Proof Delivery Form

Date of delivery:

Journal and vol/article ref: geo 1900131

Number of pages (not including this page): 15

This proof is sent to you on behalf of Cambridge University Press. Please check the proofs carefully. Make any corrections necessary on a hardcopy and answer queries on each page of the proofs.

Please return the marked proof within 2 days of receipt to:

geoproduction@cambridge.org

Authors are strongly advised to read these proofs thoroughly because any errors missed may appear in the final published paper. This will be your ONLY chance to correct your proof. Once published, either online or in print, no further changes can be made.

To avoid delay from overseas, please send the proof by airmail or courier.

If you have no corrections to make, please email geoproduction@cambridge.org to save having to return your paper proof. If corrections are light, you can also send them by email, quoting both page and line number.

• The proof is sent to you for correction of typographical errors only. Revision of the substance of the text is not permitted, unless discussed with the editor of the journal. Only one set of corrections are permitted.

• Please answer carefully any author queries.

• Corrections which do NOT follow journal style will not be accepted.

• A new copy of a figure must be provided if correction of anything other than a typographical error introduced by the typesetter is required.

• If you have problems with the file please contact geoproduction@cambridge.org

Please note that this pdf is for proof checking purposes only. It should not be distributed to third parties and may not represent the final published version.

Important: you must return any forms included with your proof. We cannot publish your article if you have not returned your signed copyright form.

NOTE - for further information about Journals Production please consult our FAQs at http://journals.cambridge.org/production_faqs
QUERIES

AQ1: The distinction between surnames can be ambiguous, therefore to ensure accurate tagging for indexing purposes online (e.g. for PubMed entries), please check that the highlighted surnames have been correctly identified, that all names are in the correct order and spelt correctly.

AQ2: Please check that affiliations of all the authors and the corresponding author details are correctly set.
Finding the VOICE: organic carbon isotope chemostratigraphy of Late Jurassic – Early Cretaceous Arctic Canada

Jennifer M. Galloway1,2, Madeleine Vickers3, Gregory D. Price4, Terence Poulton5, Stephen E. Grasby1, Thomas Hadlari1, Benoit Beauchamp6 and Kyle Sulphur1,5

1Geological Survey of Canada/Commission géologique du Canada, Natural Resources Canada/Ressources naturelles Canada, 3303 33rd St N.W., Calgary, Alberta T2L 2A7, Canada; 2Aarhus Institute of Advanced Studies, Aarhus University, Heegh-Guldbergs Gade 6B 8000 Aarhus C, Denmark; 3Faculty of Science, Geology Section, University of Copenhagen, Øster Voldgade 10, DK-1350 Copenhagen K, Denmark; 4School of Geography, Earth & Environmental Sciences, University of Plymouth, Drake Circus, PL4 8AA, UK and 5Department of Geosciences, University of Calgary, Calgary, AB T2N 1N4, Canada

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 (GSSP) level cannot be traced biostratigraphically into Arctic areas (e.g. Wimbledon, 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). Palaeomagnetic reversal data may provide direct Boreal–Tethyan correlation for the Tethyan–Berriasian boundary eventually, but data from the Boreal Nordvik section (Houa 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 substrages 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, Ryanian)
and Tethyan nomenclature follows that of the relevant original literature cited. Our data do not contribute to, or require, discussion of their detailed correlations or about the common but potentially misleading use of the term Boreal for some NW European Sub-boreal sequences.

61 The numerical age of the Jurassic–Cretaceous boundary is also under debate. The International Commission of Stratigraphy (Cohen et al. 2013, updated 2018/08) places the Jurassic–Cretaceous boundary at c. 145 Ma following Mahoney et al. (2005), who suggest a minimum age for the boundary based on mean 40Ar-39Ar ages of 144.6 ± 0.8 Ma, although recent U–Pb studies by Aguirre-Urreta et al. (2019) and Lena et al. (2019) provide new U–Pb ages that suggest that the numerical age of the boundary could be as young as 140–141 Ma.

62 A small change to lower δ13C values occurs within Magnetozones M18–M17, and within the B/C Calpionellid Zone (Weissert & Channell, 1989), that contrast with more positive values obtained from the Valanginian Stage (Lini et al. 1992; Price et al. 2016). Such variation suggests that carbon isotope anomalies may be useful to characterize the Jurassic–Cretaceous boundary interval (e.g. Michalk et al. 2009; Dzyuba et al. 2013).

