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Finding the VOICE: organic carbon isotope chemostratigraphy of Late Jurassic – Early Cretaceous Arctic Canada

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Abstract

A new carbon isotope record for two high-latitude sedimentary successions that span the Jurassic–Cretaceous boundary interval in the Sverdrup Basin of Arctic Canada is presented. This study, combined with other published Arctic data, shows a large negative isotopic excursion of organic carbon (δ13Corg) of 4‰ (V-PDB) and to a minimum of ~30.7‰ in the probable middle Volgian Stage. This is followed by a return to less negative values of c. −27‰. A smaller positive excursion in the Valanginian Stage of c. 2‰, reaching maximum values of −24.6‰, is related to the Weissert Event. The Volgian isotopic trends are consistent with other high-latitude records but do not appear in Tethyan strata δ13C values during the Volgian Age due to low global or large-scale regional sea levels, and later become effectively coupled to global oceans by Valanginian time when sea level rose. A geologically sudden increase in volcanism may have caused the large negative δ13Corg values seen in the Arctic Volgian records but the lack of precise geochronological age control for the Jurassic–Cretaceous boundary precludes direct comparison with potentially coincident events, such as the Shatsky Rise. This study offers improved correlation constraints and a refined C-isotope curve for the Boreal region throughout latest Jurassic and earliest Cretaceous time.

1. Introduction

The Jurassic–Cretaceous boundary interval was characterized by significant fluctuations in Earth system processes (Hallam, 1986; Ogg & Lowrie, 1986; Sager et al. 2013; Price et al. 2016) that resulted in the extinction of many marine invertebrates (Hallam, 1986; Alroy, 2010; Tennant et al. 2017). Despite its importance in Earth history, the precise radiometric age and correlations of the Jurassic–Cretaceous boundary interval are poorly understood compared with those of other Phanerozoic environmental crises. This is partly because of the ongoing lack of a robust, global chemostratigraphic framework for the boundary (Zakharov et al. 1996; Wimbledon et al. 2011). After long debate, the Berriasian Working Group of the International Subcommission on Cretaceous Stratigraphy has voted to adopt the base of the Calpionella alpina Subzone as the primary marker for the base of the Berriasian Stage in the Tethyan faunal realm (Wimbledon, 2017). At this time, a stratotype section has not been formally designated. This potential Global Boundary Stratotype Section and Point (GSSP) level cannot be traced biostratigraphically into Arctic areas (e.g. Wimbledon, 2017, fig. 1). Paleomagnetic reversal data may provide direct Boreal–Tethyan correlation for the Tethyan–Berriasian boundary eventually, but data from the Boreal Nordvik section (Hou et al. 2007; Bragin et al. 2013; Schnabl et al. 2015) remain to be confirmed in other Arctic sections. Alternative options for the placement of the Jurassic–Cretaceous boundary continue to find support.

Although the international chemostratigraphic terminology for the Jurassic–Cretaceous boundary interval (Tithonian and Berriasian stages) is increasingly being used in Canadian Arctic studies, interpretations of the correlations of the substages and fossil zones entailed in these Tethys-based stages into the Arctic vary among global workers. Particularly contentious and significant is how much of the upper Volgian Stage is time-equivalent with the lower Berriasian Stage. Our usage in this report of the roughly equivalent Boreal (Volgian, Ryazanian)
114 in marine strata, may therefore aid with future correlations of Cretaceous argillaceous strata from two stratigraphic sections. A new δ13Corg record from Upper Jurassic – Lower Cretaceous argillaceous strata from two stratigraphic sections in the Sverdrup Basin, Arctic Canada, is presented here. Geochemical trends are compared with data from other high-latitude successions as well as with Tethyan sections to evaluate their palaeoeceanographic and palaeoclimatic importance and potential for stratigraphic correlation. In the absence of any obvious definitive cause for VOICE, several possible contributing factors, both regional and distant, are considered and discussed.

2. Study area

The Sverdrup Basin is a 1300 × 350 km paleo-depot centre in the Canadian Arctic Archipelago that contains up to 13 km of nearly continuous Carboniferous–Palaeogene strata (Figs 1, 2; Balkwill, 1978; Embry & Beauchamp, 2019).

Basin subsidence began following rift collapse of the Ellesmerian Orogenic Belt during early Carboniferous time (Embry & Beauchamp, 2019). Rifting of the Sverdrup Basin continued during the late Carboniferous Period and led to widespread flooding of the rift basin and increasingly open-marine connections with Panthalassa and North Greenland and the Barents Sea (Embry & Beauchamp, 2019). After the first rift phase, marine deposition persisted through to the lowest Berriasian Stage. This curve shows a trend in the Late Jurassic – earliest Cretaceous interval, and then ceased in the Sverdrup Basin when seafloor spreading began in the adjacent proto-Amerasia Basin to form the Arctic Ocean (Hadlari et al., 2016). Deposition in the Sverdrup Basin ended in the Palaeogene Period due to regional compression and widespread uplift associated with the Eurekan Orogeny (Embry & Beauchamp, 2019).

