

Glendonites track methane seepage in Mesozoic polar seas

Chloé Morales¹, Mikhail Rogov², Hubert Wierzbowski³, Victoria Ershova⁴, Guillaume Suan⁵, Thierry Adatte⁶, Karl B. Föllmi⁶, Erik Tegelaar⁷, Gert-Jan Reichart^{1,8}, Gert J. de Lange¹, Jack J. Middelburg¹, and Bas van de Schootbrugge¹

¹Department of Earth Sciences, Faculty of Geosciences, Utrecht University, Heidelberglaan 2, 3584 CS Utrecht, Netherlands

²Geological Institute, Russian Academy of Sciences (RAS), Pyzhevski lane 7, 119017 Moscow, Russia

³Polish Geological Institute, National Research Institute, Rakowiecka 4, 00-975 Warsaw, Poland

⁴Institute of Earth Sciences, St. Petersburg State University, Universitetskaya nab. 7/9, 199034 St. Petersburg, Russia

⁵Université Lyon 1, ENS-Lyon, CNRS, UMR 5276 LGL-TPE, F-69622 Villeurbanne, France

⁶Institute of Earth Sciences, University of Lausanne, Géopolis, 1015 Lausanne, Switzerland

⁷Shell International Ltd., Kessler Park 1, 2288 GS Rijswijk, Netherlands

⁸Royal Netherlands Institute for Sea Research (NIOZ), Ocean Sciences Department, PO Box 59, 1790 AB Den Burg, Texel, Netherlands

ABSTRACT

During the Phanerozoic, Earth has experienced a number of transient global warming events associated with major carbon cycle perturbations. Paradoxically, many of these extreme greenhouse episodes are preceded or followed by cold climate, perhaps even glacial conditions, as inferred from the occurrence of glendonites in high latitudes. Glendonites are pseudomorphs of ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$), a hydrated carbonate mineral increasingly stable at low temperatures. Here, we show that methane seepage and oxidation provide an overriding control on Mesozoic glendonite formation (i.e., ikaite fossilization). Geochemical and petrological analyses of 33 Early Jurassic to Early Cretaceous glendonites from five sections in Siberia (Russia) reveal that most of their infilling carbonate phases are reminiscent of methane-derived authigenic carbonates. Bulk glendonites and surrounding sediments exhibit exceptionally high and low carbon isotope values (+20‰ to -45‰ VPDB [Vienna Peedee belemnite]), typical for carbon sources linked to methane generation and oxidation. Gas inclusion data confirm the presence of methane and longer-chain hydrocarbon gases, suggesting a thermogenic source for the methane. Glendonite-bearing layers can be traced for hundreds of kilometers, suggesting widespread trapping of methane in the sub-seafloor during the Jurassic. As such, glendonites constitute an unexplored archive for detecting past episodes of methane release and oxidation in polar settings.

INTRODUCTION

Methane is a potent greenhouse gas, with multiple natural sources including marine cold seeps and gas hydrates. Authigenic carbonates associated with the anaerobic oxidation of methane (AOM) can be used to document the distribution in time and space of oceanic methane seepage (Peckmann et al., 1999) and its links to carbon cycle perturbations and climate change (Sun and Turchyn, 2014). One such authigenic carbonate mineral, ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$), which can become fossilized as glendonite, remains poorly understood. The stability of ikaite is favored by low temperatures, and the mineral rapidly decomposes above 7 °C (Pauly, 1963). Three main types of ikaite are distinguished: (1) tufa and travertines in springs and alkaline lakes (Pauly, 1963; Shearman et al., 1989), (2) single microscopic crystals in Arctic and Antarctic ice (Dieckmann et al., 2010), and (3) macroscopic single euhedral to stellate crystal clusters found in marine sediments. The latter ikaite type is thought to form during early diagenesis. It has a wide range of $\delta^{13}\text{C}_{\text{carb}}$ (carb—carbonate) values (from -57‰ to +4‰; Kodina et al., 2003; Lu et al., 2012), which has been attributed to the mixing of carbon generated during organic matter degradation, methanogenesis, and AOM (Kodina et al., 2003; Lu et al., 2012). The term “glendonite” pertains to pseudomorphs after this type of ikaite (David and Taylor, 1905). The transformation of ikaite to glendonite is

thought to result from the slow decrease in the concentration of Ca^{2+} and CO_3^{2-} and high phosphate levels as ikaite grows (Bischoff et al., 1993), or to a change of carbon source and pore-water chemistry from sulfate reduction of organic-rich sediments to AOM-driven processes linked to burial and vent activity in the Sea of Okhotsk (Greinert and Derkachev, 2004).

