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Earliest Cretaceous (late Berriasian) glendonites from Northeast Siberia revise the timing of initiation of transient Early Cretaceous cooling in the high latitudes

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A B S T R A C T

The studies of past climatic changes form the basis for predicting our future anthropogenic world and are among the most prominent topics in current Earth sciences. Although the Cretaceous is generally considered as a greenhouse period in Earth's history, a number of significant cooling events based on an array of climatic proxies have been identified. Here we present the first data on Berriasian (Ryazanian) glendonite findings from the paleontologically well dated Lower Cretaceous succession of northeastern Siberia. Based on well calibrated *Buchia* and ammonite biostratigraphy, the stratigraphic interval across which the glendonites occur is restricted to the late Berriasian. Stable carbon isotope ($\delta^{13}C$) values of the studied glendonites clearly suggest the precipitation of ikaite from marine water without any significant contamination from biogenic methane. Our results, when integrated with other available paleoclimatic proxies from elsewhere in the high latitudes, suggest a revision of the initiation of Early Cretaceous cooling in the high latitudes from the Valanginian to the late Berriasian. All known occurrences of Lower Cretaceous glendonites in both the northern and southern hemispheres are reviewed.

1. Introduction

Accurate reconstructions of past climates can form the basis for predicting our future anthropogenic climate and have therefore risen to the forefront in current Earth science research. Recent studies on the climate of the Cretaceous (see Föllmi, 2012 and references therein), which has traditionally been considered as a warm and equable greenhouse world with very limited if any high latitude ice, have revealed that this greenhouse climate was interrupted a number of times by cooling events of differing magnitudes (Price, 1999 and references therein). These climatic events can be reconstructed using several climatic proxies, including sedimentological records such as ice rafted debris, tillites and glendonites (Price, 1999), changes in faunal and floral assemblages in both the marine and terrestrial realms (e.g. Vakhrameyev, 1982; Kemper, 1987; Zakharov and Rogov, 2003), inorganic and organic geochemical records such as the interpretation of stable oxygen isotope ($\delta^{18}O$) data from fossil carbonate and organic matter (e.g. Bornemann et al., 2008), and organic lipid biomarkers such as the TEX_{86} proxy (e.g. Littler et al., 2011; Jenkyns et al., 2012). Abrupt sea-level falls are also considered as connected with cooling episodes (Price, 1999; Haq, 2014). The presence of glendonites within depositional sequences is one of the most significant lines of evidence for at least seasonal near-freezing bottom water paleotemperatures, whilst other proxies are less conclusive (Price, 1999).

Glendonites, considered as calcite pseudomorphs of the metastable mineral ikaite ($CaCO_3x6H_2O$), are among the most well-known indicators of near-freezing conditions and have been commonly used for paleoclimate reconstructions for several decades (Kemper and Schmitz, 1975, 1981; Kaplan, 1978, 1980; Markwick and Rowley, 1998; de Lurio and Frakes, 1999; Price, 1999; Lippert, 2004; Selleck et al., 2007; Price and Nunn, 2010; Rogov and Zakharov, 2010; Herrle et al., 2015; Vickers et al., 2016). These calcite pseudomorphs have been recorded from deposits varying in age from Neoproterozoic to Holocene, and geological settings varying from relatively deep-marine to tidal and lacustrine environments, as well as permafrost influenced rocks (Dempster and Jess, 2015). The study of modern ikaite crystals has

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revealed an even broader array of settings in which they can form, including varying depths in the oceans ranging from littoral to bathyal, i.e. ~0–4000 m (Jansen et al., 1987; Geptner et al., 2014; Krylov et al., 2015), in lakes (Last et al., 2013), springs (Ito, 1996), melted sea ice in both the Arctic and Antarctic (Rysgaard et al., 2012), and caves (Bazarova et al., 2014). Whilst they may form in a diverse range of different environments, their occurrence is always associated with low temperatures which do not exceed 7 °C. Generally, ikaite precipitation is favored by elevated alkalinity and dissolved phosphate in the pore-waters, and in many cases its formation is associated with organic-rich marine sediments where methane oxidation is occurring (Greinert and Derkachev, 2004; Selleck et al., 2007; Krylov et al., 2015, and references therein). Teichert and Luppold (2013) have recently emphasized the significant influence of methane on ikaite precipitation, based on a study of late Pliensbachian glendonites, and similar results were also derived by Morales et al., 2015, who studied Siberian Jurassic to Early Cretaceous glendonites. Alternatively, concentrations of phosphorus in pore waters have recently been suggested as a key factor controlling ikaite precipitation (Zhou et al., 2015). However, in all known cases (including low-latitude occurrences), glendonite and its precursor ikaite occur in association with relatively cold-water environments, therefore we suggest that their occurrence in Early Cretaceous deposits can be used as a proxy for climatic cooling, although the relative importance of other factors responsible for their distribution remains debatable.

2. Review of worldwide Lower Cretaceous glendonite occurrences

Early Cretaceous glendonite records have been known for more than 100 years and have been used as a proxy for discrete cooling events over a relatively narrow temporal range (Figs. 1–2, Table 1). Valanginian (especially late Valanginian) glendonites are widely distributed across the present-day Arctic, including from Arctic Canada (Kemper and Schmitz, 1981; Kemper, 1987) and northern Siberia (Revuckaja, 1908; Migai, 1952; Kaplan, 1978; Zlobina et al., 2014). Additional records of Valanginian glendonites were also briefly described from West Siberia (Potapova, 2006). Late Berriasian to middle Valanginian glendonites have been described from the Antarctic (Varela and Cisternas, 2015), whilst late Hauterivian glendonites are known from Svalbard (Vickers et al., 2016). Glendonites have recently been discovered in the Galadriel Fjeld Formation (Kilen, N. Greenland) (Junium et al., 2004), corresponding to the upper part of the Ullaberget Member and lower part of the Helvetiafjellet Formation (Dypvik et al., 2002), and thus could also be late Hauterivian in age. Hauterivian glendonite records are also known from the Pebble Shale Unit of NE Alaska (van der Kolk et al., 2011).

