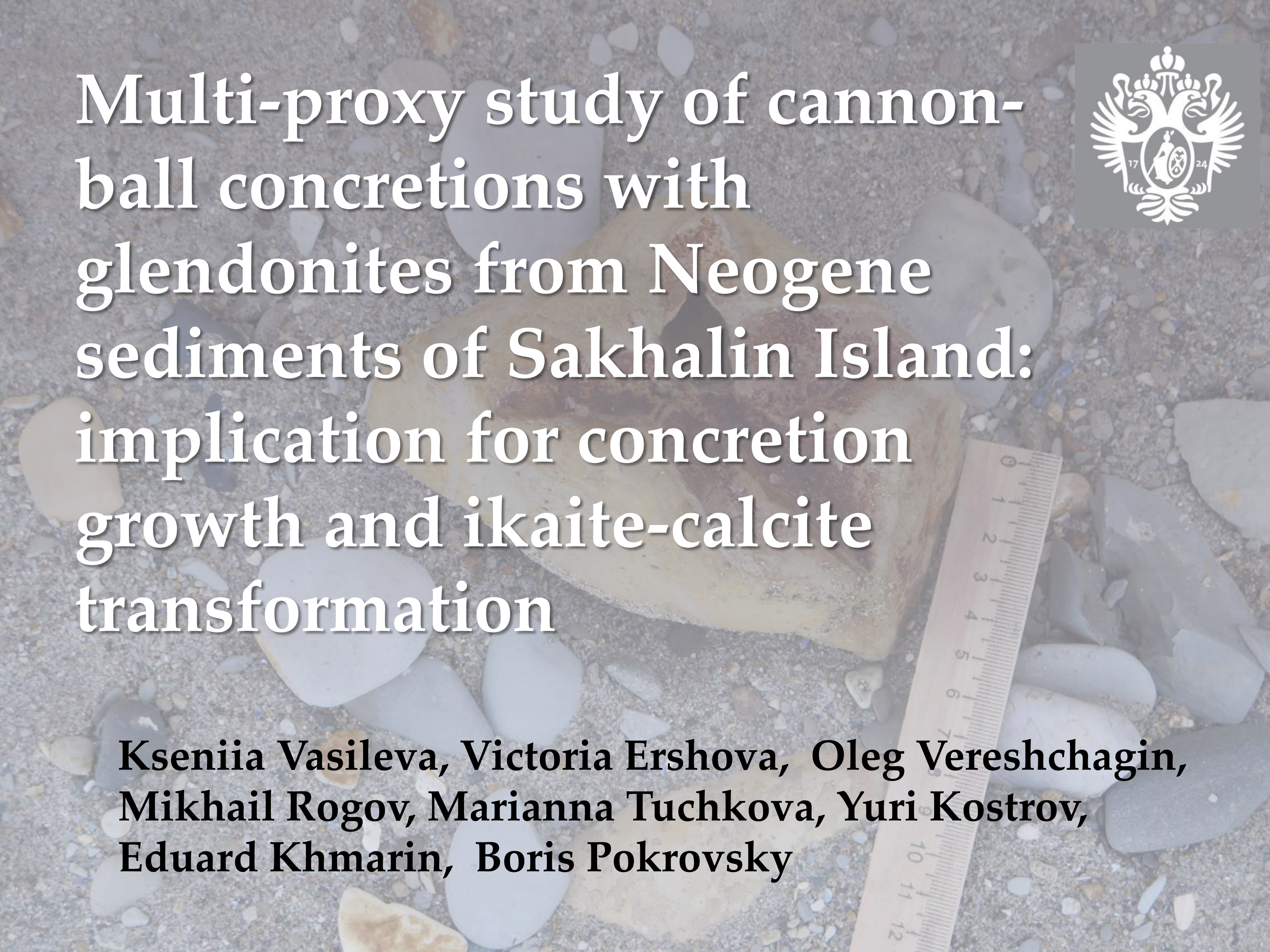
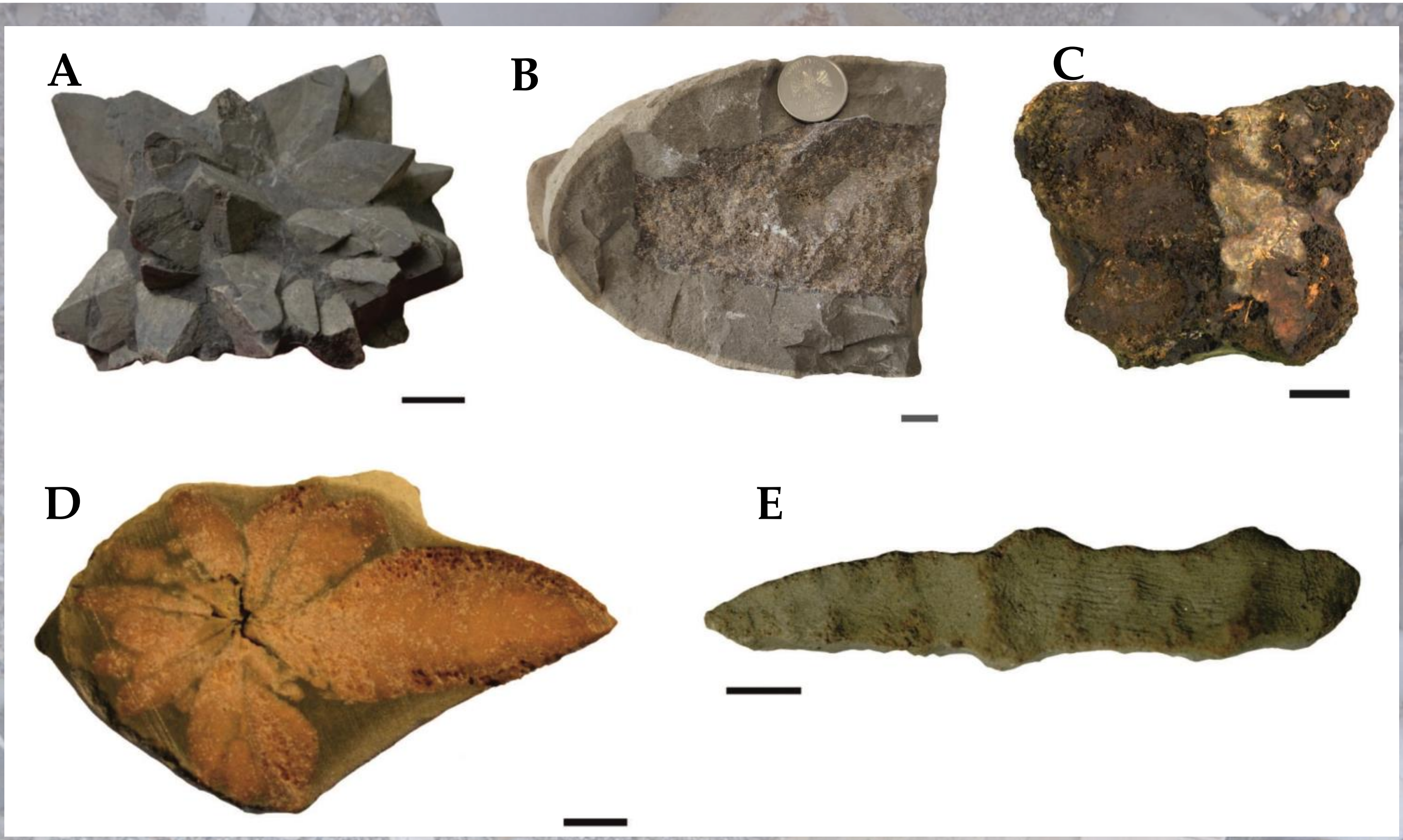


