Hydrocarbon seepage and formation of authigenic minerals in the permafrost of West Siberia

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ABSTRACT
The first overview of the major hydrocarbon-induced chemical and mineralogic changes affecting permafrost sequences was presented. Long-term leakage of hydrocarbons, either as macro- or microseepage, set up near-surface oxidation-reduction zones that favor the bacterial activity and the formation of the authigenic mineral association of carbonates, iron sulfides and oxides and siliceous microspheres.

RÉSUMÉ
Le premier aperçu des principaux changements chimiques et minéralogiques induits par les hydrocarubures affectant le pergélisol sont présentés. Les fuites à long terme des hydrocarbures, par microécoulement ou macroécoulement, forment des zones d'oxydation-réduction près de la surface qui favorisent l'activité bactérienne et la formation de roches sédimentaires associées aux carbonates, aux sulfures et oxydes de fer et aux microsphères silicieuses.

1 INTRODUCTION

A warming climate can induce environmental changes due to the release of the greenhouse gases carbon dioxide and methane. Large quantities of organic carbon are stored in permafrost (Bischoff et al. 2013). But how fast the process of the microbial breakdown of organic carbon and the release of the greenhouse gases will occur, remain uncertain (Schuur et al. 2015).

Although hydrocarbon seepages from oil and gas fields are known for decades this important environmental factor has not yet received necessary attention in the research studies within Arctic and sub-Arctic regions. Permafrost hitherto considered as an impermeable screen for gases (Hubberten and Romanovskii 2003) with low activity of biochemical processes (Yergeau 2010). However, long-term leakage of hydrocarbons, either as macro- or microseepage, set up near-surface oxidation-reduction zones that favor the bacterial activity. This adaptation opens windows of opportunity to empirically resolve at least some critical debates about permafrost carbon dynamics.

The objective of this paper is to provide the first overview of the major hydrocarbon-induced chemical and mineralogic changes affecting frozen sequences. The bacterial oxidation of light hydrocarbons can directly or indirectly bring about significant changes in the pH and Eh of the surrounding environment, thereby also changing the stability fields of the different mineral species present in that environment (Schumacher 1996).

2 SITE DESCRIPTIONS AND METHODOLOGY

Sampling was made at two sites within gas productive areas at the northern West Siberia.

The first site is located in the south of the Tazovskii peninsula and characterized by the widespread distribution of hydrolaccoliths with ice core within the territory. Their formation is related to dislocations of sedimentary strata of West Siberia, which, to a significant degree, are caused by inversion of the sediment density along the section (Kurchatova et al. 2014). The volumetric weight of diatomites (0.8–1.0 g/cm^3) is significantly lower relative to the overlapping Oligocene–Pleistocene sandy – clayey deposits (1.8–2.0 g/cm^3). At the top of the sequence, the diatomic clays are characterized by a high ice content, which exceeds the full moisture capacity. Their salinity is ~0.6% (up to 1.6%), mostly, due to sulfates (up to 90–99 mg-equiv. %) at low portion of chlorides (~0.007 mg-equiv. %). 30-m frozen core were collected from the top of one hydrolaccolith.

The second site is located in the Central Yamal peninsula, at 30 km south from Bovanenkovo gas field within Murtinskaya productive area. Samples of the massive ice were taken from the walls of crater that found in summer 2014 (Leibman et al. 2014). Studies of gas bubbles in massive ground ice of the Kara sea region have shown concentrations of methane exceeding that of the atmosphere by an order of magnitude, up to 2.2 ml/kg (Streletskaya et al., 2014). Ice samples were collected at the depth 5.8 and 23.8 m from the top level of Yamal crater.

All samples of frozen sediments and ice were collected in winter expeditions and stored at -15°C until processing. Specimens were prepared by the replica method not to disturb the structure of the frozen sediments and ice that allows to identify the meta-stable colloids and most small-sized component of the frozen sediments – microorganisms (Rogov and Kurchatova 2013). Gold-coated specimens were used for SEM and qualitative X-ray microanalyses to obtain complementary information on the elemental compositions of authigenic minerals.

3 RESULTS

Cryogenic structures of diatomic clay also crystallography of the ground ice samples: the block shifts of sediments and ice schlierens, twinning of ice crystals indicate the stress deformation of permafrost sequences (Fig. 1). Mineral grains of quartz and feldspar are characterized by features of cryogenic weathering and also crushing (Fig. 2, 3). The frozen samples and ice contain high concentration of gas bubbles that form continuous chains along the deformational cracks (Fig. 4). The rest of methane content in non-hermetically stored core samples was 2.2 and 7.6 vol % in sediments and ice, respectively, which is higher by one order of magnitude relative to the data from deposits and polygonal wedge ice (ice complex) of the Late Pleistocene (Brouchkov and Fukuda 2002). Methane homologs and helium were also identified in the gas composition.