In the Late Jurassic Period, the Sverdrup Basin was one of many rift basins that formed during the break-up of Pangea and affected paleoeceanographic connections between the western Tethys and Panthalassa in northern latitudes. Deposition of the Deer Bay Formation during latest Jurassic – earliest Cretaceous time marked a rift climax in the Sverdrup Basin prior to the break-up of the adjacent proto-Amerasia Basin, manifested as a sub-Hauterivian break-up unconformity in the Sverdrup Basin (Embry, 1985a; Galloway et al., 2013; Hadlari et al., 2016, Fig. 2). The Deer Bay Formation is therefore a lithostatigraphic unit of interest from both a tectonostratigraphic and palaeoceanographic perspective; its study may provide insight into both regional and global changes at this dynamic time in Earth’s history.

The Deer Bay Formation is a succession of mudstone with interbeds of siltstone and very fine-grained sandstone deposited in pro-delta to offshore shelf environments across the Sverdrup Basin during the Volgian to late Valanginian ages (Heywood, 1963; Balkwill, 1983; Embry, 1985b, c). The Deer Bay Formation reaches a maximum thickness of 1375 m on eastern Elles 165 Ringnes Island and 920 m on Axel Heiberg Island (Balkwill, 1983). Offshore shelf mudstones of the Deer Bay Formation are conformably overlain either the shallow-shelf sandstones of the Awingak Formation or the Ringnes Formation, its offshore-shelf mudstone equivalent (Fig. 2). Deer Bay mudstones grade conformably into delta-front and fluvial-deltaic sands of the overlying 171 Isachsen Formation along the axis of Sverdrup Basin (Fig. 2; Balkwill, 1983; Embry, 1985b), but these formational contacts are disconformable on basin margins (Hadlari et al., 2016; Embry & Beauchamp, 2019). The Deer Bay Formation is undivided except for the designation of the c. 40 m sandstone-dominated Glacier Fjord Member in its upper part on southern Axel 177
Jurassic–Cretaceous carbon isotope stratigraphy

Fig. 1. (Colour online) Upper: palaeogeographic map of Pangea at c. 150 Ma (Tithonian; modified from Scotese, 2014), with modifications from Amato et al. (2015), Midwinter et al. (2016) and Hadlari et al. (2016, 2017, 2018). Arc and microcontinental terranes that had not yet docked with the North American and Siberian accretionary margins are not illustrated in the palaeo-Pacific Ocean (Panthalassa). Lower: map of the Sverdrup Basin showing location of stratigraphic sections studied at Geodetic Hills and Buchanan Lake, Axel Heiberg Island, Nunavut. After Dewing et al. (2007).
Sverdrup Basin

3. Materials and methods

A total of 154 samples were collected every c. 1.5–2 m throughout a 255 m exposure of the Deer Bay Formation at Buchanan Lake (79° 22′ 04″ N, 87° 46′ 90.3″ W), and 92 samples were collected every c. 3–4 m from a 388 m exposure of the Deer Bay Formation at Geodetics Hills (79° 48′ 57.20″ N, 89° 48′ 20.41″ W), Axel Heiberg Island (Fig. 1). Bivalves, belemnites and ammonites were collected from the Buchanan Lake section; macrofossils were not observed at the Geodetics Hills section. All samples are stored in permanent collections of the Geological Survey of Canada.

Mudstone samples were pre-treated with 10% HCl to remove carbonates, and then δ13C analysis of organic carbon was performed using a Elemental VarioEL Cube Elemental Analyser followed by a trap-and-purge separation and online analysis by continuous flow with a DeltaPlus Advantage isotope ratio mass spectrometer coupled with a ConFlo III interface at the GG Hatch Stable Isotope Laboratory, University of Ottawa. Results are reported as ‰ relative to Vienna PeeDee belemnite (V-PDB) and normalized to internal standards calibrated to the international standards IAEA-CH-6 (−10.4%), NBS-22 (−29.91%), USGS-40 (−26.24%) and USGS-41 (37.76%). Long-term analytical precision is based on blind analysis of the internal standard C-55 (glutamine; −28.53%) not used for calibration, and is routinely better than 0.2‰. For the Buchanan Lake dataset (n = 154), 14 quality control duplicate analyses were run (representing 9% of the samples). For the Geodetics Hills dataset (n = 92), 12 quality control duplicate analyses were run (12%) (online Supplementary Material available at http://journals.cambridge.org/geo). Average relative percent difference (RPD) was 0.13 ± 0.10‰ SD (n = 14) for the Buchanan Lake samples and 0.55 ± 0.42‰ SD (n = 12) for the Geodetics Hills material. The blind standard C-55 was run in triplicate for each of the three batches to assess accuracy. The average RPD between the measured and expected value of the standard was 0.18 ± 0.13% SD (n = 9).

