#### **REVIEW ARTICLE**



# Mechanisms of Late Pleistocene authigenic Fe–Mn-carbonate formation at the Laptev Sea continental slope (Siberian Arctic)

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#### Abstract

Study of the microstructure and isotopic composition of authigenic tubule-shaped carbonate concretions from sediment core PS51/154-11 on the western Laptev Sea continental slope (present water depth 270 m) has allowed for reconstruction of the conditions prevailing during their formation and identification of the mechanisms controlling their genesis. Concretions were collected from the basal sediment unit with an extrapolated age estimate of 16.3–17.6 cal.ka. Crystallization of carbonate tubules occurred at the beginning of the last deglaciation when the site was located in the proximity to the former coastline and the mouths of the Olenek and Anabar-Khatanga rivers in water depths of about 150–170 m. Microprobe analysis showed that the studied carbonate tubules consist of the minerals belonging to the siderite-rhodochrosite isomorphic series. The measured isotopic composition of  $\delta^{13}$ C and  $\delta^{18}$ O in the carbonates varies between -21.0 and -17.0% and between -9.86and 1.72% VPDB, respectively. The  $\delta^{18}$ O values in the authigenic carbonates give evidence for the gradual transition from a freshwater affected to modern-like marine sedimentation environment during carbonate crystallization. Water freshening is confirmed by the co-occurrence of authigenic Fe-Mn carbonates and Fe-phosphate vivianite that is a typical mineral of freshwater environments. The dominant source of dissolved inorganic carbon in the pore water was the isotopically light carbon derived from the diagenetic decomposition of organic matter. Two possible scenarios of authigenic carbonates formation are proposed: penetration of freshened ground waters and/or enhanced freshwater influence during short seasonal floods in combination with geochemical processes in a narrow marginal filter zone that was located extremely close to the Laptev Sea continental slope and the studied core site.

**Keywords** Authigenic carbonates  $\cdot$  Carbon and oxygen stable isotopes  $\cdot$  Early diagenesis  $\cdot$  Oxidation of organic matter (OM)  $\cdot$  Laptev Sea  $\cdot$  Late Pleistocene

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# Introduction

Although sedimentation in polar marine environments occurs under low temperatures, i.e., slightly above or below zero, sediments undergo a relatively deep cycle of diagenetic transformation. Authigenic mineralization in the form of nodules, concretions, and separate crystals is common in modern bottom sediments on the shelf and continental slope of arctic seas [9, 13, 23, 32, 36, 37, 39, 42; and references therein]. Whereas ferromanganese nodules are abundant in the modern Arctic sediments (e.g., [34] and references therein), the newly formed carbonate and phosphate formations are relatively rare. Core PS51/154-11 from the western Laptev Sea continental slope in which both carbonates (rhodochrosite, siderite, and ikaite) and phosphates (vivianite) were found [79, 81, 82] is of, therefore, particular interest.

In natural systems, vivianite  $(Fe_3(PO_4)_2 \cdot 8H_2O)$  is stable under pH conditions from 6 to 9, and its precipitation directly from pore water solution is favored by high concentrations of ferrous iron (Fe(II)) and soluble reactive P often found in anoxic non-sulfidic environments [67]. The uniqueness of this vivianite finding is confirmed by the fact that other known occurrences of this mineral in the Arctic refer only to lakes (e.g., Lake El'gygytgyn in the Far Eastern Russian Arctic; Murdock [55]). Carbonates are among other minerals that occur together with vivianite in core PS51/154-11. One of those is ikaite-hexahydrate of calcium carbonate (CaCO<sub>3</sub>·6H<sub>2</sub>O)-that forms at temperatures around 0 °C and rapidly decomposes above 7 °C [62]. Three main types of ikaite are distinguished [53]: (a) tufa and travertines in springs and alkaline lakes [62, 73], (b) single microscopic crystals in Arctic and Antarctic ice [18], and (c) macroscopic single euhedral-to-stellate crystal clusters found in marine sediments (e.g., the Laptev Sea; [42, 72]). The latter ikaite type is thought to form during early diagenesis. It has a wide range of  $\delta^{13}$ C values (from -57 to +4%; [32, 48]), which has been attributed to the mixing of carbon generated during organic matter degradation, methanogenesis, and anaerobic oxidation of methane (AOM). Its crystallization is favored by increased concentration of PO<sub>4</sub><sup>3-</sup> ions inhibiting the growth of calcite and aragonite [16, 86].

