellet. At Janusfjellet, the sampled sections were 46.9 and 94.3 m thick, with 20 and 37 samples taken. At Knorringfjellet, 17 samples were taken from a section 89.4 m thick. Sample positions were recorded with a Leica TPS-100 total station, with error <1 cm. All levels are reported here after correction of dip, with 0 m defined as the level of a thin, yellow, silt bed 27.1 m below the Dorsoplanites marker bed at Janusfjellet. The lithological log shown in Fig. 2 is based on the Janusfjellet section. The development is similar at Knorringfjellet, with the base of the member, the yellow silt, the Dorsoplanites and the Myklegardfjellet beds observed at similar relative levels. Material was collected from freshly exposed shale excavated from under the scree cover.

Organic carbon isotope analysis and TOC determinations were carried out at IFE, Norway. Samples were
crushed and homogenised in a mortar before washing with 2N HCl and rinsing to neutral pH. The samples were dried for more than 12 hours at 80 °C. Approximately 5-10 mg of material was used. Combustion took place in the presence of O2 and Cr2O3 at 1700 °C in a Carlo Erba NCS 2500 element analyzer. Excess O2 and NOx were reduced to N2 in a Cu oven at 650 °C. H2O was removed in a chemical trap of KMnO4 before separation of N2 and CO2 on a 2 m Poraplot Q GC column. CO2 was injected on-line to a Micromass Optima Isotope Ratio Mass Spectrometer for determination of δ13C. TOC was determined on the TCD on the element analyser. Repeat measurements on standards showed a precision better than ±0.1 ‰ for δ13C, ±3 % relative for TOC. Data were smoothed using cubic splines. Spectral analysis followed the REDFIT procedure (Schulz & Mudelsee 2002), which allows uneven spacing of samples and also provides significance testing with a realistic autocorrelated null model. We used a rectangular window with two segments. In order to study possible periodicities in the Milankovitch band, it is necessary to sample with a spacing corresponding to no more than 200 kyr, which is sufficient to resolve the 400 kyr eccentricity cycle. We therefore limited the spectral analysis to a subsection of 34 samples from -6.4 to 24.8 m at Janusfjellet, where the average sample spacing was 0.95 m, estimated to correspond to c. 70 kyr (see below). The software Past, version 2.06, was used for all data analysis and plotting (Hammer et al. 2001).

Organic carbon isotopic composition is influenced by the type of organic matter input. We therefore carried out Rock-Eval pyrolysis on a subset of the samples (Geo-Lab Nor, Trondheim, Norway).

**Results**

The results of the carbonate isotope analyses are shown in Fig. 3. Dolomitic concretions (often septarian) are highly depleted in δ18Ocarb down to -18.3 ‰ VPDB, and also strongly depleted in δ13Ccarb. Sideritic carbonates form a gradient from isotopic compositions similar to those of the dolomites towards more normal-marine, as represented by a well-preserved brachiopod from a seep carbonate. A concretion from the overlying Rurikfjellet Fm. also has a more normal-marine δ18O value, but is depleted in δ13C.

Organic carbon isotope and TOC values are shown in Fig. 2. At Janusfjellet, one sample at 3.18 m had an extreme δ13Corg value of -24.2 ‰ VPDB. In addition, one sample at 7.50 m gave δ13Corg = -27.0 ‰ VPDB. Without further evidence we disregard these values as outliers due to, e.g., contamination. The curves show good congruency, with both the Janusfjellet and Knorringfjellet sections giving a clear decreasing trend from the base of the section up to c. 6.5 m, followed by an increase up to the top. The TOC curves are also in general agreement between the two sections, with peaks near the base of the Slottsmøya Member (-24 m) and also around 12 m, a few metres...
The red-noise test in REDFIT reported no significant departure from the red-noise model (runs test, 9 runs being within the 5% acceptance interval of 5-14). Although the series is short, a spectral peak at a frequency of 0.216 cycles/m (4.63 m/cycle) is significant at the 95.45% false-alarm level (Fig. 4a). A second prominent peak occurs at 0.078 cycles/m (12.8 m/cycle). There is also a spectral peak near the Nyquist limit, probably influenced by aliased frequency components but still indicating a periodicity of less than 2 m. Sinusoidal fitting using the two main periodicities from the spectral analysis (4.63 and 12.8 m/cycle) is shown in Fig. 4b. Five or six short cycles can be identified, breaking up into longer cycles towards the top of the subsection. These cycles are also seen in the SF=2 spline fit in Fig. 2.