The empty curve-cut spherical and elongated aggregates were found with gas bubbles in the ice schlierens of clay and samples of massive ice (Figure 5). The hexagonal faces of aggregates and etching figures indicate a crystal structure typical for ice. The anomalous ice forms with gas inclusions (gas-bearing crystallites) can grow along with flat faces crystals under overcooled and viscous conditions at the expense of salts and free gas.

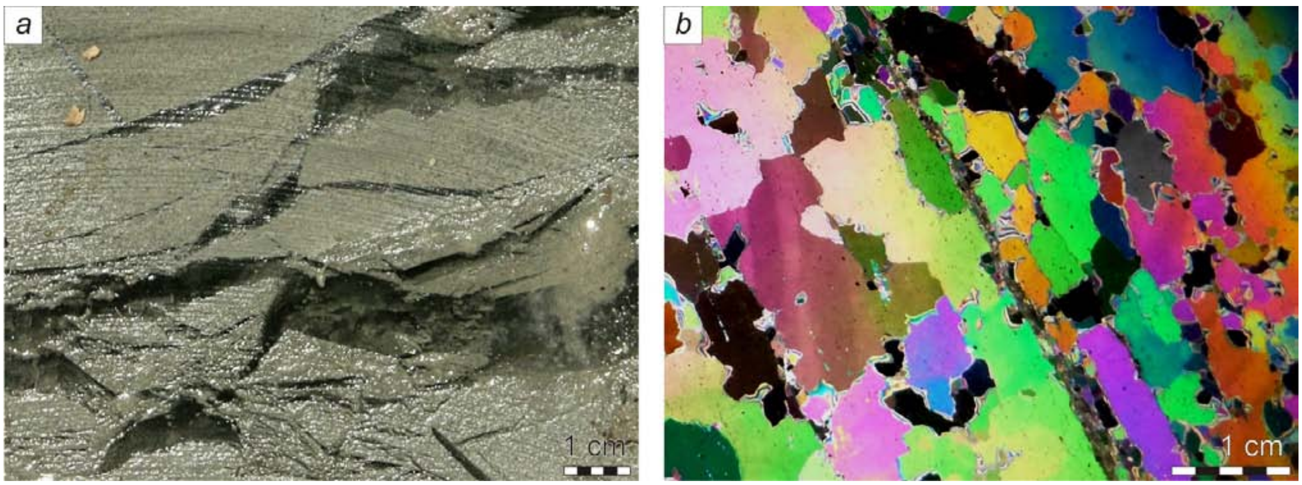


Figure 1. Deformations of cryogenic structures of diatomic clay (*a*) and crystallography of massive ice, 23.8 m depth (*b*).

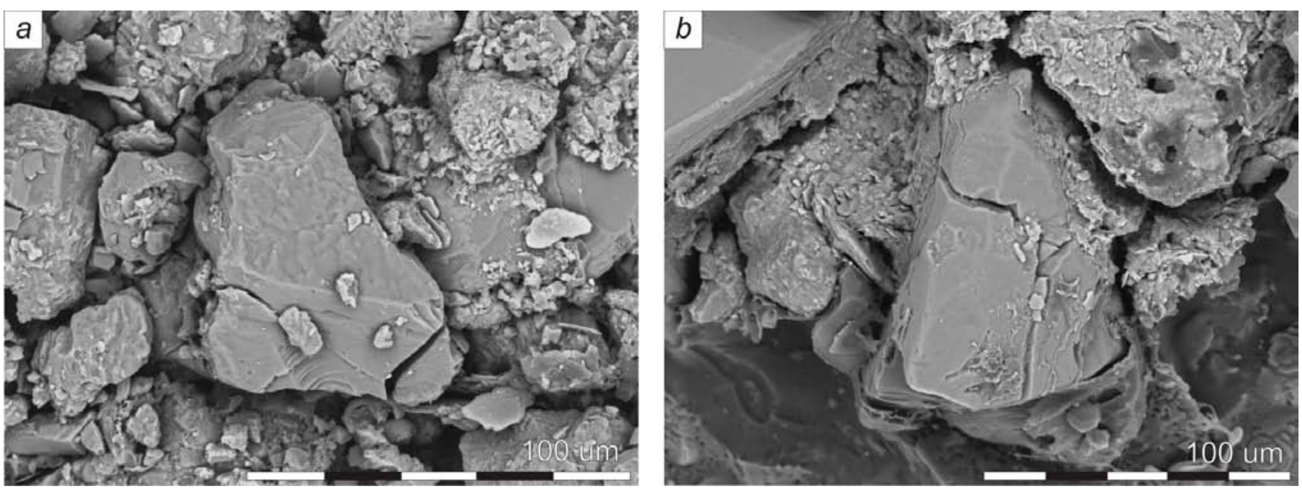


Figure 2. Quartz grains: cryogenic weathering (*a*) and crushing *in situ* (*b*).

