

ANNUAL REPORT ON GEOTRACES ACTIVITIES IN RUSSIA

May 1st, 2022 to April 30th, 2023

New GEOTRACES relevant scientific results

- The increasing influence of Atlantic inflows in the Arctic Ocean in recent decades has had a potential impact on regional biogeochemical cycles of major and trace elements. The warm and salty Atlantic water, entering the Eurasian Basin through the Norwegian Sea margin and the Barents Sea, affects particle transport, sink, phyto-, and zooplankton community structure and could have far-reaching consequences for the marine ecosystems. This study discusses the elemental composition of suspended particulate matter and fluffy-layer suspended matter (FLSM) derived from samples collected in the Barents Sea and northern Norwegian Sea in August 2017 (**Figure RU-1**). The mosaic distribution of SPM elemental composition is mainly determined by two factors: (i) The essential spatial variability of biological processes (primary production, abundance, and phytoplankton composition) and (ii) differences in the input of terrigenous sedimentary matter to the sea area from drainage sources (weak river runoff, melting of archipelago glaciers, etc.). The distribution of lithogenic, bioessential, and redox-sensitive groups of elements in the particulate matter was studied at full-depth profiles. Marine cycling of strontium in the Barents Sea is shown to be significantly affected by increasing coccolithophorid bloom, which is associated with Atlantic water. Mn, Cu, Cd, and Ba significantly enrich the suspended particulate matter of the benthic nepheloid layer relative to the fluffy layer particulate matter within the benthic boundary layer [Starodymova et al., 2023].

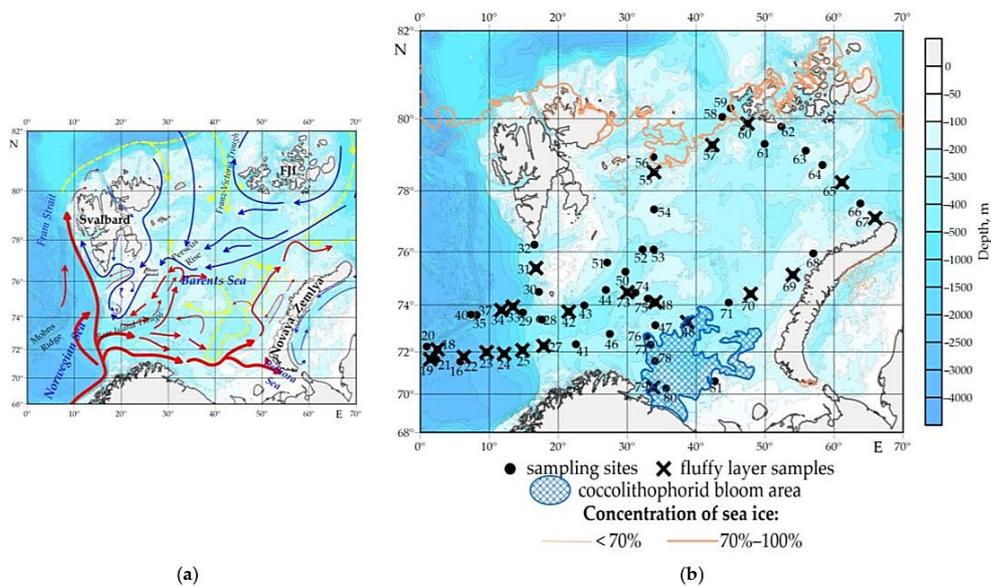


Figure RU-1. (a) Water circulation scheme after [Loeng, 1991; Pisarev, 2021]: red arrows—warm currents; blue arrows – cold currents; dashed yellow arrows – subsurface currents. (b) Map of SPM and FLSM sampling stations, July–August 2017. Station numbers are omitted in the first two digits. The area of coccolithophorid blooms ($>1.5 \cdot 10^6$ cells/l) derived from MODIS-Aqua data; images are composites over August 2017 [Kopelevich et al., 2020]; sea ice conditions from satellite imagery on August 8, 2017 [<http://old.aari.ru/odata/>]. Bathymetric data based on IB-CAO bathymetry [Jakobsson et al., 2020].

