

Evaluation of stabilization rate of high and low molecular organic matter in cryoconite holes from the Arctic, Antarctic and Caucasus mountain ecosystems by ^{13}C -NMR spectroscopy

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Abstract

Cryoconite holes are considered as a place of accumulation of organomineral matter, including black carbon. It is formed as a result of incomplete combustion of carbon-containing fragments of natural and anthropogenic origin. Such material is transported by the wind and participates in the formation of cryoconite on the ice surface. The accumulation of organic matter in cryoconite can significantly affect the climate of our planet. To assess the processes of resistance to biodegradation of organic matter in cryoconite, molecular methods of analysis were used. This work presents the qualitative and quantitative evaluation of composition of humic acids, formed in selected cryoconite holes of various geographical regions. To identify them, the ^{13}C -NMR spectroscopy method was used, which makes it possible to reveal trends in the accumulation of specific structural fragments and the rate of stabilization of cryoconite organic matter. The analysis of the elemental composition revealed that the most condensed macromolecules of humic acids accumulate in cryoconite holes on Mount Elbrus. In the molecules of humic acids, the accumulation of aliphatic structural fragments up to 71-73% occurs to a greater extent, while the composition of the aliphatic fragments depended on local precursors of humification. In the Arctic and Antarctic ecosystems, humic acids with relatively homogeneous composition are formed. These ecosystems are characterized by the domination of moss-lichen communities, which are characterized by a predominance of lipids and carbohydrates in the chemical composition. Black carbon is an important part of the planetary carbon cycle. Under the conditions of active deglaciation, cryoconite material can enter the periglacial zone, and under the action of soil microorganisms, it can become an additional source of greenhouse gases in the atmosphere.

Key words: black carbon, cryoconite, deglaciation, polar region, ^{13}C -NMR spectroscopy

DOI: 10.5817/CPR2021-2-15

Received March 1, 2021, accepted December 31, 2021.

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Acknowledgements: We would like to express our gratitude to Dmitry Bolshiyarov for his help in the selection and delivery of cryoconite to St. Petersburg, as well as his help in interpreting the data regarding the genesis of cryoconite. This work was supported by Russian Foundation for Basic Research, project No 19-05-50107.

Introduction

The stability of various groups of organic compounds from soils, water bodies, and cryoconite has been investigated for a long time (Polyakov and Abakumov 2020a, Chukov *et al.* 2015, Abakumov *et al.* 2015, Lodygin *et al.* 2014, Lodygin and Beznosikov 2010, Dziadowiec *et al.* 1994, Orlov 1990, Hatcher *et al.* 1981). Studies have focused on stabilization of organic matter, but addressed also the assessment of the soil regime, the intensity of the soil forming factor, as well as the process of removal of pollutants from ecosystems (Baccolo *et al.* 2020, Amaro *et al.* 2015, Celis *et al.* 2014, Knoblauch *et al.* 2013). Organic matter contains a large set of various structural fragments that are formed under conditions of mineralization and humification. In the course of these processes, labile (readily hydrolyzable) and stable substances are formed (Polyakov and Abakumov 2020a, Lupachev *et al.* 2017, Semenov *et al.* 2009). These substances can be accumulated and formed in soil and water systems, as well as on glacial surfaces (Polyakov *et al.* 2019a, Szymański 2017, Szymański *et al.* 2015, Dziadowiec *et al.* 1994). Nowadays, formation of these compounds and their stabilization are studied in order to identify underlying mechanisms. Under the conditions of cryoconite formation, organic matter of various origins accumulates, such as *e.g.* soil organic matter, undecomposed plant residues, and black carbon as well (Polyakov *et al.* 2019a, Szymański 2017, Polyakov and Abakumov 2020b).

Black carbon (BC) is one of the short-lived climatic factors ([1]-Council 2019, [2]-AMAP 2015, Stone 2014). BC is formed as a result of incomplete combustion of fossil fuels and biomass, mainly: emissions from transport engines; emissions from wood and coal combustion; emissions from industrial production (metallurgy and petrochemistry); emissions from oil, gas production and wild-fires (Bond *et al.* 2013,

Andreae and Gelencsér 2006, Bond and Bergstrom 2006). BC accumulates on snow and ice cover, leads to its heating, which in turn leads to their melting in the accumulation site (Reid *et al.* 2005). The Arctic region, according to the data of regular meteorological observations carried out since 1990, witnessed an increase in the average winter temperature by 3°C, and, therefore, is considered extremely sensitive and vulnerable region (Acosta Navarro *et al.* 2016). In recent decades, the area and volume of Arctic ice have been decreasing (Nordli *et al.* 2014, Notz and Stroeve 2016). Of the total amount of BC accumulated on the surface of the Arctic, pollution from Europe contributes 68%, followed by emissions from Asia, which bring 22% (Flanner *et al.* 2007). BC damages not only Arctic ice, but also the mountain glaciers in the same ways. The warming effect is more evident in mountainous areas due to the pollution of snow and ice than in Arctic or Antarctic ice areas ([1]-Council 2019, [2]-AMAP 2015).

Elbrus is the largest mountain-glacial massif in Russia (Polyakov *et al.* 2020c, Zolotarev and Kharkovets 2012). In 2007, the total area of the ice sheet was 120 km². At present, the reserves of ice and perennial firns accumulated in the second half of the 20th century are melting at an unprecedented rate, and they are almost exhausted over a large area in the 3700-4000 m zone. The recharge boundary on the glacier has risen by 200 m, and the firn consumption increases. In the area of ablation, lava ridges thaw out. The cumulative mass balance has reached its lowest value in the past 50 years. In addition to dust, various aerosols and trace elements (As, Mn, Zn, Cu, Cr, Ni, Pb, Cd and Hg), the impact of the accumulation of moraine materials on the glaciers surface was studied (Rototava *et al.* 2019). The surface moraine plays a role in the evolution of the glacier, commensurate with the climatic factor.