Organic carbon isotopic composition can be influenced by the type and maturity of organic matter; Rock-Eval pyrolysis was therefore conducted on all samples. Total organic carbon (TOC, wt%) was determined by Rock-Eval 6 (Vinci Technologies, France) pyrolysis as the sum of organic matter during pyrolysis (pyrolyserable carbon, 100–650°C) and oxidation (residual carbon, 400–850°C) on all samples. Analyses of standard reference materials (IFP 160000, Institut Français du Pétrole; internal 9107 shale standard, Geological Survey of Canada, Calgary; Ardakani et al. 2016) was run every fifth sample demonstrating a <1% relative standard deviation (RSD) for TOC, <3% RSD for S1 and S2, and 11% RSD for S3. The lower accuracy for S3 in bulk samples was expected due to poor peak integration and distinction between S3 organic matter and S3 carbonates that may occur because of the presence of siderite in standards (Ardakani et al. 2016). Duplicate analyses were conducted for assessment of analytical precision. In the Buchanan Lake dataset 22 duplicate samples were run, and in the Geodetic Hills dataset two duplicate samples were run (online Supplementary Material available at http://journals.cambridge.org/geo). Samples from both sections comprised the analytical batch from which quality control duplicate samples were randomly selected. Average RPD for TOC (wt%) was 16.75 ± 26.93, S1 is 13.21 ± 15.34, S2 is 9.56 ± 13.67 and S3 is 11.02 ± 14.30 (n = 24).

4. Results

4.1. Macrofossils and age of strata

Macrofossils were found during this study in the middle and upper parts of the Deer Bay Formation in the Buchanan Lake section and...
258 were not seen in the Geodetic Hills section. The Buchanan Lake
259 macrofossils are, from top of the section to the base: (1) small
260 impressions of *Buchia* sp., 76 m below the base of the Isachsen
261 Formation (GSC loc. C-626162); age, undeterminable within the
262 late Oxfordian – Valanginian interval; (2) several fragments of
263 ammonite *Nikitinoceras kemperi* (Jeletzky) (Fig. 3a, b), bivalve
264 *Buchia* sp. cf. *inflata* (Toula) (Fig. 3c) and belemnites *Acroteuthis*
265 and *Cylindroteuthis*? (C-626163) occur 75.5 m below the base of the Isachsen
266 Formation; age, early Valanginian; (3) numerous
267 impressions of *Buchia okensis* (Pavlow) or *B*. sp. aff. *okensis* (sensu
268 Jeletzky 1964, 1984) occur 77 m below the base of the Isachsen
269 Formation; age, early Valanginian; (4) fragments of bivalves 125 m below the base of the Isachsen
270 Formation including *Buchia* sp. aff. *okensis*, *Mclearnia*?, *Oxytoma*?
271 and *Meleagrinella*?, with unidentified gastropods and the belemnite
272 *Acroteuthis* (C-626172); of probable early Ryazanian age; and (5) sev-
273 eral fragments of relatively large *Borealites* (Pseudocraspedites)
274 (Fig. 3e, f) and of *Borealites* s.l. (Fig. 3g, h) occur 143 m below
275 the Isachsen Formation (C-626176, 15-GTA-A80) and are of
276 early Ryazanian age. Poorly preserved, unidentifiable fossil
277 fragments occur in still lower beds and above the carbon isotope
278 anomaly. Mikhail Rogov (pers. comm., 2019) has assisted us
279 with our identification of the specimens we have assigned to
280 *Nikitinoceras* and *Borealites* Klimova.

The *Borealites* specimens are the lowest in our collections and
provide a youngest age limit for the lower negative δ13C anomaly
at Buchanan Lake. A previous fossil collection from perhaps the
same level as our *Borealites* fauna and in a similarly prolific horizon
(GSC loc. 26171, 316 feet = 96.3 m above the base of the Deer Bay
Formation according to Souther, 1963, p. 438) contains ammonites
closey similar to ours. They were initially reported as Valanginian
(Frebold, in Souther, 1963) but were figured, together with associ-
ated *Buchia okensis*, as lower Berriasian *Tollia (Subcraspedites)*
aff. *suprasubditus* (Bogoslovsky) by Jeletzky (1964, plate I–III),
as *Craspedites* (*Subcraspedites*) by Jeletzky (1973, plate 6, from

\[1\] Jurassic–Cretaceous carbon isotope stratigraphy

![Image](42x294 to 354x751)
We did not find fossils to control the older age limit for the negative δ13C excursion in the sections studied. However, Jeletzky (1984, p. 221) also reported other unidentifiable ammonites and large Buchia fisherianna (d’Orbigny) from "an 8 m bed commencing 31 m above the base of the Deer Bay Formation along the Awingak River, that is, near or within our Buchanan Lake section. The collection has not been relocated but, if the fossils are correctly determined, they imply a middle, perhaps early middle, Volgian age for this interval, which would fall at about the maximum depletion point of the δ13C curve.