Latest Early Cretaceous (Aptian and Albian) glendonite occurrences are known from Arctic Canada (upper Aptian to lower Albian of Sverdrup Basin, see Kemper, 1987; Herrle et al., 2015). Glendonite concretions were also recorded from the lowermost upper Aptian of Spitsbergen, as proven by findings of the typical ammonite *Tropaeum arcticum* (Stolley) (Rogov and Zakharov, 2010). Additional records of upper Aptian to lower Albian glendonites from Svalbard were reported by Maher et al. (2004) and Vickers et al. (2016). Possible Aptian glendonites ("stellate concretions") are also known from NE Russia (Efimova et al., 1970), as well as from the southern hemisphere, including the late Aptian Bulldog Shale in the Eromanga Basin, Australia (Sheard, 1991; de Lurio and Frakes, 1999) and Aptian of the South Shetland Islands (Varela and Cisternas, 2015). Early to Middle Albian glendonite occurrences were also reported from Kamchatka, eastern NE Russia (Alabushev, 1995) (see Figs. 1–2 and Table 1 for summary).

These Early Cretaceous glendonite occurrences correlate with other proxies for climatic cooling, including episodes of southward

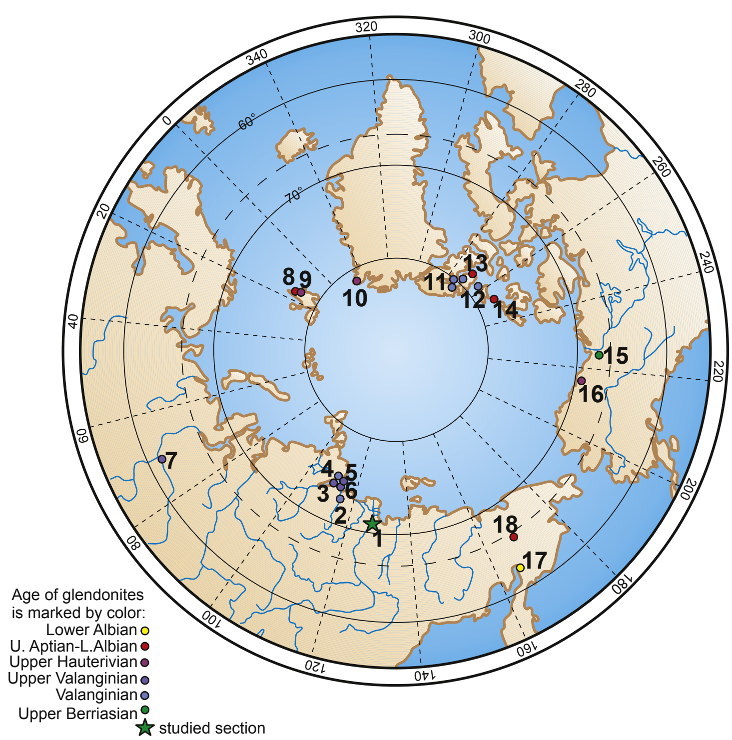

Fig. 1. Map showing geographic position of all known Lower Cretaceous glendonite records in the Northern Hemisphere. For references and ages see Table 1. 1. Studied section (Chucha Cape); 2. Srednyaya river; 3. Nordvik Bay; 4. Osipa river, AH-3 well; 5. Bolshoi Begichev and Preobrazhenia islands; 6. Nordvik Peninsula; 7. Priobskaya 8232 well; 8–9. Sassenfjorden, incl. Festningen Cape and Janusfjellet Mt; 10. Kilen; 11–12. Ellesmere, Axel Heiberg and Amund Ringnes islands; 13. Axel Heiberg Island; 14. McKenzie King Island; 15. Martin Creek; 16. Canning river; 17. Ajnyn river; 18. Umkuveem river.

