ANNUAL REPORT ON GEOTRACES ACTIVITIES IN RUSSIA

May 1st, 2016 to April 30th, 2017

New scientific results

- For the first time the trace element (Al, Fe, Mn, Cd, Cr, Co, Cu, Mo, Ni, Pb) speciation in sinking particles in the White Sea was examined using a modified method of selective chemical leaching [Tessier et al., 1979]. Sinking particles were collected by use of 18 sediment traps deployed at different layers of the water column (deployment period varied from 1 month to 1 year). Based on contribution of the lithogenic fraction, the three groups of trace metals were distinguished: 1) Al and Cr as a typical lithogenic elements (till 90% of total content); 2) Fe, Mo, Ni, Co and Cd – with the intermediate contribution of lithogenic fraction (from 50 to 75% of total content); 3) Mn, Cu and Pb as the least lithogenic elements and in the same time the most geochemically labile elements. For each of them a contribution of adsorbed, organic and associated with amorphous hydroxides fractions in sum exceeds 50% (of total content), for Mn this value is the maximal one (to 90%). In direction to the sea bottom the Mn content in the form of hydroxides as well as in the adsorbed ones distinctly increased. Partitioning of the Mn occurrence forms in the sinking particles in the near-bottom layers is close to that in the uppermost (0–2 cm) sediment layer [**Demina et al., 2017**].

- A measurement procedure for determining of Ru, Pd, Ir, Pt and Au mass fractions in ferromanganese deposits by inductively coupled plasma-mass spectrometry after acid digestion and anion exchange pre concentration is presented. To eliminate incomplete recovery after sorption pre concentration of the platinum-group elements (PGE) and Au, a standard addition method was used. Detection limits ranged from 0.02 ng (Pd, Ir) to 0.19 ng (Ru). The measurement results for ferromanganese nodule reference material NOD-A-1 and NOD-P-1 agree with earlier reported values. Intermediate precision of PGE concentration data for nodule reference materials in this work was 5–24% (1s) and could reflect sample heterogeneity [**Berezhnaya, Dubinin, 2017**].

- The age of the pelagic sediments from Brazil Basin was determined using strontium isotope stratigraphy data for biogenic apatite. For layer 0–5 cm the age of sediments was 24.1±0.2 million years, and for layer 86–90 cm it was 24.8±0.2 million years. The average sedimentation rate in the Late Oligocene was close to 13 mm per 1000 years. The chemical composition of ferromanganese micronodules, nodules, and films on weathered volcanic rocks was investigated in these sediments to study minor and major element behavior during the ore-forming process and diagenesis. Hydrogenous Fe-Mn nodule found on the surface of the sediment with Mn/Fe value 1.05–1.95 in its composition was formed at a growth rate of 1.2–2.4 mm per million years, which is 1000 times lower than the growth rate of the buried nodules (Mn/Fe = 0.4) on the horizon 83 cm. During diagenesis, the buried nodule changed the mineral composition (asbolane-buserite partially substituted by goethite), and part of elements (Mn, Ni, Li, Tl) were lost by a nodule, but it kept the elements associated with iron oxyhydroxide (Ce, Th, Be, As, V). The composition of manganese micronodules from two studied layers was determined by two steps of mineralization during oxic and suboxic diagenesis. The Sr isotope composition of manganese micronodules from both layers is the same as for Sr in contemporary ocean water. The $^{143}Nd/^{144}Nd$ value in manganese micronodules differs between sediment layers, reflecting the isotopic composition of Nd in paleoocean at the time of micronodule formation, and did not differ between the size fractions [**Dubinin et al., 2017**].

- The chemical composition of zooplankton of the Kara Sea proper and two bays of Novaya Zemlya Archipelago was determined. The results revealed similar distribution of major, trace and rare-earth elements in zooplankton from the aquatic environments that were studied. The C_{org} comprised 49.5±4.8% of the dry zooplankton weight, while the summed content of other major elements (Na, P, S, K, Mg, Ca) made up to 4.82%. The elements studied were arranged into three groups by the content level: K, S, P, Al, Ti, Sc, Cd, Se, Cs, Rb and Corg corresponded to the average chemical composition of ocean zooplankton, while the contents of Na, Ca, Mg, Fe, Mn, Zn, Sr, Ba, B, Cu, Pb, Cr, Ni, V, Co, Sb, Mo, Ag, Be, Ga and Hg were lower, and Li, As, and U significantly exceeded the respective reference values [**Lobus, 2016**].