- The study investigated vertical particle fluxes and associated environmental parameters in the southern part of the Kara Sea in September 2022 on the basis of a 5-day deployment of two moored Automatic Deep-Sea Sedimentation Observatories (ADOS) with sediment traps and CTD, currents and hydrooptical profilers (**Figure RU-2**). A significant heterogeneity (up to two orders of magnitude) in the spatial distribution of the total particle fluxes and the main components of the sedimentary matter was revealed based on data of two moorings

deployed at the same sea depth of 100 m in the area of the Yamal shelf [Klyuvitkin et al., *in press*].

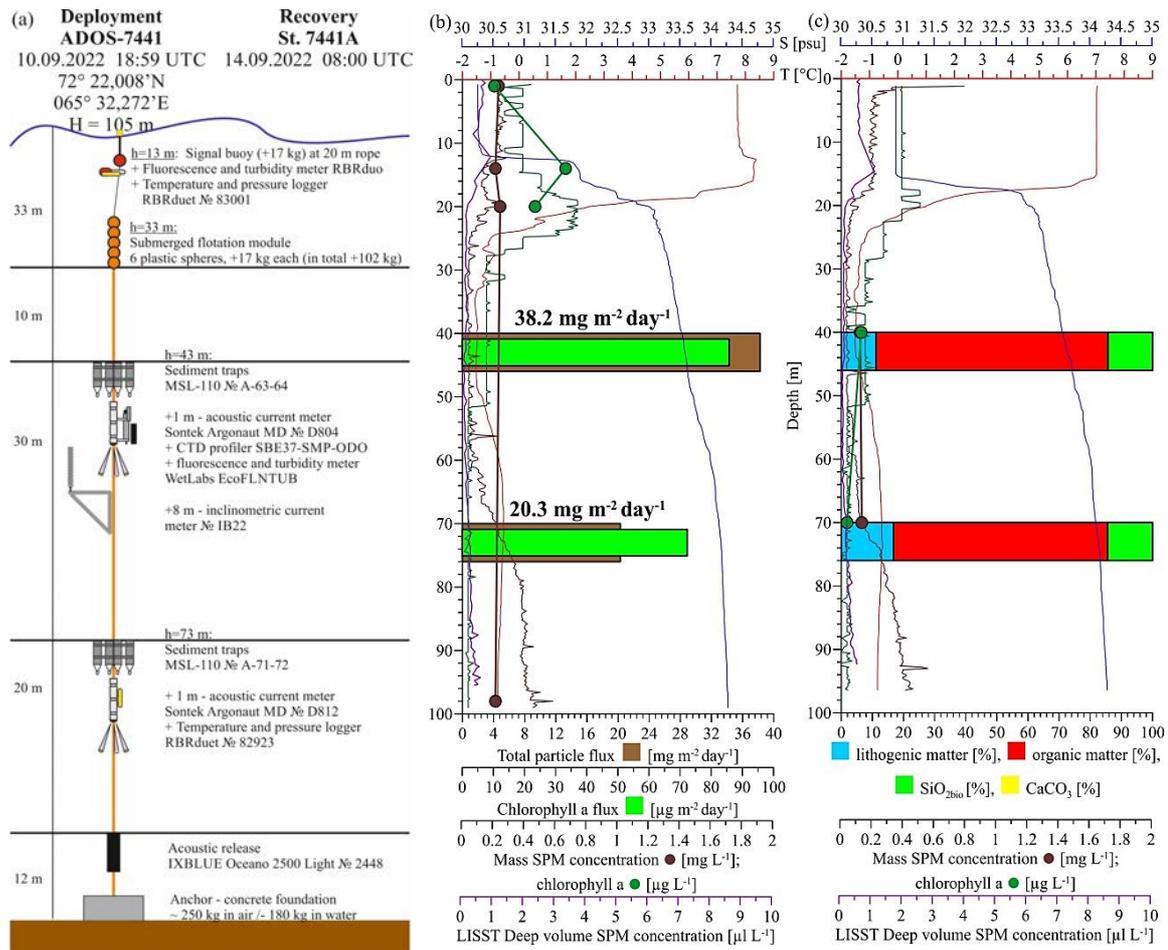


Figure RU-2. Example of ADOS-7441 deployed in the Kara Sea in September 2022: scheme (a) and total particle flux and Chl-a flux (b) and flux composition (c) with main environmental features vertical distribution: temperature, salinity, suspended particulate matter and Chl-a concentration before deployment (b) and after recovery of ADOS-7441 (c).

