Earth System
Open Access
Science
Data
Discussions

Database of global glendonite and ikaite records throughout the Phanerozoic

Mikhail Rogov[1], Victoria Ershova[1,2], Oleg Vereshchagin[2], Kseniia Vasileva[2], Kseniia Mikhailova[2], Aleksei Krylov[2,3]

5   [1] Geological Institute of RAS, Moscow 119017, Russia

[2] Institute of Earth Sciences, St. Petersburg State University, 199034 St. Petersburg, Russia

[3] VNIIOkeangeologia, 190121, St. Petersburg, Russia

Correspondence to: Mikhail Rogov (russianjurassic@gmail.com)

10

Abstract. This database of Phanerozoic occurrences and isotopic characteristics of metastable cold-water calcium carbonate hexahydrate (ikaite; $CaCO_3 \cdot 6H_2O$) and their associated carbonate pseudomorphs (glendonites) has been compiled from academic publications and open-access reports. Our database including 690 occurrences reveals that glendonites characterize cold-water environments, although their distribution is highly irregular in space and time. A significant body of evidence

15   suggests that glendonite occurrences are restricted mainly to cold-water settings, however they do not occur during every glaciation or cooling event of the Phanerozoic. While Quaternary glendonites and ikaites have been described from all major ocean basins, older occurrences have a patchy distribution, which may suggest poor preservation potential of both carbonate concretions and older sediments.

The data file described in this paper is available on Zenodo at https://doi.org/10.5281/zenodo.3991964 (Rogov et al., 2020).

1 Introduction

20

Metastable cold-water calcium carbonate hexahydrate (ikaite; $CaCO_3 \cdot 6H_2O$) and their associated carbonate pseudomorphs (glendonites) have attracted considerable attention during the past few decades, mainly due to their utility for palaeoenvironmental (especially palaeoclimatic) reconstructions (Kemper and Schmitz, 1975, 1981; Kaplan, 1978, 1979, 1980; Suess et al., 1982, among others). Carbonate pseudomorphs of metastable ikaite have acquired a number of different

25   names (anthraconite, glendonite, thinolite, jarrowite, pseudogaylussite, gennoishi, hokou-seki, White Sea hornlets, polar euhedrons, barleycorn, Gerstenkörner, hedgehogs, see Supplementary), and despite nearly 200 years of study (since the earliest papers by Sokolov, 1825; Freisleben, 1827; Pander, 1830), their distribution and formation mechanisms are still poorly understood. We use the most common name for these pseudomorphs (glendonite), which is derived from the famous glendonite-bearing locality, Glendon (NSW, Australia, see Dana, 1849; David et al., 1905). Modern ikaite occurs in a wide

30   range of cold-water environments. Ikaite microcrystals have been recorded in sea ice and cold caves, ikaite tufa has been

reported from shallow marine and lacustrine settings, and macrocrystals and their aggregates have been described from hypersaline springs, lacustrine and marine sediments, ranging from littoral environments to abyssal depths (up to ~4,700 m) (Pauly, 1963; Stein, Smith, 1985; Ito, 1996; Dieckmann et al., 2008; Last, 2012; Geptner et al., 2014; Oehlerich et al., 2015). Occurrences of ikaite pseudomorphs (glendonites) in the geological record are characterized by a slightly less diverse range

35   of palaeo-environments. Ancient glendonites have been mainly described from marine clastic rocks, although they have been discovered in caves and lacustrine deposits of Neogene age.

The first attempts at a comprehensive review of glendonite occurrences through geological time were undertaken by M.E. Kaplan (1978, 1980), who summarized the available information about glendonite findings throughout the world and publicized their importance for palaeoclimatic studies. During the last 40 years, numerous papers on glendonite and ikaite

40   occurrences have been published, along with new geochemical data. These geochemical data mainly include stable carbon and oxygen isotope values from ikaite and glendonite, along with a limited number of clumped isotope and Sr isotope data (Nenning, 2017; Rogov et al., 2018). Information on glendonite occurrences is scattered throughout hundreds of papers on regional geology, explanatory notes to geological maps, and other reports, but until now, no single reference database of global glendonite distribution throughout the Phanerozoic has been compiled.

45   This paper presents a new single reference database of ikaite and glendonite records from the Early Cambrian until the present. It is based on the analysis of numerous papers (including unpublished reports) and museum collections, as well as on data collected during the last 15 years by the authors. All records were averaged to substages (if possible) without further subdivision, and nearby occurrences were considered as a single locality if the distance between separate data points was less than 1−2 km. As glendonite occurrences were frequently mentioned but not imaged or fully described in many

50   publications, consideration of such records as true glendonites was mainly based on additional lines of evidence supporting glendonite occurrence within the same region or stratigraphic interval.

2 General information about ikaite and glendonite composition

2.1 Mineralogy

Single crystal X-ray structure determinations (e.g., Hesse and Kuppers, 1983; Swainson and Hammond, 2001;

55   Lennie et al., 2004) have shown that ikaite crystallizes in the spacegroup $C2/c$, and its structure consists of $CaCO_3 \cdot 6H_2O$ units with each Ca bound to six water molecules and a bidentate carbonate group to yield 8-fold coordination. Hydrogen bonding links $CaCO_3 \cdot 6H_2O$ moieties to form the crystal structure (Lennie et al., 2004).

Ikaite has been found in natural modern-day environments at temperatures ranging from −2°C to +7°C (Dieckmann et al., 2008; Huggett et al., 2005; Suess et al., 1982). The relative abundance of ikaite in nature is attributed to its

60   metastability (e.g., Marland 1975). Marland (1975) and Shahar et al. (2005) suggest that low temperatures and high pressures are the main factors controlling ikaite stabilization. However, Marland (1975) and Shahar et al. (2005) also suggest that

metastable ikaite should not naturally occur on Earth's surface and other carbonates (e.g., calcite, vaterite, aragonite) should crystallize instead. The main factors proposed for ikaite stabilization at Earth's surface are elevated contents of sulphate/phosphate/magnesium ion in the crystallization medium, or high pH.

65   Unfortunately, very few studies have investigated the chemical composition of modern natural ikaite (e.g., Suess et al., 1982; Pauly, 1963; Schubert et al., 1997). These few studies did not identify sulphate or phosphate ions as constituents of natural ikaite, whereas magnesium content ranged up to ~0.5 wt.% MgO (Pauly, 1963; Schubert et al., 1997). Schubert et al. (1997) reported minor amounts of Mg, Fe and Al ($540\pm27\mu g\ g^{-1}$, $43.2\pm1.2\mu g\ g^{-1}$, and $19.4\pm0.2\mu g\ g^{-1}$, respectively) in two dried ikaite subsamples, along with a total organic carbon content of 0.15%. It's important to note that ikaite unit cell

70   parameters provided in published data differ significantly (e.g., Rysgaard et al., 2013), which could indicate chemical composition variations of studied ikaites.