- For the dominant species of mesozooplankton (*Senecella siberica*, *Limnocalanus macrurus*, *Calanus* spp.) content of C_{org}, lipids, and also major (Na, Mg, P, S, K and Ca), trace (Li, Be, B, Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Y, Mo, Ag, Cd, Sb, Cs, Ba, Hg, Tl, Pb, Bi, Th and U) and rare-earth (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) elements has been determined in the Ob River-estuarine system and the adjacent shelf of the Kara Sea. We have revealed high accumulation of Li in *Calanus* spp., which concentration is approximately 350 times more than ones in *S. siberica* and *L. macrurus*. Total accumulation of chemical elements per unit of volume (1 m^3) is higher in *L. macrurus* than in *S. siberica* and *Calanus* spp., 6.63, 0.69, 0.41 mg, respectively. Intensity of biological accumulation of elements and location of the maximum accumulation of elements by zooplankton community depend on the hydrophysical mode in the Ob River estuary. Postmortem change of chemical composition in dead *L. macrurus* has multidirectional character. The revealed distinctions of the chemical composition in alive and dead zooplankton reflect depots of elements in an organism and peculiarities of lifetime accumulation and postmortem transformation of substances [**Lobus et al., *in press***].

- Continuous sampling of aerosols is carried out on the NW coast of the Kandalaksha Bay of the White Sea. Aerosol matter (PM2.5) from 30 filters collected in summer and autumn, 2013, and spring, 2014, was studied by scanning electron microscopy. The elemental composition of aerosol matter was determined by the inductively-coupled plasma mass-spectrometry (ICP-MS) with Agilent 7500. The major portion of aerosol particles collected in summer is of biogenic origin. Heavy metal concentrations in aerosols are at the Arctic background level. The distribution of trace element concentrations is characterized by simultaneous peaks of different elements. The backward trajectory analysis shows an increase in Ni and Cu concentrations corresponding to the arrival of air masses from the western part of the Kola Peninsula where metallurgical industry occurs. That suggests the influence of smelters [**Starodymova et al., 2016**].

- The data on the distribution of atmospheric black carbon (BC) in the marine boundary layer of the North Atlantic and Baltic, North, Norwegian, Barents and White Seas from the 67th research cruises of the RV "*Akademik Mstislav Keldysh*" since August 25 to October 10, 2016 are processed and interpreted. During some parts of the cruise, air masses arrived from background areas of high latitudes, and the measured BC concentrations were low. During other parts of the cruise, air masses arrived from industrially developed areas and regions with gas flaring with strong BC sources, and this led to substantially enhanced measured BC concentrations. Model-supported analyses are currently performed to use the measurement data for constraining the emission strength in these areas [**Shevchenko et al., 2016**].

- Authigenic minerals were studied in Holocene shelf sediments of the Laptev Sea (cold methane seep site, water depth 71 m). The study presents the first finds of large hard carbonate concretions with Mg-calcite cement in recent sediments of the Arctic shelf seas.

These concretions differ from previously reported glendonites and concretions from bottom sediments of the White Sea, Kara Sea, Sea of Okhotsk, etc. A study of the morphology, microstructure, and composition of these newly reported concretions revealed the multistage formation of carbonates (structural varieties of Mg-calcite and aragonite). It was shown that organic matter played an important role in the formation of authigenic carbonates, i.e., in the formation of sedimentary–diagenetic Mg-calcite. The role of methane as a possible source for authigenic carbonate formation was estimated. It was found that methane-derived Mg-calcite accounts for 17–35% of concretion materials. Mg-calcite had $\delta^{13}C\text{-}C_{carb}$ values between –24 and –23‰ and $\delta^{13}C\text{-}C_{org}$ values between –44.5 and –88.5‰. Authigenic carbonate formation in the Arctic shelf seas can act as a biogeochemical filter mechanism limiting methane emissions from bottom sediments to the water column and atmosphere [**Kravchishina et al., 2017**].