Other less exotic carbonates found in the arctic marine sediments are representatives of the isomorphic siderite-rhodochrosite series. These minerals are typical in anaerobic environments with high content of dissolved iron and manganese in pore water [12]. They often occur in the regions with elevated sedimentation rates in wellsorted deposits enriched in organic matter (OM) when it is oxidized to  $HCO_3^-$  due to reactions with iron and manganese mediated by microbial communities [33, 56]. The presence of rhodochrosite in core PS51/154-11 was revealed earlier by X-ray diffractometry (XRD) studies [82].

Under favorable conditions, the above-mentioned authigenic minerals relatively quickly form in sediments of different age in both marine and lacustrine environments. For instance, in marine environments, rhodochrosite was reported from Holocene deposits of the Baltic Sea [43, 57, 78]; from Pliocene sediments of Galapagos Ridge in equatorial Pacific aging back to 5 Ma (million years ago) [52]; from Cretaceous accretionary wedge of Barbados in association with siderite [27]; from Eocene-Quaternary deposits of the Norwegian-Greenland basin and Ermak Plateau [14]. In lacustrine environments, it was recorded in varved clays of the Big Watab Lake (Minnesota, USA) aging back to 10 ka (kiloyears ago) [77], in modern gas hydrate structures of Lake Baikal [41], and other localities [43].

Siderites were described in carbonate muds with an age of 190 ka retrieved from the deep-water submarine alluvial fan of the Congo River [22]; in gas hydrate-bearing and adjacent horizons of the Blake Ridge aging back to 6 Ma [50, 65]; in the cement of carbonate concretions from Cascadia continental margin [35, 69]; in Peru trench [83]; in Prudz Bay in Antarctica [15]; in the South China Sea sediments [75]; in the sediments of Akademicheskii Ridge [2, 19, 70]; as well as modern gas hydrate-bearing mud volcanoes and seeps of Lake Baikal [38]. In association with vivianite, siderite was observed in the sediments of the Amazon deep-sea fan accumulated 25 ka [11, 74] and in gas-saturated sediments of Lake Baikal [70].

The association of all three minerals in one section siderite, rhodochrosite, and vivianite—is much less common and has been noted; for example, in the sediments of the Lake El'gygytgyn [55] and the Norwegian Sea [20]. In the studied core PS51/154-11, a unique association of four authigenic minerals (ikaite, siderite, rhodochrosite and vivianite) was observed. This core with the extrapolated basal age of 17.6 cal.ka (calendar kiloyears) reflects the history of the Late Pleistocene and Holocene events in the western Laptev Sea [5, 60, 76, 79–82].

The aim of this paper is to reconstruct the mechanisms and conditions associated with the early diagenesis of authigenic carbonates and other minerals on the Laptev Sea continental slope. Authigenic siderite and rhodochrosite from core PS51/154-11 are essential for paleoceanographic reconstructions due to the fact that microfossils are more or less absent in the concretion-bearing sediment interval. The isotopic composition ( $\delta^{13}$ C and  $\delta^{18}$ O) of authigenic carbonates reflects the conditions of their crystallization–composition of pore water, temperature, and carbon source. Therefore, it becomes possible to reconstruct these parameters, including the degree of ambient water freshening for the period of early deglaciation. These results are important in the context of environmental changes following the Last Glacial Maximum (LGM) in terms of hydrological setting, sedimentation patterns, and pore water chemistry due to the global sealevel rise and the associated invasion of seawater into the former exposed terrestrial–fluvial shelf areas.

### **Materials and methods**

Core PS51/154-11 (77°15.56 N, 120°36.59E, 270 m water depth) was obtained from the upper continental slope of the western Laptev Sea during the Russian–German TRANSDRIFT V expedition in August 1998 aboard the German RV Polarstern. The core is 700 cm long. Its stratigraphy and paleoenvironmental interpretations are constrained by a series of 13 AMS <sup>14</sup>C datings and high-resolution micropaleontological data [5, 31, 60, 76, 79–82]. The oldest date in the core is at 572 cm is 15,372 yrs BP, and the extrapolated age of the core base is estimated as 17.6 cal.ka.