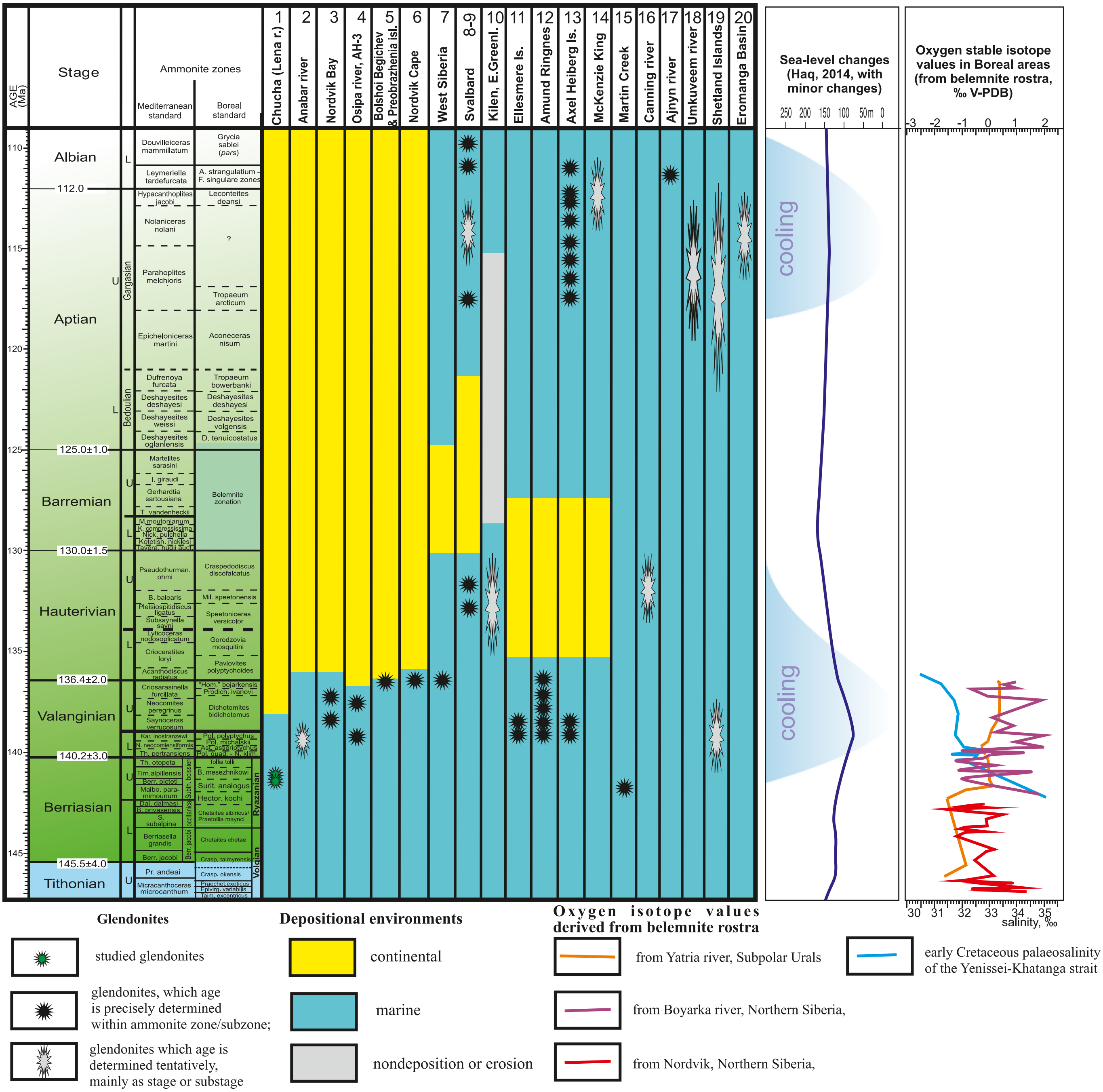

Fig. 2. Correlation chart of Early Cretaceous glendonites occurrences across the Northern Hemisphere with available stable isotopic data and see-level curve. Areas shown with numbers in the upper part of the figure are the same as on Fig. 1 except 19–20. Ages are given after Ogg and Hinnov, 2012; sea-level curve by Haq (2014) was calibrated against ammonite zones except position of three lowermost Cretaceous sequence boundaries which given after Hoedemaeker et al., 2016.
Mediterranean standard zonation is given after Reboulet et al. (2014); Boreal succession and its correlation after Baraboshkin (2004) with minor corrections. Oxygen isotope values are given after Price and Mutterlose (2004) (for Yatria river), Nunn (2007) (for Boyarka river) and Zakharov et al. (2014) (for Nordvik). Early Cretaceous palaeosalinity of the Yenissei-Khatanga strait are provided after Zakharov and Radostev (1975).

spreading of boreal faunas in the northern hemisphere (Herrle and Mutterlose, 2003; Mutterlose et al., 2009) and stable isotope data derived from belemnite rostra (e.g. McArthur et al., 2007; Price and Nunn, 2010).

Here we present the first data on Berriasian (Ryazanian) glendonite records, which provide a revised temporal constraint on the initiation of these Early Cretaceous cooling events.

3. Late Berriasian glendonites from Northeast Siberia

3.1. Geological setting

Glendonites have been found in the Upper Jurassic–Lower Cretaceous section at Cape Chucha, northeastern Siberia (Figs. 3–4). Ten glendonite-bearing levels have been found through the studied

Table 1
Cretaceous glendonite occurrences.

No in Figs. 1–2	Locality	Lithology of glendonite-bearing units	Age	Age determined by	Comments	Data source
1	Cape Chucha	Sandstones	Late Berriasian, Analogus-Mesezhnikowi Chrons	Ammonites, bivalves	Glendonites recorded from 3 members	This paper
2	Srednyaya river	No data	Valanginian	Ammonites	Presence of "pseudogaylussite crystals" is mentioned	Revuckaja, 1908
3	Nordvik Bay	Clayey siltstones	Late Valanginian	Ammonites, bivalves	Numerous glendonite occurrences are mentioned	Zlobina et al., 2014
4	Osipa river, AH-3 borehole	Sandy and clayey silts; siltstones and sandstones	Valanginian	Ammonites, bivalves	"Anthraconite roses" are mentioned (Osipa river), and glendonites were reported from AH-3 well	Migai, 1952; authors' observations
5	Bolshoi Begichev and Preobrazhenia islands	Sandstones and siltstones	Late Valanginian	Ammonites, bivalves	Numerous levels with "Stellate calcite pseudomorphoses" are mentioned	Revuckaja, 1908; Burdykina, 1981; Basov et al., 1983
6	Nordvik Peninsula	Sands. Glendonites are associated with Arctichnus burrows	Late Valanginian, Bojarkensis Chron	Ammonites	"stellate calcite pseudomorphoses" are mentioned from the single member	Zakharov et al., 1983
7	Priobskaya 8232 well	Sandstones	Late Valanginian/ earliest Hauterivian	Palynology	Single pseudomorphose was found	Potapova, 2006, age determined by palynologist O. Shurekova
8–9	Sassenfjorden, Svalbard	Sandstones (Hauterivian), sandstones and shales (Aptian–Albian)	Late Hauterivian and Late Aptian–Early Albian	Ammonites	Few levels with glendonites; Hauterivian records were studied in details (Price and Nunn, 2010)	Maher et al., 2004; Vickers et al., 2016; authors' data
10	Kilen, North Greenland	Sandstones	Hauterivian	Correlation with Svalbard succession (Dypvik et al., 2002)	δ^{13}C data are available	Junium et al., 2004
11–12	Ellesmere, Axel Heiberg and Amund Ringnes islands, Arctic Canada	Clays and silty shales	Valanginian	Ammonites, palaeomagnetic reversals	Numerous glendonites were reported and figured	Kemper and Schmitz, 1975, 1981; Kemper, 1987; Lippert, 2004
13	Axel Heiberg Island, Arctic Canada	Siltstones and shales	Late Aptian–Early Albian	Benthic foraminifera, dinoflagellates	Multiple glendonite occurrences	Herrle et al., 2015
14	McKenzie King Island, Arctic Canada	Clays	Late Aptian–Early Albian	No data	Multiple glendonite occurrences	Kemper, 1987, Taf. 17
15	Martin Creek, Arctic Canada	Shales	Late Berriasian, Buchia okensis Chron	Bivalves	Carbonate crystal rosettes are mentioned from single member	Mountjoy and Proctor, 1969
16	Canning river, Alaska	Mudstones	?Hauterivian	Palynology, benthic foraminifera	Numerous glendonite occurrences	van der Kolk et al., 2011
17	Ajnyn river, Kamchatka	Pebbly-vitroclastic unit	Early Albian	Ammonites	Glendonites were recorded in few levels	Alabushev, 1995
18	Umkuveem river, North-East Russia	Sandstones	Aptian	Bivalves	"Stellate concretions" are reported from the top of the succession	Efimova et al., 1970
19	Shetland Islands, Antarctic	Mudstones and siltstones	Late Berriasian –Valanginian, Aptian	Macroflora, palynology	"Microglendonites" were found in palynological samples	Varela and Cisternas, 2015
20	Eromanga Basin, Australia	Black mudstones	Late Aptian	Microflora, molluscs	Glendonites are found within thin interval	Sheard, 1991; de Lurio and Frakes, 1999