- Mercury (Hg) concentrations in lichens and mosses can be used as surrogates for atmospheric Hg deposition to continental surfaces. Hg concentrations ($n = 334$) and isotopic composition ($n = 67$) of epiphytic tree lichens and terricolous lichens and mosses from remote locations across the Eurasian Arctic and sub-Arctic (50° to 72° N, 30° to 180° E) were studied [Sonke et al., 2023]. The total Hg (THg) concentrations ranged from 13 to 7700 ng·g⁻¹. Epiphytic tree lichens had significantly higher median THg levels (243 ng·g⁻¹) than terricolous lichens (35 ng·g⁻¹) and mosses (74 ng·g⁻¹) (**Figure RU-3**). THg is substantially higher in both tree lichens and terricolous lichens near the Arctic Ocean shore and up to 300 km inland. The combined $\delta^{202}\text{Hg}$, $\Delta^{199}\text{Hg}$, and $\Delta^{200}\text{Hg}$ signatures suggest that the elevated coastal Hg levels are delivered by marine air masses rich in gaseous and particulate-oxidized Hg^{II} forms, such as HgBr₂. Similar to other vegetation Hg isotope studies, inland terricolous lichen and moss $\Delta^{200}\text{Hg}$ are near zero, indicating a dominant (63%) atmospheric Hg⁰ origin followed by Hg^{II} wet and dry deposition. Inland tree lichens carry a more positive $\Delta^{200}\text{Hg}$ of 0.15‰, similar to the atmospheric Hg^{II} end-member, suggesting that they preferentially accumulate Hg^{II} wet and dry deposition compared to colocated terricolous lichens. Mosses from the European sub-Arctic show a low $\delta^{202}\text{Hg}$ of -3.1‰, which we speculate to result from regional soil Hg⁰ emissions that are recaptured by mosses. Overall, the Hg isotope

variability of mosses and lichens reveals latitudinal gradients in Hg deposition pathways and identifies preferential Hg⁰ or Hg^{II} uptake [Sonke et al., 2023].

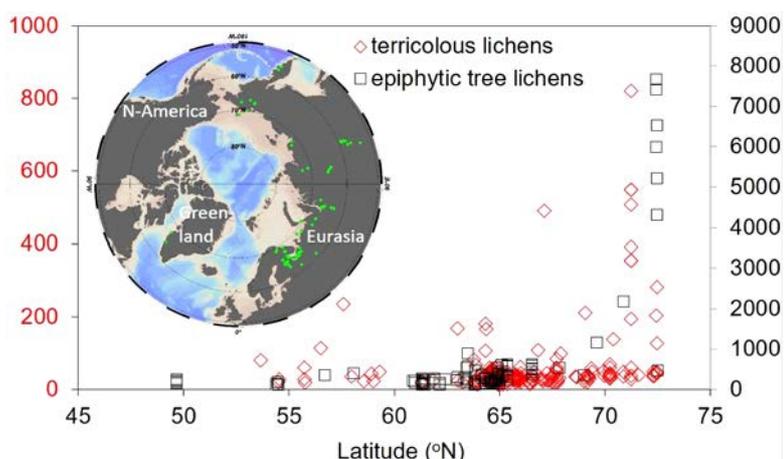
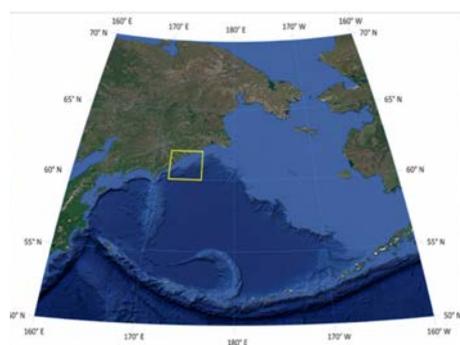
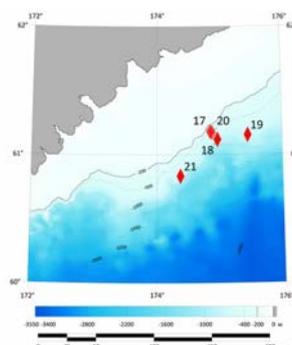