- The vertical distribution of chlorophyll *a*, particulate organic carbon and its isotopic composition, total suspended particulate matter, and the structure of the phytoplankton community were studied in the Middle and South Caspian Sea in May–June 2012. The vertical distribution of the values of the organic carbon isotopic composition was primarily controlled by the vertical structure of phytoplankton and chlorophyll *a* in the water column up to ~500 m and by biogeochemical processes at the redox barrier (~600 m layer). A significant amount of weakly transformed chlorophyll *a* was found close the sea bottom. The high level of the Caspian Sea and processes related to this phenomenon in the water column (formation of stable stratification, development of hypoxia and anoxia, availability of free hydrogen sulfide and methane in depressions, etc.) contribute to slowing the complete transformation of OM in sedimentation, removing incompletely decomposed organic substances from the carbon cycle [**Kravchishina et al., 2016**].

New publications (published or in press) GEOTRACES Compliant and GEOTRACES-related

- Alekseychik P., Lappalainen H.K., Petäjä T., Zaitseva N., Heimann M., Laurila T., Lihavainen H., Asmi E., Arshinov M., Shevchenko V., Makshtas A., Dubtsov S., Mikhailov E., Lapshina E., Kirpotin S., Kurbatova Y., Ding A., Guo H., Park S., Lavric J.V., Reum F., Panov A., Prokushkin A., Kulmala M. (2016) Ground-based Station Network in Arctic and Subarctic Eurasia: an Overview. Geography, Environment, Sustainability. V. 09. No 02. P. 75–88.
- Berezhnaya E.D., Dubinin A.V. (2017) Determination of Platinum Group Elements and Gold in Ferromanganese Nodule Reference Samples. Geostandards and Geoanalytical Research. V. 41. No 1. P. 137–145. DOI: 10.1111/ggr.12130
- Berezhnaya E.D., Dubinin A.V. (2017) Determination of the Platinum-Group Elements and Gold in Ferromanganese Nodule Reference Material NOD-A-1. Geochemistry International. V. 55. No. 2. P. 218–224. DOI: 10.1134/S0016702917010037
- Budko D.F., Demina L.L., Lisitsin A.P., Kravchishina M.D., Politova N.V. (2017) The Heavy Metal Occurrence Forms in the Modern Bottom Sediments of the White and Barents Seas. Doklady Earth Sciences. V. 474. No 1. P. 93–98.
- Demina L.L., Bud'ko D.F., Alekseeva T.N., Filippov A.S., Novigatsky A.N., Kochenkova A.I. (2017). The Distribution of Geochemically Different Fractions of the Group of Heavy Metals (Mn, Fe, Cd, Co, Cr, Cu, Mo, Ni, Pb) in the Processes of Early Diagenesis of Bottom Sediments of the White Sea. Geochemistry International. No 1. P. 107–112.