interval (within sandstone members 40, 42 and 55) (Fig. 4), represented by stellate aggregates ranging from ca. 1 to 5–6 cm in diameter and in some cases by solitary "bipyramidal crystals" (Fig. 5). Occasionally, especially within the upper part of member 42 and in member 56, glendonites occur in the central parts of relatively small cannon-ball-like carbonate concretions. The occurrence of glendonites is confined to the Berriasian part of the studied succession, represented by a thick (~400 m) sequence of deltaic to shallow marine interbedded sandstone and siltstone belonging to the Khairgass Formation. This formation overlies thin (~5 m thick) Volgian (upper Tithonian to lowermost Berriasian) shales of the Buolkalakh Formation (see Rogov et al., 2011). The Khairgass Formation contains scarce fossils, which are mainly represented by bivalves. These bivalves belong to the Boreal genus *Buchia* (*B. volgensis* and also *B. unschensis*, *B. fischeriana* in the lower part of the formation; Figs. 4, 6), which occur throughout the formation, whilst other bivalves are very uncommon. These buchiids are strongly indicative of a middle to late Berriasian (Ryazanian) age of the Khairgass Formation. *B. volgensis*, which is scattered throughout all glendonite-bearing members (Figs. 4, 6), is diagnostic of the upper part of the Berriasian stage (Rogov et al., 2011, and references therein), becoming extinct before the start of the Valanginian. The *B. volgensis* zone has been extensively studied and recognized as upper Berriasian (upper Ryazanian) in many different regions, including East Greenland, the Volga area and NE Russia (Zakharov, 1981; 1987). Ammonites occur infrequently throughout much of the studied section but can also form the basis for a biostratigraphic calibration. The ammonite genus *Bojarkia*, typical of the Mesezhnikowi ammonite zone, was identified from the topmost part of member 40 through to member 56 (Figs. 4, 6), whilst boreal phylloceratids *Boreophylloceras* occur within member 56. Below, within member 35 and member 40, a few *Surites* indicating the presence of either the Kochi or Analogus ammonite zones were collected (Fig. 6.7–8). Therefore, the integration of both ammonite and bivalve biostratigraphy provides strong support for a late Berriasian age for the stratigraphic horizon containing all of the glendonite findings.

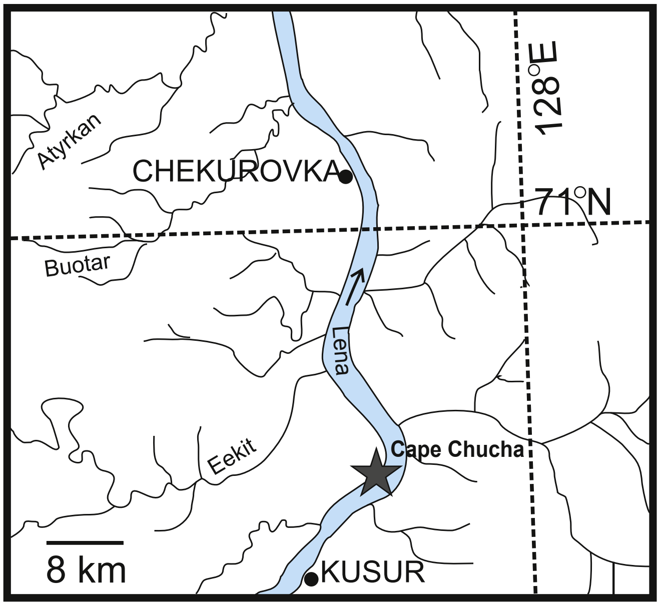

Fig. 3. Map showing position of the studied section.

3.2. Morphology of glendonites in thin section

The glendonites display a short-prismatic habit, slightly distorted due to specific growth and later corrosion. Internally they are composed of microgranular calcite, commonly discolored by dispersed ferrous oxides-hydroxides or organic matter (OM), and occasionally contaminated by terrigenous silt grains (up to 1–2%). X-ray diffraction studies reveal a predominance of calcite in the studied concretions. Cold-cathodoluminescence (CL) petrography distinguishes tabular, ovoidal, rhombohedral, fine-fibrous, spherulitic and clear mosaic calcites within the studied glendonites. The observed relationship between different calcite phases suggests multiple stages of dissolution-recrystallization and replacement (complete or partial) of pre-existing types of calcite. The obtained CL-colors are different for successive calcite generations and vary from black (no luminescence) to dark brown for the oldest (tabular, ovoidal, rhombohedral) types of calcite, and up to light brown-orange (spherulitic) and bright reddish-orange (fine-fibrous and clear mosaic) for the younger calcites (Fig. 7A–D). The CL patterns reflect a progressive increase in the iron content within the youngest calcite generations, caused by the increasing influence of burial diagenesis.

3.3. Stable isotope analysis

Stable carbon and oxygen ($\delta^{13}C$ and $\delta^{18}O$) isotope analyses were performed on the glendonites from the Chucha section (Fig. 7E, Supplementary Table 1). The results were obtained with the Thermoelectron system, including a Delta V Advantage Mass-Spectrometer with Gas-Bench-II, in the Geological Institute of the Russian Academy of Sciences, Moscow. Isotopic results were calibrated against C-O-1 and NBS-19 standards reacted with H_3PO_4 at 50°C, confirming analytical precision for both $\delta^{18}O$ and $\delta^{13}C$ of ±0.2‰.

$\delta^{13}C$ values of the studied glendonites lie within the range of −15.9 to −21.7‰ (Fig. 7E). Almost identical carbon isotope values were reported from Holocene glendonites formed in littoral environments of the White Sea (Geptner et al., 2014), as well as those of the Aptian glendonites from Australia (de Lurio and Frakes, 1999), and the Hauterivian and Eocene glendonites of Svalbard (Spielhagen and Tripati, 2009; Price and Nunn, 2010). These stable isotope values are close to those typical for recent authigenic marine carbonates (Lein, 2004). However, modern glendonites typically show a much broader range of carbon isotope values (ca. from +40 to −60‰, see Galimov et al., 2006; Last et al., 2013), which are strongly dependent on the depositional environment. The extremely negative $\delta^{13}C$ values (<−30‰) of many deep marine glendonites are likely to be due to the significant input of biogenic methane from the seafloor (Schubert et al., 1997; Greinert and Derkachev, 2004; Galimov et al., 2006), whilst ikaite precipitated in lacustrine environments often exhibits positive $\delta^{13}C$ values. The obtained range of $\delta^{13}C$ values for the glendonites in this study is typical of shallow marine depositional environments, and suggests that ikaite was precipitated in marine water without significant contamination by methane seepage. $\delta^{18}O$ values of the studied glendonites are characterized by a broad range (from −2.8‰ to −12.7‰, see Supplementary Table 1), reflecting the complex processes involved in the transformation of ikaite to glendonite, characterized by multiple calcite replacement phases. Therefore we suggest that our stable oxygen isotope values cannot be applied as a paleoclimate (temperature) proxy, due to the significant dissolution and re-precipitation of primary calcite during subsequent diagenesis. No correlation is observed between the stable carbon and oxygen isotope values in the studied glendonites ($R^2 = 0.1415$).