Figure RU-3. The plot demonstrates that Eurasian lichen Hg ($\text{ng}\cdot\text{g}^{-1}$) increases with latitude.

- Distribution of trace elements was studied in the methane seep ecosystem's components of the Koryak slope, the Bering Sea (**Figure RU-4**). Concentrations of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Zr, Mo, Cd, Ba, W, Pb, U were determined in seawater, benthic organisms, and surface layer of bottom sediments. Along with this, analysis of dissolved methane in water, as well as the total organic and inorganic carbon in organisms and sediments has been performed [Demina et al., 2022].



a)



b)

Figure RU-4. Study area, the Koryak Slope, the Western Bering Sea (a), and sampling sites (b) in cruise 82nd RV Akademik M.A. Lavrentyev, 2018.

Methane-saturated emanations from the Koryak slope serve a source of many trace elements: the near-bottom water layer is enriched in trace elements (5 to 1000 times) compared to the ocean water (**Figure RU-5**). Diffuse methane flows from reduced sediments contribute to the benthic diffuse flux of dissolved elements into seawater, providing the high concentration in near-bottom water. The data we have obtained could contribute to future quantitative analysis of the impact of methane seepage processes on the global-scale budget of the trace elements.

One of the biogeochemical features of seep ecosystems is an accumulation of trace elements by benthic organisms, particularly by gills of the pliocardiinae symbiotrophic clam *Calypotgena pacifica*. Gills of *C. pacifica* are significantly enriched in many trace elements, especially in Fe, Zn, and Cd (up to $n 10^2 \mu\text{g}/\text{g}$ dry wt.), as well as the other chalcophile metals such as Co, Mo, Ni, Pb. The soft tissues of organisms, enriched in TOC (to 52 % dry wt.) are a target not only for essential elements Fe, Cu, Zn, Co, Ni, Cr, and Mo but also for potentially toxic As, Cd, Pb, U, and W. The lithophile elements such as Ti, Mn, and Ba showed a predominant accumulation in the clam shells.

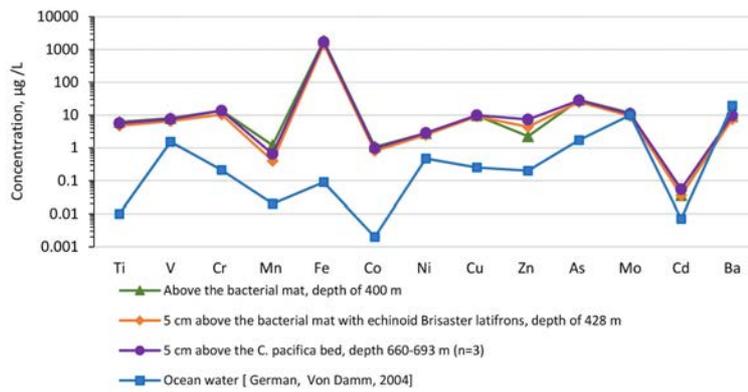


Figure RU-5. The trace element distribution in the biotope water of methane seep areas at the Koryak slope, compared to the ocean water (German, Von Damm, 2004).

Estimation of the trace element Enrichment Factor in methane seep surface sediments relative to the upper continental crust has revealed depletion in most elements that may be caused, along with the reduced conditions, by the intensive element uptake by organisms. Our data suggest that methane seeps are biogeochemically important areas where the concentration and dispersion processes of trace elements coexist [Demina et al., 2022].