The Tmax values are in the range 432-445 °C, i.e. in the early stage of maturity. There is a general trend towards lower maturity up the section (Fig. 5a). The S₂ values (amount of hydrocarbons generated by cracking of organic matter during pyrolysis) are in the range 1-6 mg HC/g, except for exceptionally high values at 11.5 and 41.8 m (19 and 37 mg HC/g, respectively; Fig 5b). The Hydrogen Index (HI=S₂/TOC × 100) is generally higher above 10 m in the section, again with peaks at 11.5 and 41.8 m (Fig. 5c). The HI implies a predominantly Type III kerogen (HI<200 mg HC/g TOC), but Type II in the two exceptional samples (Fig. 6). There is a relatively strong correlation between TOC and HI (R²=0.68, p=0.01; Fig. 5d). The strongest correlation between any Rock-Eval parameter and organic carbon isotope values is between HI and δ¹³Corg, but this correlation is still weak and not statistically significant (R²=0.27, p=0.19; Fig. 5e).

above the minimum in the δ¹³Corg curve. In both sections the values are generally in the range 1-4 % TOC. At 42 m a TOC peak of 9.7 % is observed in the Janusfjellet section, matching a similar excursion in the data from Knorringfjellet reported by Dypvik (1985). The peak was presumably missed by our sampling at that locality. There is no correlation between δ¹³Corg and TOC (R²=0.038, p=0.11).

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Discussion

Carbonate isotopes

The analyses of diverse carbonates from the Slottsmøya Member in the Knorringfjellet area (Fig. 3) confirm the results of Krajewski (2004) from the Ingebrigtsenbukta Mbr. in southern Spitsbergen, demonstrating strong diagenetic overprint and a lack of primary marine isotopic signal. This overprint includes hydrothermal alteration, as shown by the depletion in δ¹⁸O particularly in the dolomites. Combined with the finds of authigenic carbonates in the upper part of the Slottsmøya Member. (Hammer et al. 2011), this makes it impossible to acquire a stratigraphically useful carbonate isotope record.

Local correlation

The very similar organic carbon isotope logs from the sections at Janusfjellet and Knorringfjellet, c. 10 km apart, indicate similar sedimentation rates and lack of (or at least similar) major tectonic complications. Given the spatially heterogeneous sedimentology and local overthrusting and slumping in the Agardhfjellet Fm. (Dypvik et al., 1991a), this is already a useful result, allowing us to place vertebrates and other finds in the two areas.
defined by the first occurrence of Trochammina praerosacea, in the topmost Kimmeridgian, at a level corresponding to c. -60 m in Fig. 2. The base of the F5 zone, defined by the FO of Ammodiscus zaspelovae (basal Middle Volgian), was placed c. 32 m below the Dorsoplanites marker bed, corresponding to -5 m in Fig. 2, while the base of F6 (within the uppermost Middle Volgian) occurs around 40 m. The minimum in the organic carbon isotope curve, around 6.5 m, is therefore situated in the lower part of the Middle Volgian. Above 40 m, a strong reduction in sedimentation rate (Nagy & Basov 1998) combined with poor exposure and also uncertainties in Boreal and global correlations make it difficult to position precisely the Volgian-Ryazanian boundary in the section (which may or may not correspond with the international Jurassic-Cretaceous boundary, e.g. Zakharov & Rogov 2008).

Further information on the stratigraphy in the upper part of the Slottsmøya Member was provided by Wierzbowski et al. (2011), who found that well-preserved ammonites from the methane seep carbonates (Hammer et al. 2011) range from the lower Upper Volgian Okensis Zone to the Upper Ryazanian Tolli Zone. Although some of the seep carbonates are slumped, we believe that they are all confined to an interval from c. 5 to 11 m below the top of the member (Hammer et al. 2011). This confirms the condensed nature of the section above 40 m as reported by Nagy & Basov (1998), and also indicates that the base of the overlying Rurikfjellet Formation may be as young as the Valanginian.

Further foraminiferal, palynological and ammonite biostratigraphic work in the Janusfjellet section is in progress.

Correlation with other areas

A composite δ¹³Ccarb curve for the Upper Jurassic of the Russian Platform (Podlaha et al. 1998; Price & Rogov 2009) shows steady reduction in δ¹³Ccarb from the Kimmeridgian and through the Lower Volgian, reaching a minimum in the lower Middle Volgian (Virgatites virgatus zone). After a rapid increase in the upper Middle Volgian (basal Epivirgatites nikitiini zone) the curve remains at a high level until a new decrease in the uppermost Volgian (Fig. 7).