63 A recent global stack compiled by Price et al. (2016) that included data from many sites spanning a range of mainly southerly latitudes, and was therefore considered representative of the global carbon isotopic signal, showed that the composite δ13Corg curve from the base of the Kimmeridgian to the base of the Valanginian stages has no major perturbations. However, there is a paucity of published δ13C data from Arctic regions, and in those that do exist, there is notably greater variation in high-northern-latitude δ13Corg (e.g. Hammer et al. 2012) than in better-studied middle- to low-latitude carbonate records (δ13Ccarb) (Price et al. 2016) or in δ13Ccarb records from belemnites in Arctic successions (Zák et al. 2011).

Hammer et al. (2012) present δ13Corg data for the Upper Jurassic – lowermost Cretaceous systems of central Spitsbergen. This record shows a middle Volgan excursion of c. 5‰ that they term the Volgan Isotopic Carbon Excursion (VOICE). Koevoets et al. (2016) documented a middle Volgan negative excursion in δ13Corg of c. 3‰ in the Agardhfjellet Formation of central Spitsbergen. Records from northern Siberia also document a δ13Corg excursion to isotopically lighter values in the upper middle Volgan (Exoticus Zone; Zakharov et al. 2014), but with no parallel trend in δ13Ccarb measured in belemnite rostra from the same section (Zák et al. 2011); this is possibly because carbon isotopes preserved in belemnite rostra may not be in equilibrium with ambient seawater (Wierzbowski & Joachimski, 2009). Turner et al. (2018) report a δ13Corg curve from the 6406/12-2 drill core from the Norwegian Sea that spans the interval from the base of the Pallasioides Zone to the top of the Rositanda Zone in the lower middle Volgan Stage. A negative isotopic excursion occurs in the Pallasioides Zone that the authors relate to VOICE. Further south, Morgans-Bell et al. (2001) examined the carbon isotope stratigraphy of organic matter preserved in the Wessex Basin. Their record extends into the Upper Jurassic System but does not continue through to the lowest Berriasian Stage. This curve shows a trend of declining δ13Corg of much greater magnitude than the time-equivalent carbonate curve.

Alternative correlation tools, such as geochemical anomalies in marine strata, may therefore aid with future correlations of Jurassic–Cretaceous strata, particularly in high northern latitudes. 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 palaeoceanographic 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 x 350 km palaeo-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 the Permian and Triassic periods. A second phase of rifting began in the Early Jurassic Period, continued through 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 (Hadalari 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 palaeoceanographic 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 lithostratigraphic unit of interest from both a tectonostatigraphic 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 Volgan to late Valanginian ages (Heywood, 1963; Balkwill, 1983; Embry, 1985b, c). The Deer Bay Formation reaches a maximum thickness of 1375 m on eastern Elftp 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 stratigraphic 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).
Heiberg Island, south of the study area (Emby, 1985b). In other localities, the member is absent from shale facies or because of truncation below an intra- or sub-Isachsen unconformity (Emby, 1985b). Concretions of various compositions, size and shape occur throughout the Deer Bay Formation, with large (up to 5 m long) calcitic and sideritic mudstone concretions common in its lower portion. Glendonites occur in multiple horizons that range in thickness from 2 to 20 m throughout the Deer Bay Formation and are most common in its upper Valanginian portion (Kemper, 1975, 1983, 1987; Kemper & Jeletzky, 1979; Selmeier & Grosser, 2011; Grasby et al. 2017). This upper interval is further characterized by finely laminated siltstones and fissile shales that host rare thin rusty-weathering calcareous layers and irregularly distributed intervals of calcareous concretions (Heywood, 1957; Kemper, 1975; Balkwill, 1983). The biostrophic framework of the glendonite-bearing Valanginian succession was described by Kemper (1975, 1975, 1977, 1987) based on ammonites in successions exposed on Amund Ringnes (lower Valanginian) and Ellef Ringnes (upper Valanginian) islands. These strata also contain age-diagnostic marine bivalves, including Bucharie keyserlingi (Lahusen) and belemnites (Jeletzky, 1973; Kemper, 1977).