- Study of the current level and origin of hydrocarbons (HC): aliphatic – AHC and polycyclic aromatic – PAH (September 2021, May and September 2022) in suspended particulate matter in surface water layer and in bottom sediments of the coastal areas of the Caucasian sector of the Black Sea has established a decrease in concentrations in surface waters. HC accumulation occurs in finely dispersed sediments. The Kerch Strait is one of the most polluted water areas of the Black Sea where AHC and PAH content in sediments reached 200 µg/g and 320 ng/g, respectively. It is shown that natural processes (productivity of the water area, fluid flows from the sedimentary strata) have a great influence on the HC values [Nemirovskaya et al., 2022].
- AMK 5188, 5189, 5190, 5191 and 5536 cores were sampled during the 2015-2016 IO RAS expeditions in the Norwegian Sea (**Figure RU-6**). Major and trace element contents are derived from XRF core scanner analyses. The distribution of the Ti/Ca ratio as one of the main stratigraphic proxies (**Figure RU-7**) has shown that its highest values for the North Atlantic correlate with glacial events (MIS 8, 6 and 4). The minimum Ti/Ca values associated with biogenic calcite input are typical for MIS 7, 5 and 1. Our data correlate well with results for the Greenland Sea and the southern Norwegian Sea (Sabine et al., 2022) and can be used for the integrated stratigraphy of the Norwegian-Greenland Basin [Novichkova et al., *in press*].

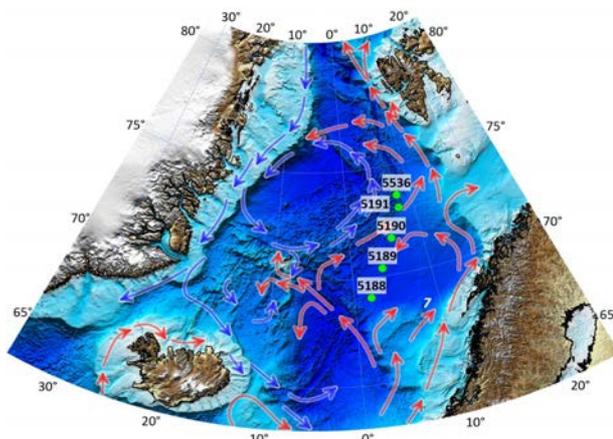


Figure RU-6. Overview map of main North Atlantic surface (red arrows) and bottom (blue arrows) currents [Blindheim, Rey, 2004] and location of studied cores.



Figure RU-7. Ti/Ca ratio stratigraphy along a south-north profile of the Norwegian Sea. The interglacial MIS 1, 3, 5, 7 shown as shadow [Novichkova et al., in press].

- The distribution of particulate organic carbon in the seas of the Russian Arctic is characterized by circumcontinental and vertical zonalities. They are expressed in decreasing concentrations and fluxes ($\text{mgC}/\text{m}^2/\text{day}$) of suspended organic carbon in the transition from the near-continental to pelagic regions of the Arctic Ocean, as well as from the surface photic layer to the near-bottom layer by two orders of magnitude, which is confirmed by instrumental data of sedimentation traps and correlates with the zonality of bioproduction processes (**Figure RU-8**).