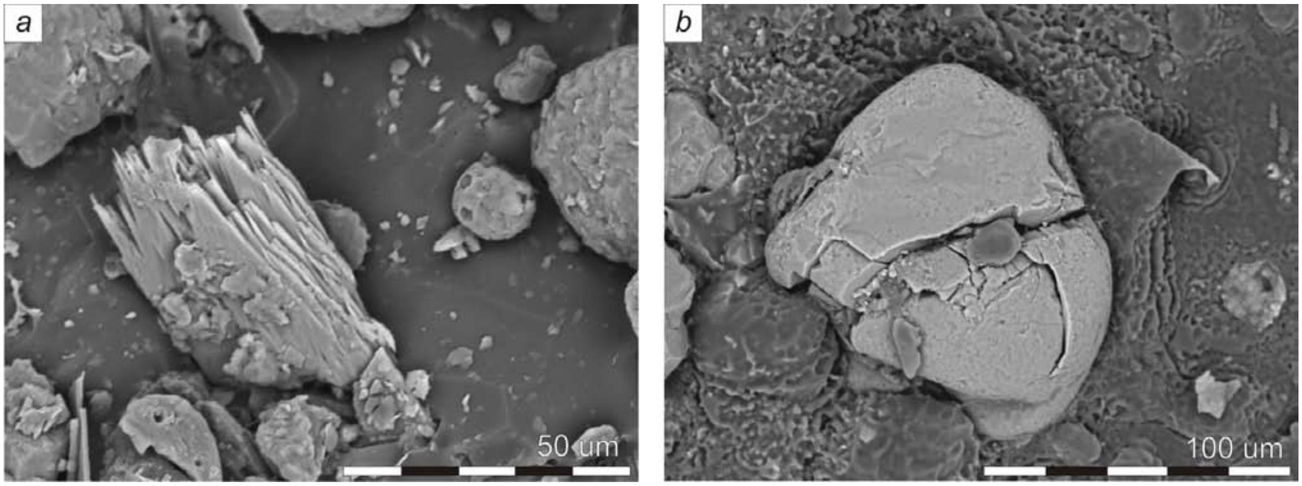


Figure 3. Feldspar grains: cryogenic weathering (*a*) and crushing *in situ* (*b*).

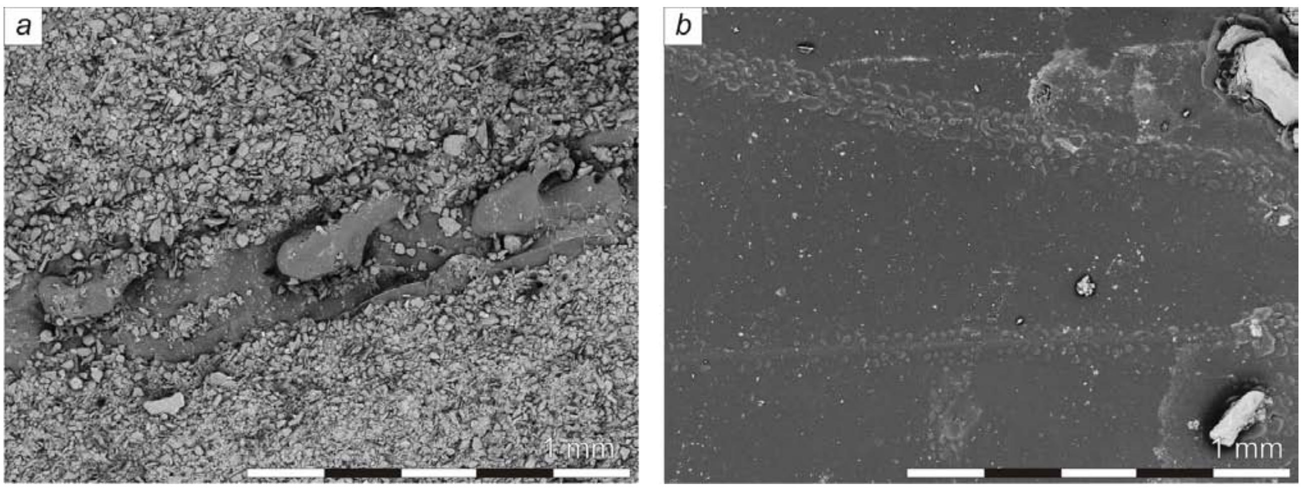


Figure 4. Chains of gas bubbles: along ice schlieren (*a*) and deformational cracks in the massive ice (*b*).