Sediments below 600 cm core depth (extrapolated age > 16 cal.ka) that contain carbonate concretions are almost barren of fossils and contain only a few tests of planktic and benthic foraminifers, with the exception of a single-layer aging back to c.17.2 cal.ka derived from subpolar planktic foraminifers [60, 79-82]. Abundant small-sized plant debris and mica evidence proximity to the paleocoastline and the active influx of terrigenous material. Prior to 16 cal.ka, water depth at the core site was about 100-120 m less than at present, i.e., about 150-170 m. Strong freshwater influence of the Anabar-Khatanga and Olenek rivers is evidenced by the composition of water palynomorphs and dinoflagellate cysts [31]. Severe sea-ice conditions prior to 16 cal.ka are reconstructed from the composition of dinocysts represented by heterotrophic cold-water species [31], biomarker data [26], and high input of iceberg and sea-ice rafted debris (IRD) [82].

Measurements of the total organic carbon (TOC) content were carried out with a carbon–nitrogen–sulphur analyzer Elementar Vario EL III in GEOMAR (Kiel, Germany). In the upper part of the core down to 150 cm, sampling was carried out at 5 cm interval and the rest part of the sediment section was sampled every 10 cm. Samples were freezedried and homogenized. All samples were run in duplicate of which the average was used [79, 80].

We analyzed samples of authigenic Fe–Mn carbonates collected at four core intervals: 620–622, 642–644, 652–654 and 674–677 cm (Fig. 1). Spot analyses of Ca, Mg, Mn, and Fe were carried out at VSEGEI (St.Petersburg, Russia) using a Scanning Electron Microscope equipped with Energy Dispersed Spectrometer—SEM–EDS system (Cam-Scan MV2300 with BSE Detecor: excitation voltage, 20 kV;

peak count time, 120 s; background count time, 10 s; spot diameter 255 nm).

Isotopic composition of carbon and oxygen ( $\delta^{13}C$  and  $\delta^{18}$ O) in Fe–Mn carbonates was determined with a massspectrometer IRMS Delta V adventure with Gas-Bench device at the Faculty of Geology of the Lomonosov Moscow State University. Carbonate samples (1-3 mg) were subject to total dissolution in 100% phosphoric acid during 14 h at 72 °C. CO<sub>2</sub> gas was automatically directed for measurement into a mass spectrometer with the help of Gas-Bench device. The reference limestone NBS-19 is used as a standard ( $\delta^{13}$ C = + 1.95% and  $\delta^{18}O = -2.2\%$  VPDB; [24]). Results are expressed in VPDB scale. Isotopic composition of oxygen in carbon dioxide produced by the reaction between phosphoric acid and carbonates is known to be approximately 10% heavier than in original carbonate. Oxygen fractionation factor depends on temperature and mineral (chemical) composition of carbonates. For stoichiometric calcites, rhodochrosites, and siderites, it is calculated using the following equations [10, 17, 66]:

$$10^3 \ln \alpha_{\rm H_3PO_4\text{-}CaCO_3} = 3.89 + 5.61 \times \frac{10^5}{T^2}$$

$$10^3 \ln \alpha_{\rm H_3PO_4-MnCO_3} = 3.77 + 5.72 \times \frac{10^5}{T^2}$$

$$10^{3} \ln \alpha_{\mathrm{H_{3}PO_{4}}\text{-FeCO}_{3}} = 3.85 + 6.84 \times \frac{10^{5}}{T^{2}}.$$

These values were obtained for 72 °C:

 $10^{3} \ln \alpha_{H_{3}PO_{4}-CaCO_{3}} = 8.6\% co, \quad 10^{3} \ln \alpha_{H_{3}PO_{4}-MnCO_{3}} = 8.1\% co$ and  $10^{3} \ln \alpha_{H_{2}PO_{4}-FeCO_{3}} = 9.6\% co.$ 

Since the standard NBS-19 is calcite, the following corrections are often introduced into  $\delta^{18}$ O values:

$$10^3 \ln \alpha_{\text{CaCO}_3 - \text{MnCO}_3} = -0.5\% oo,$$

 $10^3 \ln \alpha_{\text{CaCO}_3 - \text{FeCO}_3} = 1.0\% oo.$ 

There is no common approach for calculating fractionation between phosphoric acids and non-stoichiometric carbonates. Hence, as the estimates of fractionation between rhodochrosite and siderite with the acid generally compensate each other, we decided not to introduce any corrections into the measured  $\delta^{18}$ O values of carbonates.