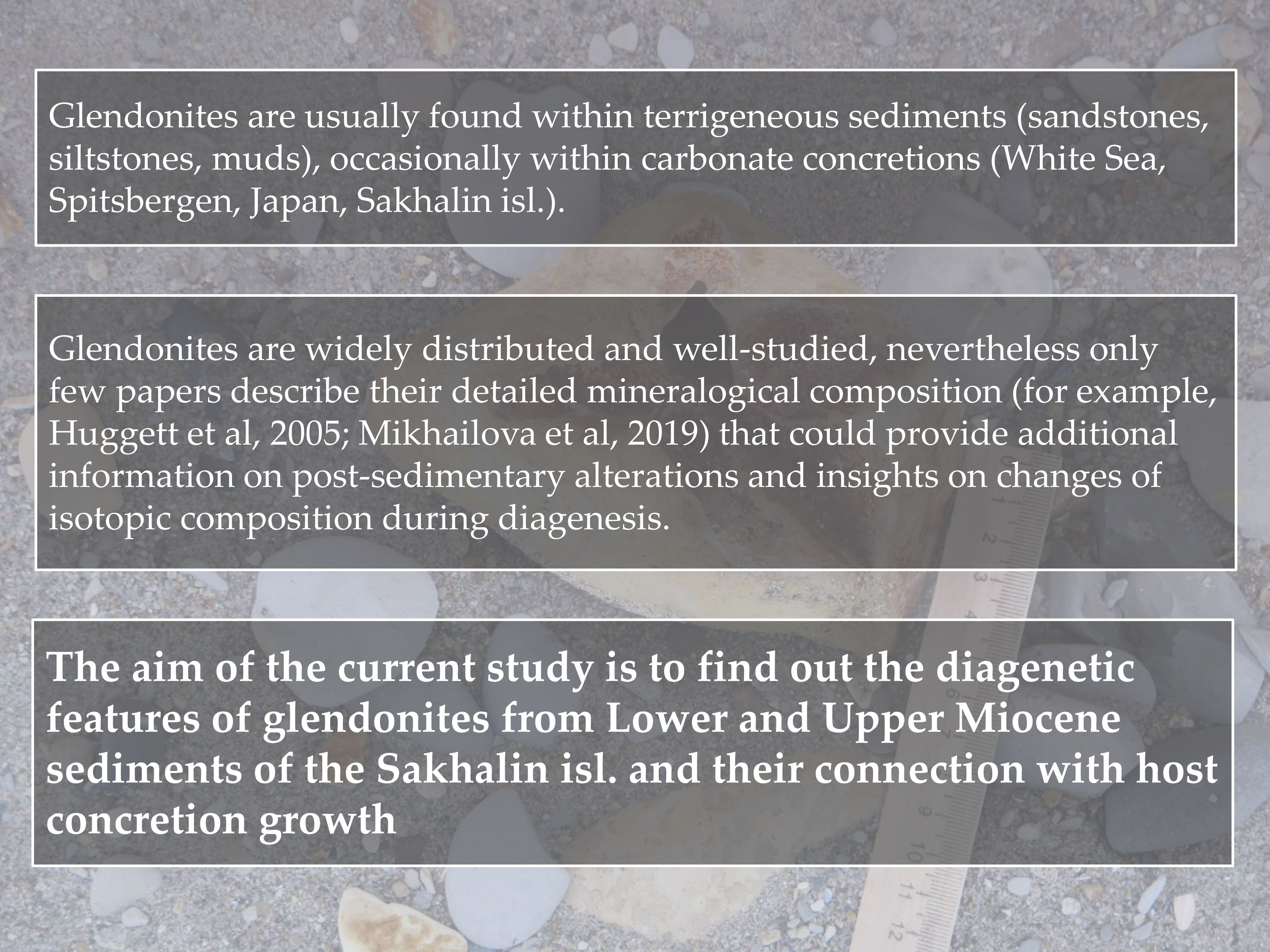
Multi-proxy study of cannon-ball concretions with glendonites from Neogene sediments of Sakhalin Island: implication for concretion growth and ikaite-calcite transformation

Kseniia Vasileva, Victoria Ershova, Oleg Vereshchagin, Mikhail Rogov, Marianna Tuchkova, Yuri Kostrov, Eduard Khmarin, Boris Pokrovsky

Ikaite, metastable hexahydrate of calcite, is considered to indicate cold water environments and findings of ikaite pseudomorphs (glendonites) point at cold climate of the past. Glendonites are found all over the World in sediments of different ages – from Mesoproterozoic to modern.