Žák et al. (2011) presented a δ¹³Ccarb log from the Oxfordian to the Ryazanian at the Nordvik Peninsula, Northern Siberia. A replotting of their data is shown in Fig. 7, with a smoothing spline curve. Although the biostratigraphic control is slightly imprecise in the Lower to lower Middle Volgian, a broad minimum is evident around 32-33 m, again in the lower Middle Volgian.

Nunn & Price (2010) recorded a marked negative excursion in their δ¹³Ccarb curve from Helmsdale, Scotland, in the Boreal Pavlovia rotunda-Virgatopavlovia fittoni
zones, and comment on the correlation with the lower Middle Volgian excursion on the Russian Platform (Price & Rogov 2009).

Going outside the Boreal and High Boreal Realms, Katz et al. (2005) recorded a marked negative excursion in δ¹³C_carb in the middle Tithonian of DSDP site 534A, Blake-Bahama Basin, Western Central Atlantic (Fig. 7). The most negative values were found at 148.7 Myr in their age model based on Gradstein et al. (1995), placing the excursion in the Pavlovia pallasioides zone. They correlate this excursion with a much less prominent negative excursion in the western Tethys (Padden et al. 2002).

In summary, the negative excursion in δ¹³C_carb in the lower Middle Volgian (Dorsoplanites panderi zone) of Svalbard seems to show robust correlation with a similar excursion in δ¹³C_carb elsewhere in the Boreal and High Boreal Realms, with the central Atlantic and to a lesser degree with the western Tethys.

Published curves for δ¹³C_carb in the Upper Jurassic are scarcer. The highly detailed curve for the Kimmeridge Clay in Dorset (Morgans-Bell et al. 2001; Jenkyns et al. 2002) ends within the Lower Tithonian V. fittoni zone, but the declining trend from the Kimmeridgian is evident and the most negative value (-29.1 ‰ VPDB) is recorded in the Pavlovia pallasioides zone, correlating with the lowermost Dorsoplanites panderi High Boreal zone (Ogg 2004). The data from Morgans-Bell et al. (2001) are replotted in Fig. 2. In the low-resolution global δ¹³C_carb curve given by Katz et al. (2005), derived from Hayes et al. (1999), the two lightest values in the Mesozoic through to the Recent are found in the Aalenian (-32 ‰ VPDB) and the Tithonian (-29 ‰ VPDB). On the other hand, the δ¹³C_carb curve at DSDP site 534A reported by Falkowski et al. (2005) does not record any negative excursion in the Tithonian. Nunn et al. (2009) reported an organic carbon curve from a Callovian to Lower Kimmeridgian succession in Scotland.

Above the negative excursion, from the Upper Volgian/Upper Tithonian, the Northern Siberia and the Central Atlantic carbon isotope values remain consistently lighter than below (Kimmeridgian). Because the Spitsbergen and Russian Platform curves do not extend down to the Kimmeridgian, we do not know whether this persistent shift is also present there.
Cyclostratigraphy

Dypvik (1992) identified coarsening-upwards lithological cycles in the Agardhfjellet Formation, varying from 2 to 7 m in thickness and capped by sands or carbonates. In the Kimmeridgian-Volgian part of the succession, Dypvik reported an average cycle thickness of 6.4 m, estimated to correspond to 900 kyr at a sedimentation rate of 0.8 cm/kyr. In the latest geological time scale for the Boreal Upper Jurassic (Ogg & Hinnov 2012), partly based on cyclostratigraphy, the Middle Volgian has a total duration of 3.0 Myr. Based on the carbon isotope excursion reported here, and foraminiferal biostratigraphy (Nagy & Basov 1998), we can roughly equate the Middle Volgian with the interval from -5 to 35 m in the sections, giving an average sedimentation rate of about 1.3 cm/kyr. This is comparable with the rates given by Nagy & Basov (1998) for the Middle Volgian in central Spitsbergen, varying from 1.1 to 2.0 cm/kyr. The strong cycles of 4.63 m thickness observed in the middle part of the section at Janusfjellet (Figs. 2 and 4) would then correspond to a period of c. 360 kyr. Considering the large uncertainties and probable variation in sedimentation rate, this may represent the 405 kyr long eccentricity cycle, which is the strongest Milankovitch cycle in the Late Jurassic (Laskar et al. 2004; Huang et al. 2010). Tuning to this cycle, the 12.8 m period would correspond to 1120 kyr, which is also in the long eccentricity band. The possible <2 m cycle would correspond to less than 150 kyr, i.e. generally in the short eccentricity band. Tuning to the 405 kyr cycle also makes it possible to calculate the true duration of the -6 to 12.5 m subsection, containing four well-defined cycles, as 1.62 Myr, giving a sedimentation rate of 1.14 cm/kyr in this part.