In the context of the unpredicted global climatic changes, special attention is also focused on the Arctic and Antarctic ecosystem. Research in the Arctic shows that at current levels of temperature rise, the Arctic Ocean could be ice-free in summer over the next 30-40 years (Serreze et al. 2007, Wang and Overland, 2009, Tunved et al. 2013). This can have a powerful effect on the sources and sinks of atmospheric aerosols, as well as on the properties and distribution of clouds in the Arctic.

The Antarctic ice sheet is an important indicator of climate change and a driver of sea level rise. The Antarctic ice streams contribute about 10% of the observed global sea level rise. According to some authors, if the glaciers of Antarctica, with the ice in the Arctic, completely melted, the global sea level will rise by 65 m (Amaro et al. 2015, Feldmann et al. 2019, Hara et al. 2019, Zwally et al. 2017). The mass of Antarctic ice in the coastal and terrestrial parts does not remain unchanged and substantially depends on climate fluctuations. Many studies have been devoted to the issue of degradation/accumulation of glacier mass, but there is still no conclusive view on local/regional/global level. It is true for *e.g.* cryoconite holes formation on the surface of glaciers. They are formed under the influence of local accumulation of material within the continent, although the transfer of particles from the Pacific basin has also been noted (Amaro et al. 2015, Dickens et al. 2019, Groeneweg and Beunk 1992).

Cryoconite holes, in addition to changing albedo and their contribution to the deglaciation process, have a threat from the accumulation of priority toxicants (Akilan et al. 2019, Amaro et al. 2015, Baccolo et al. 2020, Casey et al. 2017). Trace elements, radionuclides, and polycyclic aromatic hydrocarbons are transported here with particles of BC (Polyakov et al. 2020a). Cryoconite holes are small ecosystems with a closed cycle of nutrients and a specific microbiome community (Bond et al. 2013, Christner et al. 2003, Singh et al. 2020). In

conditions of active deglaciation, this material can be quickly involved in the modern soil-forming process. This can adversely affect the state of soils in the most vulnerable ecosystems of the Arctic and Antarctic, as well as mountainous regions. In these conditions, soil cryogenesis and mass transfer, contaminated material can persist in the soil for a long time and inhibit the microbiological activity of the soil (Ejarque and Abakumov 2016, Szymański et al. 2015, Zubrzycki et al. 2014, Boike et al. 2013). However, cryoconite material can also serve as a biologically active substance and introduce a significant amount of nutrients into the soils of periglacial environments (Polyakov et al. 2020a, b; Abakumov 2008). Taking into account the fact that in cryoconite are in fact accumulations of black and elemental carbon, the process of humification can also take place, with formation of humic acids (HAs) (Polyakov and Abakumov 2020b, Polyakov et al. 2019a).

Normally, the HAs are heterogeneous systems of high and low molecular compounds formed from the decay of plant and animal remnants in terrestrial and aquatic ecosystems (Polyakov and Abakumov 2020a, Polyakov et al. 2019b, Vasilevich et al. 2019, Vasilevich et al. 2018, Lodygin et al. 2017). BC of biogenic origin (formed mainly during wildfires) (Warneke et al. 2009) accumulates under the conditions of cryoconite formation. In general, the material of cryoconite holes is a biologically active substance in which humification, accumulation and destruction of humic substances under the influence of microorganisms occurs (Polyakov and Abakumov 2020b, Polyakov et al. 2019a). This mechanism is quite different from soil humification, because there is no seasonal input of humification precursors, and the climatic conditions in which the transformation of BC is very different (Vasilevich et al. 2019, Dziadowiec et al. 1994, Orlov 1990, Hatcher et al. 1981). In addition to information on the molecular com-

position of HAs, data on the elemental composition of HAs play an important role. The elemental composition of HAs represents the percentage of C, H, N, and O elements in them. The high variability of the elemental composition of HAs among different soils is explained by the varying degree of accumulation of elements in the HAs (Polyakov and Abakumov 2020a, Vasilevich *et al.* 2019, Lodygin *et al.* 2017). By the ratio of elements, we can determine the leading processes of humification occurring in the soil. Information on the elemental composition of organic substance contribute to understanding of the general principles of molecular construction and some of their properties (Orlov 1990). Nevertheless, along with humification, the processes of weathering of material also occur, which accumulates mainly from local rocks, and BC is mainly introduced from other regions (Szymański *et al.* 2015, Abakumov *et al.*

2013, Bronnikova 2011, Schaefer *et al.* 2008). Therefore, under conditions of active deglaciation in polar and alpine regions, materials saturated with HAs will enter the soil, which will be involved in the modern process of soil formation and will contribute to the transformation of the most vulnerable ecosystems of our planet.

The aim of this work is an estimation of stabilization of organic matter, which is accumulated and formed in cryoconite holes selected from the Arctic, Antarctic and mountain ecosystem based on qualitative and quantitative composition of HAs. To achieve the aim, the following tasks have been set:

- to investigate the elemental composition of HAs;
- to determine the qualitative and quantitative composition of HAs;
- to evaluate the stabilization of organic matter formed in cryoconite holes.

Material and Methods

The study sites

The study area is confined to the Arctic, Antarctic and Mount Elbrus (Central Caucasus) (Fig. 1).