Examples of glendonites: A - stellate (Middle Jurassic, Anabar Bay), B – crystal-like in concretions (Lower Miocene, Sakhalin isl.), C – cross-like (Lower Oligocene, Sakhalin isl.), D – stellate in concretion (cross section, Holocene, White Sea), E - crystal like (Holocene, White Sea). Scale bar is 1 cm.



Glendonites are usually found within terrigeneous sediments (sandstones, siltstones, muds), occasionally within carbonate concretions (White Sea, Spitsbergen, Japan, Sakhalin isl.).

Glendonites are widely distributed and well-studied, nevertheless only few papers describe their detailed mineralogical composition (for example, Huggett et al, 2005; Mikhailova et al, 2019) that could provide additional information on post-sedimentary alterations and insights on changes of isotopic composition during diagenesis.

The aim of the current study is to find out the diagenetic features of glendonites from Lower and Upper Miocene sediments of the Sakhalin isl. and their connection with host concretion growth

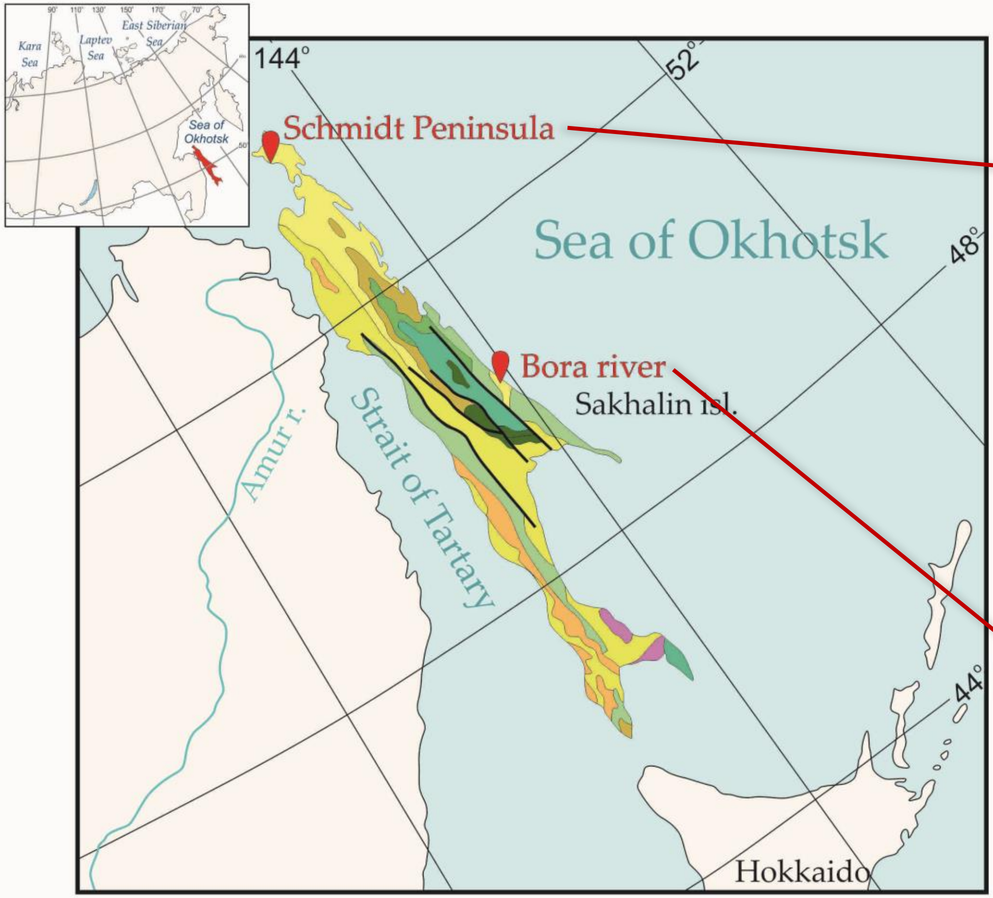
Materials and methods

6 samples of glendonites within host concretion from Bora (3 samples) and Vengeri (3 samples) formations were studied.

Polished thin-sections were studied under the polarizing Olympus BX-53 microscope with CL8200 Mk-5 Optical CL System for cold cathodoluminescence, accelerating voltage 6-10 kV and current of 220-250 μA (Department of the Regional Geology, Saint Petersburg State University).

The morphology of minerals and their chemical composition was studied on carbon-coated polished sections by means of an Hitachi S-3400 N scanning electron microscope equipped with an Oxford Instruments AzTec Energy X-Max 20 energy dispersive spectrometer (“Geomodel” Resource Centre of Saint-Petersburg State University (RC SPbSU)). EDX spectra were obtained under the following conditions: 20 kV accelerating voltage, 1 nA beam current.