- Dubinin A.V., Uspenskaya T.Yu., Rimskaya-Korsakova M.N., Demidova T.P. (2017) Rare Elements and Nd and Sr Isotopic Composition in Micronodules from the Brazil Basin, Atlantic Ocean. Lithology and Mineral Resources. V. 52. No. 2. P. 81–101. DOI: 10.1134/S0024490217020043
- Kravchishina M.D., Lein A.Yu., Savvichev A.S., Reykhard L.E., Dara O.M., Flint M.V. (2017) Authigenic Mg-Calcite at a Cold Methane Seep Site in the Laptev Sea. Oceanology. V. 57. No. 1. P. 174–191. DOI: 10.1134/S0001437017010064
- Kravchishina M.D., Lein A.Yu., Pautova L.F., Klyuvitkin A.A., Politova N.V., Novigatsky A.N., Silkin V.A. (2016) Vertical Distribution of Suspended Particulate Matter in the Caspian Sea in Early Summer. Oceanology. V. 56. No. 6. P. 819–836. DOI: 10.1134/S0001437016050064
- Lobus N.V. (2016) Elemental Composition of Zooplankton in the Kara Seaand the Bays on the Eastern Side of Novaya Zemlya. Oceanology. V. 56. No 6. P. 809–818. DOI: 10.1134/S0001437016050088
- Lobus N.V., Drits A.V., Flint M.V. (In press) Accumulation of Chemical Elements in the Dominant Species of Copepods in the Ob Estuary and the Adjacent Kara Sea Shelf. Oceanology.
- Makarov V.I., Popova S.A., Shevchenko V.P. (2016) Long-term Trends in Black (Elemental) Carbon Concentrations in the Ambient Air of West Siberia and the White Sea Region. Chemistry for Sustainable Development. V. 24. No. 4. P. 459–465.
- Shevchenko V.P., Kopeikin V.M., Evangeliou N., Lisitzin A.P., Novigatsky A.N., Pankratova N.V., Starodymova D.P., Stohl A., Tompson R. (2016) Atmospheric Black Carbon Over the North Atlantic and the Russian Arctic Seas in Summer–Autumn Time. Chemistry for Sustainable Development. V. 24. No. 4. P. 441–446.
- Shevchenko V.P., Vinogradova A.A., Lisitzin A.P., Novigatsky A.N., Panchenko M.V., Pol'kin V.V. (2016) Aeolian and Ice Transport of Matter (Including Pollutants) in the Arctic. In: Implications and Consequences of Anthropogenic Pollution in Polar Environments. From Pole to Pole (Ed. R. Kallenborn). Springer. P. 59–73.
- Starodymova D.P., Shevchenko V.P., Sivonen V.P., Sivonen V.V. (2016) Material and Elemental Composition of Surface Aerosols on the North-Western Coast of the Kandalaksha Bay of the White Sea. Atmospheric and Oceanic Optics. V. 29. No 6. P. 507–511. DOI: 10.1134/S1024856016060154

New projects and/or funding

- Russian Science Foundation (RSF) project No. 14-27-00114-P "Sediment-biogeochemical studies of seas of the European part of Russia (dispersed sedimentary matter, bottom sediments, diagenesis). Interaction of geospheres, particle and energy fluxes", 2017–2018, under the direction of Academician A.P. Lisitzin.
- Programme of Presidium of Russian Academy of Sciences, project No. 0149-2015-0056 "Biogeochemistry of heavy metals and natural processes of biosorption purification of seas and oceans" under the direction of Dr L.L. Demina.
- Russian Foundation of Basic Research (RFBR) grant No. 16-05-00037 "Pelagic "biofilter" at the river-sea boundary: patterns of functioning in the large Arctic rivers estuaries" under the direction of Ph.D. A.V. Drits.

Meetings

- EGU General Assembly, Vienna, 23–28 April 2017. Poster presentation: Evangeliou N., Shevchenko V.P., Yttri K.E., Echhardt S., Sollum E., Pokrovsky O.S., Kobelev V.O., Korobov V.B., Lobanov A.A., Starodymova D.P., Vorobyev S.N., Thompson R., Stohl R. Elemental carbon in snow from Western Siberia and Northwestern European Russia during spring 2014, 2015 and 2016.
- XXIII Workshop "Siberian Aerosols" in Tomsk, Russia, November 29 – December 02, 2016. Oral presentation by Starodymova D.P., Vinogradova A.A., Zaharova E.V., Shevchenko V.P., Sivonen V.P., Sivonen V.V. Trace-elemental composition of near-the-ground aerosols on NW Kandalaksha Bay coast of the White Sea (in Russian).

Cruises GEOTRACES-related

- Shirshov Institute of Oceanology of Russian Academy of Sciences (IO RAS) cruise to the North Atlantic along 60°N: the 51th cruise of *RV Academik Ioffe*, June 3 – July 13, 2016, cruise leader is Dr Sergey Gladyshev. Our objectives for the expedition include 1) studying of the Deep Winter Convection – Labrador Sea water formation in the Irminger Sea; 2) Western Boundary Current System formation – role of the cascading from the shelf; 3) studying of lateral and vertical fluxes of suspended particulate matter – concentration, quantity, chemical composition (macro- and microelements including metals); 4) paleoclimatic reconstructions (sediment corer sampling) with which her research interests are well aligned (Fig. 14).