3.4. Rock eval pyrolysis

A few samples from the Berriasian of the Chucha section, derived from glendonite-bearing members 42 and 56 along with members 36 and 39, were analyzed using a Delsi-Nermag Rock-Eval II analyzer. They generally exhibit low Total Organic Carbon (TOC) values (except two samples containing fossil wood, see Supplementary Table 2) and a low Hydrogen Index (HI), suggesting the dominant input of terrestrial organic matter (OM). Such low TOC values are in agreement with the negligible influence of OM on the $\delta^{13}C$ values. Tmax values, measured from sediments surrounding the glendonites, indicate that the studied sections were not deeply buried and just entered the oil window, suggesting the organic material is immature to early mature. Therefore, our rock eval pyrolysis results confirm that the studied glendonites did not form in an area with thermogenic or biogenic methane seepage and can be used as a paleoclimate proxy.

4. Discussion

Prior to this study, there were only a few strands of tentative evidence for earliest Cretaceous (pre-Valanginian) climatic cooling. Earliest Cretaceous tillites of the southern hemisphere are dated as Berriasian–Valanginian by palynology (Alley and Frakes, 2003), but their precise age range is unknown. Glendonites reported from Berriasian–Middle Valanginian deposits of the Shetland Islands (Varela and Cisternas, 2015) are also imprecisely dated. Vakhrameyev (1982) pointed out the disappearance of thermophilic *Classopolis* pollen grains (Traverse, 2007) in the Berriasian–Valanginian of northern Eurasia, which could be evidence of a climatic cooling during this time. Independently, Krassilov (1973) suggested a temperature decrease in eastern Asia from the Berriasian to the Albian based on the decline of cycadophytes. There is evidence for a southward penetration of Boreal ammonites and buchiid bivalves during the latest Berriasian, albeit less significant than during the Valanginian, with boreal ammonites known from western Kazakhstan (Mangyshlak, see Luppov et al., 1988) and Boreal buchiid bivalves recorded from the Berriasian of Crimea and

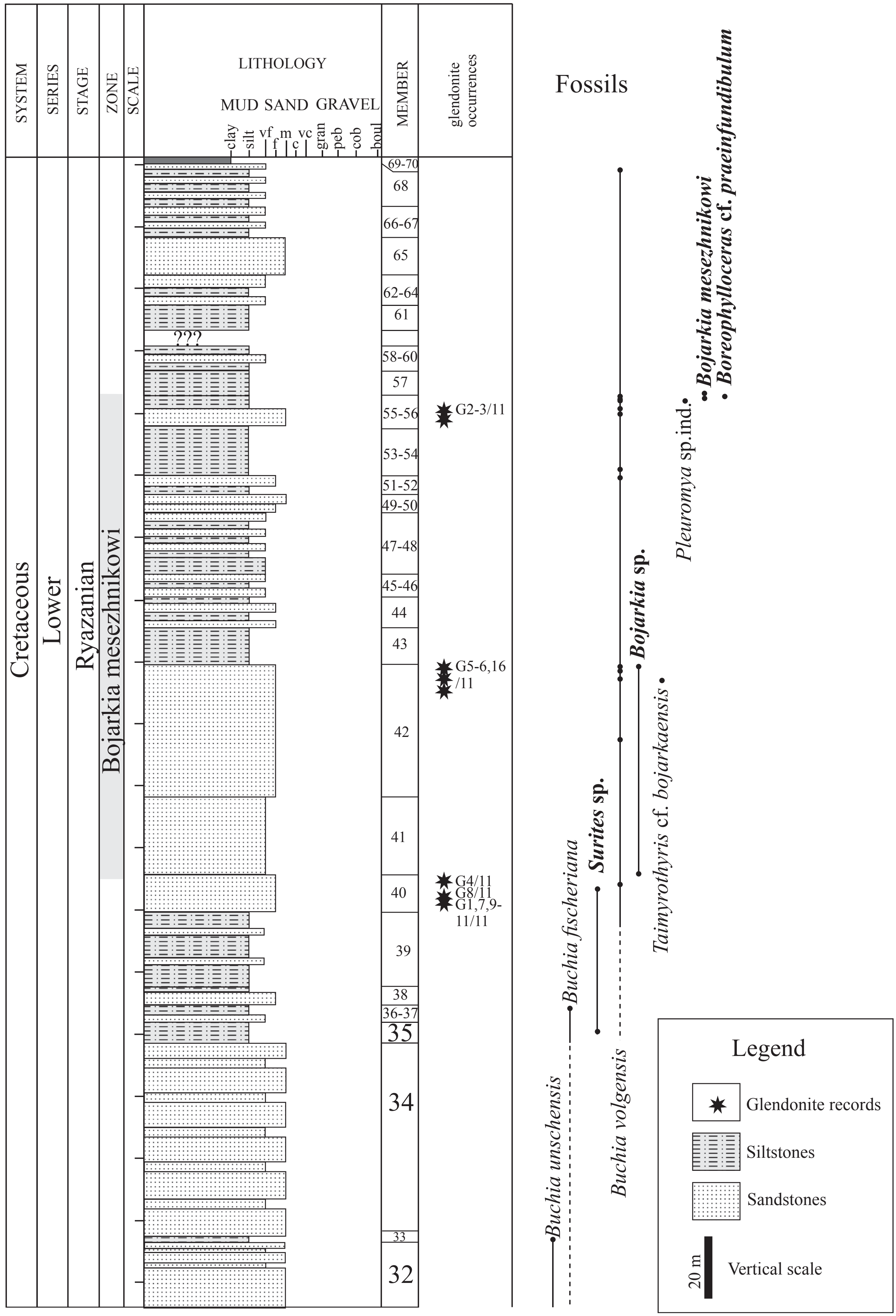

Fig. 4. Stratigraphic log and distribution of fossils and glendonites through the Chucha section.