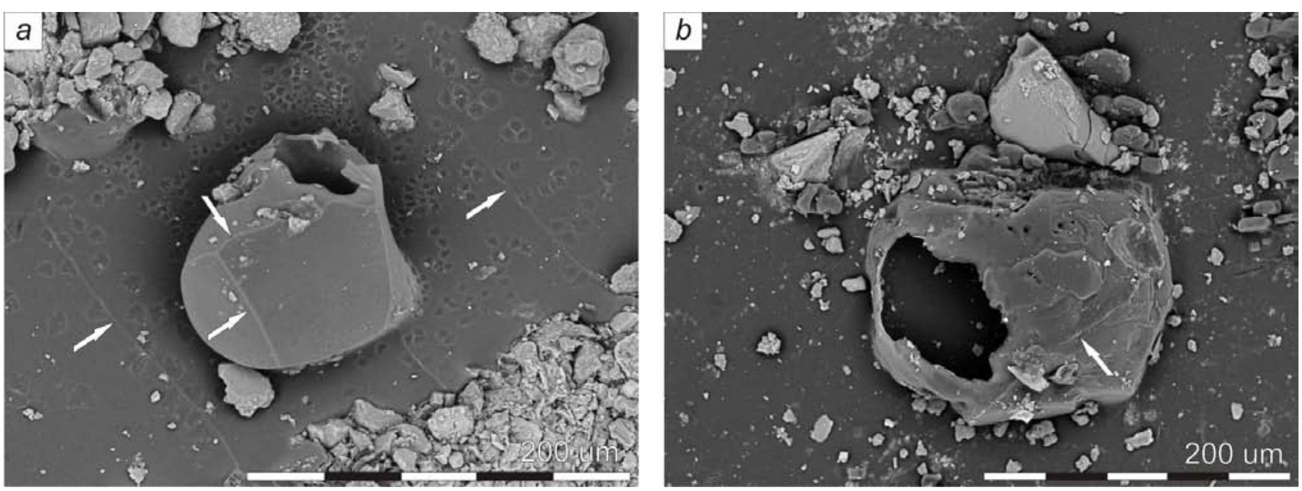


Figure 5. Gas-bearing ice crystallites: within ice schlierens (*a*) and in the massive ice (*b*), (*arrows show boundaries of crystals)*.

Bacterial colonies were found in specimens from 30 m depth beneath ice-core of hydrolaccolith ((Fig. 6). The results of the microbiological analyses are still not received. But examples of bacterial activity were found in the diatomic clay and also in ice samples and mineral inclusions including the different generations of iron sulfides: amorphous framboids - marcasite clusters - pyrite (Fig. 7). Diagenetic carbonates (siderite) and gypsum that usually form at the flanks of the gas and petroleum field were determined in the same specimens (Fig. 8). Other examples of possible microbial biomineralization include amorphous silica, as well as the formation of authigenic iron oxides - magnetite that is wide distributed in hydrocarbon-induced biogeochemical aureoles in non-permafrost regions (Fig. 9).

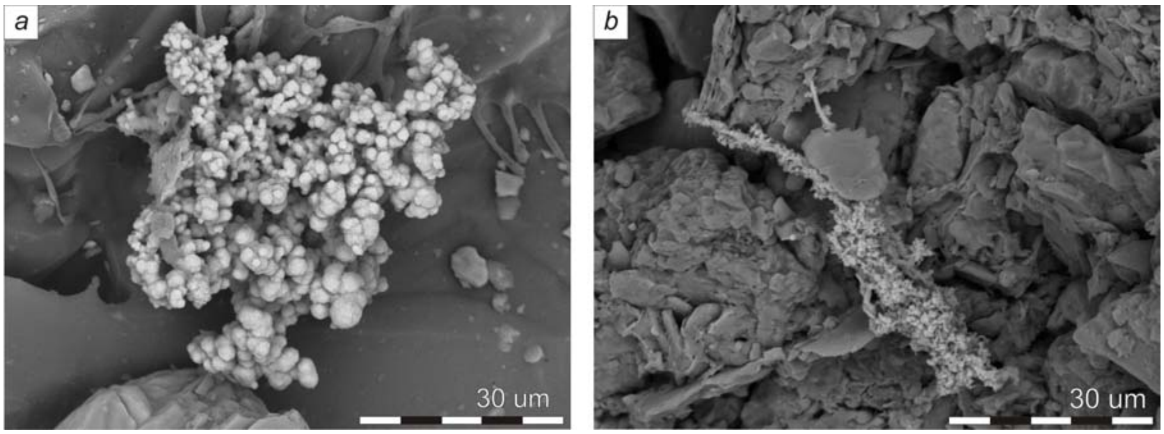


Figure 6. Bacterial colonies.