Although ikaite formation has been linked to *in situ* methane generation and oxidation in previous work (Kodina et al., 2003; Lu et al., 2012), glendonites have thus far mostly been used as a proxy record for cold temperatures, due to the peculiar thermodynamic parameters that control ikaite formation. Emphasis has been put on the reconstruction of seawater temperature from bulk glendonite $\delta^{18}\text{O}_{\text{carb}}$ values, but unexpectedly low $\delta^{18}\text{O}_{\text{carb}}$ values have proved ambiguous (Price and Nunn, 2010). Besides, and similarly to ikaite, glendonites show $\delta^{13}\text{C}$ values ranging from -45‰ to 0‰ (Selleck et al., 2007; Teichert and Luppold, 2013), suggesting a connection between certain glendonite-bearing sites and methane seepage (Greinert and Derkachev, 2004; Teichert and Luppold, 2013). Based on petrological and geochemical analyses on glendonites and host sediments, as well as on the molecular and isotopic composition of gas inclusions trapped in glendonites, we demonstrate that the ikaite-to-glendonite transformation was an early diagenetic process linked to AOM. Glendonites may thus be used to document past events of methane release and oxidation in cold environments.

GEOLOGICAL SETTING AND METHODS

A total of 33 glendonites were sampled from five sections in Siberia (Russia), composed of marine sandstone, siltstone, and mudstone, spanning the late Pliensbachian (Anabar Bay; Suan et al., 2011), the late Bajocian (Cape Kystatym and Cape Khorongkho), the late Bajocian–early Bathonian (Chekurovka), and the early Bathonian and late Berriasian (Chucha) (Figs. 1A and 1B). The sedimentary successions were deposited in shallow to deep continental shelf settings (corresponding to shoreface to offshore environments) near the North Pole (Fig. 1C; see the GSA Data Repository¹). The sampled sections are stratigraphically constrained by the occurrence of age-diagnostic ammonites, brachiopods, and bivalves, as well as accessory microfossils and chemostratigraphy in the Anabar Bay section (see the Data Repository). Except for some specimens found in a conglomerate bed, none of the glendonites were transported (shown by the preservation of their angular shape). All glendonites and enclosing nodules and sediments were subjected to petrographical (optical and ultraviolet-light microscope), bulk stable isotope (inorganic carbon and

¹GSA Data Repository item 2017159, coordinates of the sections, details on stratigraphy, methods and geochemical results (Rock-Eval and CSIA), and tables of raw geochemical data, is available online at <http://www.geosociety.org/datarepository/2017/> or on request from editing@geosociety.org.

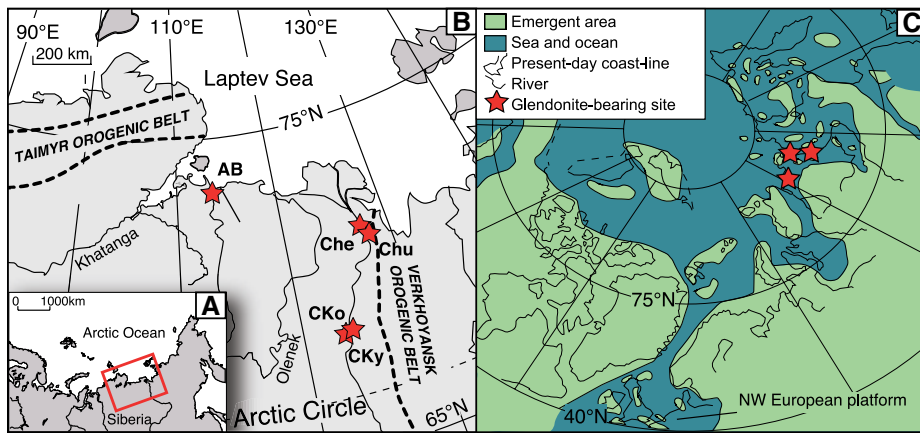


Figure 1. A,B: Location of North Siberian Basin (Russia), with red stars denoting location of sampled sections along Lena River (CKy—Cape Kystatym; CKo—Cape Khorongkho; Chu—Chucha; Che—Chekurovka) and along Laptev Sea (AB—Anabar Bay), modified after Suan et al. (2011). **C:** Paleogeographic map of Early Jurassic (late Pliensbachian) showing past locations of glendonite formation (after Meledina et al., 2005).

oxygen), and Rock-Eval (Espitalié et al., 1985) analyses. Gas inclusions of glendonites were examined by compound-specific isotope analyses (CSIA) on five selected specimens.