The Cape Baranov is located in the Severnaya Zemlya Archipelago, samples collected from the Mushketov glacier (Bolshevik Island, Severnaya Zemlya Archipelago, 23 km south of the “Cape Baranov” Arctic Station). The Mushketov Glacier is a glacial dome with an area of about 89 km² and an ice thickness of about 160 m. It is located on the surface of the upper denudation leveling (Bolshiyarov *et al.* 2016). The island is composed of the Upper Proterozoic terrigenous complex (sandstones, siltstones, granodiorites). Average annual air temperature is -14°C. The area is characterized by stable winds mainly from the southern direction with an average speed of 10–15 m/s (Manousakas *et al.* 2020). By the personal observation

we suppose that mineral material of cryoconite holes is released from under the glacier, *i.e.* it was formed a long time ago and, due to the movement of the glacier, is pulled up from the lower part to the surface, where it continues to develop at present time.

The Garabashi glacier is part of the Caucasian Mountains and located on Mt. Elbrus. The glacier begins at an altitude of about 4900 m and ends at 3330 m; its area in the 1980s and 90s was 4.47 km². Since 1982, the glacier has lost 14% of its volume and 11.4% of its area. This zone is subjected to active deglaciation, and cryoconite material is, therefore, involved in modern soil formation with the formation of highly productive systems in the regions of seasonal streams. The average annual temperature is -12°C (Rototaeva *et al.* 2019).

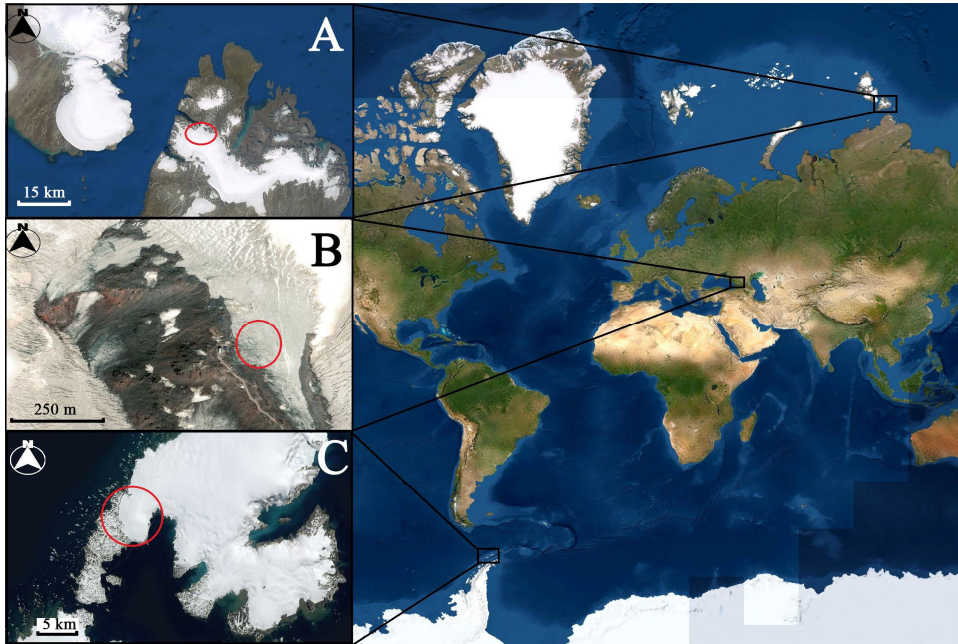


Fig. 1. Study area. **A** – Mushketov glacier, Cape Baranov, Severnaya Zemlya; **B** – Elbrus Mountain, Central Caucasus; **C** – Collins Ice Cap, Antarctica.

The Collins Ice Cap is located in the West Antarctica region on King George Island, Fildes Peninsula. The maximum height of the ice cap reaches 700 m. The peninsula consists of volcanic rocks, mainly andesites, basalts, and various tuffs. The

average annual temperature is -2.8°C . A characteristic feature of cryoconite material is its chemical composition corresponding to volcanic sediments (Polyakov et al. 2020a, b). The studied cryoconites are presented in Fig. 2.

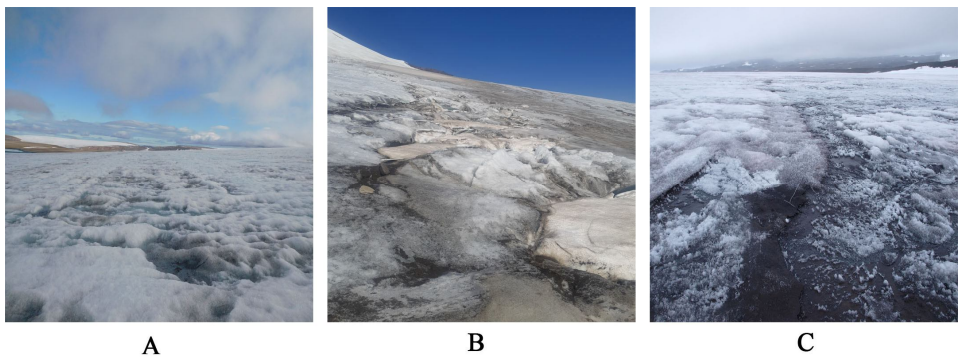


Fig. 2. Studied cryoconites. **A** – Mushketov glacier, Severnaya Zemlya; **B** – Elbrus Mountain, Central Caucasus; **C** – Collins Ice Cap, Antarctica.