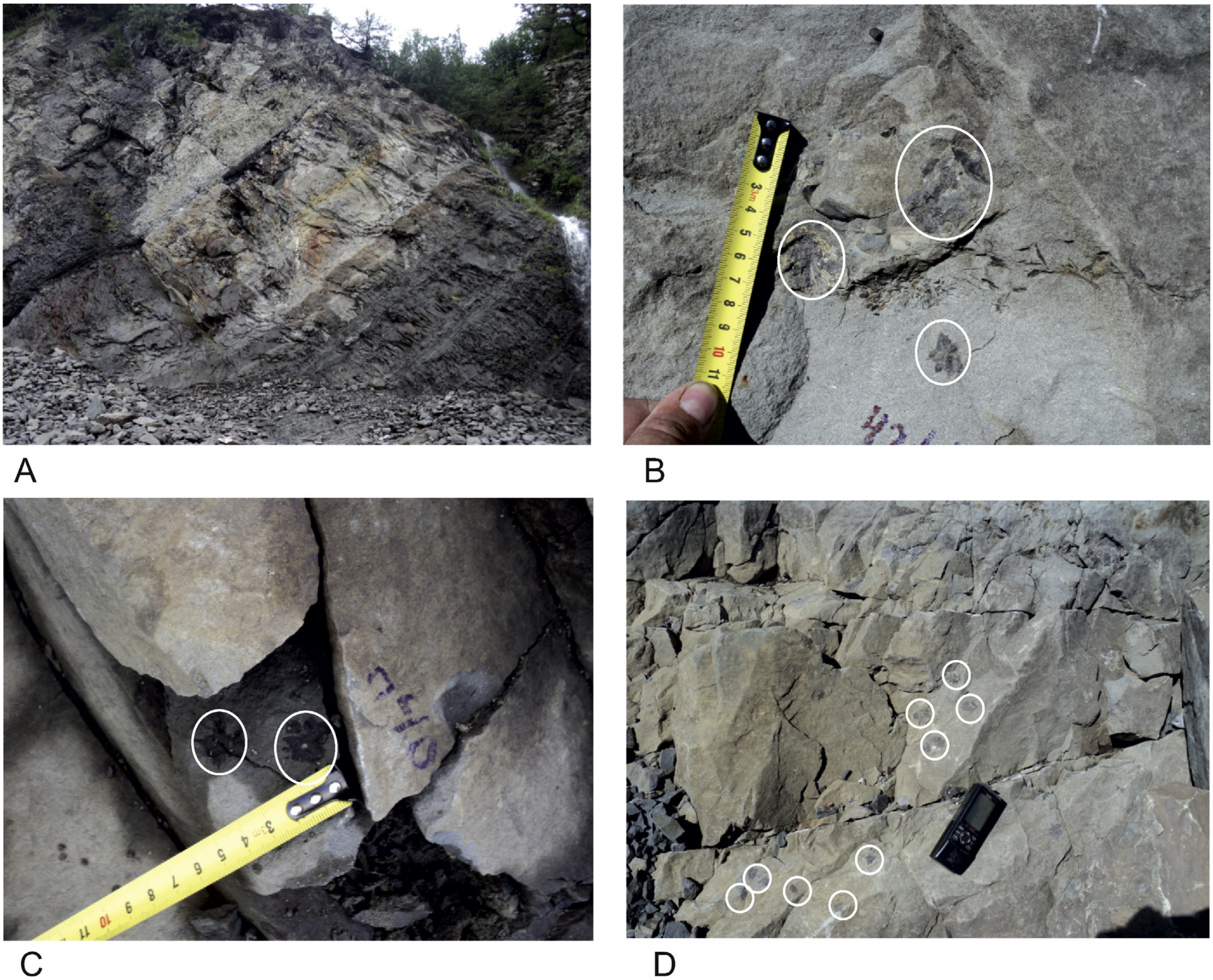

Fig. 5. Field photos of the Chucha section and glendonites. A – general view on the members 54–57; B – glendonites in the member 42; C – glendonites in the member 40; D – glendonites from the top of member 42. Glendonites at figures B–D are marked by white circles.

the northern Caucasus (Zakharov and Kasumzadeh, 2005). Recent studies of Berriasian ammonites (Mitta and Ploch, 2012) in Poland also indicate the presence of Boreal *Surites* in the Polish Trough. During the late Berriasian, northward penetration of Tethyan bivalves and ammonites was relatively weak, as their records are known only from the Russian Platform, with the northernmost penetration of the himalayitid ammonite *Riasanites* restricted to the Pechora basin and berriasellids only discovered south of the latitude of Moscow. Such a pattern of molluscan immigration could be caused by a global climatic cooling during the late Berriasian. In contrast with the distribution of Boreal and Tethyan molluscs described above, Late Jurassic molluscan immigrations in many cases were characterized by nearly equal northward penetration of Tethyan taxa and southward penetration of Boreal taxa, and thus were controlled primarily by the presence of suitable ocean gateways (Zakharov and Rogov, 2003). Although published TEX_{86} data suggest a generally warm and equable climate during the Early Cretaceous (Littler et al., 2011; Jenkyns et al., 2012), this paleoclimatic interpretation could be challenged as the studied samples come from marine localities surrounded by continental landmasses. The TEX_{86} proxy is strongly influenced by the influx of additional organic material from terrestrial sources, which can increase temperature estimates calculated using the TEX_{86} proxy and lead to an overestimation of ambient seawater temperature (Ho et al., 2014). Nunn (2007) describe oxygen isotope data from the Boyarka reference section (Khatanga depression) indicating a wide range of palaeotemperatures, including near-freezing, during the Berriasian–Valanginian (see Fig. 2). It should be noted that Zakharov and Radostev (1975) (Fig. 2) reported the gradual decrease of salinity during the Berriasian–Valanginian in the Boyarka area, which could shift oxygen isotope data to more negative values and result in warmer paleotemperature estimates if this salinity effect is not taken into account. The late Berriasian–Hauterivian time interval is also associated with a sea-level drop (Haq, 2014, see also Fig. 2). Additional evidence for cold-climate intervals during the Early Cretaceous could also be derived from the distribution of ice-rafted material. It should be noted, however, that lots of examples of late Aptian dropstones in both the northern and southern hemispheres are known (Pickton, 1981; Frakes and Francis, 1988; Markwick and Rowley, 1998; Rodríguez-López et al., 2016), while suspected ice-rafted dropstones of Berriasian age have only been reported by Epshteyn