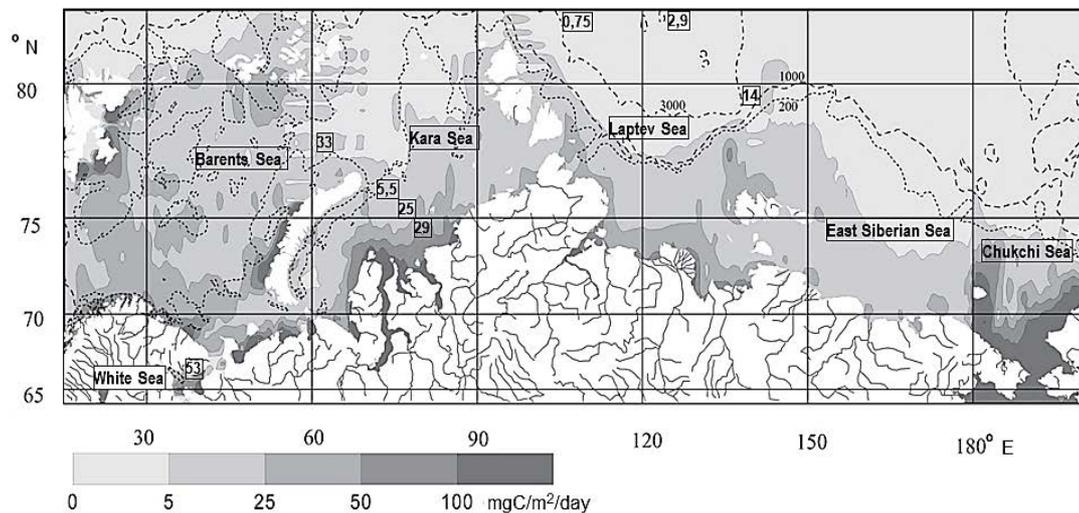


Figure RU-8. Schematic map of the calculated primary production average annual flux of organic carbon ($\text{mgC}/\text{m}^2/\text{day}$) to the bottom in the Arctic seas of Russia [Vetrov, Romankevich, 2019] in comparison with the mean annual instrumental data of sedimentation traps installed in the bottom horizon, the figures show: White Sea 53 $\text{mgC}/\text{m}^2/\text{day}$ [Novigatsky et al., 2020]; Barents Sea 33 $\text{mgC}/\text{m}^2/\text{day}$ [Agafonova et al., 2023]; Kara Sea 5.5 $\text{mgC}/\text{m}^2/\text{day}$ [Drits et al., 2021], 25 and 29 $\text{mgC}/\text{m}^2/\text{day}$ [Gaye et al., 2007]; Laptev Sea 0.75 $\text{mgC}/\text{m}^2/\text{day}$ [Nöthig et al., 2020], 2.9 $\text{mgC}/\text{m}^2/\text{day}$ [Fahl et al., 2009], 14 $\text{mgC}/\text{m}^2/\text{day}$ [Lalande et al., 2007].

However, the rarity and relatively large uncertainty of annual organic carbon fluxes obtained by the sediment trap method makes it difficult to estimate them accurately. Additional observations of suspended organic carbon fluxes over a broader range of environmental regimes are needed to thoroughly evaluate and validate the calculated primary production model results and to better understand the processes controlling the flux of suspended organic carbon to depth in the ocean [Novigatsky et al., *in press*].

- Mineralogical, geochemical, and isotopic studies of the Fe–Mn crust collected in the Jan Mayen vent field area have been carried out for the first time. The crust (about 3 cm thick) has a distinct microstratified structure, sharp contact with the underlying volcanic substrate, and colloform Fe and Mn oxyhydroxides at its bottom. The crust is composed mainly of Mn oxyhydroxides: birnessite and buserite with an impurity of volcanic glass. As follows from the layer-by-layer study of the crust, the Mn content increases by 3–10 times from bottom to top, whereas Fe and REE decrease in the same direction. The samples are marked by a positive Eu anomaly ($\text{Eu}/\text{Eu}_{\text{NASC}}$ 1.08–1.41). $\text{Ce}/\text{Ce}_{\text{NASC}}$ is 0.89 ± 0.05 . $^{87}\text{Sr}/^{86}\text{Sr}$ in the crust's lower and middle layers is within 0.70621–0.70713, while ϵNd reaches 5.6–6.2. These parameters are 0.70740 and -0.1 , respectively, in the uppermost layer of the crust. The REE composition, positive Eu anomaly, high ϵNd values, and low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the crust are indicative of the fact that the ore material mainly originated from hydrothermal solutions (**Figure RU-9**). Changes in the Sr and Nd isotope characteristics and REE composition in the crust layers are due to a decrease in the hydrothermal material contribution as the crust grew at a high crust deposition velocity in the Jan Mayen vent field area [Kravchishina et al., 2022].