### 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′ 0.47″ N, 87° 46′ 9.03″ 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 Vario El 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/gec). Average relative percent difference (RDP) was 0.13 ± 0.10‰ (n = 14) for the Buchanan Lake samples and 0.55 ± 0.42‰ (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 RDP between the measured and expected value of the standard was 0.18 ± 0.13‰ (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 (pyrolysable 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 Geodetics Hills dataset two duplicate samples were run (online Supplementary Material available at http://journals.cambridge.org/gec). 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...
were not seen in the Geodetic Hills section. The Buchanan Lake macrofossils are, from top of the section to the base: (1) small impressions of Buchia sp., 76 m below the base of the Isachsen Formation (GSC loc. C-626162); age, undeterminable within the late Oxfordian – Valanginian interval; (2) several fragments of ammonite Nikitinoceras kemperi (Jeletzky) (Fig. 3a, b), bivalve Buchia sp. cf. inflata (Toula) (Fig. 3c) and belemnites Acroteuthis? and Cylindroteuthis? (C-626163) occur 75.5 m below the base of the Isachsen Formation; age, early Valanginian; (3) numerous impressions of Buchia okensis (Pavlow) or B. sp. aff. okensis (sensu Jeletzky 1964, 1984) occur 77 m below the base of the Isachsen Formation; age, early Valanginian; (4) fragments of bivalves 125 m below the base of the Isachsen Formation including Buchia sp. aff. okensis, Mclearnia?, Oxytoma? and Meleagrinella?, with unidentified gastropods and the belemnite Acroteuthis (C-626172); of probable early Ryazanian age; and (5) several fragments of relatively large Borealites (Pseudocraspedites) (Fig. 3e, f) and of Borealites s.l. (Fig. 3g, h) occur 143 m below the Isachsen Formation (C-626176, 15-GTA-A80) and are of early Ryazanian age. Poorly preserved, unidentifiable fossil fragments occur in still lower beds and above the carbon isotope anomaly. Mikhail Rogov (pers. comm., 2019) has assisted us with our identification of the specimens we have assigned to 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 closely similar to ours. They were initially reported as Valanginian (Frebold, in Souther, 1963) but were figured, together with associated 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
4. Carbon isotopes

4.1. ROCK-EVAL 6 pyrolysis

TOC measured by Rock-Eval 6 pyrolysis on samples of the Buchanan Lake section (median TOC 1.16 wt%; range 0.09–37% 4.36 wt%; n = 154) and Geodetic Hills section (median TOC 1.48 wt%; range 0.48–5.87 wt%, n = 92) are typical for high latitude Upper Jurassic and Lower Cretaceous mudrock successions. The TOC range indicates poor to excellent source rock (see online Supplementary Material available at http://journals.cambridge.org/geo). Thermal alteration material indicated by T_{max} (the temperature corresponding to maximum S2 during pyrolysis) ranges from 427 to 499°C in samples collected from the Buchanan Lake section and from 436 to 448°C in samples collected from the Geodetic Hills section; the majority of samples from both sections are in the oil window. The S2 values (amount of hydrocarbons generated by thermal cracking of organic matter) and S3 (the amount of CO2 released during thermal breakdown of kerogen) range from 0.15 to 2.42 mg HC/g and 0.27–2.41 mg HC/g at Buchanan Lake, respectively (n = 154). S2 and S3 range from 0.22 to 6.13 mg HC/g TOC 0.13–1.27 mg HC/g TOC, respectively, at Geodetic Hills (n = 92). The hydrogen index (HI = S2/g TOC) and oxygen index (OI = S3/g TOC) suggest that organic matter is predominantly Type III kerogen at Buchanan Lake and a mixture of Type II and III kerogen in the Geodetic Hills samples (Fig. 5). The Geodetic Hills locality was more distal and in a deeper part of the basin during latest Jurassic – earliest Cretaceous times than the Buchanan Lake locality, and this is reflected in the higher proportion of Type III kerogen at Buchanan Lake. Samples with very low TOC resulted in HI or OI values > 200 (Buchanan Lake A22, A43, A56, A65, A76, A82, A121 and A124) and are not plotted on the Van Krevelen diagram (Fig. 5) or stratigraphically (Fig. 6).

4.2. Stratigraphic trends in TOC, HI and OI are shown in Figure 6. In both the Buchanan Lake and Geodetic Hills sections, TOC increases near the top of the Deer Bay Formation. Trends in HI and OI are also similar between the two sections, with marginally higher HI values near the base of the Deer Bay Formation.