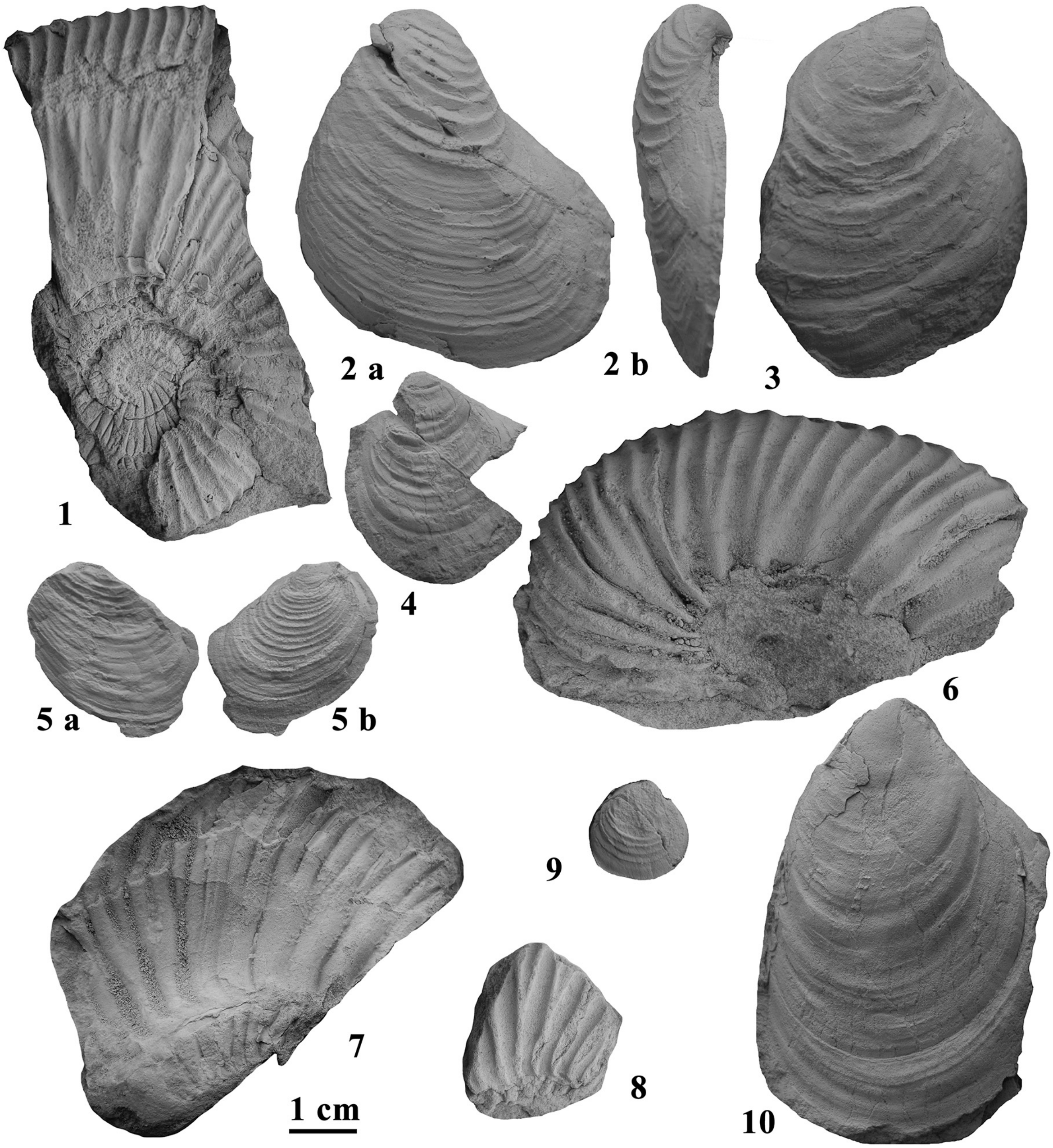

Fig. 6. Upper Berriasian (upper Ryazanian) key ammonites and bivalves from the Chucha section. These specimens are stored in the Vernadsky Geological Museum (Moscow). All specimens are coated with ammonium chloride. Scale bar = 1 cm. 1 – *Bojarkia mesezhnikovi* Schulgina, specimen no. BP-11307, member 56; 2–3, 10. *Buchia volgensis* (Lahusen), 2 – specimen no. BP-11314, 0,7 m below the top of the member 56, left valve; 3 – specimen no. BP-11309, member 56, right valve; 10 – specimen no. BP-11315, member 39; 4, 9. *Buchia unschensis* (Pavl.), 4 – specimen no. BP-11312, 0,1 m below the top of the member 33, left valve; 9 – specimen no. BP-11318, member 33; 5. *Buchia fischeriana* (d'Orb.), specimen no. BP-11320, 1 m below the top of the member 37, a – left valve, b – right valve; 6. *Bojarkia* sp., specimen no. BP-11316, 0,4 m below the top of the member 42; 7–8. *Surites* sp., 7 – specimen no. BP-11308, member 35; 8 – specimen no. BP-11319, member 40.