Dorsoplanitid ammonites and various associated Buchia species including B. fisherianna (d’Orbigny) are widespread on nearby Ellesmere Island (Jeletzky, 1984; Schneider et al. 2019) and indicate a middle Volgian age for the lower Deer Bay Formation and its initial transgression event throughout eastern Sverdrup Basin.

Jeletzky (1984, p. 223) also reported other unidentified ammonites and bivalves in lower parts of the Buchanan Lake succession.

Two reports of Buchia mosquensis (von Buch) from Amund Ringnes Island (Jeletzky, in Balkwill et al. 1977, p. 1136) may be early Volgian, rare indicators of this interval in the more axial portion of the basin, or they may be late Kimmeridgian in age.

Stratigraphically close juxtaposition of early Ryazanian and early Valanginian fossils supports the interpretation of a strongly condensed interval or basinal disconformity at the Buchanan Lake locality near the depocentre of the Sverdrup Basin. The apparent absence of diagnostic fossils of late Berriasian age across the Sverdrup Basin has been used previously to suggest a widespread sub-Vangianian disconformity (Jeletzky, 1973; Kemper, 1975; Embry, 2011).

The Valanginian strata in the northern and eastern parts of Sverdrup Basin, as across the Arctic, are replete with glendonites (Kemper & Schmitz, 1975; Grasby et al., 2017; Rogov et al., 2017), but minor occurrences of 'stellate nodules' or 'carbonate crystal rosettes' have been reported in upper Oxfordian or lower Kimmeridgian strata to Berriasian strata in the western Sverdrup Basin (Poulton, 1994, p. 183), northern Yukon (Poulton, 1996, p. 285), and the Northwest Territories (Mountjoy & Procter, 1969).

While their appearance in only the upper 104 m of the Buchanan Lake section of the Deer Bay Formation at Buchanan Lake might suggest pre-Vangianian ages for the underlying strata, the interval with glendonites overlap with strata containing Buchia okensis, or B. cf. and aff. okensis, collected in this study and reported by Jeletzky (1984, p. 221, 223). They may indicate an age for the associated glendonites as old as early Ryazanian, although it is possible that they developed within the lower Ryazanian strata exposed on the sea floor during Valanginian time.

4.6. Carbon isotopes

We did not find fossils to control the older age limit for the negative δ13C excursion, with a magnitude of c. 4% and reaching minimum values of −29.8% at Buchanan Lake and −30.7% at Geodetic Hills, is observed within the lower Deer Bay Formation. All of the recovered macrofossils from the Buchanan Lake section occur stratigraphically above the negative carbon isotope excursion, dating the overlying strata as late Volgian or Ryazanian in age and younger in the Buchanan Lake section. This negative δ13C excursion is followed by a return to less negative values of c. −27%. A small negative shift of c. 1.5% occurs in strata that are likely late middle Volgian or early late Volgian in age, and this is followed by an interval of generally increasing values across the interpreted Jurassic-Cretaceous boundary until the upper Valanginian part of the Deer Bay Formation. A positive carbon isotope excursion is evident in its upper part in both sections, with a magnitude of c. 1.5% (interpreted here as the Weissert Event; Erba et al. 2004). Carbon-13 isotope ratios reach maximum values of −24.6% at Buchanan Lake and −24.9% at Geodetic Hills during this event (Fig. 4).
Lake samples, $\delta^{13}$C$_{org}$ is also significantly ($P < 0.001$) correlated with S1 ($r_s = -0.34$), S3 ($r_s = 0.33$) and HI ($r_s = -0.3$), but these relationships are insignificant in the Geodetic Hills samples. In both sections the relationships between $\delta^{13}$C$_{org}$, $T_{max}$ and S2 are insignificant ($P > 0.05$). While statistically significant, the relationships between $\delta^{13}$C$_{org}$ and organic matter parameters (TOC in both sections, S1 and S3 for Buchanan Lake) are weak as shown by the low values of $r_s$ suggesting that the influence of organic matter source, diagenesis and thermal maturation on the $\delta^{13}$C$_{org}$ values is limited. The high thermal maturity ($T_{max}$ 427–499°C Buchanan Lake and 436–448°C in Geodetic Hills) of the material could complicate interpretations of the Rock Eval pyrolysis data. Thermal degradation may disguise a change in organic matter source as heating pushes kerogen types to low HI (Hunt, 1996). Degraded, oxidized, residual ‘dry-gas-type’ kerogen (Type IV) falls into the same category as Type III on a van Krevelen-type plot (Tyson, 1995); a change in organic matter source from dominantly terrestrial (Type III) to marine (Type II) may therefore not be recognizable in an HI–OI cross-plot/van Krevelen-type diagram if the organic matter became highly thermally degraded. However, the reproduction of the carbon isotope curve in two stratigraphic sections, and consistency with curves from other Arctic areas, lends confidence to the hypothesis that the signals are not overly influenced by changes in organic matter source.