PETROLOGICAL CHARACTERISTICS

Thin-section analyses of the investigated glendonites reveal a number of genetic phases of carbonate growth alternating with phases of dissolution

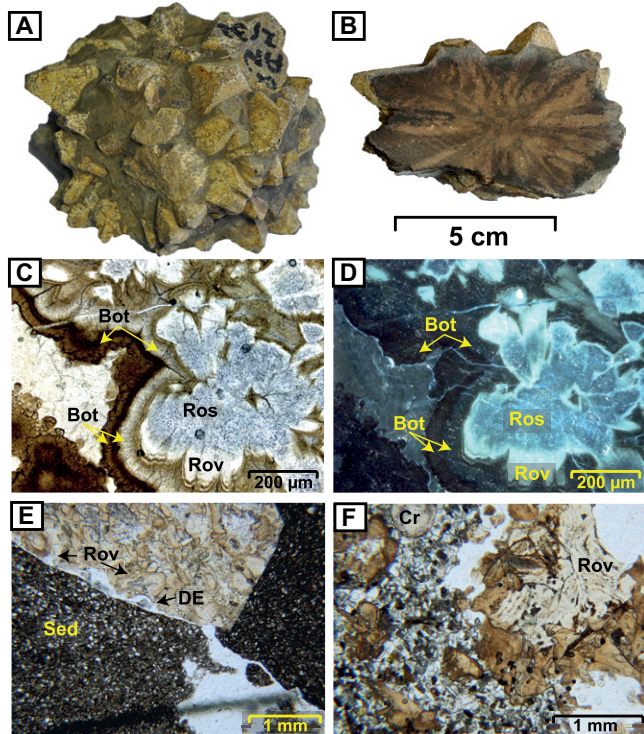


Figure 2. Macroscopic and microscopic views of glendonite specimens from Siberia (Russia). **A,B:** Medium-size stellate-shape glendonite; upper Pliensbachian, profile and transverse views, respectively. **C,D:** Succession of carbonate cements observed in glendonites (Ros—rosette oriented crystals; Rov—rosette calcite overgrowths; Bot—botryoids); upper Bajocian, transmitted and ultraviolet light (UV), respectively. Rosettes contain black UV-fluorescent impurities resulting from organic particles. Some botryoidal carbonates have highly fluorescent rim that may be due to microbial film. **E:** Fluid exhaust microstructure associated with dissolution event (DE) disbanding rosette overgrowths (Rov) of glendonite and reworking nonconsolidated host sediment (Sed); upper Bajocian. **F:** Conglomerate of reworked and broken glendonites containing rosette overgrowths (Rov) in sandy matrix with crinoid fragments (Cr), and highlighting early fossilization of ikaite; upper Bajocian.

(Fig. 2). The following genetic phases are recurrent, independent of location and age:

(1) Whitish calcite crystals organized into “rosettes”, containing organic matter impurities and which are overgrown by replacive calcite cements. Rosettes likely result from the direct recrystallization of ikaite into calcite (Teichert and Luppold, 2013).

(2) Fibrous to botryoidal carbonates in different shades of yellowish amber, in some cases also characterizing nodules surrounding glendonites.

(3) Anhedral irregular to clotted amber-colored calcites that have recrystallized part (or most) of the glendonite.

In a conglomerate bed at Cape Kystatym (Bajocian-Bathonian; Fig. 2F), reworked glendonites bear genetic phases 1 and 2, which are equally observed in Quaternary ikaites from the Nankai Trough (Stein and Smith, 1986). Hence, these cements precipitated during very early diagenesis. Similar cementation patterns have been observed in glendonites from distant regions and different age (Greinert and Derkachev, 2004; Huggett et al., 2005; Teichert and Luppold, 2013), indicating that they represent widespread features of ikaite fossilization.