**Fig. 1** Location of core PS51/154-11, lithological description vs depth (cmbsf—cm below sea floor), calendar ages (cal.yrs BP) estimated from AMS<sup>14</sup>C datings [5, 82], TOC and C/N records [79, 80], and photos of carbonate tubule samples from different downcore intervals

## Results

Brownish grey carbonate concretions occur below 620 cm core depth and are represented by separate and joined (parallel or ramified) tubules and their fragments are partly filled with sand-size material. Tubule diameter does not exceed 1–2 mm, and their length ranges between 1 and 2 cm. Sediment matrices consists of sandy silt with numerous organic and sulphide inclusions. Carbonate tubules in association with vivianite concretions occur down to the core base; and vivianite concretions alone occur up to 585 cm core depth [82] (Fig. 1). Ikaite crystals were found during onboard core description at 360 cm core depth.

Originally, rhodochrosite was identified in carbonate tubules by means of XRD [82]. SEM–EDS analysis allowed us now to determine the elemental composition of carbonate minerals more precisely and to reveal their globular microstructure (Fig. 2). According to their chemical composition, carbonates from the studied samples are represented by minerals of the isomorphic siderite–rhodochrosite series with considerable admixture of calcium. Thus, in addition to the previously determined rhodochrosite, we established now the presence of a siderite phase (Fig. 3).

Chemical analysis at certain points showed that the tubules from the depths of 620–622 and 642–644 cm consist of rhodochrosite; Mn (42–79 mol%) in their crystal lattice is substituted by Fe (6–37 mol%) and Ca (up to 20 mol%). Siderite composition of carbonates was determined in the samples from the depths of 652–654 and 674–677 cm. Besides Fe (42–56 mol%), they include Mn (13–25 mol%) and Ca (up to 20 mol%). All studied samples contain small amounts of Mg (up to 8 mol%). The trace element composition of varying Fe:Mn ratios and low Mg content testify that siderites were formed from fresh or brackish pore water [29, 84].

Mass-spectrometer measurements of carbonates showed generally low concentrations of heavy carbon <sup>13</sup>C and oxygen <sup>18</sup>O isotopes. The measured  $\delta^{13}$ C values vary between -21.0 and -17.0% VPDB, and those of  $\delta^{18}$ O range from -9.86 to 1.72% VPDB (Table 1).

TOC content varies within 0.4–1.35% of the dry sediment averaging 1.0% (Fig. 1). It reaches its maximum (1.35%) at 261 cm, while minimum values are recorded at 661–671 cm. TOC distribution in core PS51/154-11 suggests that it is partly utilized for reduction of iron oxides to carbonate/phosphate and/or sulphides (in the Holocene section). C/N values range between 7.4 and 13.1 averaging < 10 (Fig. 1; [79, 80]). Therefore, abundant marine OM is preserved in the sediments.

#### Discussion

# Mechanisms of carbonate formation in the course of diagenesis

Based on the analysis of sediment lithology, the association of Fe–Mn carbonates with other authigenic minerals (vivianite and ikaite) and the isotopic composition of carbon and oxygen in Fe–Mn carbonates, we attempt to reconstruct the mechanism of their formation.

Crystallization of biochemical carbonate minerals during early diagenesis is directly controlled by microbial activity. Microbes participate in major diagenetic processes such as OM disintegration, methane oxidation and methane generation (e.g., [46]).

The first process largely results from microbial destruction of OM in the course of sulphate reduction under anaerobic conditions, as described by the following general reaction:

$$2CH_2O + SO_4^{2-} \rightarrow 2HCO_3^{-} + H_2S \tag{1}$$

In the Arctic, this process leads to the formation of siderites and rhodochrosites as described from sediments drilled on the Lomonosov Ridge close to the North Pole [39]. The same is suggested for ikaite formation in the Laptev Sea shelf sediments [42].