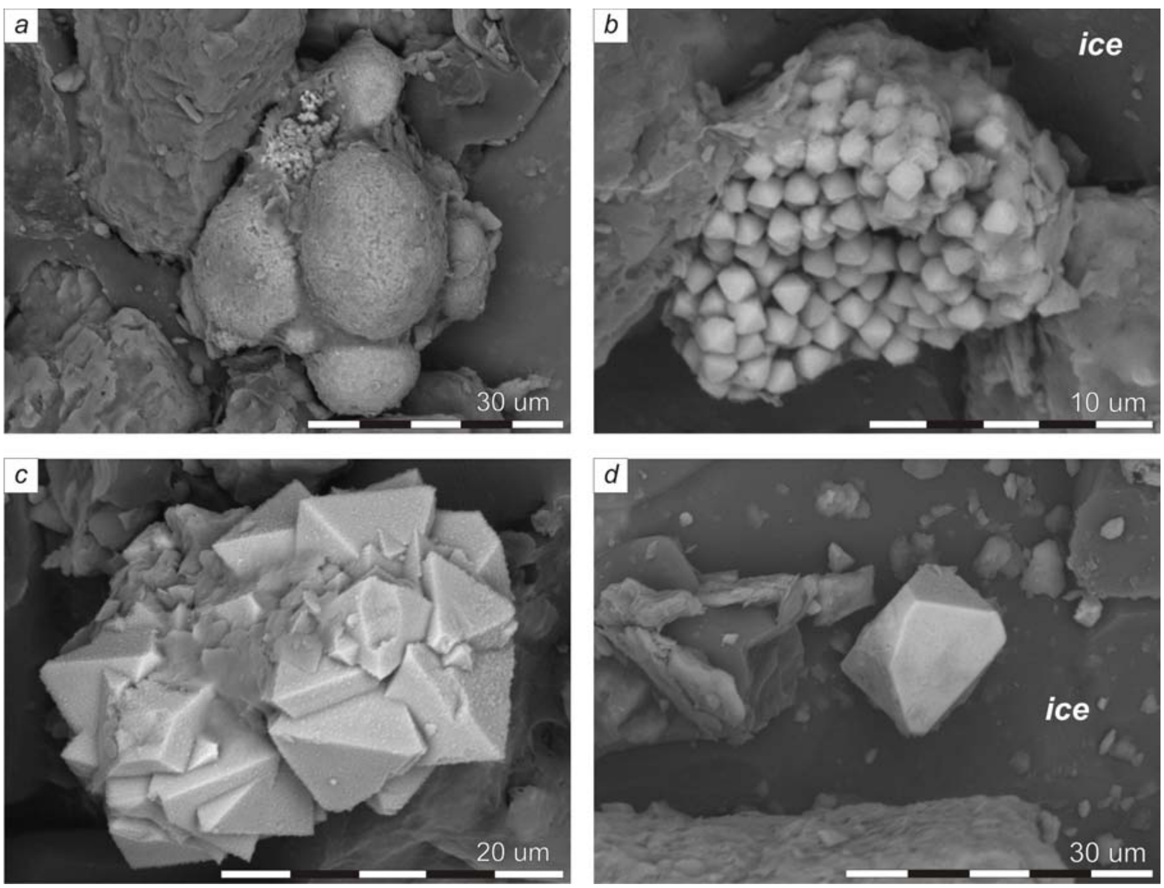