Outside of the aqueous environment, ikaite rapidly disintegrates into a mush of water and anhydrous calcium carbonate (e.g., Pauly, 1963; Bischoff et al., 1993), which can be in the form of vaterite (e.g., Shaikh, 1990; Ito, 1996; Ito et al., 1999), aragonite (e.g., Stein and Smith, 1986; Council and Bennett, 1993), or calcite (e.g., Pauly, 1963; Bischoff et al.,

75   1993). Ito (1998) suggested that the rate of ikaite transformation is dependent on the availability of water (which increases the rate of transformation) and the presence of magnesium ion (which inhibits the transformation to both calcite and vaterite). Purgstaller et al. (2017) showed that the formation of anhydrous calcium carbonates is controlled mainly by the prevailing physicochemical conditions, such as the Mg/Ca ratio of the aqueous medium and water availability.

Ikaite-glendonite transformation begins with ikaite destabilization, resulting in a cloudy (Suess et al, 1982) or

80   whitish (Kodina, 2003) interior of the ikaite crystals. The replacement of ikaite by anhydrous calcium carbonate ($CaCO_3 \cdot 6H_2O \rightarrow CaCO_3 + 6H_2O$) leads to a primary volume loss of 70−80% (Suess et al, 1982; Fairchild et al., 2016) and disintegration, as the density of ikaite is much less than of anhydrous calcium carbonates. However, the primary morphology of ikaite can be preserved due to fast seawater cementation (Huggett et al., 2005; Selleck et al., 2007). Seawater diagenesis of ikaite takes place in the sulphate-reduction zone and glendonite can be subsequently altered during burial diagenesis,

85   where it can be replaced by younger carbonate generations or non-carbonate minerals such as silica (Wang et al., 2017), dolomite (Loog, 1980) or gypsum (Mikhailova et al., 2019).

2.2 Morphology

Unlike calcite and aragonite, ikaite is typically characterized by pyramidal, spear-like (e.g., Dieckmann et al., 2008; Tang et al., 2009; Rysgaard et al., 2014) or stellate crystals (e.g., Selleck et al., 2007) with square-prismatic cross-sections

90   (e.g., Swainson and Hammond, 2001) (Fig. 1). In some cases, the shape of the original ikaite crystal is preserved as a pseudomorph (e.g., Kaplan, 1978; Shearman and Smith, 1985; Kemper, 1987). The size of natural modern ikaite clusters and solitary crystals varies from ~ 5 μm to ~10 cm. Glendonites display a number of internal structures, including (1) visible core and rim with no apparent zonation; (2) core and alternating mm-scale rims, forming distinct zonation and (3) homogeneous

bodies from the centre to the edges. Glendonites are characterized by a size range which mainly lies between 0.5 and 15−20
95   cm, with some of the largest specimens ranging up to 1 m in diameter or in length. Microglendonites are rarely reported;
however, their size is similar to that of ikaite microcrystals, ranging from 5 to 10 μm (Oehlerich et al., 2013). Glendonite
colour varies from light yellow and whitish if weathered to dark brown.

Due to water removal during ikaite to anhydrous calcium carbonate transformation, glendonites are frequently
porous and contain small pieces of adjacent sediment (such as sand grains, microfossils, clay particles etc) and several
100   successive carbonate generations.

2.3 Petrography and cathodoluminescence

Several mineralogical studies have been performed on glendonites (David et al., 1905; Boggs, 1972; Kaplan, 1979;
Larsen, 1994; McLachlan et al., 2001; Greinert and Derkachev, 2004; Huggett et al., 2005; Selleck et al., 2007). These
studies showed that glendonites are composed of 2−4 consecutive carbonate generations, which differ in morphology and
105   chemical composition (Fig. 2). Calcite is the only anhydrous calcium carbonate, which was found as replacive phase after
ikaite in natural pseudomorphs (glendonites).

The first carbonate generation comprises blocky calcite crystals, which typically show euhedral, triangular, or
bipyramidal shapes, or irregular habits (e.g., Greinert and Derkachev, 2004; Huggett et al., 2005; Qu et al., 2017). Crystals
are clear to opaque, with concentric zonation formed by an admixture of clay or organic matter (Huggett et al., 2005) and
110   show no luminescence (e.g., Larsen, 1994; Morales et al., 2017). These crystals are always Mg and Fe depleted or almost
pure $CaCO_3$. This first generation is interpreted as ikaite-derived calcite (Huggett et al., 2005).

Ikaite-derived calcite does not form the frame of the glendonite and is always supported by cements of different
morphology. The first ikaite-derived calcite generation can be overgrown by needle-like or spherulitic calcite cement (e.g.,
Boggs, 1972; Kaplan, 1979; Huggett et al., 2005). Crystals are a yellowish or amber colour under the optical microscope
115   with a bright cathodoluminescence (Frank et al., 2008; Teichert, Luppold, 2013, among others). This carbonates are typically
Mg or/and Fe-rich. These carbonates can contain inclusions of pyrite (either as idiomorphic crystals or with framboidal
habits; Greinert and Derkachev, 2004). Blocky, sparry or radiaxial fibrous calcite can occupy the residual pore space
(Teichert, Luppold, 2013) or replace carbonate rims and ikaite-derived calcite (Vasileva et al., 2019), typically displaying an
orange to dark red cathodoluminescence.

120   Besides multiple carbonate generations, some detrital material is typically also found in glendonites. Inclusions of
quartz, feldspar (plagioclase/K-feldspar), volcanic glass, olivine, pyroxene, amphibole, magnetite, hematite, and mica can
also occur (e.g., Astakhova and Sorochinskaya, 2000).

3 Isotopic composition of ikaite and glendonite

Stable carbon and oxygen isotopic values of glendonites and ikaites can encompass a broad range of values (fig. 3).
125 $\delta^{13}C$ values of ikaite range from −42.7 to +8.3 ‰PDB, while $\delta^{18}O$ values range from −17 to +3.60 ‰PDB (Dahl, Burchardt, 2006; Chaikovsky, Kadebskaya, 2014; Kodina et al., 2003; Krylov et al., 2015; Last et al., 2013; Lu et al., 2012, Stein, Smidt, 1985; Zabel, Schultz, 2001). The stable isotopic compositions of bulk glendonites and individual carbonate generations differ significantly. $\delta^{13}C$ values of bulk glendonite samples range from −52.4 to +0.6 ‰PDB, while $\delta^{18}O$ values range from −16.6 to +4.8 ‰PDB (Derkachev et al., 2007; Geptner et al., 1994, 2014; Qu et al., 2017; Willscroft, 2013;
130 Vickers et al., 2018; Morales et al., 2017; Teichert, Luppold, 2013, among others). $\delta^{13}C$ values of ikaite-derived calcite range from −27.7 to −14.3 ‰PDB, while $\delta^{18}O$ values range from −5.1 to +1.3 ‰PDB (Frank et al., 2008). Lastly, $\delta^{13}C$ values of secondary carbonate cements range from −20.2 to −3.9 ‰PDB, while $\delta^{18}O$ values range from −23.1 to −6.2 ‰PDB (Frank et al., 2008; Vasileva et al., 2019; see fig. 3). Based on the range of $\delta^{13}C$ values, the source of carbon during ikaite crystallization and ikaite-glendonite transformation was derived from dissolved inorganic carbon (DIC), decaying organic
135 matter or methane seeping through underlying strata.