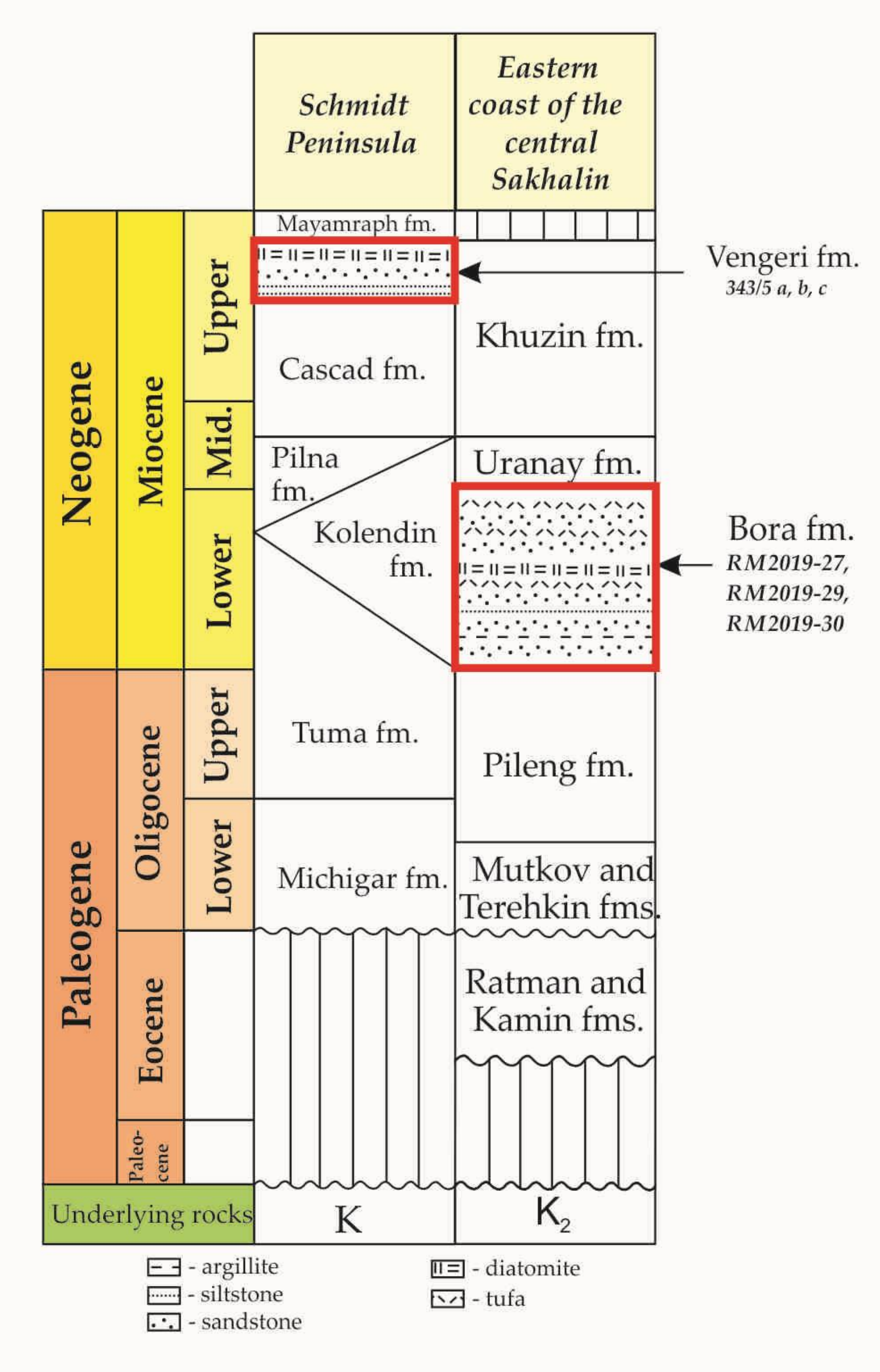
Carbon and oxygen isotope data were collected with the Thermo electron system, including a Delta V Advantage Mass-Spectrometer with Gas-Bench-II (Geological Institute of the Russian Academy of Sciences, Laboratory of Geochemistry of Isotope and Geochronology, Moscow). An analytical precision for both $\delta^{18}O$ and $\delta^{13}C$ of ±0.2‰.



N_2	- Pliocene pebble, sandstone, clay and basalt
N_1	- Miocene pebble, sandstone, clay, basalt and tuff
N	- Neogene terrigeneous rocks, coal, basalt and tuff
p	- Paleogene terrigeneous rocks, coal, basalt and tuff
K_2	- Cretaceous terrigeneous rocks, tuff, basalt, dacite, rhyolite
K	- Cretaceous terrigeneous rocks, tuff, basalt, dacite, rhyolite
$J\text{-}K_1$	- Jurassic to Lower Cretaceous terrigeneous rocks, tuff and siliceous rocks
T-J	- Triassic to Jurassic terrigeneous rocks, tuff, limestone and siliceous rocks
PZ	- Paleozoic terrigeneous rocks, tuff, limestone, siliceous rocks and metamorphic rocks
╲	- main faults

Outcrop of Vengeri Formation, Schmidt Peninsula

Outcrop of Bora Formation, Schatun stream

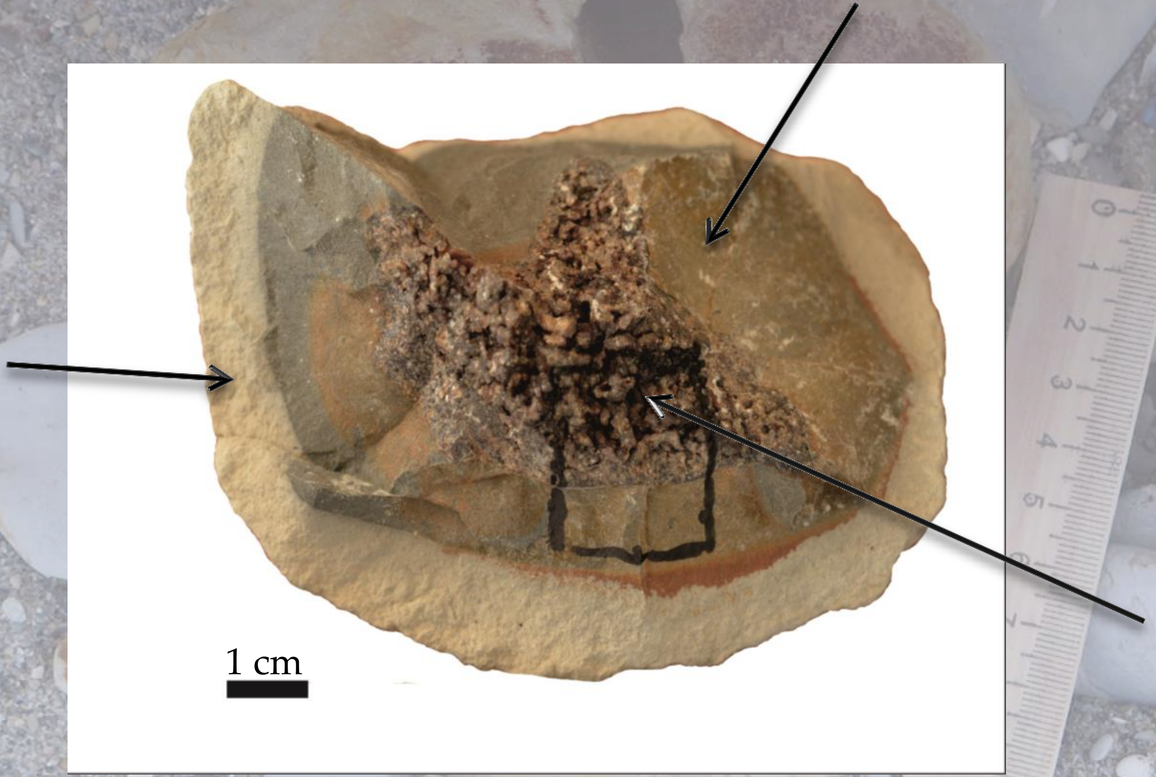


Bora and Vengeri formations are composed with terrigeneous sediments (sandstones, siltstones, argillites), comprises diatomite layers. Tufa interlays are found within Bora Formation

Carbonate concretions are found within terrigeneous layers , some of concretions contain glendonite in the center.