5. Discussion

The $\delta^{13}$C$_{org}$ and TOC curves across Upper Jurassic – Lower Cretaceous strata from the Buchanan Lake and Geodetic Hills sections show similar trends, and this permits confidence in...
extrapolating fossil age control from the Buchanan Lake section
to the Geodetic Hills section. A marked negative excursion of up
to ~4‰, reaching to ~30‰ (Fig. 4), occurs in probable middle
Volgian strata of the lower Deer Bay Formation. This is followed
by a return to less negative values near ~27‰, a brief negative
excursion of an additional c. 1.0–1.5‰ that may be late
Volgian in age, an interval of generally increasing values and then
a relatively positive carbon isotope excursion in strata of
Valanginian age of the upper part of the Deer Bay Formation.

5.4. VOICE

Trends in δ13Corg from the Buchanan Lake and Geodetic Hills
sections of the Deer Bay Formation are consistent with other
δ13Corg curves spanning the Jurassic–Cretaceous boundary
interval in the High Arctic (Hammer et al. 2012; Zakharov
et al. 2014; Koevoets et al. 2016; Fig. 7). In those records, rela-
tively positive carbon isotope values of c. −28‰ are observed in
the Kimmeridgian and lowest Volgian strata and are followed by
an up to 4–6‰ more negative excursion in the middle Volgian
strata. This event is followed by a return to relatively more
positive values during late Volgian and Ryazanian time.
Hammer et al. (2012) term the negative excursion they document
in lower middle Volgian strata of the Slottsmyea Member
(Agardhfjellet Formation) the Volgan Isotopic Carbon Excursion
(VOICE). Hammer et al. (2012) correlate the VOICE with a lower
middle Volgian broad minimum in the δ13Ccarb record from belemn-
ite rostra of Žák et al. (2011) that spans the Oxfordian–Ryazanian
interval at the Nordvik Peninsula, Siberia. Hammer et al. (2012) also
relate the VOICE to a negative excursion in δ13Ccarb from Helmsdale,
Scotland in the Sub-boreal lower middle Volgian Rotunda–Fittoni
ammonite zone (Nunn & Price, 2010) and a negative δ13Ccarb
excursion in DSDP site 534A in the ?Tithonian strata (western cen-
tral Atlantic; Katz et al. 2005). Hammer et al. (2012) conclude that
the lower middle Volgian negative excursion seen in their δ13Corg
record from Spitsbergen is consistent with carbonate records from
elsewhere in the Boreal and High Boreal realms, the central
Atlantic and, to a lesser degree with the western Tethys. Koevoets et al. (2016) also examined the organic carbon isotope
record preserved in the Upper Jurassic – Lower Cretaceous
Agardhfjellet Formation of central Spitsbergen. A marked negative
excursion of c. 4‰ is measured and dated as middle Volgian.
Koevoets et al. (2016) argue that the VOICE is also recognized
in δ13Ccarb curves from the Russian Platform (Price & Rogov, 2009).
Zakharov et al. (2014) document an irregular but overall decline in δ13Ccarb (as determined in belemnite rostra; Žák et al. 2011)
throughout Upper Jurassic strata from the Nordvik section
and that they relate to a gradual increase in CO2 in the atmosphere–
ocean system, and that may have led to warming based on coeval
changes in a belemnite oxygen isotope record. They also present a
δ13Corg record that shows a negative excursion of c. 3% within the
Exoticus Zone and extending into the basal part of the [Craspedites
Okensis Zone (late middle Volgian – early late Volgian). Trends
observed in the δ13Corg at this locality are not observed in the
δ13Ccarb of belemnite rostra from the same section (Žák et al. 2011; Zakharov et al. 2014). Morgans-Bell et al. (2001) examined
the Kimmeridgian–Berriasian interval of the Wessex Basin from
Dorset, UK. A prominent middle Tithonian negative excursion of
δ13Corg is not apparent in their record, although a short-lived excur-
sion may be related to the VOICE (Turner et al. 2018). Turner et al.
(2018) also interpret a short-lived decline in δ13Corg values in the
lower middle Volgian Pallasioides Zone in Core 6406/12-2 from the
Norwegian Sea as the VOICE. The composite δ13Ccarb curve
in the Kissimett–Berriasian interval of the Wessex Basin is based
on Tethyan data, shows no major negative
carbon isotope events (Fig. 7; Price et al. 2016).  