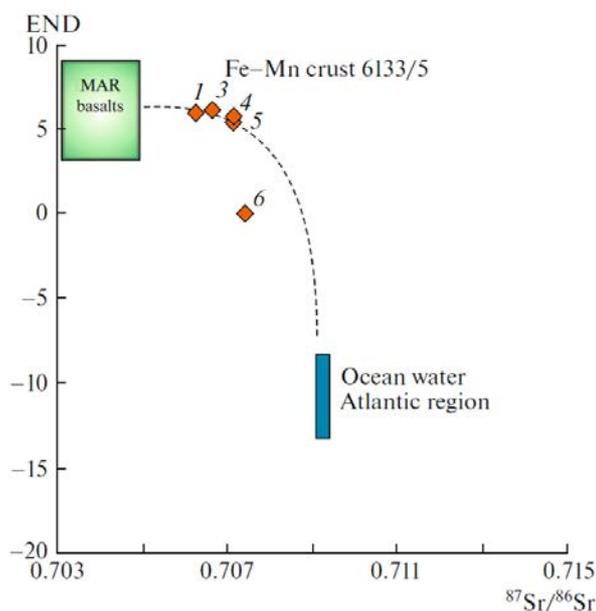


Figure RU-9. Sr and Nd isotopic composition in several layers of the Fe–Mn crust 6133/5. The dotted line indicates the mixing of the average isotopic compositions of MAR oceanic basalts and seawater after [Faure, 1986; Kuznetsov et al., 2012].

GEOTRACES relevant cruises

- A unique climate experiment was carried out to study the composition of air and characteristics of the underlying surface in the Russian sector of the Arctic and Siberia. Synchronized research on board the R/V *Akademik Mstislav Keldysh* and the unique scientific facility the *Tu-134 Optik* flying laboratory were carried out in the South Kara Sea from September 5 to 18, 2022 (**Figure RU-10**). The cruise leader is Dr. Kravchishina M.D. The airborne and spaceborne optical satellite algorithms were validated to retrieve the sea surface characteristics during the cruise. For the first time on the Arctic shelf, data on methane concentration in the natural troposphere–near-surface atmosphere over sea–water

column–bottom sediments system was obtained. Greenhouse gases fluxes were estimated simultaneously from the shelf area and adjacent land. Related research on recent and ancient sedimentation conditions and processes was carried out in the South Kara sedimentary basin, where huge oil and natural gas reserves are located.