Although Mesozoic and Cenozoic glendonites are enriched in Sr, they do not record primary $^{87}Sr/^{86}Sr$ ratios of seawater and show enrichment in ^{86}Sr compared to coeval marine carbonates (Rogov et al., 2018; author's data).

4 General information about ikaite and glendonite composition

4.1 Data mining

140 The authors have collected ikaite and glendonite specimens belonging to different stratigraphic intervals from numerous localities over the last 15 years. In addition to our specimens, we also studied glendonites from museum collections and analyzed information about glendonite/ikaite occurrences from numerous publications, using advanced online searches (including all of the different glendonite names mentioned above) along with library searches (see supplementary information for details). The locations of all ikaite/glendonite-bearing sites are shown on Fig. 4. The total amount of records
145 included in the database is 690, based on 323 references, our investigations and communications by our colleagues.

4.2 Database contents

The database is provided as an Excel 2003 file (.xls). The main sheet of the database includes the following information: locality, age (substage/formation/Ma), modern coordinates, palaeolatitudes (calculated using paleolatitude.org; see van Hinsbergen et al., 2015), references, depositional settings, and host rock. Some datapoints lack information about
150 palaeolatitude (as they were derived from terrains with an uncertain geographic position) or host rock (in the case of some museum specimens). We aim to provide locality and coordinate information as precisely as possible. However, in some cases the available locality information was rather imprecise (for example, 'basin of river 'X'', or 'mountain ridge 'Y''),

although the effects of such imprecise location details on our analysis of (palaeo)latitude distribution are considered insignificant. Palaeolatitudes of Paleogene and Neogene glendonites from the northern margin of the Pacific cannot be

155   determined using paleolatitude.org. We chose a similar palaeolatitude to the present-day for the Paleogene and Neogene based on Bazhenov et al. (1992), Harbert et al. (2000) and Kovalenko and Chernov (2003). Palaeomagnetic data from Sakhalin (Weaver et al., 2003; Zharov, 2005) are more complicated and suggest a northward drift during the Cenozoic. The complex tectonic structure of the island precludes an accurate calculation of palaeolatitude for each time slice and locality from Sakhalin.

160   Additional sheets include stable carbon and oxygen isotope data and references.

5 Data overview

5.1 Glendonite distribution in space and time

A significant irregularity in Phanerozoic glendonite distribution is apparent in Fig. 4, which illustrates glendonite locations plotted on present-day geography. However, when the palaeolatitudes of glendonite samples are taken into account,

165   it becomes clear that they mainly formed in high latitudes throughout the Phanerozoic (Fig. 5). Interestingly, most glendonite occurrences have been reported from the northern Hemisphere, which is challenging to explain. Only Quaternary records of ikaite/glendonite occurrences are fairly evenly distributed across the cold-water environments of both the northern and southern Hemispheres and within all ocean basins, including deep-water sites at low and near-equatorial latitudes. Glendonite occurrences within the Arctic Ocean (Kara Sea, Laptev Sea, Chukchi Sea) and the Sea of Okhotsk are more

170   abundant compared to other regions, which can be partially explained by sampling bias, as these regions have been particularly actively studied during the past few decades. In contrast to other time slices, Neogene glendonites are restricted to the northern margin of the Pacific, except for a single reported occurrence in Arctic Canada. Glendonite occurrences are particularly common at numerous localities along the western coast of the Pacific Ocean, including from Japan, Sakhalin and Kamchatka, where their presence is used as a diagnostic feature for numerous formations and members. Furthermore, one of

175   these formations (Gennoishi Formation of Sakhalin Island) is named after the Japanese name for glendonites (gennoishi, 玄 能石). Coeval glendonite records also occur along the eastern Pacific coast, where they were first recognized by Dana (1849). Paleogene glendonites typically occur in the same region as Neogene occurrences but are also abundant in the North Atlantic area. North Atlantic occurrences include giant glendonites from the Mors and Fur islands (Denmark), as well as abundant Spitsbergen glendonites. It should be noted that the giant glendonites from Denmark are mainly embedded in post-

180   PETM rocks, but clumped isotope data from the glendonites are indicative of near-freezing temperatures (Nenning, 2017).

The Late Cretaceous was characterized by a global greenhouse climate and lacks any glendonite occurrences. Lower Cretaceous glendonites are known from all stages and occurred in high latitudes of both the northern and southern Hemispheres. However, no occurrences are known from the most prominent warming event (early Aptian) and only a single

185   occurrence has been reported from the Barremian. The paucity of Barremian glendonites may be related to the HALIP-induced regression in the Arctic and scarcity of marine deposits of this age in the high northern latitudes. Glendonites are particularly abundant within the Valanginian, Aptian and Albian sediments of Svalbard (Kemper, Schmitz, 1981; Vickers et al., 2018) and Arctic Canada (Herrle et al., 2015), along with the Aptian of Australia (de Lurio, Frakes, 1999). Berriasian glendonites, which mark the initiation of the Early Cretaceous cold interval, are rare and mainly described from Siberia (Rogov et al., 2017).

190   Peak glendonite abundance, comparable to that of the Quaternary, occurs during the Middle Jurassic, but nearly all occurrences of this age have been described from northern Eurasia, with no occurrences in the southern Hemisphere. The numerous Middle Jurassic glendonite occurrences coincide with long-term cooling of the Arctic Ocean, primarily instigated by changes in oceanic circulation following closure of the Viking corridor (Korte et al., 2015). The Late Jurassic is characterized by a significant decrease in glendonite abundance towards the end of this time interval. Lower Jurassic

195   glendonite occurrences are restricted to the upper Pliensbachian and a few in the upper Toarcian.

No glendonites have been confidently identified from the Triassic Period. Only two suspicious reports of pseudomorphs resembling glendonites from low-latitude lagoonal environments were mentioned by Kaplan (1979), based on reports by van Houten (1965) and Kostecka (1972).

Permian glendonite occurrences display a similar distribution to Lower Cretaceous occurrences. They are also

200   known from both the northern and southern Hemisphere, but are especially abundant in Tasmania and Australia (Selleck et al., 2007), while in the northern Hemisphere they are mainly found in north-east Asia (Biakov et al., 2013), accompanied by rare findings in the rest of Siberia and Novaya Zemlya. Possible glendonites from Turkey and Saudi Arabia are poorly described.

Carboniferous glendonites are uncommon and mainly known from the Upper Carboniferous of Gondwana. In

205   addition, glendonites were also reported from low-latitude carbonate deposits of Alberta, Canada (Brandley, Krause, 1994).

There is a notable absence of glendonite occurrences for a prolonged period of time below the Carboniferous, spanning the Devonian, Silurian and Middle−Upper Ordovician. Lower Ordovician glendonites have only recently been discovered and described (Popov et al., 2019; Mikhailova et al., 2019), as until recently, they were known as a kind of 'anthraconite' and were not considered as glendonites. Their findings are restricted to Baltoscandia. Cambrian glendonites

210   are less frequent but are mainly known from the same region and same facies (black shales) as the Lower Ordovician glendonites. A few Cambrian glendonites were also found in sandstones, and a single occurrence is known from outside the Baltic region in South Korea (Chon, 2018).