Carbonates formed due to methane (and its homologues) oxidation under anaerobic conditions (or under aerobic ones given the strong methane influx) occur in regions with focused hydrocarbon fluid discharge. The most common mechanism in marine settings is sulphate reduction according to the following scheme:

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^{-} + HS^{-} + H_2O,$$
 (2)

where sulphates are limited, such as freshwater environment or in marine settings depleted in sulphate ion, methane can be oxidized according to Eqs. (3) and (4), where there is enough iron and manganese to form siderites-rhodochrosites [6, 40]:

$$CH_4 + 4Fe_2O_3 + 15H^+ \rightarrow HCO_3^- + 8Fe^{2+} + 9H_2O$$
(3)

$$CH_4 + 3MnO_2 + 3H^+ \rightarrow HCO_3^- + 3Mn^{2+} + 3H_2O.$$
(4)

Microglobular structure of the studied siderites/rhodochrosites (Fig. 2) is typical for diagenetic conditions when microbial destruction of OM produces pH increase. Such authigenic concretions occur in Ice Complex deposits of the eastern Arctic coastal lowlands [44].



◄Fig. 2 Microstructure of carbonates and measurement points on SEM images: a–d general view of the samples, e, f globular structures, and g, h globules with the marks corresponding to measurement points

#### Isotopic composition of carbon

Variations of the measured  $\delta^{13}$ C in the studied siderite/ rhodochrosite samples of -21 to -17% give evidence for a possible combination of carbon from different sources. Usually, isotopic composition of  $C_{\text{org.}}$  ranges from -20to -30%, whereas  $\delta^{13}$ C of dissolved inorganic carbon in the modern seawater is close to 0% [21, 24, 71]. Thus, the studied carbonates are on the mixing line between these end members. Values of  $\delta^{13}$ C–CH<sub>4</sub> in bottom sediments are normally lighter than -40%, although in rare cases, they rise up to -20%, and even more if abiogenic sources are involved [63, 85]. Considerably higher  $\delta^{13}$ C values than biogenic methane (up to -7%) were thought to be the characteristic feature of abiogenic methane [24]. The measured  $\delta^{13}$ C values of carbonates show that enrichment in light isotope <sup>12</sup>C is insufficient to assume that methane contributed carbon for their crystallization. However, this mechanism should not be completely excluded, because kinetic isotope effects accompanying methane oxidation produce heavier  $\delta^{13}$ C bicarbonate-ion (following reactions 2-4). On the other hand, notable signs of gas saturation were not observed during onboard lithological description of core PS51/154-11. Therefore, it is unlikely that carbon of methane origin was present in the pore fluid from which the studied carbonates crystallized (otherwise, its participation was minimal).

This leads to the likely conclusion that a reduction of  $Fe^{3+}$  and  $Mn^{4+}$  cations produced siderites and rhodochrosites as described by the following general reactions:

 $4\text{Fe}(\text{OH})_3 + C_{\text{org}} \rightarrow \text{Fe}\text{CO}_3 + 3\text{Fe}(\text{OH})_2 + 3\text{H}_2\text{O}, \quad (5)$ 

 $2\mathrm{MnO}_2 + C_{\mathrm{org}} + \mathrm{H}_2\mathrm{O} \to \mathrm{MnCO}_3 + \mathrm{Mn(OH)}_2.$ (6)

## Isotopic composition of oxygen

Oxygen isotope values  $\delta^{18}$ O can be used to estimate the temperature of carbonate crystallization and to reconstruct the  $\delta^{18}$ O composition of carbonate-forming pore fluid, hence, its origin.

The Laptev Sea shelf and continental slope receive considerable amount of river water, primarily controlled by the Lena River runoff. Isotopic composition of river water is strongly different from isotopic composition of both, seawater and sea ice. Therefore, this parameter is a good indicator for the presence of river water in the water column. For the Arctic shelf regions, and particularly for the Laptev Sea,  $\delta^{18}$ O of seawater (primarily of Atlantic origin) typically equals 0.3% VSMOW at 35% salinity, and  $\delta^{18}$ O of river water is as light as -20% VSMOW [3, 4].