There is some similarity between these cycles and the ones observed in the pectinatus to rotunda zones in the Kimmeridge Clay in Dorset (Fig. 2, data from Morgans-Bell et al. 2001). The organic carbon isotope cycles there are on the order of 30 m thick. Given the probable sedimentation rates in the Dorset Kimmeridge Clay based on cyclostratigraphy in the precessional and obliquity bands (Weedon et al. 2004; Huang et al. 2010), this corresponds to a c. 405 kyr eccentricity cycle.

Environmental correlations

As discussed by, e.g., Jenkyns et al. (2002) the organic carbon isotope record is influenced by a large number of environmental parameters, and is in general difficult although not impossible to interpret (e.g., Jenkyns et al., 2002; Kump & Arthur, 1999). A major factor controlling the organic carbon isotope composition is the type of the organic material, e.g., marine or terrestrial, which again is influenced by both local and regional or global parameters such as sea level, productivity and climate. A decrease in the burial rate of organic matter (which is enriched in $^{12}$C) leaves more light carbon in the remaining carbon pool, potentially leading to a negative carbon isotope shift both in carbonates and in organic matter. Common explanations for negative carbon isotope excursions include decreased burial of organic carbon, e.g., by decreased riverine phosphate delivery (Kump & Arthur, 1999), upwelling of bottom water enriched in light carbon, and methane release from gas hydrates or other reservoirs (e.g., Hesselbo et al. 2000).

The $\delta^{13}$C$_{org}$ curves for the Upper Jurassic in central Spitsbergen can be compared with the global sea-level curve of Haq et al. (1987). There is a very general correspondence, with a sea-level maximum near the Kimmeridgian-Volgian boundary corresponding with relatively heavy isotope values, lower sea level in the Middle Volgian near the negative isotope excursion, and a new maximum near the Volgian-Ryazanian boundary. In addition, the possible 405 ka-long eccentricity cycle observed here is likely to be associated with third-order sequences, as described, e.g., from the Kimmeridge Clay (Huang et al. 2010). In this perspective, it is difficult to explain the negative carbon isotope excursion as an effect of decreased productivity due to a diminishing supply of nutrients from rivers. In addition, such a reduction in organic matter burial is not clearly reflected by trends in organic carbon content in the Slottsmøya Member (Fig. 3). For the Valanginian (Lower Cretaceous) positive carbon isotope excursion (Lini et al. 1992), it has been suggested (Wortmann & Weissett 2000; Weissett & Erba 2004) that it was caused by sea-level rise and drowning of carbonate platforms. The details of local sea level through the Volgian in Spitsbergen are not known, but a maximal flooding surface is inferred at 42 m in the section, based on geochemical and sedimentological data indicating low sedimentation rates (Collignon & Hammer, this volume). This level is near the Volgian-Ryazanian boundary, in accordance with the Haq et al. (1987) global sea-level curve.

Inspired by current practice for naming carbon isotope excursions in the Palaeozoic, we propose the name VOICE (Volgian Isotopic Carbon Excursion) for this event. We prefer Volgian to Tithonian as all our examples of this excursion so far (except possibly the Central Atlantic site) are found in the Boreal realm, and the Volgian-Tithonian correlations are still under debate.

Conclusions

The complexity of the organic carbon isotope record requires that stratigraphic correlation must be cross-validated by biostratigraphy or other correlation tools. Still, $\delta^{13}$C$_{org}$ can provide improved resolution and increased confidence in correlations. Pending additional data, the curves from Svalbard indicate that a negative excursion in the lower Middle Volgian (Dorsoplanites panderi or possibly Virgatites virgatus zone) can be correlated across the Boreal and High Boreal Realms, and perhaps
even further. This excursion (here called VOICE) may prove a useful chemostratigraphic tool for resolving the difficulties in tying the Boreal to the Tethyan and global time scales. A strong cyclicity, possibly in the order of 400 kyr in parts of the section, indicates that organic carbon isotopes can be used to identify astronomical forcing in the Boreal Mesozoic, allowing the use of cyclostratigraphy for precise correlation.

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