5.2 Glendonites as palaeoenvironmental indicators

Over the past few decades, glendonites have been used as a proxy for cold-water environments and/or cooling

215   towards glaciation events (Kaplan, 1980; Kemper, Schmitz, 1981; Suess et al., 1982; De Lurio, Frakes, 1999; Price, 1999; Swainson, Hammond, 2001; Selleck et al., 2007; Rogov et al., 2017, among others). This interpretation is grounded on the discovery of ikaite precipitation during early diagenesis at low temperatures in Holocene−Pleistocene marine sediments,

confined to layers with elevated carbonate alkalinity, high pH, and high concentrations of dissolved phosphate (e.g., Kodina et al., 2003; Greinert & Derkachev, 2004; Zhou et al., 2015). The increase in alkalinity, which promotes crystallization of

220   ikaite, is caused by biogeochemical processes in marine sediments, such as organoclastic sulphate reduction and/or anaerobic oxidation of methane (Schubert et al., 1997; Suess et al., 1982; Kodina et al., 2003; Krylov et al., 2015; Lu et al., 2012; Zabel & Schulz, 2001).

However, experiments carried out during the last few years have revealed at least short-term ikaite stability at much higher temperatures, up to 30-35° C (Clarkson et al., 1992; Rodríguez-Ruiz et al., 2014; Purgstaller et al., 2017; Tollefsen et

225   al., 2020). Ikaite stability at high temperatures had only previously been demonstrated under high pressures (van Valkenberg et al., 1971). It is important to note that high-temperature experiments were only conducted on ikaite microcrystal precipitates, and there is currently no evidence for stability of 'typical' centimetre to decimetre-sized ikaite crystals and ikaite clusters at similarly high temperatures.

Our analysis of glendonite distribution through space and time has revealed a complex relationship between climate

230   change and glendonite occurrence. On the one hand, nearly all glendonite findings known to date (except for a few doubtful ones) are associated with cold-water environments and are usually found in sediments with high-latitude low diversity faunas and dropstones (e.g., Price, 1999). On the other hand, no glendonites have been discovered from two prominent glacial intervals in Earth's history (the Late Ordovician and Late Devonian), and their pre-Quaternary occurrences are very irregular, changing to the southern Hemisphere in early Paleozoic to mostly northern Hemisphere in Mesozoic and Cenozoic.

235   However, the roles of additional factors influencing ikaite precipitation remain unclear.

6 Data availability

The .xls file containing this database is available on Zenodo https://doi.org/10.5281/zenodo.3991964 (Rogov et al., 2020). Updates will be available under the same web address as well as through direct hyperlink (http://jurassic.ru/_pdf/glendonites_database.xls) or can be requested directly from the first author of this paper.

240 # 7 Conclusions

Our new reference glendonite and ikaite database can be used to show that glendonites typically occur in cold-water environments throughout the Phanerozoic, but their distribution is highly irregular in space and time. Although there is no evidence for glendonite formation in warm-water settings, not all of Earth's major glaciations and other cooling events are associated with glendonite occurrences. Significant irregularity also occurs in spatial glendonite distribution throughout the

245   Phanerozoic. Quaternary glendonites and ikaites have been described from all ocean basins of the world, while pre-Quaternary glendonites have not been found in many regions which would appear to be suitable for ikaite precipitation.

Earth System
Science
Data
Open Access
Discussions

Author contributions

MR designed the study and collected data on stratigraphic and geographic distribution of glendonite, VE did the overall editing and supervision, OV collected data on morphology and mineralogical composition, KV and KM were responsible for data on isotopic composition, petrography and cathodoluminescence, AK provided data on ikaite distribution and diagenesis. All authors discussed the results and participated in preparation of the paper.

Competing interests

The authors declare that they have no conflict of interest.

Acknowledgements

Earth System
Science Data
Open Access
Discussions

Financial support

References

Bazhenov, M. L., Burtman, V. S., Krezhovshikh, O. A. and Shapiro, M. N.: Paleomagnetism of Paleogene rocks of the Central—East Kamchatka and Komanorsky Islands: tectonic implications, Tectonophysics, 201(1–2), 157–173, doi:10.1016/0040-1951(92)90181-5, 1992.

280   Biakov, A. S., Goryachev, N. A., Davydov, V. I. and Vedernikov, I. L.: The first finds of glendonite in permian deposits of the North Okhotsk Region, Northeastern Asia, Doklady Earth Sciences, 451, 716–718, doi: 10.1134/S1028334X13070210, 2013.

Brandley, R. T. and Krause, F. F.: Thinolite type pseudomorphs after ikaite: Indicators of coldwater on the subequatorial western margin of Lower Carboniferous North America, GSPG Memoir, 17, 333–334, doi: 10.11575/PRISM/30223, 1994.

285   Chon, S.-J.: First report of glendonite in the uppermost Cambrian, in GSA, Indiana, USA, 4-7 November 2018, 265-3, doi: 10.1130/abs/2018am-321990, 2018.

Clarkson, J. R., Price, T. J. and Adams, C. J.: Role of metastable phases in the spontaneous precipitation of calcium carbonate, J. Chem. Soc. Faraday Trans., 88(2), 243–249, doi:10.1039/ft9928800243, 1992.

Dana, J. D.: United States Exploring Expedition. During the years 1838, 1839, 1840, 1841, 1842. Under the command of
290   Charles Wilkes., 735 pp., 1849.

David, T. W. E., Taylor, T. G., Woolnough, W. G. and Foxall, H. G.: Occurrence of the pseudomorph glendonites in New South Wales, Records of the Geological Survey of New South Wales, 8, 162–179, 1905.

Dieckmann, G. S., Nehrke, G., Papadimitriou, S., Gottlicher, J., Steininger, R., Kennedy, H., Wolf-Gladrow, D. and Thomas, D. N.: Calcium carbonate as ikaite crystals in Antarctic sea ice, Geophys. Res. Lett., 35(8), doi:10.1029/2008GL033540,
295   2008.

Frakes, L. A., Francis, J. E. and Syktus, J. I.: Climate Modes of the Phanerozoic, Cambridge Univ. Press, Cambridge., 2005.

Freisleben, J. K.: Ueber einige interessante Vorkommnisse im Schlotztenleimen (Alluvialthon) bey Obersdorf, ohnweit Sangerhausen, Isis von Oken, 20, 334–337, 1827.

Geptner, A. R., Vetoshkina, O. S. and Petrova V.V.: New data on the composition of stable isotopes in glendonites of the
300   White Sea and their genesis, Lithol. Mineral. Resources, 49(6), 473–490, doi:10.1134/S0024490214060042, 2014.

Harbert, W., Kepezhinskas, P., Krylov, K., Grigoriev, V., Sokolov, S. and Aleksuitin, M.: Paleomagnetism and Tectonics of the Kamchatka Region, Northeastern Russia: Implications for Development and Evolution of the Northwest Pacific Basin, Polarforschung, 68, 297–308, 2000.