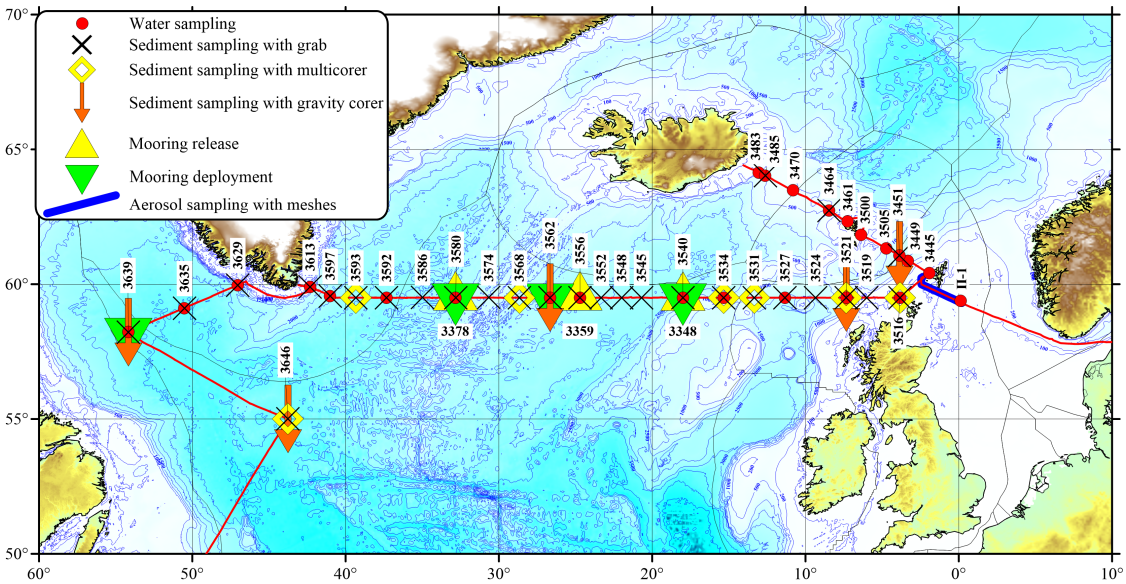

Figure 14. *The map of sampling sites in 51th cruise of RV Akademik Ioffe, June–July 2016.*

- IO RAS cruise to the Kara Sea. The 66th cruise of RV *Academik Mstislav Keldysh*, from July 16 to August 16 2016, cruise leader is Prof. Mikhail Flint. Multidisciplinary researches of the Kara Sea ecosystem (**Fig. 15**). One of the main object was to evaluate the specificity of the physical, hydrochemical, biological and geochemical processes of the ecosystems of the Kara Sea in the areas of large-scale impact desalinating runoff of the Ob and Yenisei rivers.