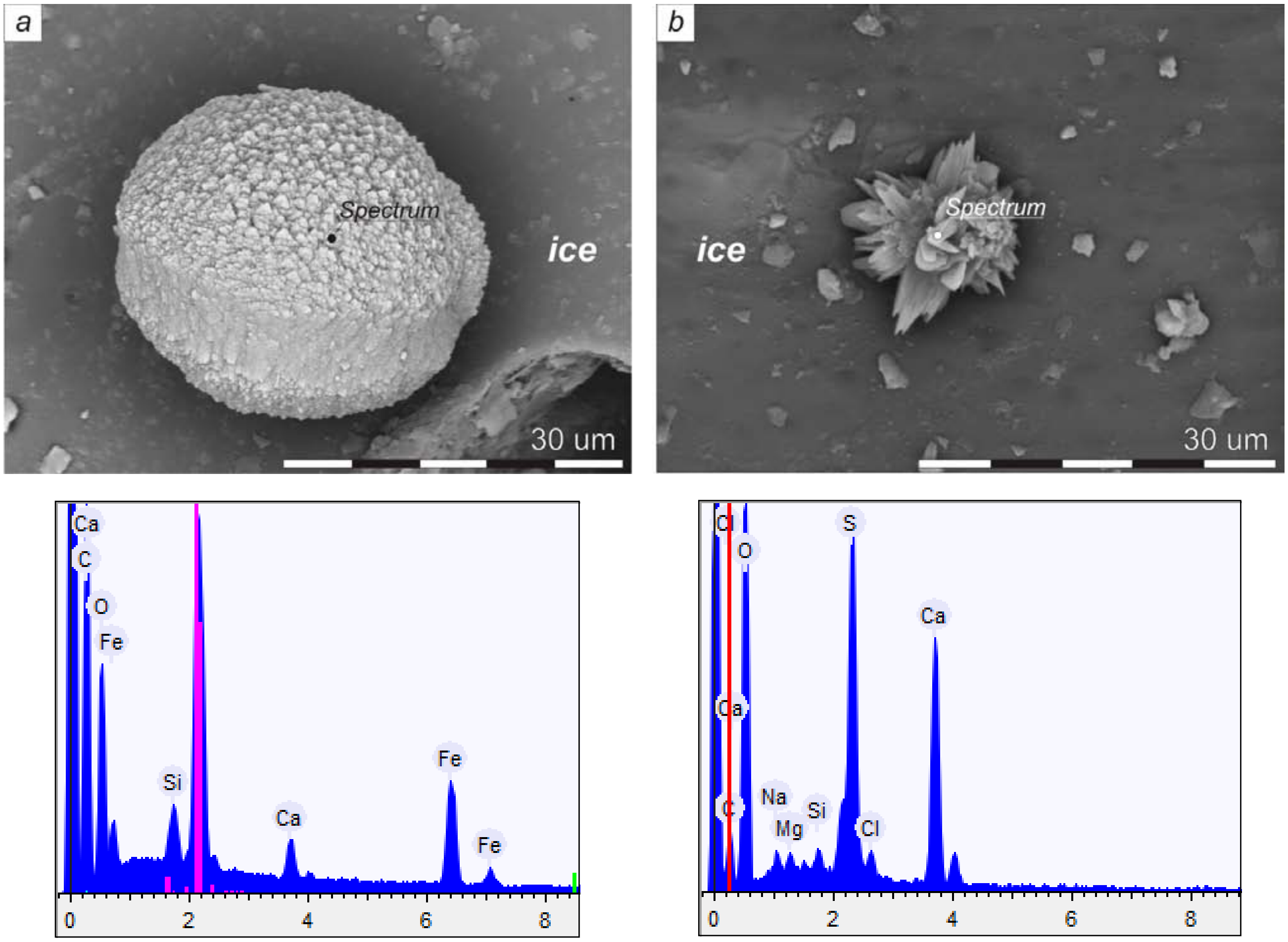