Spearman’s rank correlation was conducted to evaluate relationships between δ^{13}C_{org} and organic matter source and maturity. In both sections, δ^{13}C_{org} is significantly related to TOC (Buchanan Lake δ^{13}C_{org}:TOC r_{s} = 0.3, P < 0.001, n = 146 with outliers A22, A43, A56, A65, A76, A82, A121 and A124 removed; Geodetic Hills δ^{13}C_{org}:TOC r_{s} = 0.43, P < 0.001, n = 92). In 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 δ^{13}C_{org} 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, $^{13}\text{C}_{\text{org}}$ 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 $^{13}\text{C}_{\text{org}}$, $T_{\text{max}}$ and S2 are insignificant ($P > 0.05$). While statistically significant, the relationships between $^{13}\text{C}_{\text{org}}$ 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 $^{13}\text{C}_{\text{org}}$ values is limited. The high thermal maturity ($T_{\text{max}}$ 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 $^{13}\text{C}_{\text{org}}$ 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. a. 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, relatively 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 Slottsmeja Member (Agardhfjellet Formation) the Volgian Isotopic Carbon Excursion (VOICE). Hammer et al. (2012) correlate the VOICE with a lower middle Volgian broad minimum in the δ13Ccarb record from belemnite 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 central 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 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 Okenis 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. (2005) 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 excursion may be related to the VOICE (Turner et al. 2018). Turner et al. (2018) also interpreted 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 from the base of the Kimmeridgian to the base of the Valanginian sections, based mostly 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 effectively decoupled during this time, or that there was latitudinal decoupling between the Arctic and Tethyan seas. Typically, covariant 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 composition (e.g. Kump & Arthur, 1999; Meyer et al. 2013). Coupled terrestrial organic (e.g. derived from fossil wood or charcoal) and carbonate 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), 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 decoupling of high-northern-latitude regions from the global carbon pool.
Jurassic – Cretaceous carbon isotope stratigraphy

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.
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 $^{13}$C 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 $^{13}$C value involves a relative increase in $^{12}$C 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 (Weisert & Channell, 1989; Weisert & Erba, 2004), increased flux of $^{12}$C into surface waters by upwelling of $^{12}$C-rich bottom waters (Küspert, 1982) or intensified weathering and riverine input of dissolved inorganic carbon (Weisert & Mohr, 1996). A geological rapid release of $^{12}$C 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 $^{13}$C (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 $^{13}$Corg values seen in the middle Jurassic volcanic records and an absence from $^{13}$C$_{carb}$ records (Price et al. 2016). As modelled by Kump & Arthur (1999), an increase in volcanism sufficient to perturb atmospheric $p$CO$_2$ levels could drive down the carbon isotopic value in the ocean–atmosphere system. However, any trend in $^{13}$C$_{carb}$ could be relatively quickly countered as burial of anomalously depleted organic matter may overcompensate for additional input of depleted volcanic CO$_2$ (Kump & Arthur, 1999). Notwithstanding this, the Shatsky Rise, a vast shield volcano with a surface area of c. 480 000 km$^2$, formed in the NW Pacific Ocean at about the Jurassic–Cretaceous boundary (Sager et al. 2013). Recent $^{39}$Ar/$^{40}$Ar age determinations of basaltic lava samples from Tamu Massif, the oldest and largest edifice of the submarine Shatsky Rise, provide an age of c. 144 Ma (Geldmacher et al. 2014), similar to the widely used c. 145 Ma $^{40}$Ar/$^{39}$Ar 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 (Yashara 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. Ogg & Hinnov, 2012; Aguirre-Ureña 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 (Omuma et al. 2011; Evenchick et al. 2015; Dockman et al. 2018; Kingsbury et al. 2018; Fig. 2). Seep carbonates are also found in the Janusfellet section of Spitsbergen; these are of late Volgian – earliest Valanginian age (Wierzbowksi et al. 2011), and are therefore younger than the carbon isotope excursion documented in Sverdrup Basin.

Eustatic sea-level fall was invoked by Nunn & Price (2010) to explain a general trend towards more negative $^{13}$C$_{carb}$ values in their belemnite record from Helmsdale, Scotland, in the Tithonian Stage. A sea-level fall could result in enhanced release of $^{13}$C 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 $^{13}$C values in relatively isolated epeiric seas (e.g. Holmden et al. 1998; Immensehauser et al. 2003). ‘Local’ depletion in $^{13}$C is caused by isotopically light CO$_2$ 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 CO$_2$ (‘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 circulated 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 $^{13}$C values.

The Deer Bay Formation is the result of regional marine transgression that was preceded by a sea-level lowstand in Sverdrup Basin (Embry & 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 sub-sidence 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 Hauterivian Age (e.g. Embry, 1991). The Sverdrup Basin and other high-latitude Boreal basins (e.g. Dyvik & Zakharov, 2012) could have experienced compositional evolution away from global marine $^{13}$C values during middle Volcanian 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 Volcanian 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
5.b. Weissert Event

A particularly prominent feature of Early Cretaceous global carbon isotope records is the Valanginian (Weissert) δ13C 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 δ13C 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) δ13C 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 δ13Csub 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
δ13C values during the middle Volgian Age 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.