CARBON AND OXYGEN ISOTOPE DATA

The occurrence of fibrous/botryoidal carbonates in high latitudes, in association with clotted and anhedral carbonates (genetic phase 3) and repeated dissolution events, is reminiscent of mineralogical features described from hydrocarbon seep carbonates (Savard et al., 1996). A link to hydrocarbon oxidation is also apparent from stable isotope analyses. Glendonite samples show bulk $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ values ranging from -44.5‰ to 0‰ VPDB (Vienna Peedee belemnite) and from -14.7‰ to -0.8‰ VPDB, respectively, displaying a generally strong inverse correlation (Fig. 3). Carbonate nodules surrounding glendonites have less-variable $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ values, ranging between -30.4‰ and -16.4‰ VPDB and -4.0‰ to -2.7‰ VPDB, respectively. Diagenetic carbonates of bulk sediment enclosing glendonites exhibit low to exceptionally high $\delta^{13}\text{C}_{\text{carb}}$ values ranging from -29.5‰ to $+21.3\text{‰}$ VPDB, and $\delta^{18}\text{O}_{\text{carb}}$ values between -2.6‰ and -20.6‰ VPDB. A late diagenetic overprint of bulk sediment carbon and oxygen isotope values cannot be completely ruled out (Jacobsen and Kaufman, 1999). Cracking temperatures of organic material (T_{max}) show a wide range of values (between 412 and 482 °C) corresponding to immature and mature material. However, this large uncertainty can be ascribed to very low values of S2 peaks linked to an intense oxidation of the organic material, and to low total organic contents (TOC) (Behar et al., 2001). Jurassic sediments on the Siberian craton were probably never deeply buried (Drachev et al., 2010). The preservation of aragonitic bivalves and T_{max} data of Suan et al. (2011) also suggest that sediments only reached the uppermost part of the oil window. In our samples, sparry (blocky) calcite related to burial cementation represents only a minor carbonate phase, and no correlation has been observed between its relative occurrence and changes in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values.