Figure 7. Secondary iron sulfides: colloidal aggregates of “buds” (*a*), framboid (*b*), marcasite cluster (*c*), pyrite crystal (*d*).



Element	Weight %	Weight % σ	Atomic %
Carbon	45.639	0.636	61.134
Oxygen	31.491	0.631	31.668
Silicon	1.400	0.105	0.802
Calcium	1.865	0.118	0.749
Iron	19.604	0.444	5.648

Element	Weight %	Weight % σ	Atomic %
Carbon	11.540	1.457	17.436
Oxygen	59.552	1.162	67.549
Sodium	0.797	0.182	0.629
Magnesium	0.600	0.132	0.448
Silicon	0.565	0.108	0.365
Sulfur	11.505	0.363	6.511
Chlorine	1.191	0.145	0.609
Calcium	14.250	0.407	6.452

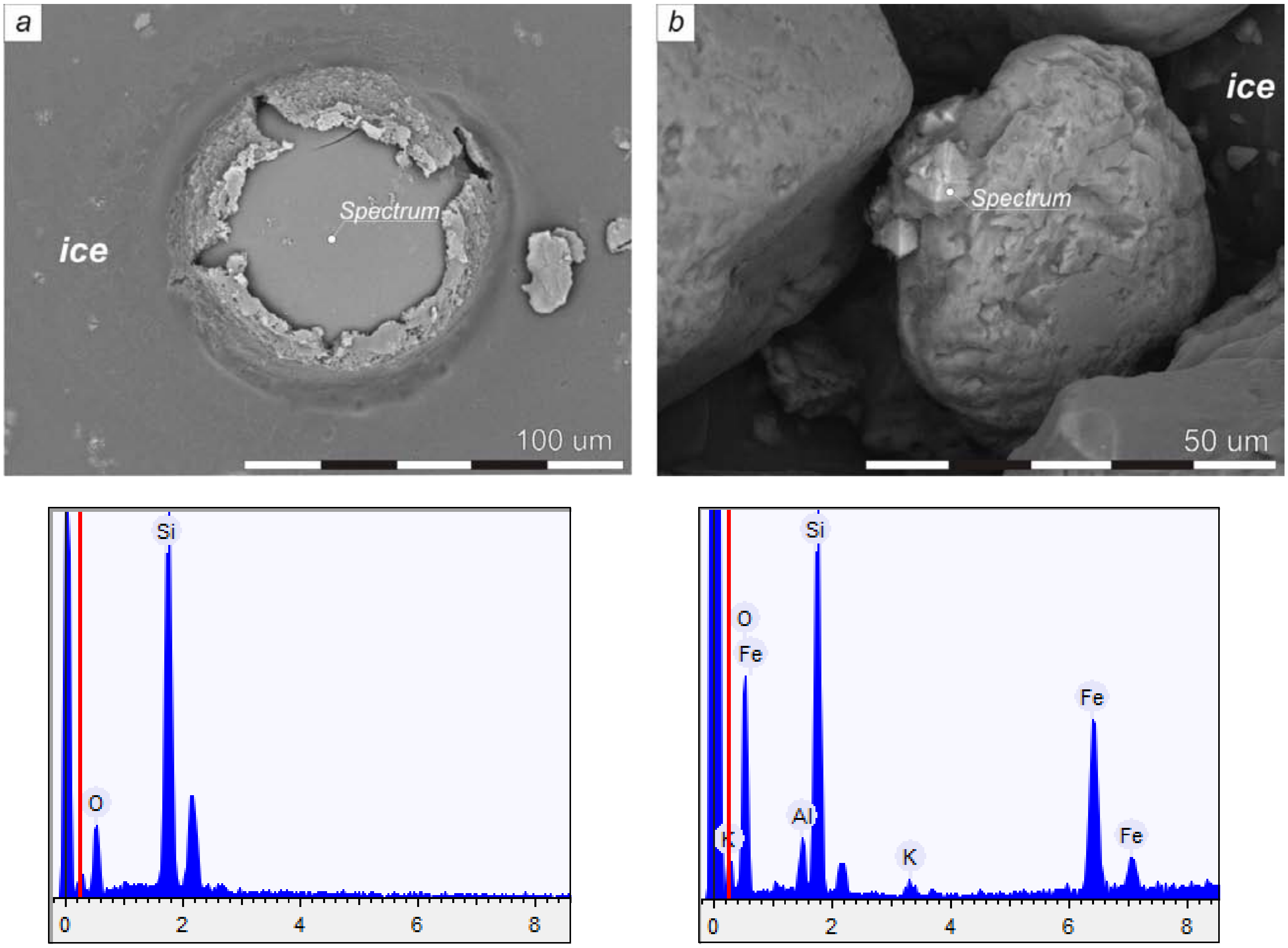
Figure 8. SEM and EDS analyses of siderite (*a*) and gypsum (*b*) concretions in the massive ice.

4 DISCUSSION

Hydrocarbon migration through permafrost sequences of West Siberia, mostly methane, is confirmed by seismic survey and geochemical studies of gas content in the ice and deposits. Thus, geochemical survey of free gas content (C1 – C6, H2, CO2, N2) in pore space of snow and soils is used to identify hydrocarbon prospective areas.

Numerous destructed mineral grains (quartz, feldspars) indicate the cyclic phase transitions of water – ice in the sediments as a result of the pulsating gas microbubbles and pore-water flow through the framework of the plastic-frozen clay. If cryogenic weathering and crushing of quartz are difficult to distinguish due to mechanical cracking in the both cases the delicate dissolution features that are formed on the surfaces of feldspar grains are evidence for *in situ* chemical weathering during freezing–thawing cycles (Gibson et al. 1983).