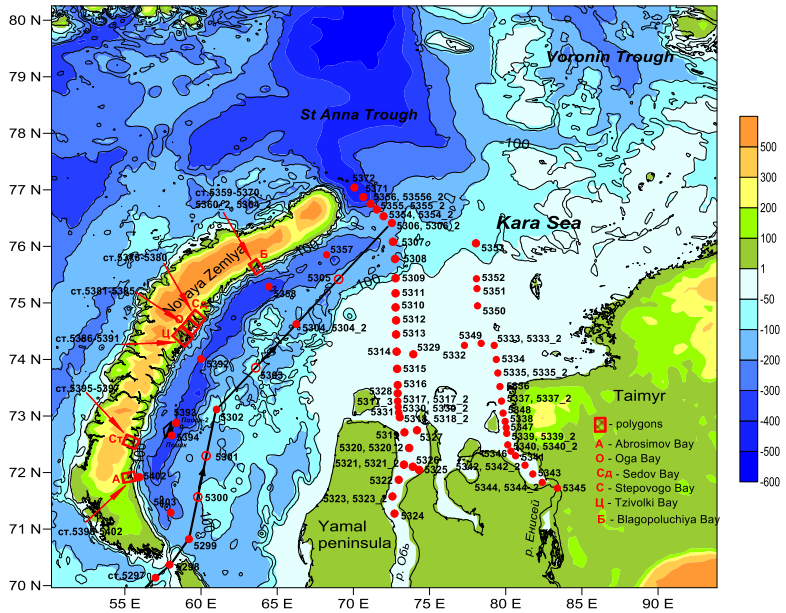

***Figure 15**. The map of sampling sites during 66th cruise of RV Academik Mstislav Keldysh, July–August 2016.*

- IO RAS cruise to the Barents Sea: the 67th cruise RV *Academik Mstislav Keldysh* from August 25 to October 10, 2016. The main objectives were modern sedimentation processes researches including biogeochemical studies of suspended particulate matter and bottom sediments [**Fig. 16**].

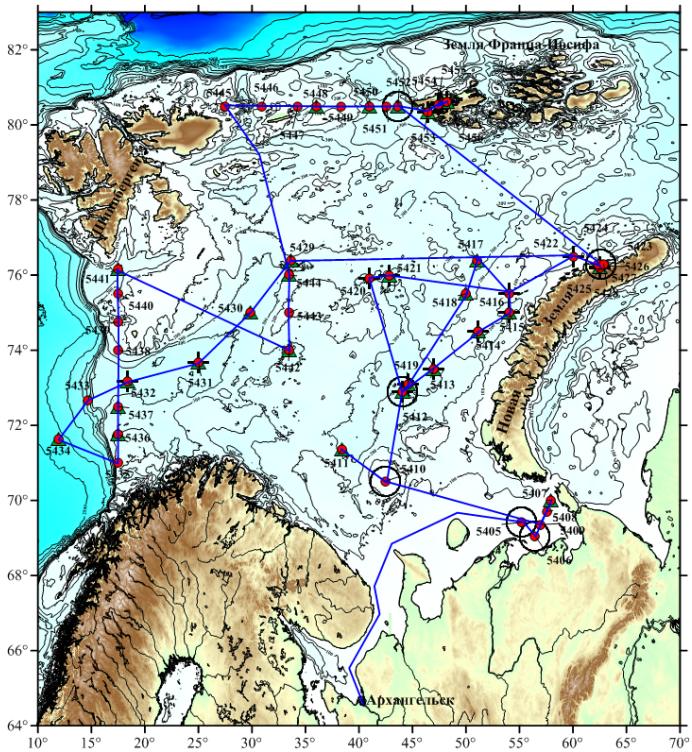

***Figure 16**. The map of sampling sites during 67th cruise of RV Academik Mstislav Keldysh, August–October 2016. Circle – water samples collecting; triangle – multicorer samples; cross – geological gravity corer; big circle – mooring deployment.*

- Marine Hydrophysical Institute of RAS and IO RAS cruise to the Black Sea: the 91th cruise of RV *Professor Vodyanitsky*, November 16 – December 5, 2016. The related studies of the system – particulate matter of the water column (suspended particulate matter, trapped matter) and the upper sediment layer makes it possible to reveal most fully the processes of sedimentogenesis and early diagenesis.

Outreach activities

- We announced the opportunities for cooperation in trace element research with Russia: http://www.geotraces.org/news-50/news/116-news/1215-opportunities-for-cooperation-in-trace-element-research-with-russia
  We noted a great interest to our expedition in 2017. We've received some proposals from Europe, United States of America and Australia. The expedition was planned by IO RAS (http://ocean.ru/) on board *RV Akademik Mstislav Keldysh*. The main purpose of the complex researches is studying of the Arctic Seas' ecosystems, including the climate change, continental discharge and biological productivity, particulate and dissolved matter pathways.
  We are planning to collect samples for joint trace element researches with our colleagues from University of Southern Mississippi (USA) and Macquarie University (Australia).

Other activities

- New sediment traps and other necessary equipment for moorings deployment in the Barents Sea and the North Atlantic.

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