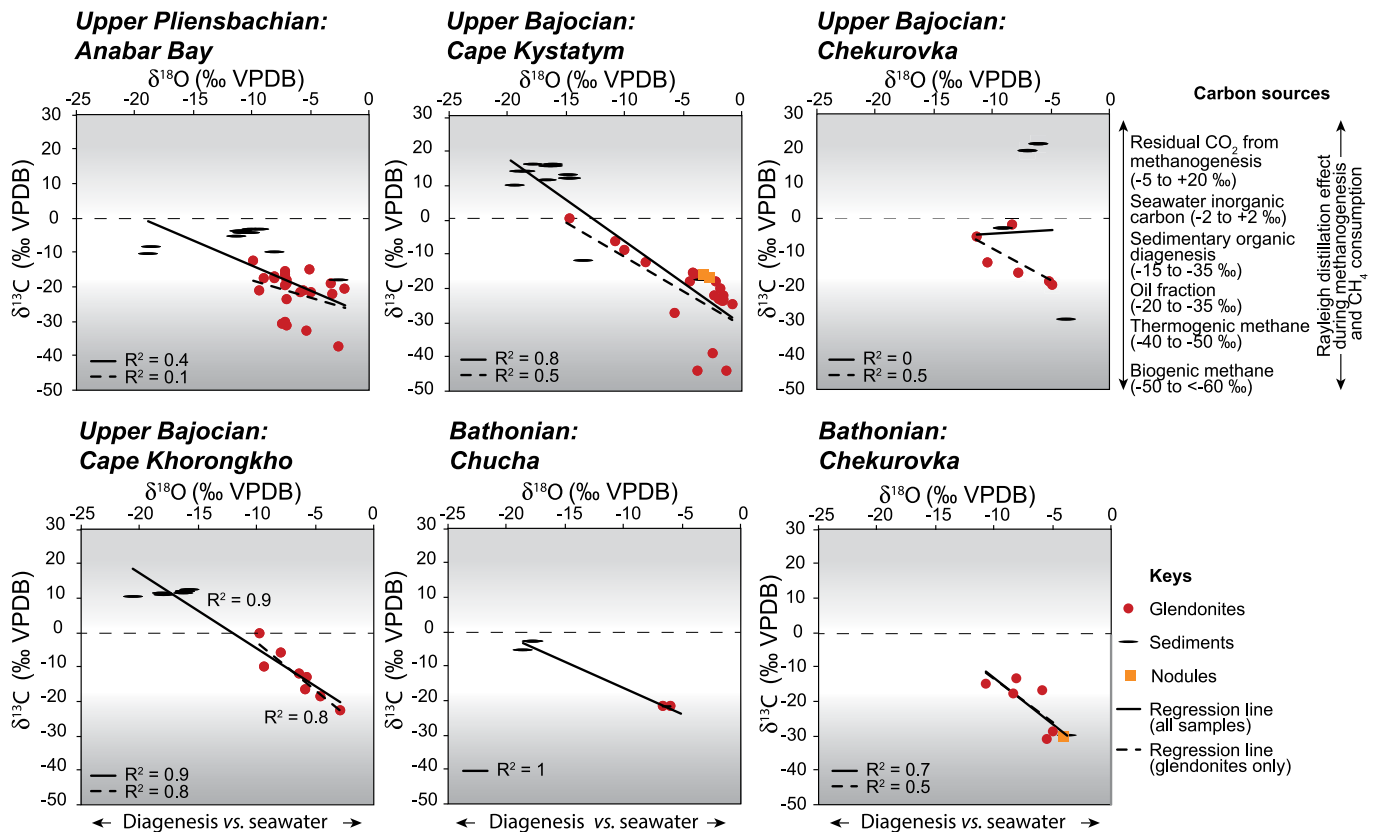


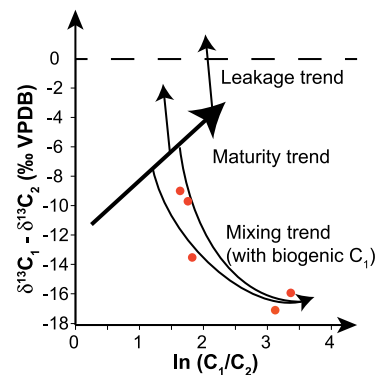
Figure 3. Carbon and oxygen stable isotope distribution of carbonates belonging to bulk glendonites from Siberia (Russia; see Fig. 1 for sample locations), surrounding nodules, and enclosing sediment. Methane oxidation is a central process contributing to carbonate carbon sources. VPDB—Vienna Pee Dee belemnite.

The isotopic data from bulk glendonite samples can be separated into two groups. The first has normal marine $\delta^{18}\text{O}_{\text{carb}}$ values (up to -0.8‰ VPDB) that are accompanied by extremely low $\delta^{13}\text{C}_{\text{carb}}$ values (-25‰ to -45‰ VPDB), implicating methane as a carbon source. The less-negative $\delta^{13}\text{C}_{\text{carb}}$ values obtained for some glendonites ($\sim -25\text{‰}$ VPDB) could be related to the mixing of various carbon sources and geochemical processes, including aerobic oxidation of organic matter, sulfate reduction, and/or fermentation (Whiticar, 1999), or to a changing proportion of biogenic versus thermogenic methane. The second group is strongly ^{13}C enriched, which is explained by a residual CO_2 source from microbial methanogenesis. The ^{18}O -depleted values indicate the late diagenetic circulation of fluids (Jacobsen and Kaufman, 1999).

IMPLICATION OF GAS INCLUSIONS FOR FORMATION OF GLENDONITES

Compound-specific isotope analyses performed on gas inclusions of bulk glendonites (Fig. 4) document the average gas composition during the ikaite-to-glendonite transformation. In addition to methane (C_1), significant concentrations of higher-molecular-weight hydrocarbon gases (C_{2+}), including ethane (C_2), propane (C_3), butane (C_4), and pentane (C_5), were detected. The investigated glendonites samples have $\delta^{13}\text{C}_{\text{carb}}$ values between -13‰ and -28‰ VPDB, showing the limitations of bulk $\delta^{13}\text{C}_{\text{carb}}$ values as proxies for the role of methane in authigenic carbonate precipitation. Biogenic degradation of organic matter produces strongly ^{12}C -enriched methane (up to -110‰ VPDB), whereas thermogenic cracking leads to the formation of various hydrocarbon gases (C_1 to C_5) with a $\delta^{13}\text{C}$ signature closer to that of the parent organic matter (-30‰ to -50‰ VPDB; Schoell, 1980). A gas interpretation plot (Prinzhofer and Huc, 1995) shows that a mixture of thermogenic and biogenic hydrocarbon gas was likely involved in ikaite/glendonite formation at the investigated locations (Fig. 4). The