305 Herrle, J. O., Schroder-Adams, C., Davis, W., Pugh, A. T., Galloway, J. M. and Fath, J.: Mid-Cretaceous High Arctic stratigraphy, climate, and oceanic anoxic events, Geology, 43(5), 403–406, doi:10.1130/G36439.1, 2015.

van Hinsbergen, D. J. J., de Groot, L. V., van Schaik, S. J., Spakman, W., Bijl, P. K., Sluijs, A., Langereis, C. G. and Brinkhuis, H.: A Paleolatitude Calculator for Paleoclimate Studies, PloS one, 10(6), doi:10.1371/journal.pone.0126946, 2015.

310 van Houten, F. B.: Crystal casts in Upper Triassic Lockatong and Brunswick Formations, Sedimentology, 4(4), 301–313, doi:10.1111/j.1365-3091.1965.tb01553.x, 1965.

Ito, T.: Ikaite from cold spring water at Shiowakka, Hokkaido, Japan, Journal of mineralogy, petrology and economic geology, 91, 209–219, doi:10.2465/ganko.91.209, 1996.

Kaplan, M. E.: Calcite pseudomorphoses from the Jurassic and lower Cretaceous deposits of northern East Siberia, Soviet geology and geophysics, 12, 62–70, 1978. (in Russian)

315 Kaplan, M. E.: Calcite pseudomorphs (pseudogaylussite, jarrowite, thinolite, glendonite, gennoishi, White Sea hornlets) in sedimentary rocks. Review of major localities., VINITI., 39 pp., 1979. (in Russian)

Kaplan, M. E.: Calcite pseudomorphs (pseudogaylussite, jarrowite, thinolite, glendonite, gennoishi, White Sea hornlets) in sedimentary rocks: origins of the pseudomorphs, Lithol., Miner., Resour., 14, 623–636, 1980.

Karpinsky, A.: Ueber die cambrische, silurische und einige andere Ablagerungen in Gouwernement Pskow, Mining journal (Gorny zhurnal), 2, 261–270, 1887. (in Russian)

Kemper, E. and Schmitz, H. H.: Stellate nodules from the upper Deer Bay formation (Valanginian) of Arctic Canada, Geological Survey of Canada Paper, 75, 109–119, doi: 10.4095/103040, 1975.

Kemper, E. and Schmitz, H. H.: Glendonite - Indikatoren des polarmarinen Ablagerungsmilieus, Geol. Rundsch, 70(2), 759–773, doi: 10.1007/bf01822149, 1981.

325 King, C.: Report of the Geological Exploration of the Fortieth Parallel, Volume I: Systematic Geology, Professional papers of the Engeneer department US army, 761 pp., 1878.

Korte, C., Hesselbo, S. P., Ullmann, C. V., Dietl, G., Ruhl, M., Schweigert, G. and Thibault, N.: Jurassic climate mode governed by ocean gateway, Nat. Commun., 6, doi:10.1038/ncomms10015, 2015.

Kostecka, A.: Calcite paramorphs in the aragonite concretions, Ann. Soc. Geol. Pol., 42, 289–296, 1975.

330 Kovalenko, D. V. and Chernov, Ye. Ye.: Paleomagnetism and tectonic evolution of Kamchatka and Southern Koryakia, Russ. J. Pac. Geol., 22(3), 48–73, 2003.

Krylov, A. A., Logvina, E. A., Matveeva, T. M., Prasolov, E. M., Sapega, V. F., Demidova, A. L. and Radchenko, M. S. Ikaite (CaCO3*6H2O) in bottom sediments of the Laptev Sea and the role of anaerobic methane oxidation in this mineral-forming process, Proceedings of the Russian Mineralogical Society, 4, 61-75, 2015. (in Russian])

335 Last, F. M. and Last, W. M.: Lacustrine carbonates of the northern Great Plains of Canada, Sediment. Geol., 277–278, 1–31, doi:10.1016/j.sedgeo.2012.07.011, 2012.

Loog, A.: On the geochemistry of postsedimentary mineral formation in the Tremadocian graptolithic argillites of North

Estonia, Acta et Commentationes Universitatis Tartuensis, 527, 44–50, 1980. (in Russian)

de Lurio, J. and Frakes, L. A.: Glendonites as a paleoenvironmental tool: implications for early Cretaceous high latitude
340 climates in Australia - its composition and evolution, Geochim. Cosmochim. Acta, 63(7), 1039–1048, doi:10.1016/S0016-7037(99)00019-8, 1999.

Mikhailova, K., Vasileva, K., Fedorov, P., Ershova, V., Vereshchagin, O., Rogov, M. and Pokrovsky, B.: Glendonite-Like
Carbonate Aggregates from the Lower Ordovician Koporye Formation (Russian Part of the Baltic Klint): Detailed
Mineralogical and Geochemical Data and Paleogeographic Implications, Minerals, 9(9), doi:10.3390/min9090524, 2019.

345 Nenning, F.: Mega-glendonites in the Early Eocene Fur Formation. Unraveling paleoenvironmental conditions in the Danish
Basin and their influence on glendonite formation, Ph.D. thesis, Westfälischen Wilhelms-Universität Münster., 177 pp.,
2017.

Oehlerich, M., Mayr, C., Griesshaber, E., Lucke, A., Oeckler, O. M., Ohlendorf, C., Schmahl, W. W. and Zolitschka, B.:
Ikaite precipitation in a lacustrine environment–implications for palaeoclimatic studies using carbonates from Laguna Potrok
350 Aike (Patagonia, Argentina), Quat. Sci. Rev., 71, 46–53, doi:10.1016/j.quascirev.2012.05.024, 2013.

Oehlerich, M., Mayr, C., Gussone, N., Hahn, A., Holzl, S., Lucke, A., Ohlendorf, C., Rummael, S., Teichert, B. M. A. and
Zolitschka, B.: Lateglacial and Holocene climatic changes in south-eastern Patagonia inferred from carbonate isotope
records of Laguna Potrok Aike (Argentina), Quat. Sci. Rev., 114, 189–202, doi:10.1016/j.quascirev.2015.02.006, 2015.

Pander, C. H.: Beiträge zur Geognosie des Russischen Reiches. St.Petersburg, Karl Kray., 1830.

355 Pauly, H.: "Ikaite", a new mineral from Greenland, Arctic, 16(4), 263–264, doi: 10.14430/arctic3545, 1963.

Popov, L. E., Alvaro, J. J., Holmer, L. E., Bauert, L. E., Pour, M. G., Dronov, A. V., Lehnert, O., Hints, O., Mannik, P.,
Zhang, Z. and Zhang, Z.: Glendonite occurrences in the Tremadocian of Baltica: first Early Palaeozoic evidence of massive
ikaite precipitation at temperate latitudes, Sci. Rep., 9(1), 1–10, doi:10.1038/s41598-019-43707-4, 2019.

Price, G. D.: The evidence and implications of polar ice during the Mesozoic, Earth-Sci. Rev., 48(3), 183–210,
360 doi:10.1016/S0012-8252(99)00048-3, 1999.