Association of glendonite in the studied formations with dropstones is an indicator of cold conditions, which is well-corresponding with view on glendonites as a proxy for cooling events.

60-90% of the cannon-ball concretion is occupied by sandy limestone (cemented with high-magnesium calcite) and occasionally contains dolomite and pyrite. Central part of the cannon-ball concretion is occupied by glendonite (crystal-like or star-like cluster of crystals).

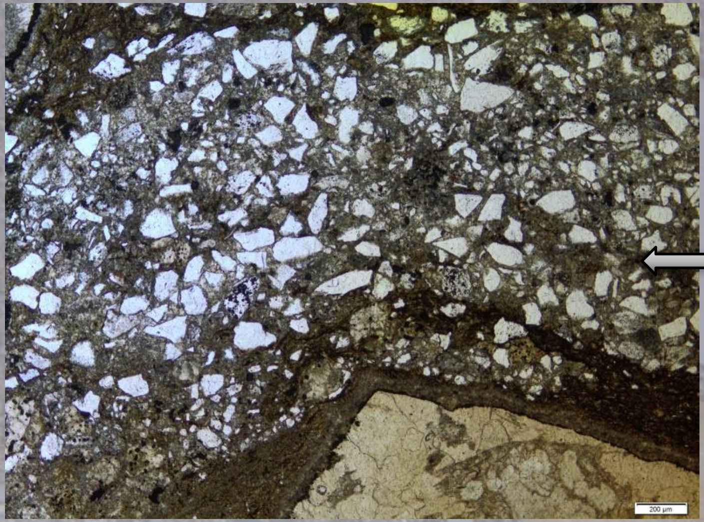


host cannon-ball concretion

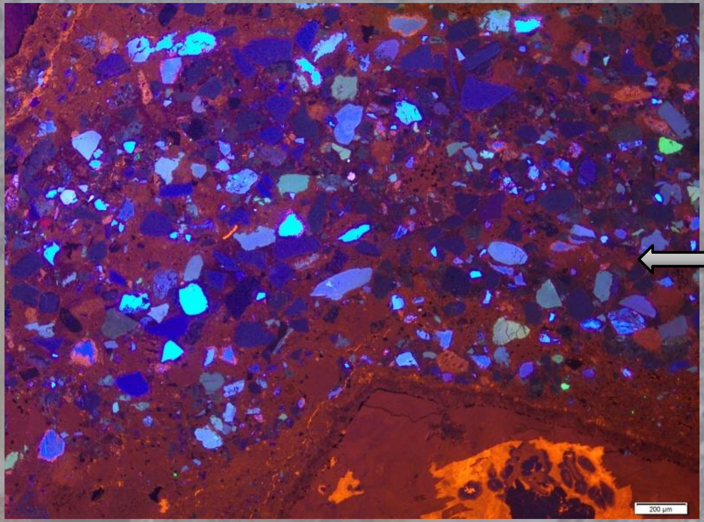
Sandstone
(host sediments)

glendonite

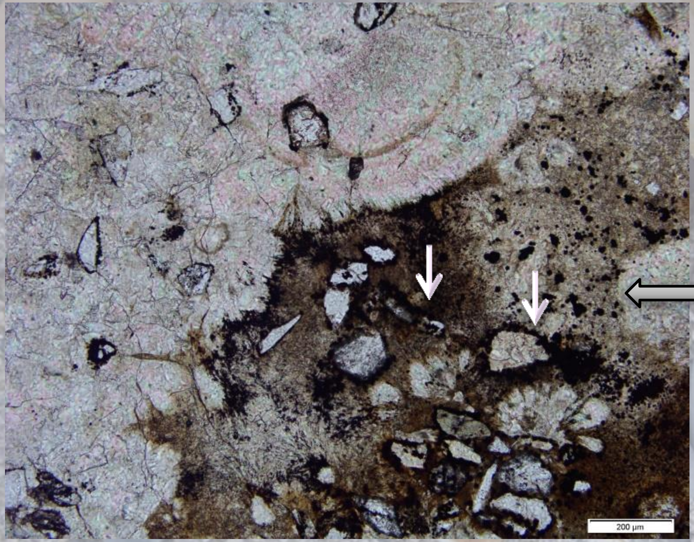
Sample 343/5a



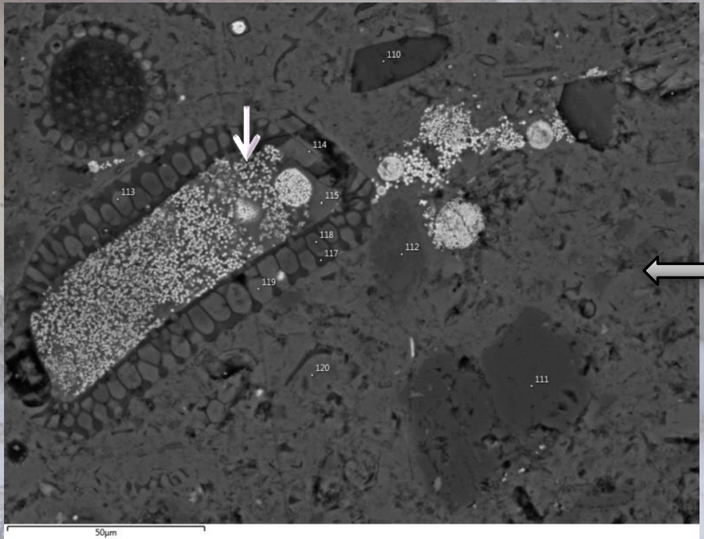
Sample RM2019/27, plane-polarized photo. Internal structure of host concretion