Figure 4. Model of gas genetic fractionation based on analyses of relative hydrocarbon composition of glendonites and their specific stable carbon isotope content. Leakage and mixing can influence the molecular and isotopic composition of hydrocarbon gases at various stages of gas maturation (narrow arrows). The $\delta^{13}\text{C}_1$ - $\delta^{13}\text{C}_2$ versus $\ln(\text{C}_1/\text{C}_2)$ diagram (Prinzhofer and Huc, 1995) confirms occurrence of mixed thermogenic and biogenic methane within glendonite samples. VPDB—Vienna Pee Dee belemnite.



proportion of biogenic and thermogenic methane is difficult to evaluate due to additional CO_2 -reduction and Rayleigh-distillation processes (Whiticar, 1999). However, the high concentration of C_{2+} gas (varying between 5%–28% of total hydrocarbons) and $\text{C}_1 / (\text{C}_2 + \text{C}_3)$ ratios between 3 and 24 (Martin et al., 1997) indicate a major contribution of thermogenic gas in the inclusions (Schoell, 1980). Especially propane, which is known to be rapidly biodegraded both anaerobically and aerobically (Kinnaman et al., 2007; Quistad and Valentine, 2011), shows no significant carbon isotope fractionation. This confirms the very rapid transformation of ikaite to glendonite and argues against a slow late diagenetic incorporation of hydrocarbons during the recrystallization of carbonates.

A local (i.e., *in situ*) methane source equally appears questionable, as glendonites are associated with clay, silt, and sandstone, which have a very low TOC (0–0.8 wt%, see the Data Repository). Conversely, glendonites

are not observed in certain nearby sections where TOC values are higher (Suan et al., 2011). Methane was likely sourced from a deeper reservoir with thermogenic methane diffusing upwards, perhaps linked to the activity of the Verkhoysk and Taimyr fault zones (Fig. 1). Typical seep structures and fauna are not observed, suggesting that methane did not reach the sediment-water interface and that fluxes were diffusive (Teichert and Luppold, 2013).

CONCLUSIONS

Our new multi-proxy data set clearly demonstrates that Siberian glendonites record the occurrence of methane seepage during the Jurassic and the Early Cretaceous. Their occurrence is decoupled from local TOC content, pointing to a deeper hydrocarbon source. The complex sequence of ikaite-calcite precipitation leading to glendonite formation, as well as the large range of $\delta^{18}\text{O}_{\text{carb}}$ values found here, prevent the use of bulk glendonite $\delta^{18}\text{O}_{\text{carb}}$ values to monitor past seawater temperatures. Instead, the relationship between glendonite formation and methane oxidation is of interest with regards to past intervals of global carbon cycle perturbations. The Toarcian oceanic anoxic event (OAE), the Valanginian Weissert event, the Aptian-Albian OAEs, and to some extent the Paleocene-Eocene Thermal Maximum (Kaplan, 1978; Kemper, 1987; Price, 1999; Spielhagen and Tripathi, 2009) were all accompanied by widespread glendonite formation.

ACKNOWLEDGMENTS

We thank three anonymous reviewers and Jörn Peckman for constructive feedback, as well as Otto H. Stiekema and Arnold E. van Dijk for their technical assistance. The Swiss National Science Foundation (grant P2LAP2-155097 to Morales), The Netherlands Organisation for Scientific Research (project n° NWO ALWOP.145 to van de Schootbrugge), Utrecht University, the Russian State program (grant 0135-2014-0064, Geological Institute, RAS), Program II.3 (RAS), the Russian Foundation for Basic Research (grant 15-05-03149 to Rogov), and Shell International (Netherlands) are acknowledged for their financial support and access to laboratory facilities. This research contributes to the Netherlands Earth System Sciences Center.