Mass-spectrometer measurements of our siderite and rhodochrosite samples revealed a depletion in <sup>18</sup>O isotope, from – 9.86 to 1.72‰ VPDB (Table 1). Based on the modern  $\delta^{18}$ O values of seawater, river water, and pore water (conventional regional average) given in [3, 4] and near-bottom water temperature of + 0.3 °C [25], as well as temperatures of – 1.6 °C at the subbottom depth of 5.5 m [4], it is possible to deduce whether carbonates were formed in equilibrium following these equations [7, 30, 87]:

$$10^3 \ln \alpha_{\text{FeCO}_3\text{-}\text{H}_2\text{O}} = 2.89 \times \frac{10^6}{T^2} - 2.81$$

$$10^3 \ln \alpha_{\text{FeCO}_3 - \text{H}_2\text{O}} = 2.56 \times \frac{10^6}{T^2} + 1.69$$

$$10^3 \ln \alpha_{\text{MnCO}_3-\text{H}_2\text{O}} = 17.84 \pm 0.18 \times \frac{10^3}{T} - 30.24 \pm 0.62,$$

where  $\alpha$ —factor of oxygen isotope fractionation and *T* temperature of carbonate crystallization in K. This approach was used for calculating the theoretical oxygen isotope composition of carbonates in relation to the  $\delta^{18}$ O composition of original fluid (Table 2).

Calculation results (Table 2) show that the studied carbonates crystallized from the fluid formed through the mixing of pore water (seawater) and river water. However,  $MnCO_3$  from the upper interval (620–622 cm) formed from the pore water that was isotopically close to seawater, while isotopic composition of the lower samples indicates considerable contribution of oxygen from freshwater sources (Table 1).

The above equations [7, 30, 87] can be also used for calculating the equilibrium crystallization temperatures for siderites and rhodochrosites with the measured  $\delta^{18}$ O values in carbonates and ambient water. The obtained values vary from – 57 to +81 °C depending on the applied  $\delta^{18}$ O of water (seawater, pore water, or river water). Obviously, these extreme temperature estimations are unrealistic for the conditions of early diagenesis in the Laptev Sea. It is very unlikely that the real temperatures of rhodochrosite/siderite crystallization were much different from +0.3 °C typical for the modern bottom sediments of the region. If so, then one can calculate the equilibrium  $\delta^{18}$ O values of the carbonateforming fluid using the same equations. The resultant values are as follows:

- 2.9% VSMOW for MnCO<sub>3</sub> from the interval 620– 622 cm;
- 14.1% VSMOW for MnCO<sub>3</sub> from the interval 642– 644 cm;



Fig. 3 Ternary diagram showing the results of SEM-EDS analyses of Fe-Mn carbonates

Table 1 Stable isotope  $\delta^{18}O$  and  $\delta^{13}C$  (VPDB) composition of carbonates, TOC,  $C_{\rm carb}$  and  $C\!/N$ 

Sediment inter- val, cm/mineral	$\delta^{18}O\%$	$\delta^{13}C\%$	TOC, % <sup>a</sup>	$C_{\rm carb}$ , % <sup>a</sup>	C/N <sup>a</sup>
620–622/MnCO <sub>3</sub>	1.7	- 17.0	0.5	0	8.8
642–644/MnCO <sub>3</sub>	- 9.6	- 19.2	0.4	0.2	8.3
652–654/FeCO <sub>3</sub>	- 6.7	- 21.0	0.5	0	9.0
674–677/FeCO <sub>3</sub>	- 9.9	- 18.4	0.4	1.5	8.5

<sup>a</sup>[79, 80]

**Table 2** Theoretical value of  $\delta^{18}O_{FeCO3}$  and  $\delta^{18}O_{MnCO3}$  [7, 30, 87] calculated for crystallization conditions (T, °C, and  $\delta^{18}O$  values) from marine, pore, and river waters of the Laptev Sea region