Same, in CL Internal structure of host concretion



Sample RM2019/27, plane-polarized photo. White arrows point at pyrite overgrowth on detrial quatrz grains

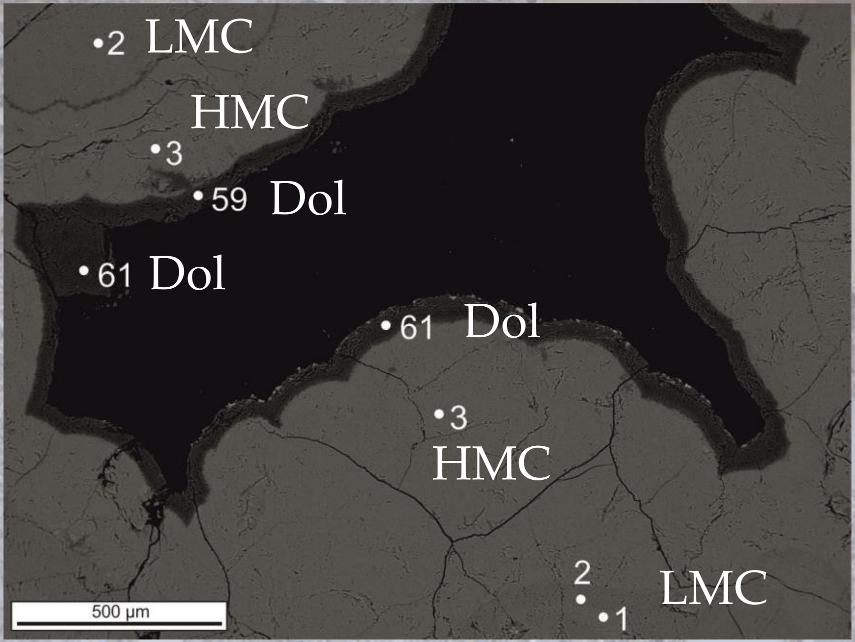


Sample 343/5a, SEM photo. White arrows point at framboidal pyrite in diatom shell

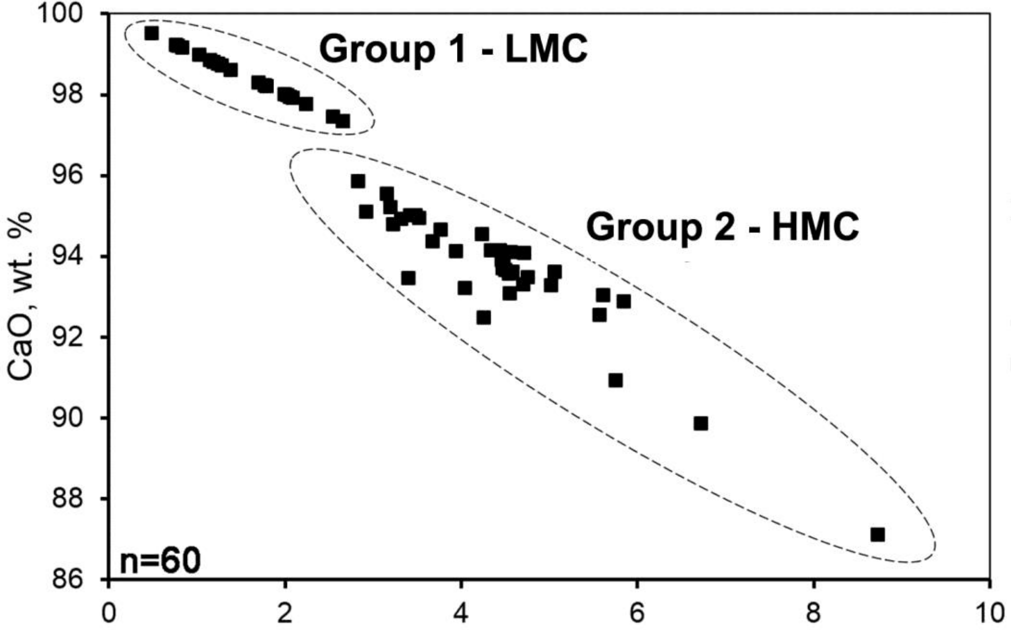
Host concretion is composed of sandstone cemented with high-magnesium calcite and occasionally contains microfossils, dolomite and pyrite; quartz grains are often corroded.

Scanning electron microscopy and microprobe analyses

There are three generations of carbonate minerals in the studied glendonites. Calcite with Mg content<2% is low-magnesium calcite (LMC), it replaced ikaite; calcite with Mg content 2-8% is high-magnesium calcite (HMC), HMC forms acicular cement crystals around ikaite-derived calcite; dolomite (Mg content>37%) forms thin fringe at the edge of HMC.