REFERENCES CITED

- Behar, F., Beaumont, V., and Pentead, H.L.D.B., 2001, Rock-Eval 6 technology: Performances and developments: *Oil & Gas Science and Technology*, v. 56, p. 111–134, doi:10.2516/ogst:2001013.
- Bischoff, J.L., Fitzpatrick, J.A., and Rosenbauer, R.J., 1993, The solubility and stabilization of ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) from 0° to 25°C: Environmental and paleoclimatic implications for thimolite tufa: *The Journal of Geology*, v. 101, p. 21–33, doi:10.1086/648194.
- David, T.W., and Taylor, T.G., 1905, Occurrence of the pseudomorph glendonite in New South Wales, Sydney: *Records of the Geological Survey of New South Wales*, v. 8, p. 161–179.
- Dieckmann, G., Nehrke, G., Uhlig, C., Göttlicher, J., Gerland, S., Granskog, M.A., and Thomas, D.N., 2010, Ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) discovered in Arctic sea ice: *The Cryosphere*, v. 4, p. 227–230, doi:10.5194/tc-4-227-2010.
- Drachev, S.S., Malyshev, N.A., and Nikishin, A.M., 2010, Tectonic history and petroleum geology of the Russian Arctic Shelves: An overview, in Vining, B.A., and Pickering, S.C., eds., *Petroleum Geology: From Mature Basins to New Frontiers—Proceedings of the 7th Petroleum Geology Conference*: Geological Society of London Petroleum Geology Conference Series 7, p. 591–619, doi:10.1144/0070591.
- Espitalié, J., Deroo, G., and Marquis, F., 1985, La pyrolyse Rock-Eval et ses applications: *Revue de l'Institut Français du Pétrole*, v. 40, p. 563–579.
- Greiner, J., and Derkachev, A., 2004, Glendonites and methane-derived Mg-calcites in the Sea of Okhotsk, Eastern Siberia: Implications of a venting-related ikaite/glendonite formation: *Marine Geology*, v. 204, p. 129–144, doi:10.1016/S0025-3227(03)00354-2.
- Huggett, J.M., Schultz, B.P., Shearman, D.J., and Smith, A.J., 2005, The petrology of ikaite pseudomorphs and their diagenesis: *Proceedings of the Geologists' Association*, v. 116, p. 207–220, doi:10.1016/S0016-7878(05)80042-2.
- Jacobsen, S.B., and Kaufman, A.J., 1999, The Sr, C and O isotopic evolution of Neoproterozoic seawater: *Chemical Geology*, v. 161, p. 37–57, doi:10.1016/S0009-2541(99)00080-7.
- Kaplan, M.E., 1978, Calcite pseudomorphs in Jurassic and Lower Cretaceous deposits of the northern area of eastern Siberia: *Geologiya i Geofizika (Russian Geology and Geophysics)*, v. 19, p. 62–70.
- Kemper, E., 1987, *Das Klima der Kreide-Zeit*, Hannover, Bundesanstalt für Geowissenschaften und Rohstoffe und Geologische Landesämter in der Bundesrepublik Deutschland, *Geologisches Jahrbuch Reihe A: Allgemeine und regionale Geologie Bundesrepublik Deutschland und Nachbargebiete, Tektonik, Stratigraphie, Paläontologie*: Stuttgart, Germany, Schweizerbart, 96 p. (in German).
- Kinnaman, F.S., Valentine, D.L., and Tyler, S.C., 2007, Carbon and hydrogen isotope fractionation associated with the aerobic microbial oxidation of methane, ethane, propane and butane: *Geochimica et Cosmochimica Acta*, v. 71, p. 271–283, doi:10.1016/j.gca.2006.09.007.
- Kodina, L.A., Tokarev, V.G., Vlasova, L.N., and Korobeinik, G.S., 2003, Contribution of biogenic methane to ikaite formation in the Kara Sea: Evidence from the stable carbon isotope geochemistry, in Stein, R., et al., eds., *Siberian River Run-Off in the Kara Sea: Characterisation, Quantification, Variability and Environmental Significance*: Amsterdam, Elsevier, *Proceedings in Marine Sciences*, v. 6, p. 349–374.
- Lu, Z., Rickaby, R.E.M., Kennedy, H., Kennedy, P., Pancost, R.D., Shaw, S., Lennie, A., Wellner, J., and Anderson, J.B., 2012, An ikaite record of late Holocene climate at the Antarctic Peninsula: *Earth and Planetary Science Letters*, v. 325–326, p. 108–115, doi:10.1016/j.epsl.2012.01.036.
- Martin, J.B., Orange, D.L., Lorenson, T.D., and Kvenvolden, K.A., 1997, Chemical and isotopic evidence of gas-influenced flow at a transform plate boundary: Monterey Bay, California: *Journal of Geophysical Research*, v. 102, p. 24,903–24,915, doi:10.1029/97JB02154.