Decoupling of high-latitude δ13Corg Records and Tethyan
records, the latter based mostly on carbonates, suggests either that
pools of organic carbon and dissolved inorganic carbon were effec-
tively decoupled during this time, or that there was latitudinal
decoupling between the Arctic and Tethyan seas. Typically, covari-
ant marine δ13Ccarb and δ13Corg are seen and interpreted as evidence
that both carbonate and organic matter were originally produced in
the surface waters of the ocean and retained their original δ13C com-
position (e.g. Kump & Arthur, 1999; Meyer et al. 2013). Coupled ter-
restrial organic (e.g. derived from fossil wood or charcoal) and
515 carbonates records suggest strong coupling of the ocean–atmosphere
system (e.g. Gröcke et al. 2005; Vickers et al. 2016), whereas
decoupled δ13Ccarb and δ13Corg records have been interpreted as
evidence for diagenetic alteration (Meyer et al. 2013; Han et al.
2018). In these latter examples, a large negative excursion in δ13Ccarb is typically not accompanied by a large response in the
δ13Corg record (e.g. Fike et al. 2006). Alternatively, Bodin et al.
(2016) have recently suggested lithological control on decoupling
between δ13Ccarb and δ13Corg Records during Early Jurassic time, whereby δ13Ccarb signatures were affected by regional variation in
carbonate composition. As the Arctic middle Volgian negative event
is observed in organic carbon records from Canada (this study),
252 Spitsbergen and Siberia (Fig. 7), it is unlikely that diagenesis or
regional differences in the composition of bulk organic carbon are
significant factors in explaining the contrast with its absence from
lower-latitude areas. Instead, the absence of the negative excursion
from lower-latitude carbonate records may be explained by decou-
ppling of high-northern-latitude regions from the global carbon pool.
Fig. 6. (Colour online) Stratigraphic trends in Rock Eval parameters TOC, HI and OI from the Buchanan Lake and Geodetic Hills sections. Events recognized in δ13Corg curves are shown in yellow. The International Chronostratigraphic Chart (ICS) v 2018/08 (Cohen et al. 2013; updated) and Boreal Stage and Sub-stage (after Shurygin & Dzyuba et al. 2015) are shown.
<table>
<thead>
<tr>
<th>Location</th>
<th>Site/Region</th>
<th>Period</th>
<th>Ammonite Zones</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nordvik, Siberia</td>
<td>(Zakharov et al. 2014)</td>
<td>Jurassic</td>
<td>Ryazanian - LowerUpper</td>
</tr>
<tr>
<td>Janusfjellet, Svalbard</td>
<td>(Hammer et al. 2012)</td>
<td>Jurassic</td>
<td>Kimm. Brachyconodontus</td>
</tr>
<tr>
<td>Boreholes DH2 and DH5R, Svalbard</td>
<td>(Koevoets et al. 2016)</td>
<td>Jurassic</td>
<td>Boreal (Siberian)</td>
</tr>
<tr>
<td>7120/2-3, Barents Sea</td>
<td>(Turner et al. 2019)</td>
<td>Jurassic</td>
<td>Sub-Boreal</td>
</tr>
<tr>
<td>1406/3-4, North Sea</td>
<td>(Turner et al. 2018)</td>
<td>Jurassic</td>
<td>Sub-Boreal</td>
</tr>
<tr>
<td>33/12, North Sea</td>
<td>(Turner et al. 2018)</td>
<td>Jurassic</td>
<td>Sub-Boreal</td>
</tr>
<tr>
<td>Dorset, UK</td>
<td>(Morgans-Bell et al. 2001)</td>
<td>Jurassic</td>
<td>Sub-Boreal</td>
</tr>
<tr>
<td>Wollaston Forland</td>
<td>(Pauly et al. 2013)</td>
<td>Jurassic</td>
<td>Sub-Boreal</td>
</tr>
<tr>
<td>Rio Corna, Italy</td>
<td>(Lini et al. 1992)</td>
<td>Jurassic</td>
<td>Sub-Boreal</td>
</tr>
<tr>
<td>DSDP Site 535</td>
<td>(Cotillion and Rio 1984)</td>
<td>Jurassic</td>
<td>Sub-Boreal</td>
</tr>
<tr>
<td>DSDP Site 416</td>
<td>(Wortmann and Weissert 2000)</td>
<td>Jurassic</td>
<td>Sub-Boreal</td>
</tr>
</tbody>
</table>

**Fig. 7.** (Colour online) Summary of published data for Late Jurassic – Early Cretaceous organic carbon isotope data from Atlantic and Tethyan sections, the global stack of Tethyan carbonate records and the new Arctic curves. Sub-Boreal ammonite zones from Mutterlose et al. (2014) and Turner et al. (2018). Boreal (Siberian) ammonite zones after Zakharov et al. (1997), Baraboshkin (2004) and Shurygin & Dzyuba (2015). The International Chronostratigraphic Chart (ICS) v. 2018/08 (Cohen et al. 2013; updated) and Boreal Stage and Sub-stage (after Shurygin & Dzyuba et al. 2015) are shown.
The organic carbon isotope record is influenced by a number of environmental factors (Kump & Arthur, 1999) and, as such, can be difficult to interpret (Jenkyns et al. 2002). Organic carbon isotope composition is strongly controlled by the type of organic matter (marine v. terrestrial) and, therefore, by both local and regional variables such as sea level, productivity and climate. Burial rate of organic matter enriched in 13C is also important, as more heavy carbon would remain in the global carbon pool. This process leads to a positive isotopic shift in both carbonates and organic matter.