Sampling procedure

Samples of cryoconite material were taken from the studied glaciers. Samples were taken during the Russian Antarctic and High Latitude expeditions in 2020, from the ice and delivered to the laboratory. A standard BC isolation method is described by Hegg *et al.* (Hegg *et al.* 2010). Dried samples were investigated at the De-

partment of Applied Ecology of St. Petersburg State University, St. Petersburg. The description of the studied cryoconite is presented in Table 1. Soil from the Elbrus region was sampled according to international standard methods and classified as Calcic Chernozems ([3]-WRB 2015).

Site	Sample	Coordination	Description	Initial material
Mushketov glacier, Cape Baranov, Severnaya Zemlya	1	N 79° 05'46.61'' E 101° 51'25.35''	Melting cryoconite from the glacier	Moraine sediments
	2	N 79°02'56.00'' E 101°51'34.52''	Melting cryoconite from the glacier	
Collins Ice Cap, Antarctica	3	S 62°9'21.8'' W 58°54'48.1''	Cryoconite is formed during the accumulation of material from the atmosphere and bird activity	Volcano
Elbrus Mountain, Central Caucasus	4	N 43° 33' 21.7'' E 43° 13'40.1''	Calcic Chernozems from the Kiendelen village	Soil
	5	N 43° 18' 18'' E 42° 27'49''	The cryoconite from the ice crack of Garabashi glacier	Volcano
	6		The cryoconite underlain by ice	

Table 1. The description of studied cryoconites.

Cryoconite material analysis, ¹³C NMR spectroscopy and elemental analysis procedure of HAs

Cryoconite samples were air-dried (20°C), ground, and passed through 2 mm sieve. Humic acids were extracted according to a published IHSS protocol (Swift 1996). Solid-state CP/MAS ¹³C-NMR spectra of HAs were measured with a Bruker Avance 500 NMR spectrometer in a 3.2-mm ZrO₂ rotor. The magic angle spinning (MAS) frequency was 20 kHz in all cases and the nutation frequency for cross polarization (CP) was $\omega_1/2\pi = 1/4 \cdot 62.5$ kHz.

Repetition delay was 3 seconds. The number of scans was 6500-32000. Contact time is 0.2 μ s (Polyakov and Abakumov 2020a).

To conduct a graphical analysis of the elemental composition (C, O, N, H), we used the van Krevelen diagram (van Krevelen 1950), using the H/C-O/C ratios to identify the direction of the transformation processes of various organic compounds in natural conditions. Under the conditions of

cryoconite formation, BC and soil organic carbon accumulates from the atmosphere and has no direct connection with local soil processes in the study region. At the same time, this analysis allowed to evaluate the processes taking place in the studied cryoconite and compare them with soil samples. Elemental compositions were cor-

rected for gravimetric water and ash content. Oxygen content was calculated by difference of whole samples mass and gravimetric concentration of C, N, H and ash.

To identify the statistical relationship between the studied compounds, we proposed Spearman's correlation.

Results and Discussion

Elemental composition of studied cryoconite

The elemental composition of HAs is quite different depending on the geographic location and factors influencing the accumulation of BC. Atomic ratios (C/N, H/C, O/C) are suitable for assessing their composition. The elemental composition and atomic ratios of the studied HAs are presented in Table 2. C/N ratio varied from 7.58 to 17.58 and was determined from a high to a very low degree of carbon enrichment with nitrogen. At the same time, the average values of carbon were found rather low relative to natural soils (46-62%) with a high content of oxygen (45-50%).

In Table 2, a comparison of the studied cryoconite with HAs from natural soils located in the Arctic, Antarctic and a cryoconite sample is presented and supplemented with data from the Spitsbergen archipelago (Polyakov et al. 2019a). Arctic samples (No. 1-2) showed C/N ratio quite close to natural soils, similarly to the cryoconite from the Spitsbergen archipelago. Apparently, this is due to a single principle of material accumulation and homogeneity of this material. In the sample from Antarctica (No. 3), the carbon content is estimated as the lowest due to the fact that local ecosystems in general have a low content of organic content (Gedgafova et al. 2019, Khakunova et al. 2018). The low carbon content in the HAs composition can also be associated with increased acidity and moisture content of the initial samples (Orlov 1990). Under such conditions, the condensation process is difficult and

the hydrolytic decomposition of humic compounds is enhanced (Vasilevich et al. 2018, Lodygin et al. 2017). Moreover, the elemental composition varied quite strongly in the studied samples, and this is due to the intensity of biological (biochemical) processes occurring in the soils.

A relatively high carbon content was found in the samples from cryoconite holes from Mount Elbrus No. 5-6 (37-39%). Actually, here, as well as in the soils formed at the foothills of the mountain (No. 4), the most favorable conditions for the humification of organic compounds are apparent. The foothills of Elbrus are quite productive ecosystems. Here, in the conditions of the formation of Chernozems, a large number of agricultural crops are grown. Dry conditions, plowing of land and erosion processes lead to the transfer of organomineral particles by the aeolian process to the nearest obstacles, which can be mountain ranges.

The van Krevelen diagram for the H/C-O/C ratios makes it possible to identify the direction of the transformation processes of various organic compounds into natural conditions (Orlov 1990). Under the conditions of studying cryoconite deposits selected from completely different natural conditions, the accuracy of this method increases significantly. Figure 3 shows the resulting diagram of the average molar ratios $H / C_{mod-O} / C$ in the studied HAs.