Purgstaller, B., Dietzel, M., Baldermann, A. and Mavromatis, V.: Control of temperature and aqueous Mg2+/Ca2+ ratio on
the (trans-)formation of ikaite, Geochim. Cosmochim. Acta, 217, 128–143, doi:10.1016/j.gca.2017.08.016, 2017.

Rodriguez-Ruiz, I., Veesler, S., Gomez-Morales, J., Delgado-Lopez, J. M., Grauby, O., Hammadi, Z., Candoni, N. and
Garcia-Ruiz, J. M.: Transient Calcium Carbonate Hexahydrate (Ikaite) Nucleated and Stabilized in Confined Nano- and
365 Picovolumes, Cryst. Growth. Des., 4(2), 792–802, doi:10.1021/cg401672v, 2014.

Rogov, M. A., Kuznetsov, A. B., Konstantinova, G. V. and Turchenko, T. L.: The Strontium Isotopic Composition in
Glendonites of the Middle Jurassic in Northern Siberia, Doklady Earth Sciences, 482, 1168–1172,
doi:10.1134/S1028334X1809009X, 2018.

Rogov, M. A., Ershova, V. B., Shchepetova, E. V., Zakharov, V. A., Pokrovsky, B. G. and Khudoley, A. K.: Earliest
370 Cretaceous (late Berriasian) glendonites from Northeast Siberia revise the timing of initiation of transient Early Cretaceous
cooling in the high latitudes, Cretac. Res., 71, 102–112, doi:10.1016/j.cretres.2016.11.011, 2017.

Rogov, M., Vasileva, K., Mikhailova, K. and Ershova, V.: Database of global glendonite and ikaite records throughout the
Phanerozoic. doi: 10.5281/zenodo.3991964, 2020.

Schlitzer, R.: Ocean Data View: https://odv.awi.de, last access 2 August 2020

375   Selleck, B. W., Carr, P. F. and Jones, B. G.: A review and synthesis of glendonites (pseudomorphs after ikaite) with new data: assessing applicability as recorders of ancient coldwater conditions, J. Sediment. Res., 77(11), 980–991, doi:10.2110/jsr.2007.087, 2007.

Sokolov, D.: On White Sea mineral, Mining journal (Gorny zhurnal), 6, 117–120, 1825. (in Russian)

Stein, C. L. and Smith, A. J.: Authigenic carbonate nodules in the Nankai Trough, Site 583, Init. Repts. DSDP., 87, 659–668,
380   doi:10.2973/dsdp.proc.87.115.1986, 1986.

Suess, E., Balzer, W., Hesse, K.-F., Muller, P. J., Ungeree, C. A. and Wefer, G.: Calcium Carbonate Hexahydrate from Organic-Rich Sediments of the Antarctic Shelf: Precursors of Glendonites, Science, 216(4550), 112801131, doi:10.1126/science.216.4550.1128, 1982.

Tollefsen, E., Balic-Zunic, T., Morth, C.-M., Bruchert, V., Choo, C., Skelton, L. and Skelton, A.: Ikaite nucleation at 35 °C
385   challenges the use of glendonite as a paleotemperature indicator, Sci. Rep., 10(1), doi:10.1038/s41598-020-64751-5, 2020.

Valkenberg, van A., Mao, H. K. and Bell, P. M.: Ikaite (CaCO$_3$x6H$_2$O), a phase more stable than calcite and aragonite (CaCO$_3$) at high water pressure, Carnegie Inst. Wash. Yearb., 70, 237–238, 1971.

Vickers, M., Watkinson, M., Price, G. D. and Jerret, R.: An improved model for the ikaite-glendonite transformation: evidence from the Lower Cretaceous of Spitsbergen, Svalbard, Nor. J. Geol., 98(1), 1–15, doi:10.17850/njg98-1-01, 2018.

390   Wang, Z., Wang, J., Suess, E., Wang, G., Chen, C. and Xiao, S.: Silicified glendonites in the Ediacaran Doushantuo Formation (South China) and their potential paleoclimatic implications, Geology, 45(2), 115–118, doi:10.1130/G38613.1, 2017.

Weaver, R., Roberts, A. P., Flecker, R., Macdonald, D. I. M. and Fot`yanova, L. M.: Geodynamic implications of paleomagnetic data from Tertiary sediments in Sakhalin, Russia (NW Pacific), J. Geophys. Res., 108(B2),
395   doi:10.1029/2001JB001226, 2003.

Zharov, A.: South Sakhalin tectonics and geodynamics: A model for the Cretaceous-Paleogene accretion of the East Asian continental margin, Russian Journal of Earth Sciences, 7(ES5002), doi:10.2205/2005ES000190, 2005.

400 **Figure 1: Ikaite and glendonite morphology (all specimens are figured in natural size). Abbreviation for museum collections: FMM – Fersman Mineralogical Museum, Moscow; GIN – Geological Institute of RAS, Moscow; NHMO – Natural History Museum, Oslo; TsNIGR – Academician F.N. Chernyshev Central Geological Research Museum, Saint-Petersburg; SGM – Vernadsky State Geological Museum, Moscow. 1-3 ikaite; 4-12 glendonite. 1 – Laptev sea, station IP1806, water depth 696 m, level of ikaite sampling 135-137 cm; 2 – Chukchi sea, station 2-2, water depth 50,4**

405 **m, level of ikaite sampling 200-230 cm; 3 – Laptev sea, station 12, water depth 31 m, level of ikaite sampling 130-140 cm (Krylov et al., 2015); 4 – specimen embedded in concretion attached to glacial boulder, littoral of the White sea near to Olenitsa river mouth, Holocene (coll. FMM); 5 – glendonite 'twins', Bolshaya Balakhnya river (Taimyr), Quaternary (specimen SGM-276-45/MN-61203, coll. by L.D. Sulerzhitsky, 1981); 6 – south from Pyatibratsky Cape, Western Kamchatka, Eocene (specimen SGM- 445-05/MN-61735, coll. by A.I. Chelebaeva, 1988); 7 – Aralskaya**

410 **river, Sakhalin, upper Eocene (specimen TsNIGR 4/8561, coll. by Kuzina I.N.); 8 – Tochilinsky section, Western Kamchatka, Eocene-Oligocene transition (specimen GIN, coll. by Palechek T.N.); 9 – Basilika Mt., Spitsbergen, lower Albian (specimen NHMO 924, coll. J.Nagy, 1964); 10 – Olenek river (near Kolumas river mouth), Yakutia, Middle Jurassic, upper Bajocian – lower Bathonian (specimen TsNIGR100/6266, coll. by Gusev A.I., 1939); 11 - Taas-Ary Island, Yakutia, middle Permian, Roadian (field photo by V.B. Ershova); 12 – borehole 60, depth 97,6 m, Saint-**