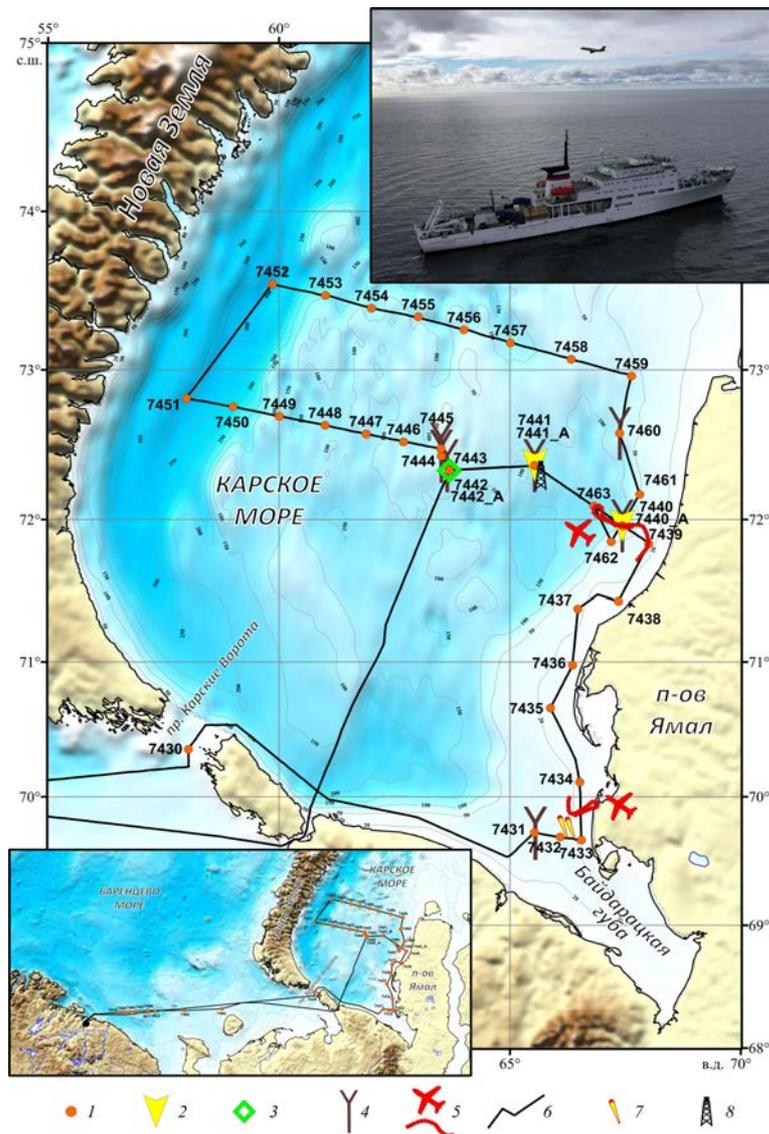


Figure RU-10. Map of marine expeditionary research in South Kara Sea, September 08–15, 2022: (1) integrated stations (set of optical, hydro-optical, hydrological, hydrochemical, hydrobiological, microbiological, and sedimentological measurements and lithological and geochemical works for sampling upper undisturbed sediment layer using a multicorer); (2) integrated mooring stations with deployment and raising of automatic deep-sea sedimentation observatories; (3) mooring station with inclinometers; (4) integrated stations with samplings of long sediment cores using large-diameter gravity corer; (5) research polygons for direct overflight measurements with flight path of Tu-134 Optik; (6) vessel's route with continuous en route measurements (gas-chemical, optical, and hydro-optical); (7) gas flares according to echo-sounding profiling data; (8) Leningradskoe gas condensate field.

Bathymetry is based on data from [Miroshnikov et al., 2021]. Insets: (bottom) entire route of vessel; (top) photo of synchronous works aboard RV Akademik Mstislav Keldysh and Tu-134 Optik flying laboratory.

The climate experiment consisted of a set of measurements in situ in the water column and the nearsurface atmospheric layer continuously along the vessel's entire route of (2275.4 nautical miles) and works at 44 oceanographic stations with the participation of the flying laboratory and satellite remote sensing of sea surface characteristics. The aircraft made direct passes over the ship at an altitude of ~90–200 m above the sea surface on September 9 and 10, 2022, to validate airborne algorithms for retrieving the characteristics of the underlying surface (suspended particulate matter, chlorophyll, dissolved OM, etc.) and measuring the composition of air and aerosols in the atmosphere and troposphere over the sea [Kravchishina et al., 2023].

New projects and/or funding

- Prolongation of the grant of Russian Science Foundation “The role of hydrothermal and thermogenic processes in recent sedimentation in the subpolar North Atlantic and Arctic Oceans”, no. 20-17-00157, 2020–2024. Dr. Marina Kravchishina is a project leader. URL: <https://rscf.ru/project/20-17-00157/> The main purpose of the grant is to investigate the combined role of hot (hydrothermal) and cold (methane seepage) fluids in recent sedimentation processes in the Arctic (Mohns Ridge and Eurasian Arctic shelf).

New GEOTRACES or GEOTRACES-relevant publications (published or in press)

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Completed GEOTRACES related PhD or Master theses (please include the URL link to the pdf file of the thesis, if available)

- Evgenia Berezhnaya completed PhD thesis “Geochemistry of platinum-group elements in ocean ferromanganese ores”, Shirshov Institute of Oceanology, Russian Academy of Sciences. Scientific advisor is Dr. Alexander Dubinin (IO RAS).

GEOTRACES presentations in international conferences

- Kravchishina V.D., Kusnetsov A.B., Starodymova D.P., Dara O.M., Chebotareva V.A., Klyuvitkin A.A., Baranov B.V., Lein A.Yu. Genesis of ferromanganese crusts in the Jan Mayen hydrothermal vent field area, Mohn’s Ridge. 10th International Conference on Mineral Resources of the World's Oceans. June 2023. г. FSBI "VNIIOkeangeologia", Angliyskiy prospect, 1, St. Petersburg, Russia.
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