Sample	C	H	N	O	C/N	H/C	O/C	H/Cmod	w
1	14	3	1	82	16.33	2.55	4.40	8.44	6.24
2	17	3	2	78	9.92	2.10	3.44	6.71	4.79
3	8	2	1	89	9.33	2.97	8.35	14.16	13.73
4	52	5	3	38	17.58	1.31	0.56	2.06	-0.19
5	39	6	6	49	7.58	1.83	0.94	3.09	0.06
6	37	5	5	53	8.63	1.61	1.08	3.05	0.54
Mean	28	4	3	65	11.56	2.06	3.13	6.25	4.19
SD	17.29	1.55	2.10	20.80	4.27	0.61	2.98	4.59	5.39
Coeff. var.	62.12	38.73	69.92	32.07	36.91	29.80	95.43	73.42	128.43
Cryoconite from Spitsbergen ¹	43	6	5	46	10.5	1.62	0.80	2.69	-0.02
Soil-like body from Lena river Delta ²	36	5	3	42	16.82	1.38	0.72	2.35	0.06
Soil from King-George isl., Antarctica ³	35	5	6	54	6.23	1.70	1.16	3.25	0.62
Cryosol from Vaigach isl., Arctic ⁴	48	6	5	36	11.29	1.42	0.55	2.2	-0.3

Table 2. Elemental composition of the studied HAs from cryoconite. Gravimetric concentration is given for C, H, O and N content. C/N, H/C, O/C, H/Cmod and “w” were calculated from mole fraction of C, H, O and N content. H/Cmod is the number of substituted hydrogen atoms in HAs; W indexes were calculated according to (Orlov 1990). Sample numbers correspond to Table 1. Note: ¹ (Polyakov et al. 2019a), ² (Polyakov and Abakumov 2020a), ³ (Polyakov and Abakumov 2020b), ⁴ (Polyakov et al. 2019b).

The studied samples are located in three clusters relative to their geographical location and their carbon content (Fig. 3). The lower H/Cmod index indicate the higher level of condensation of macromolecules in HAs samples. As expected, the highest level of macromolecule condensation is observed in the Chernozems from Elbrus (No. 4). In addition, local biological (biochemical) processes determine the intensity of condensation of macromolecules in cryoconite holes. Thus, the most condensed macromolecules accumulated on the Mount Elbrus, followed by samples from Mushketov glacier (Cape

Baranov). The lowest level of molecular condensation was found in Antarctic samples. The “w” index used in Table 2 reflects the oxidation state of the HAs. The oxidizing conditions of the environment are generally associated with the ability to migrate elements, in particular iron and aluminum ions, which actively migrate in weakly acidic to acidic solutions (Vasilevich et al. 2018, 2019; Lodygin et al. 2017). Weak reduction conditions are associated with the formation of fresh organic residues and the process of humification (Orlov 1990). All cryoconite samples are in oxidizing conditions, while the weakest

processes are observed in HAs from Mount Elbrus, which may indicate the transformation of organic matter. A clear process of humification is observed in the soil sample under weakly reduction conditions. This might be also confirmed by the low degree of the H/C_{mod} ratio. Nowadays, it is difficult to identify which processes affect the condensation of macromolecules in cryoconite samples. In our opinion, the leading factor influencing the condensa-

tion is the initial origin and composition of BC. Under the conditions of cryoconite formation, a weak transformation of organic matter is observed, and the leading process is mineralization. Based on this, this material can potentially be quickly absorbed by soil microbiota during deglaciation and make a significant contribution to climate change in the planet ([1]-Council 2019, [2]-AMAP 2015).

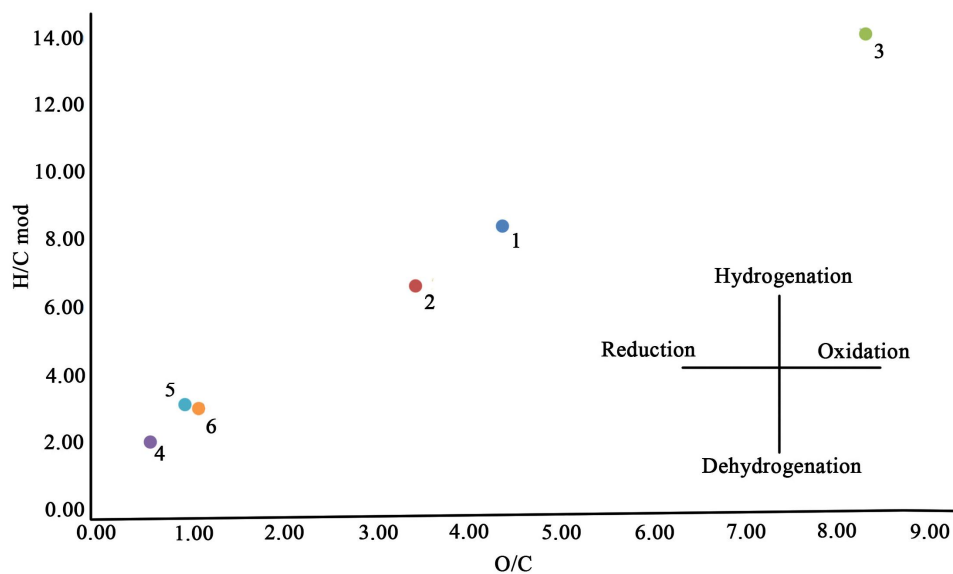


Fig. 3. Elemental composition of the studied HAs isolated from study cryoconite. H/C_{mod} – the number of substituted hydrogen atoms in the HA. Sample numbers correspond to Table 1.