415 **Petersburg region, lower Ordovician, Tremadocian (specimen TsNIGR 9/13261, coll. by G.S. Iskul, 2012).**
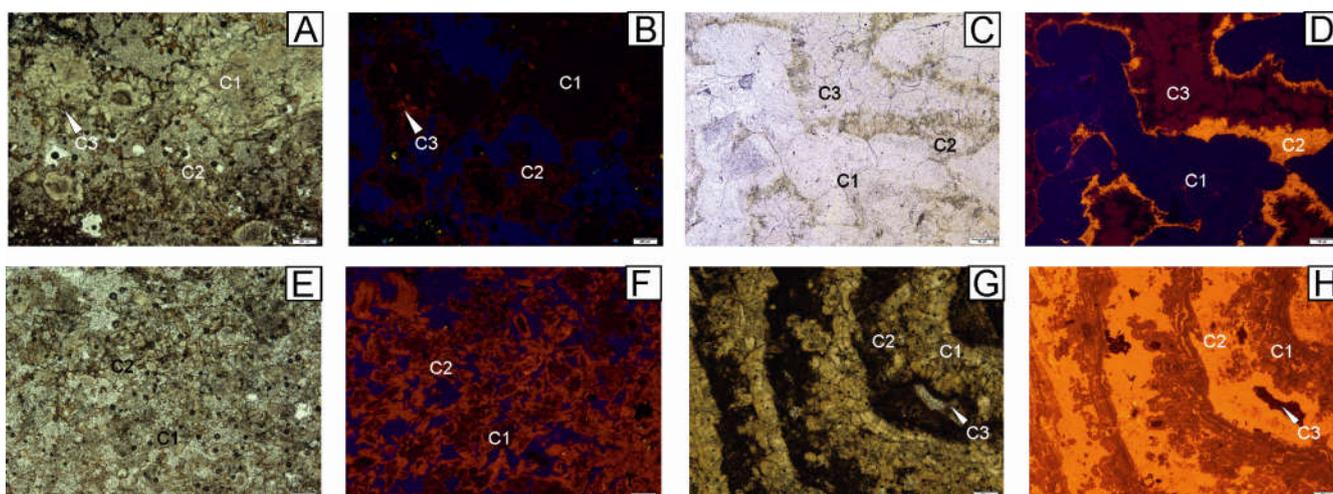

Figure 2: The internal structure of glendonite that are mainly composed of several calcite phases (C1; C2; C3) A – B. Sample L-1-3, Middle Jurassic (Bajocian-Bathonian), Ludlovskaya-1 well, Barents Sea, Russia, depth 1592+6 meters (authors` data); A - under plane-polarized light; the first calcite phase represents rosette-like crystals showing

420 **distinct core; B – the same thin-section under CL. C – D. Sample RM2019-27, Lower Neogene (Lower Miocene), Eastern coast of Sakhalin Island, Russia (authors` data). C - under plane-polarized light; D - the same thin-section under CL. E – F. Sample Led-1-3, Middle Jurassic (Bajocian-Bathonian), Ledovaya-1 well, Barents Sea, Russia,**