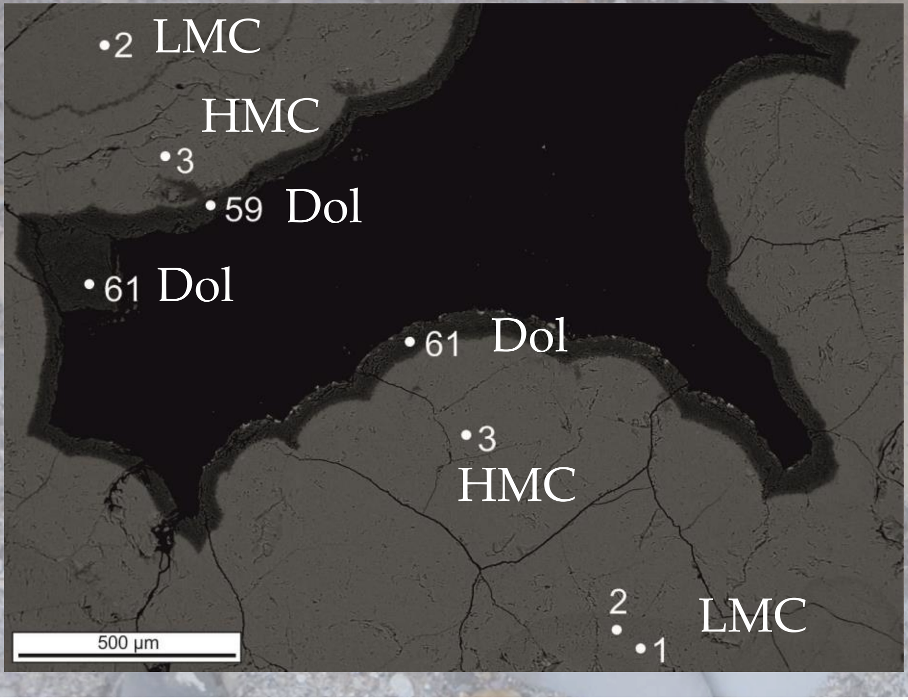


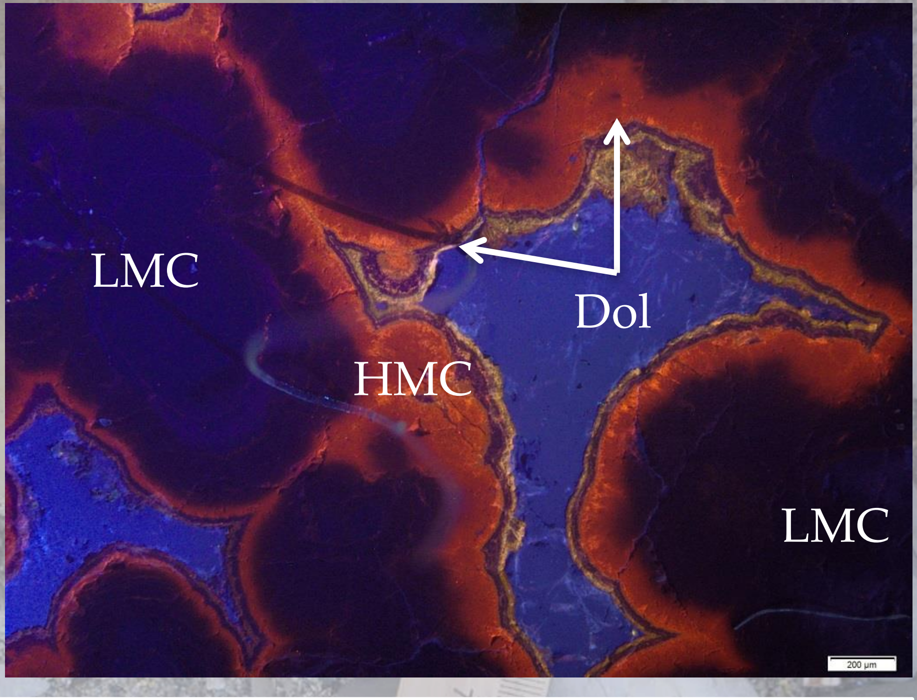
Mg content in carbonate generations within glendonite (sample RM2019/29). Mg content increases from LMC through HMC, and becomes maximum in dolomite.



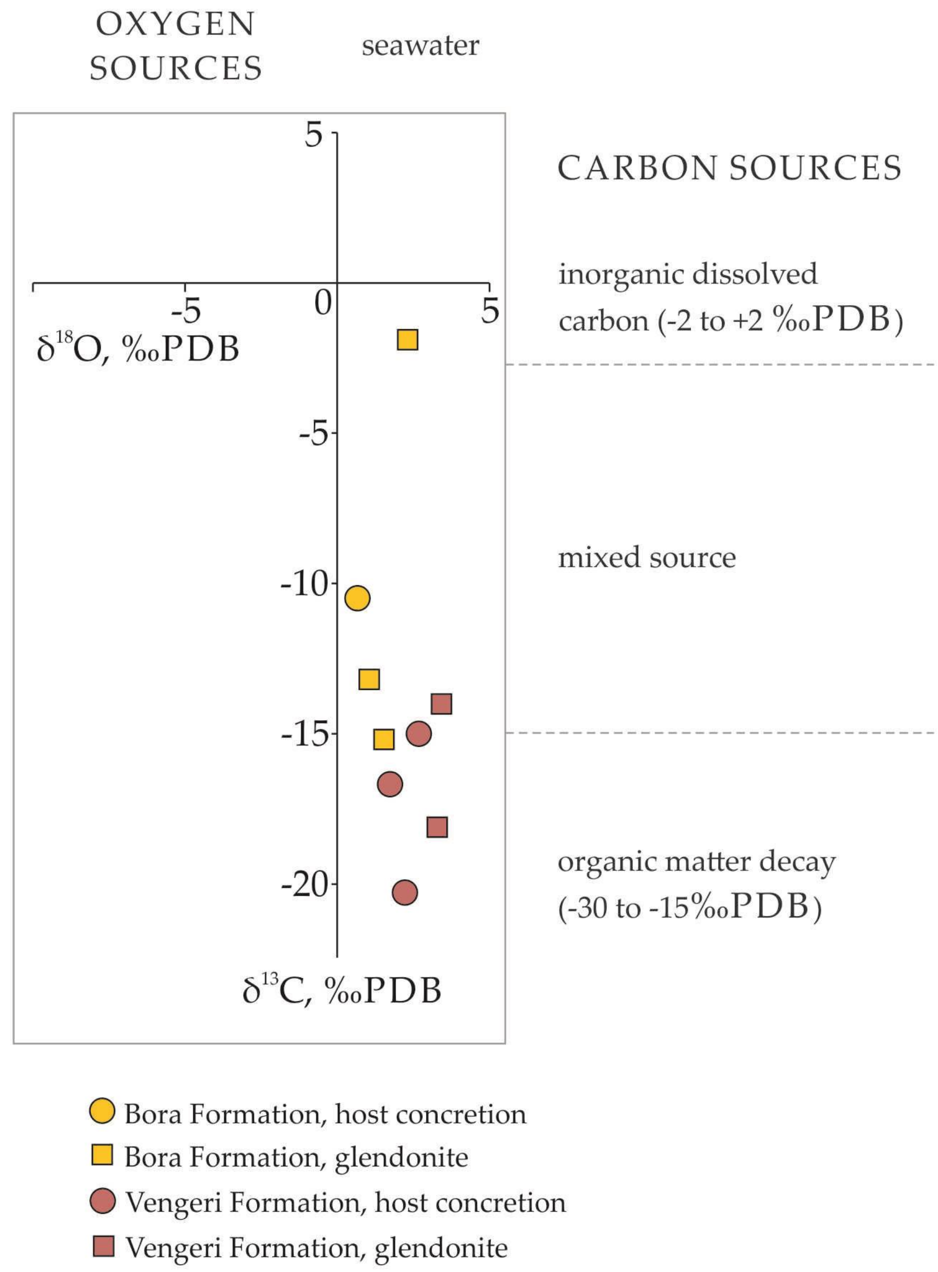
Mg-Ca ratio variation in calcites from the studied glendonite samples