Characterization of HAs by ¹³C-NMR spectroscopy

Six chemical groups in HAs were identified according to the ¹³C-NMR spectroscopy method. C_nH-alkyl in 0-46 ppm (C, H-substituted aliphatic fragments), O,N-alkyl in 46-60 ppm (methoxy and O,N-substituted aliphatic fragments), OCH/OCq in 60-110 ppm (aliphatic fragments doubly substituted by heteroatoms (including carbohydrate) and methine carbon of ethers and esters), C-C/C-H – AR in 110-160 ppm (C,H-substituted aromatic fragments; O,N-substituted aromatic frag-

ments), COO/N-C=O in 160-185 ppm (carboxyl groups, esters, amides and their derivatives), RC(=O)R' in 185-200 ppm (quinone groups; groups of aldehydes and ketones) (Chukov et al. 2015, Dziadowiec et al. 1994, Hatcher et al. 1981). The chemical shifts are calculated by absolute spectral signals. Samples 1-3 show noises in the signals; this may be due to the relatively high content of clay in the soil samples. Such noises are most typical for soil types such as Chernozems and Fluvisols.

This is due to the presence of clay in the parent materials, as well as the intake of clay materials by the river. In the studied samples, the wind can transfer the clay and dust particles in the cryoconite holes.

The obtained spectra are presented in Fig. 4. Most of the peaks corresponded to the aliphatic regions (C, H – alkyl ((CH₂)_n/CH/C and CH₃) and OCH/OC_q groups, as well as the carbonyl group COO/NC=O. The aromatic group was cal-

culated from the sum of the shifts of 110–185 ppm. Aliphatic fragments were calculated from the sum of the shifts of 0–110 ppm, 185–200 ppm. Chemical shift in 130 ppm, which corresponds to aryl carbons of charcoal (Pengerud *et al.* 2017) and indicates the pyrogenic origin of organic matter, have been detected in cryoconite holes. Data of chemical shifts in the studied soils are presented in Table 3.

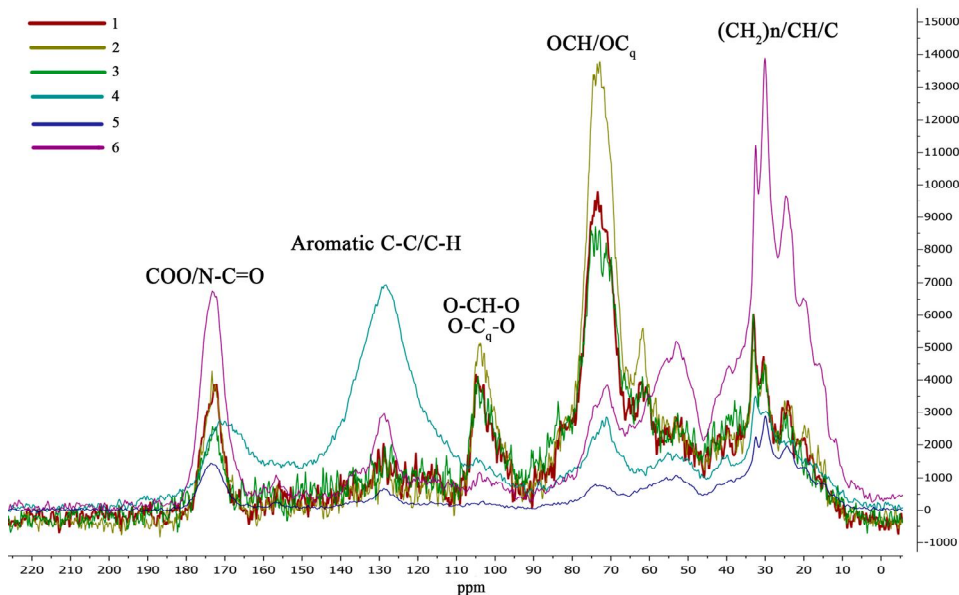


Fig. 4. CP/MAS ¹³C-NMR spectra of HAs from studied cryoconites and soil. Numbers correspond to sample numbers (*see* Table 1). Axis OX – chemical shifts in ppm; Axis OY – Intensity of signal.

Aliphatic fragments of HAs dominate in the studied cryoconite materials and are approximately in the same range of values (71-73%) (Table 3). This fact indicates that the mechanism of transformation of organic residues in various cryoconite was quite similar. At the same time, the polar regions have practically no differences in the qualitative composition of HAs. Cryoconite's HAs from Elbrus are dominated by C,H- and O,N-alkyl groups; samples from Arctica and Antarctica are dominated

by OCH/OC_q (aliphatic fragments doubly substituted by heteroatoms (including carbohydrate) and methine carbon of ethers and esters) group. Most of the BC is pyrogenic carbon, which is released into the atmosphere during fires (Abakumov *et al.* 2018, Knicker 2007). During a fire, thermal destruction of HA occurs and the peripheral part of the molecule is separated from the nucleus (Alexis *et al.* 2010). In HAs molecules, the periphery is represented by aliphatic fragments, which are sepa-

rated from the aromatic nucleus during a fire and involve in the formation of BC. It is then transported a considerable distance from the fire site and settles on the surface of soil and glaciers (Polyakov et al. 2019a). Therefore, the aliphatic part of HAs in cryoconite carries information about the precursors of humification. In the HAs isolated from polar soils of the Arctic and Antarctica, the content of OCH/OCq group is significantly higher com-

pared to the background of samples from Elbrus. The content of this group may be associated with the precursors of humification (conifers residues) and the content of complex and light ethers in them. In the samples from the Garabashi glacier, the accumulation of C,H-substituted aliphatic fragments occurs; these fragments are formed mainly from woody and herbaceous vegetation and are quite widespread in the structure of HAs of various soils.