depth 1824+6,6 meters (authors` data); E - elongated calcite crystals (C1), surrounded by the second calcite phase (C2), sample Led-1-3 under plane-polarized light; F - the same thin-section under CL. G - H – Sample F3-1-1, Lower
425 **Cretaceous (Upper Hauterivian), Festningen, Svalbard (authors` data); G - microzoning glendonite under plane-polarized light; the first calcite phase is distinguished zoning as well; H - the same thin-section under CL**
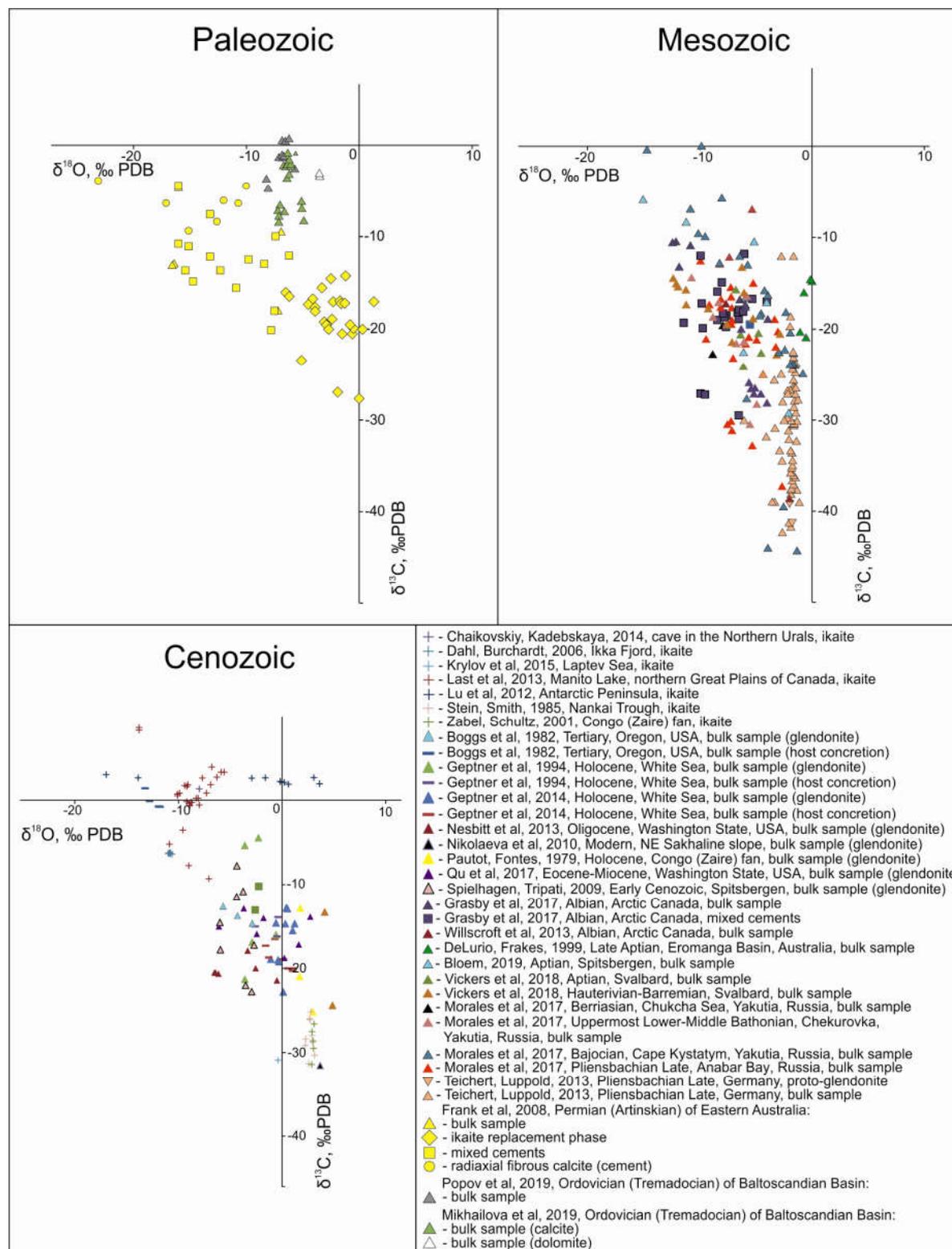
Figure 3: Isotopic composition of glendonites (including different generations), host concretions and ikaites for
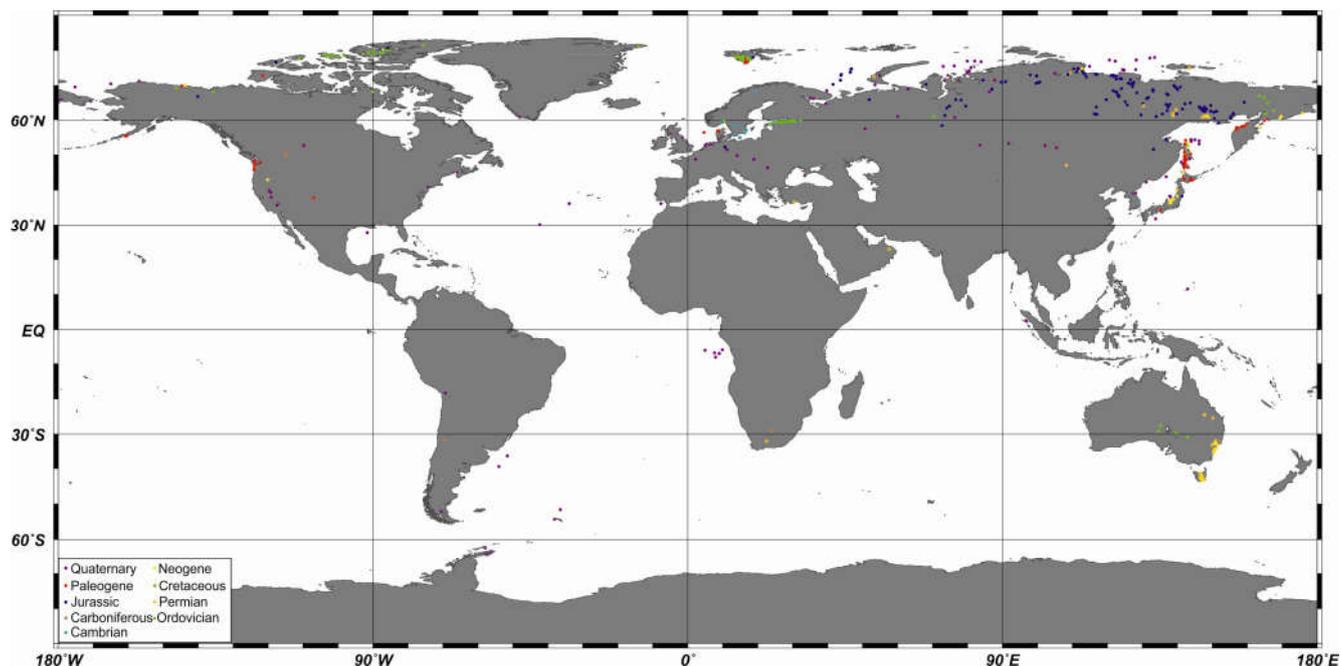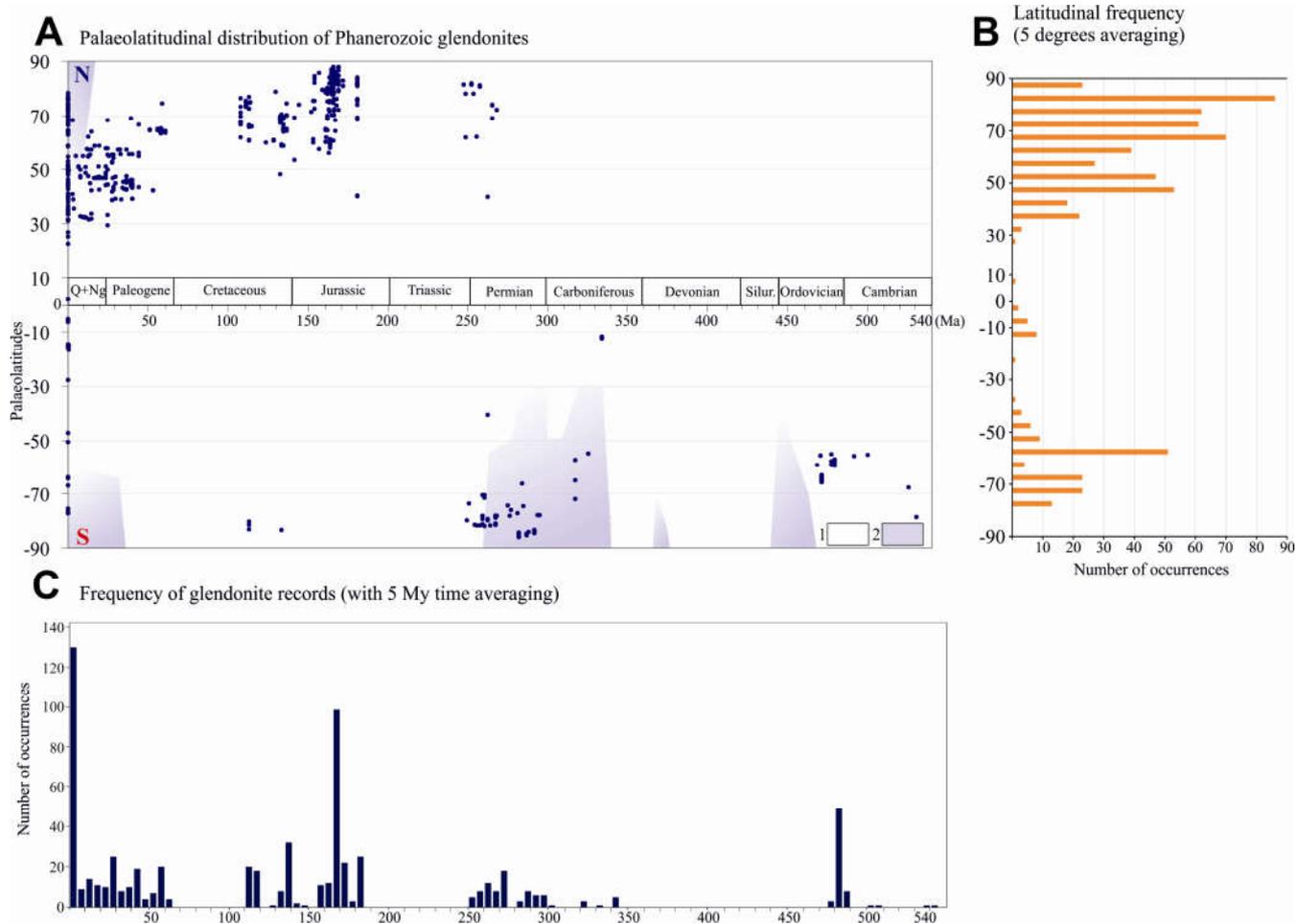430 **Paleozoic, Mesozoic and Cenozoic samples**

Fig. 4. Map showing location of all ikaite and glendonite occurrences included to the database (prepared through Ocean Data View, Schlitzer, 2020).

Fig. 5. Palaeolatitudinal distribution of glendonite and ikaite records through time. A – palaeolatitudinal occurrence; 1 – non-glacial intervals, 2 - glaciations (after Frakes et al., 2005); B – latitudinal frequency of glendonite occurrences (with 5 degrees averaging); C – frequency of glendonite occurrence through time (with 5 Ma averaging).