These phase transitions provide the required amount of water and oxygen for the oxidation of hydrocarbons to form carbon dioxide or bicarbonate that eventually precipitates mainly as siderite concretions in the ice and carbonate cement in sediments while calcium chloride accumulates in the mineralized lenses - cryopegs. Fe in



Element	Weight %	Weight % σ	Atomic %
Oxygen	44.967	1.842	58.922
Silicon	55.033	1.842	41.078

Element	Weight %	Weight % σ	Atomic %
Oxygen	28.014	1.043	50.688
Aluminum	2.688	0.304	2.884
Silicon	20.175	0.661	20.794
Potassium	0.767	0.210	0.568
Iron	48.357	1.155	25.066

Figure 9. SEM and EDS analyses of silica sphere (*a*), authigenic magnetite (*b*).

the siderite is partly substituted by Mn, and to a lesser amount by Ca. The authigenic siderite concretions were also found in the near-bottom sediments at gas hydrate-bearing mud volcanoes in fresh water of Lake Baikal, Eastern Siberia (Krylov et al. 2008). These carbonates are formed principally as a byproduct of methane oxidation using one of two reaction pathways, as summarized below:

Aerobic:

$CH_4 + 2\ O_2 + Fe^{2+} = FeCO_3 + H_2O + 2\ H^+$ (1)

Anaerobic:

$CH_4 + SO_4^{2-} + Fe^{2+} = FeCO_3 + H_2S + H_2O$ (2)

When oxygen is depleted within the sediment or pore fluid, the secondary sulfides (pyrrhotite – marcasite – pyrite) are formed. Sulfate reduction depends on geology and pore-water geochemistry of the permafrost sequences, and the nature of the bacterial degradation. Sources of iron include colloidal grain coatings, pore-filling clays, and rock fragments.

Anaerobic oxidation of methane (AOM) efficiently controls CH_4 emission. Most of this AOM is attributed to sulfate (SO_4^{2-}) reduction (SR-AOM, eq 3), but oxidized solid phases such as iron (Fe)-oxides are also thermodynamically favorable electron acceptors for the biological oxidation of CH_4 (eq 4):

$CH_4 + SO_4^{2-} \rightarrow HS^- + HCO_3^- + H_2O$ (3)

$CH_4 + 8Fe(OH)_3 + 15H^+ \rightarrow HCO_3^- + 8Fe^{2+} + 21H_2O$ (4)

The co-occurrence of reactive Fe-oxides and CH_4 in freshwater and some brackish sediments suggests that AOM coupled to Fe-oxide reduction (FeR−AOM) has the potential to remove CH_4 in SO_4^{2-}-poor environments (Egger et al. 2015).

The hydrocarbon-induced reducing environment that promotes the precipitation of a variety of magnetic iron oxides and sulfides, including magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3), pyrrhotite (Fe_7S_8), and greigite (Fe_3S_4) leads to the formation of magnetic anomalies over oil and gas fields.

The anaerobic oxidation of methane with sulfate reduction generating HCO_3^- and HS^- as products increases the alkalinity of the microenvironment. Consequently, the precipitation of carbonates and the dissolution of silica are stimulated. The dissolved silica, mainly diatoms, in the form of $Si(OH)_4$, which is initially amorphous and may eventually crystallize upon aging to form opal-cristobalite spheres (Fig. 9).

Chen and et al. (2014) discovered the formation of a thick siliceous envelope around bacteria consortia and suggested that microspheres with a particular Si-Al composition in cold methane seeps may be fossilized AOM consortia.

5 CONCLUSION

Therefore, long-term hydrocarbon seepage can directly or indirectly bring about significant changes in the pH and Eh of the permafrost sequences, thereby result in the precipitation or solution and remobilization of various mineral species and elements.

Although bacterial activity is most pronounced in surface soils in humid areas, it can occur within permafrost sequences. Bacterial activity can increase in pH and initiate the precipitation of calcium carbonate. Similarly, sulfide production by sulfate-reducing bacteria can bring about the precipitation of generations of iron sulfides and oxides, Fe(III)-reducing microorganisms produce magnetite, siderite, vivianite and rhodochrosite.

But microbial processes that produce the observed effects in hydrocarbon-induced permafrost areas are not well understood and even less well documented. This requires answers to the following questions. Is the authigenic mineral association seep-related or of non-seep origin? If seep-related, does the anomaly result from an active hydrocarbon seep or a paleoseep? Although the occurrence of microorganisms in permafrost is well established, considerable scientific research is needed before we understand carbon dynamics in Arctic and sub-Arctic regions.

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