Sample	Chemical shifts, %						AR	AL	AR/AL	AL h,r + AR h,r, %	C,H- AL/ O,N- AL
	C, H- AL	O,N - AL	OCH/ OC _q	C- C/C- H - AR	COO/ N-C=O	RC(=O) R'					
1	24	8	37	18	10	3	28	72	0.39	42	0.53
2	22	8	40	17	10	3	27	73	0.37	39	0.46
3	24	8	38	18	9	3	27	73	0.37	42	0.52
4	20	6	21	38	12	3	50	50	1.00	58	0.74
5	40	11	19	15	13	2	28	72	0.39	55	1.33
6	36	10	20	18	11	5	29	71	0.41	54	1.20
Mean	27.67	8.50	29.16	20.67	10.83	3.17	31.5	68.5	0.48	48	0.80
SD	8.23	1.76	10.11	8.57	1.47	0.98	9.1	9.1	0.25	8.21	0.37
Coeff. var.	29.77	20.71	34.65	41.47	13.58	31.05	28.9	13.2	51.4	16.99	47.34
Cryoconite from Spitsbergen ¹	34	8	16	31	10	1	41	59	0.69	65	1.42
Soil-like body from Lena river Delta ²	22	7	21	33	14	3	47	53	0.89	76	0.79
Soil from King- George isl., Antarctica ³	44	8	18	21	8	1	29	71	0.41	65	1.69
Cryosol from Vaigach isl., Arctic ⁴	23	8	37	12	18	2	29	71	0.42	42	0.52

Table 3. Percentage of carbon in the main structural fragments of HAs from cryoconites and soil by CP/MAS ¹³C-NMR spectroscopy. Sample numbers correspond to Table 1; AR – aromatic fraction; AL – aliphatic fraction; AL h,r + AR h,r % – hydrophobicity degree; C,H-AL/O,N-AL – the degree of decomposition of organic matter. *Note:* ¹ (Polyakov et al. 2019a), ² (Polyakov and Abakumov 2020a), ³ (Polyakov and Abakumov 2020b), ⁴ (Polyakov et al. 2019b).

The studied soil from the Kiendelen village accumulated up to 50% of aromatic fragments. The peaks are located in the regions C, H – alkyl ((CH₂)_n/CH/C and CH₃), OCH/OC_q, C–C/C–H- AR and COO/N–C=O groups. This sample is more condensed; the high content of aromatic fragments is associated with the predominance of herbaceous vegetation, which contains a relatively high content of lignin (Orlov 1990). Lignin is the main building material for aromatic HAs fragments. The pathways of lignin transformation in soils are represented by both the decomposition of monomers and partial changes in the macromolecule. The transformation of lignin leads to a decrease in the group of fragments –OCH₃, which is also reflected in the structure of HAs. Demethylation is a characteristic elementary process of humification; the decomposition of lignin leads to the accumulation of the COOH group. Thus, an increase in the proportion of vascular plants and lignin may indicate the formation of macromolecules that are more resistant to microbial degradation, and indicates the “maturity” of HAs. As a result of the growing season, straw is formed here, which is a fodder base for animals. Plant residues are enriched with nitrogen, carbohydrates, easily and difficultly hydrolyzed

polysaccharides and lignin, during the transformation of which high-molecular compounds condense (Polyakov and Abakumov 2020a, Orlov 1990). From the results obtained, it can be seen that the soil sample formed in the Elbrus region is significantly different from the samples from cryoconite that are formed on the Garabashi glacier. This suggests that active processes of humification of organic matter are taking place in the soil, which leads to its stabilization in resistance to biological degradation. It can be seen from the Fig. 4 that peaks in the aromatic region are observed in a similar region, which suggests that aromatic fragments, together with dust, can settle in the Elbrus foothills and form cryoconite. Nevertheless, this is not the main source of organomineral matter in the foothills, since the source of aliphatic compounds is not local soils.

Thus, the studied cryoconite have a very close quantitative composition of structural fragments in the HAs, the AR/AL ratio is 0.37-1. At the same time, significant differences were noted in the qualitative composition of HAs. Depending on the precursors of humification, the quality of plant residues, there are significant differences in the structure of HAs.

Stabilization of organic matter in studied cryoconite and soils

An important issue is the stabilization of organic matter that accumulates in cryoconite holes. Under the conditions of active deglaciation of the glacier surface, every year more and more material is involved in the current process of soil formation, which leads to significant changes in the landscapes adjacent to the glaciers. This is due to the accumulation of nutrients, risk elements, radionuclides, and the formation of specific microbial communities, under the influence of which a closed cycle of nutrient transformation is formed. A characteristic feature of HAs that are

formed in cryoconite holes is their low degree of condensation and accumulation of aliphatic fragments of HAs (up to 73%). With the accumulation of such material on the surface of glaciers, their slight transformation occurs due to permanently low temperatures and the absence of seasonal influx of the humification precursors. That organic matter is similar in structure to organic residues that are part of permafrost-affected soils in the Arctic, so we can talk about the deposition of black carbon on the surface of glaciers (Lupachev *et al.* 2017, Lodygin *et al.* 2017, Ejarque and

Abakumov 2016). At the same time, in the context of a climatic crisis, if this organic matter enters the environment, its active mineralization will be observed, which will lead to the emission of carbon dioxide into the atmosphere.

To visualize the process of humification and hydrophobicity of the studied samples, we proposed a diagram of integrated indicators of the molecular composition of HAs (Fig. 5).