- Meledina, S.V., Shurygin, B.N., and Dzyuba, O.S., 2005, Stages in development of mollusks, paleobiogeography of Boreal seas in the Early–Middle Jurassic and zonal scales of Siberia: *Geologiya i Geofizika (Russian Geology and Geophysics)*, v. 46, p. 239–254.
- Pauly, H., 1963, “Ikaite,” a new mineral from Greenland: *Arctic*, v. 16, p. 263–264, doi:10.14430/arctic3545.
- Peckmann, J., Thiel, V., Michaelis, W., Clari, P., Gaillard, C., Martire, L., and Reitner, J., 1999, Cold seep deposits of Beauvoisin (Oxfordian; southeastern France) and Marmorito (Miocene; northern Italy): Microbially induced authigenic carbonates: *International Journal of Earth Sciences*, v. 88, p. 60–75, doi:10.1007/s005310050246.
- Price, G.D., 1999, The evidence and implications of polar ice during the Mesozoic: *Earth-Science Reviews*, v. 48, p. 183–210, doi:10.1016/S0012-8252(99)00048-3.
- Price, G.D., and Nunn, E.V., 2010, Valanginian isotope variation in glendonites and belemnites from Arctic Svalbard: Transient glacial temperatures during the Cretaceous greenhouse: *Geology*, v. 38, p. 251–254, doi:10.1130/G30593.1.
- Prinzhofer, A.A., and Huc, A.Y., 1995, Genetic and post-genetic molecular and isotopic fractionations in natural gases: *Chemical Geology*, v. 126, p. 281–290, doi:10.1016/0009-2541(95)00123-9.
- Quistad, S.D., and Valentine, D.L., 2011, Anaerobic propane oxidation in marine hydrocarbon seep sediments: *Geochimica et Cosmochimica Acta*, v. 75, p. 2159–2169, doi:10.1016/j.gca.2011.02.001.
- Savard, M.M., Beauchamp, B., and Veizer, J., 1996, Significance of aragonite cements around Cretaceous marine methane seeps: *Journal of Sedimentary Research*, v. 66, p. 430–438, doi:10.1306/D4268365-2B26-11D7-8648000102C1865D.
- Schoell, M., 1980, The hydrogen and carbon isotopic composition of methane from natural gases of various origins: *Geochimica et Cosmochimica Acta*, v. 44, p. 649–661, doi:10.1016/0016-7037(80)90155-6.
- Selleck, B.W., Carr, P.F., and Jones, B.G., 2007, A review and synthesis of glendonites (pseudomorphs after ikaite) with new data: Assessing applicability as recorders of ancient coldwater conditions: *Journal of Sedimentary Research*, v. 77, p. 980–991, doi:10.2110/jsr.2007.087.
- Shearman, D.J., McGugan, A., Stein, C., and Smith, A.J., 1989, Ikaite, $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$, precursor of the thimolites in the Quaternary tufas and tufa mounds of the Lahontan and Mono Lake Basins, western United States: *Geological Society of America Bulletin*, v. 101, p. 913–917, doi:10.1130/0016-7606(1989)101<0913:ICOPOT>2.3.CO;2.
- Spielhagen, R.F., and Tripathi, A., 2009, Evidence from Svalbard for near-freezing temperatures and climate oscillations in the Arctic during the Paleocene and Eocene: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 278, p. 48–56, doi:10.1016/j.palaeo.2009.04.012.
- Stein, C.L., and Smith, A.J., 1986, Authigenic carbonate nodules in the Nankai Trough, Site 583, in Kagami, H., Karig, D.E., Coulbourn, W.T., et al., *Initial Reports of the Deep Sea Drilling Project, Volume 87*: Washington, D.C., U.S. Government Printing Office, p. 659–668.
- Suan, G., et al., 2011, Polar record of Early Jurassic massive carbon injection: *Earth and Planetary Science Letters*, v. 312, p. 102–113, doi:10.1016/j.epsl.2011.09.050.
- Sun, X., and Turchyn, A.V., 2014, Significant contribution of authigenic carbonate to marine carbon burial: *Nature Geoscience*, v. 7, p. 201–204, doi:10.1038/ngeo2070.
- Teichert, B.M.A., and Luppold, F.W., 2013, Glendonites from an Early Jurassic methane seep: Climate or methane indicators?: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 390, p. 81–93, doi:10.1016/j.palaeo.2013.03.001.
- Whiticar, M.J., 1999, Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane: *Chemical Geology*, v. 161, p. 291–314, doi:10.1016/S0009-2541(99)00092-3.

Manuscript received 9 November 2016

Revised manuscript received 2 February 2017

Manuscript accepted 2 February 2017

Printed in USA