(1978) from the Oloy trough (North-East Russia). The presence of "carbonate crystal rosettes" (potentially glendonites) has been noted by Mountjoy and Proctor (1969) from the upper Berriasian of Arctic Canada. The stratigraphic position of these records, in the upper part of an interval characterized by *Buchia okensis*, a little below the FAD of *B. volgensis*, is slightly older than those from Cape Chucha. Therefore, our finding of glendonites from well dated upper Berriasian strata of northeastern Siberia is one of the most conclusive indicators of a late Berriasian cooling event. However, the relative scarcity of Berriasian glendonite occurrences compared with their Valanginian distribution suggests that near-freezing conditions suitable for ikaite precipitation occurred only occasionally and during short discrete episodes in the late Berriasian. In the studied section, glendonites occur only within sandstones (members 40, 42 and 55) and are missing from the fine-grained strata (Fig. 3). Modern glendonites usually form between ~0.5 m and ~30 m below the sediment/water interface, mainly within the range from 1 to 3 m (see examples Kodina et al., 2003; Lu et al., 2012; Geptner et al., 2014). We suggest that ikaite precipitation occurred during the deposition of silty members 43 and 56, which are overlain by glendonite-bearing sandy units, as the higher porosity of sandy sediments was more favorable for ikaite

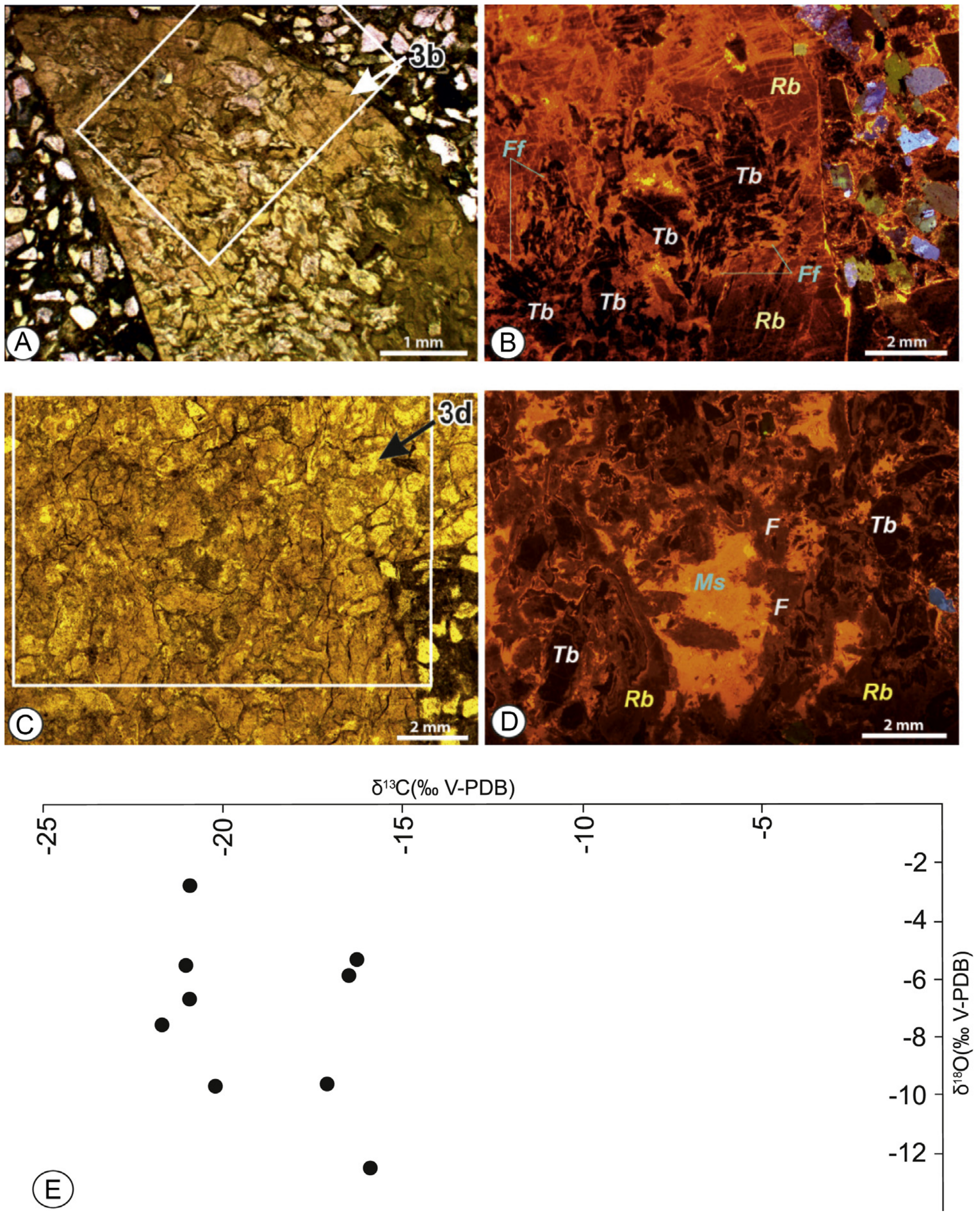

Fig. 7. Thin sections and CL-images of glendonites, showing microgranular aggregates and most of the morphological and respective chemical, types (generations) of calcite: (A) – single glendonite in siltstone, G-11-16; (B) – magnified fragment of (A) under cathodoluminescence; (C) – glendonite cluster, G-11-3; (D) – magnified fragment of (C) under cathodoluminescence; (E) – Oxygen vs. carbon stable isotope values in studied glendonites. The older generations of calcite (none and weakly luminescent): *Tb* – tabular, *Rb* – rhombohedral, *F* – fibrous; the younger generations (bright): *Ff* – fine-fibrous; *Ms* – mosaic; (E) – plot showing stable isotope composition of studied glendonites.

formation. We suggest that the few discrete levels of glendonite occurrences indicate near-freezing temperatures of the sea bottom and could reflect transient abrupt cooling events during the late Berriasian.

5. Conclusions

We present here the first data on Berriasian (Ryazanian) glendonite findings from the paleontologically well dated Lower Cretaceous succession of northeastern Siberia, which suggest a revision of the timing of initiation of Early Cretaceous cooling in the high latitudes. The stratigraphic interval across which the glendonites have been found in Northeast Siberia is restricted to the late Berriasian, based on detailed *Buchia* and ammonite biostratigraphy. Stable carbon isotope ($\delta^{13}C$) values of studied glendonites suggest the precipitation of ikaite from normal shallow marine water and along with other lines of evidence, support their usage as a paleoclimate proxy. A review of all known occurrences of Lower Cretaceous glendonites in both the northern and southern hemispheres reveals that peaks in glendonite distribution correlate with episodes of global climatic cooling, with the most prominent during the Valanginian and late Aptian. However, our finding of glendonites within late Berriasian strata in northeastern Siberia, accompanied by a significant shift in fossil assemblages reported from other high latitude regions (Vakhrameyev, 1982), suggests that the initiation of the high-latitude Early Cretaceous cooling events should be dated as late Berriasian rather than Valanginian. Late Berriasian to Hauterivian, along with late Aptian, cooling events also correspond to long-term sea-level falls, which may have a glacio-eustatic control (Fig. 2).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.cretres.2016.11.011.