δ <sup>18</sup> O of water, ‰ VSMOW	δ <sup>18</sup> O <sub>FeCO3</sub> , % VPDB		$ \begin{array}{c} \delta^{18}O_{MnCO3}, \ \% o \\ VPDB \end{array} $	
	+0.3 °C	– 1.6 °C	+0.3 °C	– 1.6 °C
- 20.0 <sup>a</sup> (river water)	- 15.5	- 15.0	- 14.7	- 14.1
- 5.25 <sup>b</sup> (pore water)	- 0.7	- 0.2	0.2	0.7
- 2.09 <sup>b</sup> (pore water)	2.5	3.0	3.4	3.9
$+0.3^{\circ}$ (near-bottom water)	4.9	5.4	5.8	6.3

<sup>a</sup>[3] <sup>b</sup>[4]

<sup>c</sup>[25]

- 12.1% VSMOW for FeCO<sub>3</sub> from the interval 652– 654 cm;
- 15.3‰ VSMOW for FeCO<sub>3</sub> from the interval 674–677 cm.

The isotopic data obtained confirm our previous conclusion that rhodochrosite from the uppermost interval (with extrapolated age of 16.3 cal.ka) crystallized from a fluid with  $\delta^{18}$ O composition almost similar to the modern pore water, whereas carbonates from the underlying sediment layers (with extrapolated age of 16.3–17.6 ka) were formed under freshened conditions.

#### Vivianite and ikaite

The fact that pore water was freshened during the times when carbonates with light  $\delta^{18}O$  composition were formed (extrapolated age 16.3-17.6 cal.ka) gains support in the coexistence of abundant vivianite concretions ranging in size from 1 mm to 1 cm [82]. Vivianite forms in reducing alkaline environments with highly active iron and phosphate ions and low concentration of sulphides [58]. Low contents of HS<sup>-</sup>- and SO<sub>4</sub><sup>2-</sup> ions are typical for freshwater environments; as a result, iron ions produce phosphates instead of sulphides (by means of microbially controlled sulphate reduction typical for marine settings). Association of siderite and vivianite is common for freshwater lakes (e.g., [55, 70]. However, vivianite is rare in marine sediments and has been reported only in a few locations: in quaternary sediments of the Amazon deep-sea fan, where millimeter-sized vivianite nodules precipitated within the sulphate-free zone [11]; in sediments from Zambezi deep-sea fan, formation of vivianite is suggested to take place below the sulphate/methane transition zone [49]. Carbonate fluorapatite is considered to be the most important authigenic sink for P in marine realm, accounting for an estimated 50% of global P burial [28, 68]. However, we have not found this mineral.

Crystallization of vivianite can be described by the following reaction:

$$3Fe_4(P_2O_7)_3 + 6H_2 + 41H_2O \rightarrow 4Fe_3(PO_4)_2(H_2O)_8 + 10H_3PO_4.$$
(7)

Besides siderite, rhodochrosite, and vivianite, the studied core sediments also contain ikaite crystals at the depth of 360 cm aging back to 13.3–13.4 cal.ka. Ikaite is unstable under normal conditions, and its crystallization occurs only in the presence of inhibitors that slow down the growth of calcite and aragonite. Phosphates belong to such inhibitors [16, 86]. For instance, ikaites in the Kara Sea occur exactly in the layers with increased concentration of dissolved  $PO_4^{3-}$  [32]. Vivianite findings in core PS51/154-11 give, therefore, indirect evidence for a high content of phosphate ion in its pore waters. Although no data on the pore water chemistry are available, we can still assume from the downcore pattern of mineral phase distribution that during the period of ikaite crystallization, OM oxidation proceeded due to sulphates rather than iron and manganese ions.

# Paleoenvironmental conditions during the period of authigenic carbonates formation

The lower part of the sediment section enriched in authigenic Fe–Mn carbonates corresponds in time to the early deglaciation with cold marine conditions, extensive sea-ice cover, and water mass stratification. At that time, Laptev Sea shelf was exposed, and rivers penetrated far northward with their mouths located close to the present shelf break and upper continental slope. Rivers actively transported terrigenous material, and icebergs delivered sediment load from Severnaya Zemlya and the decaying Barents-Kara ice sheet [60, 82].