A decline in the δ13C value involves a relative increase in 13C in the oceanic carbon reservoir (Price & Gröcke, 2002). This could occur through a combination of mechanisms, including decreased carbon burial rate as a result of decreased preservation (e.g. deep basin ventilation), decreased sea-surface productivity (Weissert & Channell, 1989; Weissert & Erba, 2004), increased flux of 13C into surface waters by upwelling of 12C-rich bottom waters (Küspert, 1982) or intensified weathering and riverine input of dissolved inorganic carbon (Weissert & Mohr, 1996). A geological rapid release of 13C into the atmosphere associated with volcanism, methane release from dissociation of gas hydrates or combustion of organic matter associated with emplacement of large igneous bodies are other mechanisms that can cause a negative excursion in δ13C (Dickens et al. 1995; Hesselbo et al. 2000; Padden et al. 2001; Schröder-Adams et al. 2019).

A geologically sudden increase in volcanism could potentially explain the large negative δ13Corg values seen in the middle Jurassic volcanic Arctic records and an absence from δ13Ccarb records (Price et al. 2016). As modelled by Kump & Arthur (1999), an increase in volcanism sufficient to perturb atmospheric pCO2 levels could drive down the carbon isotopic value in the ocean–atmosphere system. However, any trend in δ13Ccarb could be relatively quickly countered as burial of anomalously depleted organic matter may overcompensate for additional input of depleted volcanic CO2 (Kump & Arthur, 1999).

Notwithstanding this, the Shatsky Rise, a vast shield volcano with a surface area of c. 480,000 km², formed in the NW Pacific Ocean at about the Jurassic–Cretaceous boundary (Sager et al. 2013). Recent 40Ar/39Ar age determinations of basaltic lava samples from Tamu Massif, the oldest and largest edifice of the submarine Shatsky Rise, provide an age of 145.5 Ma. 40Ar/39Ar minimum age for the Jurassic–Cretaceous boundary proposed by Mahoney et al. (2005). However, new U–Pb ages from Argentina and Mexico suggest that the numerical age of the Jurassic–Cretaceous boundary may lie between 140.7 and 140.9 Ma; this evidence would place an age of c. 145 Ma (the current ICS age for the base of the Berriasian stage) into the middle of the Tithonian age (Lena et al. 2019), whether the base of the Tithonian is of age 152.1 Ma (Cohen et al. 2013; updated 2018/08) or 148 Ma (Lena et al. 2019) or somewhere between. Sub-aerial volcanism and summit weathering and/or erosion of the emergent phase of the Shatsky Rise is thought to have occurred as early as during the Valanginian age (Yasuhara et al. 2017), suggesting possible further complications in the interpretation of significance of the age of the sills associated with the Shatsky Rise. The ages of the base of the Tithonian and Berriasian stages are yet to be established (e.g. Oggi & Hinnov, 2012; Aguirre-Urreta et al. 2015).

Hydrocarbon seeps are widely distributed in Upper Jurassic and Jurassic–Cretaceous boundary beds in Spitsbergen. Seeps characterized by authigenic carbonates in the uppermost Jurassic Slottsmoya Member of the Agardhfjellet Formation in the Sassenfjorden area of central Spitsbergen (Hammer et al. 2011) may be related to the release of gas hydrates (Kiel, 2009), early thermal steepening of the geothermal gradient and/or tectonic activity associated with the initial phases of High Arctic Large Igneous Province (HALIP) activity (Maher, 2001; Hammer et al. 2011). HALIP, a major magmatic event, may therefore be relevant to the VOICE carbon isotope record, although the currently known ages of the HALIP intrusives are younger than those of the VOICE, ranging from 95–91 Ma to c. 127 Ma (Ommen et al. 2011; Evenchick et al. 2015; Dockman et al. 2018; Kingsbury et al. 2018). 40Ar/39Ar minimum age for the base of the Tithonian and Berriasian stages are yet to be established.

Eustatic sea-level fall was invoked by Nunn & Price (2010) to explain a general trend towards more negative δ13C values in their belemnite record from Helmsdale, Scotland, in the Tithonian Stage. A sea-level fall could result in enhanced release of 13C from weathering, erosion and oxidation of organic-rich sub-aerially exposed rock (Voigt & Hilbrecht, 1997; Price & Gröcke, 2002) as well as compositional deviation away from open-marine δ13C values in relatively isolated epeiric seas (e.g. Holmden et al. 1998; Immenhauser et al. 2003). ‘Local’ depletion in δ13C is caused by isotopically light CO2 input from respiration of marine organisms, as well as oxidation of terrestrial organic matter and input of isotopically light riverine dissolved inorganic carbon (Patterson & Walter, 1994; Holmden et al. 1998). Progressive oxidation of organic matter to CO2 (‘sea water ageing’, Holmden et al. 1998), which then forms dominantly bicarbonate in sea water, is greatest during a long residence time of water masses in shallow, poorly circulating settings (Patterson & Walter, 1994). The uptake of this bicarbonate in carbonates or marine organic matter in isotopic equilibrium with dissolved inorganic carbon results in carbonate or organic materials with depleted 13C values.