Data on SEM and microprobe analysis corresponds well with petrographic and cathodoluminescence characteristics of the glendonites



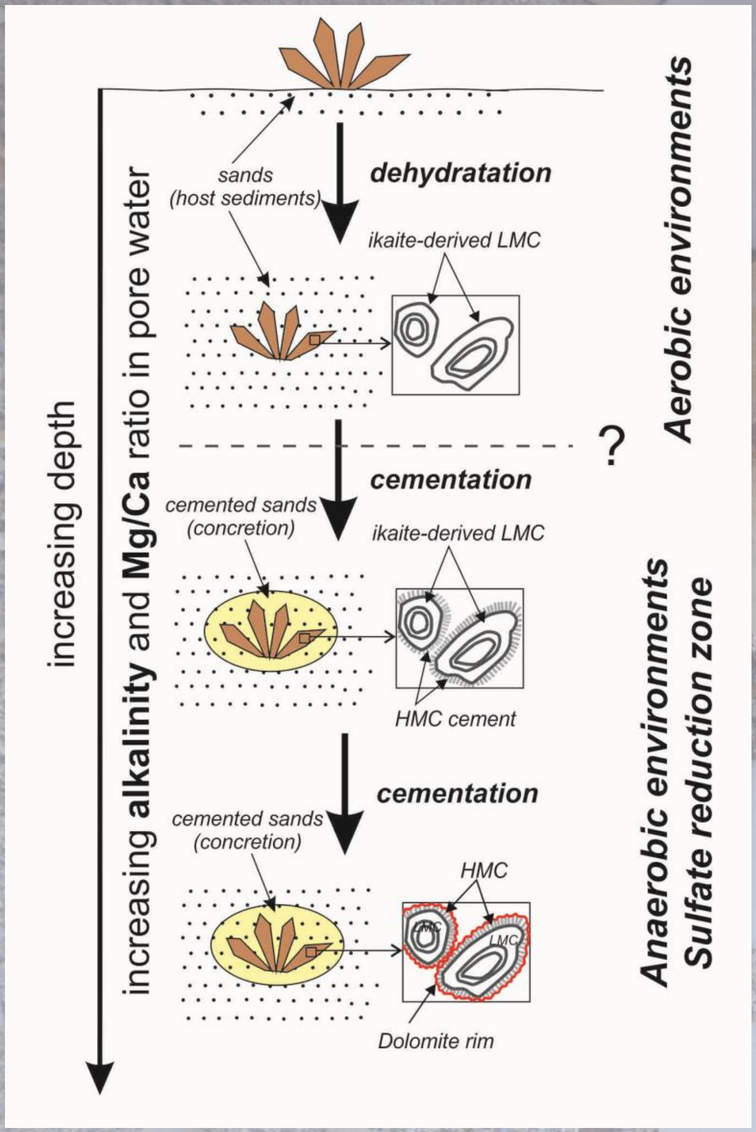


Glendonites are composed of several calcite generations. Rosette-like and blocky zonal calcite crystals ("ikaite-derived calcite") are composed of low-magnesium calcite (LMC), they are non-luminescent. Needle-like and radiaxial fibrous calcite cement is composed of high-magnesium calcite (HMC, bright orange or yellow cathodoluminescence) and dolomite (rim) and show dark red to bright-yellow cathodoluminescence.



Isotopic ratios of glendonites are close to those of host concretions. For host concretions $\delta^{13}C$ varies from -20.3 to -10.5 ‰PDB, $\delta^{18}O$ varies from +1.7 to +2.7 ‰PDB; for glendonites $\delta^{13}C$ varies from -18.1 to -1.9 ‰PDB, while $\delta^{18}O$ varies from +0.7 to +3.4 ‰PDB.

Ikaite-glendonite transformations and concretion growth



Close mineralogical and isotopic composition of the studied glendonites and host cannon-ball concretions suggest they were formed in ***common geochemical environment.***

Cementation of surrounding sediment (formation of the cannon-ball concretions) and glendonite formation were simultaneous and occurred during early diagenesis in the sulfate-reduction zone. The source of calcium and magnesium ions was seawater ($\delta^{18}O$ values are characteristic for seawater). Carbon was derived from seawater (DIC) and from decaying organic matter. Cementation of the cannon-ball concretion with high-magnesium calcite occurred together with needle-like high-magnesium calcite growth in the glendonite with increasing concentration of magnesium due to calcite extraction from the pore water.

Conclusions

Studied samples from and Vengeri formations of the Sakhaline Island were studied using mineralogical, optical, geochemical and isotopic methods. Studied glendonites are found along with cold-water fossils and dropstones thus indicating cold climate or at least seasonal cold temperatures.

Mineralogy of the studied samples was caused by geochemical changes during ikaite-glendonite transformations: increasing in Mg/Ca ratio and alkalinity in pore waters.

Isotopic (C, O) composition of the studied glendonites was caused by DIC and organic matter.

Common geochemical characteristics (mineralogy, $\delta^{18}O$ and $\delta^{13}C$ values) of host carbonate concretions and enclosed glendonites reflect ikaite-glendonite transformation and concretion growth in common geochemical environment in the sulfate-reduction zone.

Thank you for attention!

The study is supported by RFBR, project number 20-35-70012.
The **research** project is being carried out in the SPSU Research Park