The most "ancient" of the studied carbonates from the sediments with extrapolated age of 16.3-17.6 cal.ka were formed in freshwater-affected environment with brackish pore waters. Several scenarios might explain the presence of these waters on the upper continental slope of the Laptev Sea. For instance, freshwater might have percolated through the "degradation zones" that appeared in the areas of permafrost flood plains and multi-arm river channels [51] of the Olenek and Anabar-Khatanga rivers. They were likely produced by suffusion processes in granulometrically heterogeneous grounds and high-pressure gradients in low permeable zones [1]. There is an opinion that submarine groundwater discharge is an important transportation route for dissolved terrestrial material to the ocean (e.g. [45]). Therefore, it is possible to assume that Fe, Mn, and P, essential for crystallization of authigenic Fe-Mn carbonates and vivianite, were delivered to the core site with ground waters. The tubular shape of carbonate concretions supports this version, since carbonates could cement water discharge channels.

Another possible scenario considers the period of short but intense seasonal river flood—hyperpycnal mud plumes [64]—delivering huge amounts of freshwater enriched in suspended load and OM to the surface and, probably, also to near-bottom water layers. This can happen quickly, within hours or days of the initial river flood [8, 61]. Similar scenarios are observed in the Mississippi, Po, Amazon, and other deep-sea fans [8, 54, 59, 64].

Due to high density, these waters might have been able to cascade down the relatively steep upper continental slope located close to the former coastline and affect the bottom water layer. A marginal filter, i.e., the mixing zone of river and sea waters which represents a kind of a "colloidal plug", was likely narrow and also located close to the former coastline and the studied core site. Marginal filters are characterized by rapid processes of active precipitation of iron colloids, predominantly hydroxides, decomposition, and mineralization of suspended terrigenous and marine OM, and increased content of chlorophyll, nitrates, and phosphates [47]. Under such sedimentation conditions, when the bicarbonate-ion content is high due to diagenetic oxidation of OM, the formation of carbonates and vivianite starts. A certain role in water freshening can be also played by meltwater; its presence is confirmed by IRD peaks [82].

It is possible that the observed freshening of pore waters recorded in the oxygen isotopic composition of authigenic carbonates from lower sediment layers could be the result of the combined action of both scenarios. Probably, the changes in the composition of pore waters that became close to the modern seawater occurred rather quickly, as evidenced by the isotopic composition of the "youngest" rhodochrosite concretions.

# Conclusions

Authigenic carbonates represented by siderites and rhodochrosites were found in core PS51/154-11 from the western Laptev Sea continental slope (water depth 270 m) at > 600 cm core depth. They were formed during the Late Pleistocene under freshwater-affected cold-water environment of the relatively steep slope at past water depths of 150–170 m and in close proximity to the former coastline and river mouths. Sulphide-free anaerobic conditions of subaquatic diagenesis favored crystallization of siderites and rhodochrosites that cemented the walls of thin channels through which freshened waters enriched with Fe<sup>2+</sup> and Mn<sup>2+</sup> filtrated, thus forming carbonate tubules. The dominant source of inorganic carbon dissolved in the pore water was the isotopically light carbon  $CO_2$  inherited in the diagenetic decomposition of organic matter.

The general conceptual model of authigenic mineral formation in core PS51/154-11 (since ~17.6 cal.ka until the present) is represented in Fig. 4. Based on sediment lithology and mineral associations, three stages in the formation



Fig.4 General conceptual model of authigenic mineral formation at core site PS51/154-11. Timing of each diagenetic stage is shown beneath its number

of authigenic minerals have been identified. The *first stage* (c. 17.6–16.3 cal.ka) corresponds to the formation of predominantly siderites together with vivianite under the influence of freshened pore water, the sources of which could be groundwater and/or riverine flood water affected by geochemical processes in the marginal filter zone. There were reducing alkaline conditions with a high activity of iron and phosphate ions and a low concentration of sulphides. During the *second stage* (c. 16.3–15.5 cal.ka), vivianite and predominantly manganese carbonates were formed under lessfreshened conditions. The "youngest" rhodochrosite concretions crystallized from the pore water that was similar to the modern seawater as evidenced by the  $\delta^{18}$ O values. The *third*  *stage* (c. 15.5 cal.ka to present) is related to the formation of ikaite crystals that testifies to the high content of phosphates in pore waters. Fe–Mn authigenic carbonates probably started to dissolve, as evidenced by their appearance.

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#### **Compliance with ethical standards**

**Conflict of interest** On behalf of all authors, the corresponding author states that there is no conflict of interest.

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