The Deer Bay Formation is the result of regional marine transgression that was preceded by a sea-level lowstand in Sverdrup Basin (Emby & Beauchamp, 2019), with restricted marine connections and a large number of restricted environments (e.g. Ziegler, 1988; Hardenbol et al. 1998). The Deer Bay rift climax of the Sverdrup Basin occurred during this time and basin subsidence was associated with contemporaneous rift margin uplift. Due to low global sea-level during the Tithonian Age, the only direct connection between the North Atlantic and the Sverdrup Basin was the narrow and shallow Norwegian–Greenland Seaway, which was more than 1500 km long and only 200–300 km wide (Ziegler, 1988; Dore, 1991). Connections between the western Sverdrup Basin and Panthalassa were similarly constricted prior to rift-opening of the Canada Basin in the Haueterian Age (e.g. Embry, 1991). The Sverdrup Basin and other high-latitude Boreal basins (e.g. Dyrvik & Zakharov, 2012) could have experienced compositional evolution away from global marine δ13C values during middle Volcanic time, but effectively became re-coupled by Valanginian time due to global sea-level rise. The hypothesis of restriction of Sverdrup Basin water masses during Volcanic time, followed by more open circulation during Valanginian time, is consistent with global sea-level fluctuations (Haq et al. 2017), and may be supported by the greater number of known ammonite occurrences in the Valanginian part of the Deer Bay Formation, and the greater similarity of inter-marine faunas between the Arctic and Europe at this time. Embry (1991, p. 408, 414) noted three transgressive–regressive cycles during the Kimmeridgian – late Berriasian interval in the Sverdrup Basin, a gradual decline in sediment supply and a shift of the basin axis to the west, with sandstones occupying the basin margins. Sea-level rise during
Early Cretaceous time would have increased ventilation of the incipient Arctic Ocean and thus coupled the carbon dynamics of the Sverdrup Basin to the open-marine system. This interpretation would imply a similar oceanographic restriction to explain the middle Volgian negative $\delta^{13}C$ events in Svalbard and Siberia. It might also partly explain and support the ongoing difficulties with correlating Tethyan and Boreal marine faunas, especially if exacerbated by concurrent climate-influenced biogeographic differentiation.

### 5.2. Weissert Event

A particularly prominent feature of Early Cretaceous global carbon isotope records is the Valanginian (Weissert) $\delta^{13}C$ positive excursi-
on (Lini et al. 1992; Price et al. 2016). This isotope event is widely documented globally in marine carbonates, fossil shell material, terrestrial plants and marine organic matter (e.g. Lini et al. 1992; Gröcke et al. 2005; Aguirre-Urreta et al. 2008; Price et al. 2016). Marine organic matter (Lini et al. 1992; Wortmann & Weissert, 2000) typically shows a c. 2% excursion. Despite the noisy pattern seen in these published records, which possibly relate to changes in the composition of the bulk organic carbon, the shape of the $\delta^{13}C$ curve is characterized by a rapid rise from the pre-
exursion background, a plateau and a less steep decline to a new steady state that is slightly more positive than prior to the event. Only in the record from Greenland is the Valanginian (Weissert) $\delta^{13}C$ positive excursion less clear, possibly due to high condensation of the strata and related sample density, or a hiatus in the sedimentary record (Pauly et al. 2013). Given the overall pattern and magnitude of the marine records, the positive carbon isotope excursion of up to 1.5% in the upper part of the Deer Bay Formation is interpreted to represent the Valanginian (Weissert) event in Arctic Canada.

### 6. Conclusions

Carbon isotope stratigraphy from two sections in the Canadian High Arctic that span the Jurassic–Cretaceous boundary documents a marked middle Volgian negative excursion with a magnitude of c. 4% followed by a return to less negative values. A positive excursion is evident with a magnitude of c. 1.5% in the Valanginian Stage. The Volgian isotopic trends are consistent with other high-latitude records but are decoupled from Tethyan $\delta^{13}C_{sub}$ records. The globally recognized isotopically positive Weissert Event in the Valanginian Stage is also recognized in the Canadian Arctic sections. The Sverdrup Basin and other Arctic basins may have experienced compositional evolution away from open-marine $\delta^{13}C$ values during the middle Volgian time in relatively isolated basins due to low global sea levels, and became effectively re-coupled by Valanginian time when global sea level rose. As well as providing another correlation tool in a time interval with chal-
 lenging inter-provincial biostratigraphic correlations, C isotope excursions such as that presented here offer further insight into the causes of major global ocean–atmosphere perturbations beyond the conventional volcanic interpretation.

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### Supplementary material

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