Acknowledgements. Financial support for field work and analyses was
provided by the GeoMapping for Energy and Minerals (GEM) Program,
(Natural Resources Canada, Geological Survey of Canada). Collections and
research on those collections were made under the Government of Nunavut
Archaeology and Palaeontology Research Permit 2015-03P. Data analysis
and production of this research paper was conducted at the Geological
Survey of Canada and at the Aarhus Institute of Advanced Studies at Aarhus
University. JMG received funding from the AIAAS-COFUND II fellowship
programme that is supported by the Marie Skłodowska-Curie actions under the
European Union’s Horizon 2020 (grant agreement no. 754513) and the
Aarhus University Research Foundation. We are grateful to Dr Keith Dewing
for project management and Dr Lisa Neville (Calgary, AB) and Pål Liddell
Iqaluk (Hamlet of Resolute Bay, NU) for assistance with sample collection and
field logistics. We acknowledge the logistics support provided by the Polar
Continental Shelf Program (NRCAN) and UHL Helicopters (Pilot Lorne Pike).
We are grateful for the staff of the Environment and Climate Change Canada
Eureka Weather Station and, in particular, Station Manager André Beauchard.
Dr Mikhail Rogov particularly, as well as Drs Aleksandr Igolnikov and
Victor Zakharov, offered important advice concerning the current taxonomic
assignments and ages of the ammonites and a Buchia specimen. Glen
Edwards produced the photographs and the fossil plate. This publication
represents NRCan Contribution Number/Numéro de contribution de
RNCan 20190001. We are grateful for the comments of Dr Manuel Bringué
(Geological Survey of Canada) for his internal review and to Dr Óyvind
Hammer and Dr Mikhail Rogov for detailed external reviews that greatly
improved this contribution. We also thank the Editor Dr Bas Van de
Schoolbrugge for comments and suggestions.

Supplementary material.

To view supplementary material for this article, please visit https://doi.org/10.1017/S0016756819001316.

references

Cretaceous radioisotopic ages from the Anides. Geological Magazine 152
557–64.
Aguirre-Urreta MB, Naipauer M, Lescano M, López-Martínez R, Pujaña I,
chrono-biostratigraphy of the Neuquén Basin, Argentine Andes: a review
Aguirre-Urreta MB, Price GD, Ruffell AH, Lazo DG, Kalin RM, OGle N and
Early Barremian) carbon and oxygen isotope curves from the Neuquén basin.
Alroy J (2010) Geographical, environmental and intrinsic biotic controls on
Amato JM, Toro J, Akinin VV, Hampton BA, Salnikov AS and Tuchkova MI
(2015) Tectonic evolution of the Mesozoic South Anyu suture zone, eastern
China: a critical component of paleogeographic reconstructions of the Arctic
region. Geosphere 11, 1330–64.
Ardakani OH, Sanei H, Snowden LR, Outridge PM, Obermaier M, Stewart R,
Vanden Bogaard and Boyce K (2016) The accepted values for the internal
Bragin VY, Dzyuba OS, Kazansky AY and Shurygin BN (2010) Geographical, environmental and intrinsic biotic controls on
Bodin S, Krencker F, Kothe T, Hoffmann R, Mattioli E, Heimhofer U and
Bodin S, Krencker F, Kothe T, Hoffmann R, Mattioli E, Heimhofer U and
Amato JM, Toro J, Akinin VV, Hampton BA, Salnikov AS and Tuchkova MI
(2015) Tectonic evolution of the Mesozoic South Anyu suture zone, eastern
China: a critical component of paleogeographic reconstructions of the Arctic
region. Geosphere 11, 1330–64.
Ardakani OH, Sanei H, Snowden LR, Outridge PM, Obermaier M, Stewart R,
Vanden Bogaard and Boyce K (2016) The accepted values for the internal
Bragin VY, Dzyuba OS, Kazansky AY and Shurygin BN (2010) Geographical, environmental and intrinsic biotic controls on
Bodin S, Krencker F, Kothe T, Hoffmann R, Mattioli E, Heimhofer U and
Amato JM, Toro J, Akinin VV, Hampton BA, Salnikov AS and Tuchkova MI
(2015) Tectonic evolution of the Mesozoic South Anyu suture zone, eastern
China: a critical component of paleogeographic reconstructions of the Arctic
region. Geosphere 11, 1330–64.


Jurasic–Cretaceous carbon isotope stratigraphy


Geological Association of Canada, St John’s, Mineral Deposits Division, Special Publication no. 5.


Jurassic–Cretaceous carbon isotope stratigraphy


Carnets de Geologie, Madrid, Book 2019/01 (CG2019_B01).