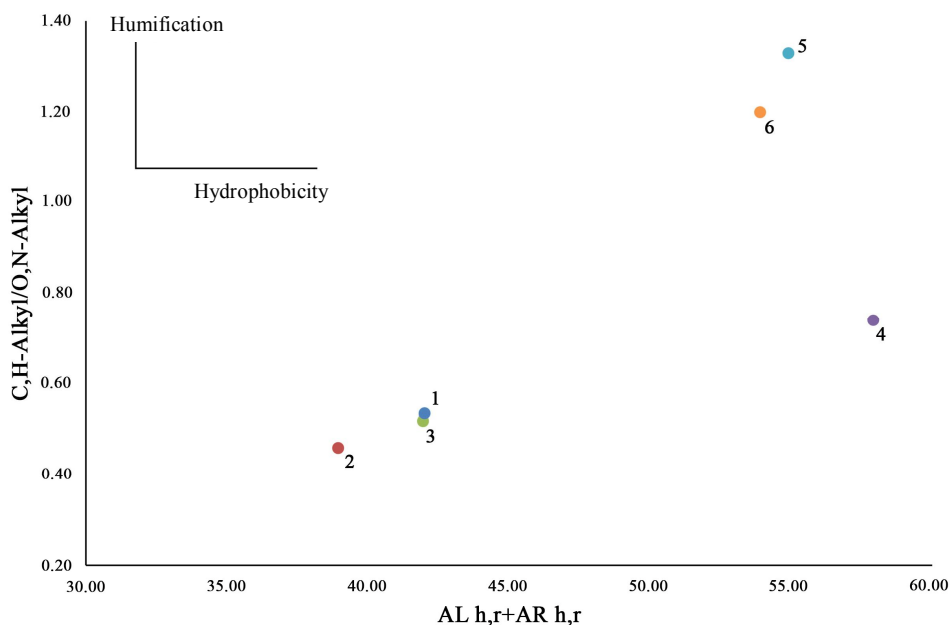


Fig 5. The diagram of integrated indicators of the molecular composition of HAs from cryoconite holes and soil. Samples correspond to Table 2; AL h,r + AR h,r indicates the total number of unoxidized carbon atoms.

The highest degree of humification was observed in the cryoconites from Elbrus (Fig. 5). This is due to the qualitative composition of the precursors of humification. The most hydrophobic HAs molecules were found in the soil of the Elbrus region. An increase in the proportion of aromatic fragments of HAs leads to the stabilization of organic matter in the cryoconites of Elbrus. The condensation of macromolecular compounds that include aromatic/unsaturated structures between 110-185 ppm indicates an increase in the degree of hydrophobicity of the soil organic matter and its

low availability for the soil microbiome (Vasilevich et al. 2019). Thus, reducing the contribution of greenhouse gases to the climate crisis.

The high correlation was observed in the RC(=O) R'group with C, O, C/N, H/C, O/C, OCH/OCq ($r = 1$) and O, N-AL with C, O, H/C, O/C ($r=1$), see Fig. 6. The composition of HAs from cryoconite varied greatly, depending on biological (biochemical) processes, which was reflected in the elemental and qualitative composition of HAs.

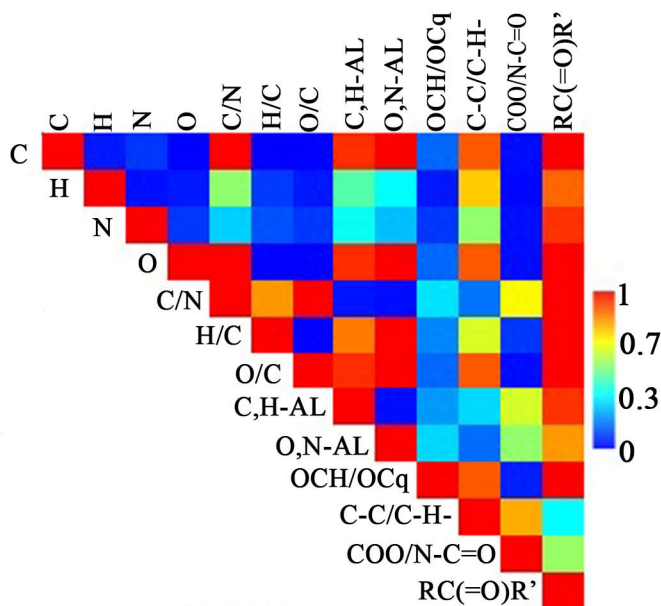


Fig. 6. Spearman's correlation matrix of HAs fractions.

Conclusions

Humic compounds formed in cryoconite holes are rather heterogeneous in comparison with natural soils. The elemental composition showed that the most condensed macromolecules accumulated in cryoconites in the area of the Mount Elbrus, while the weak-condensed macromolecules were present in the samples from Antarctica. The composition of HAs of cryoconite is dominated by aliphatic structural fragments (71-73%), while the qualitative composition of the aliphatic group is quite different depending on the study area and may be associated with the vegetation cover formed in the immediate vicinity. In conditions of active deglaciation, weakly condensed cryoconite material can be quickly involved in the process of soil formation in the periglacial zone and serve as an additional source of or-

ganic carbon. The predominance of aliphatic fragments in the HAs of cryoconite sediments can negatively affect climate change in these regions and on a planetary scale. Aliphatic fragments in HAs are less stable than aromatic fragments. They are more susceptible to hydrolysis and biodegradation, therefore, under conditions of degradation of the ice cover in mountain and polar regions, the organominerals compounds can enter the environment and make an additional contribution to climate change. The studied HAs mainly consist of straight and branched carbon chains, which can be rapidly absorbed during transformation by soil microbiota. With their rapid transformation, a significant amount of carbon dioxide or methane can enter the atmosphere, and have a great impact to the climate crisis.

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