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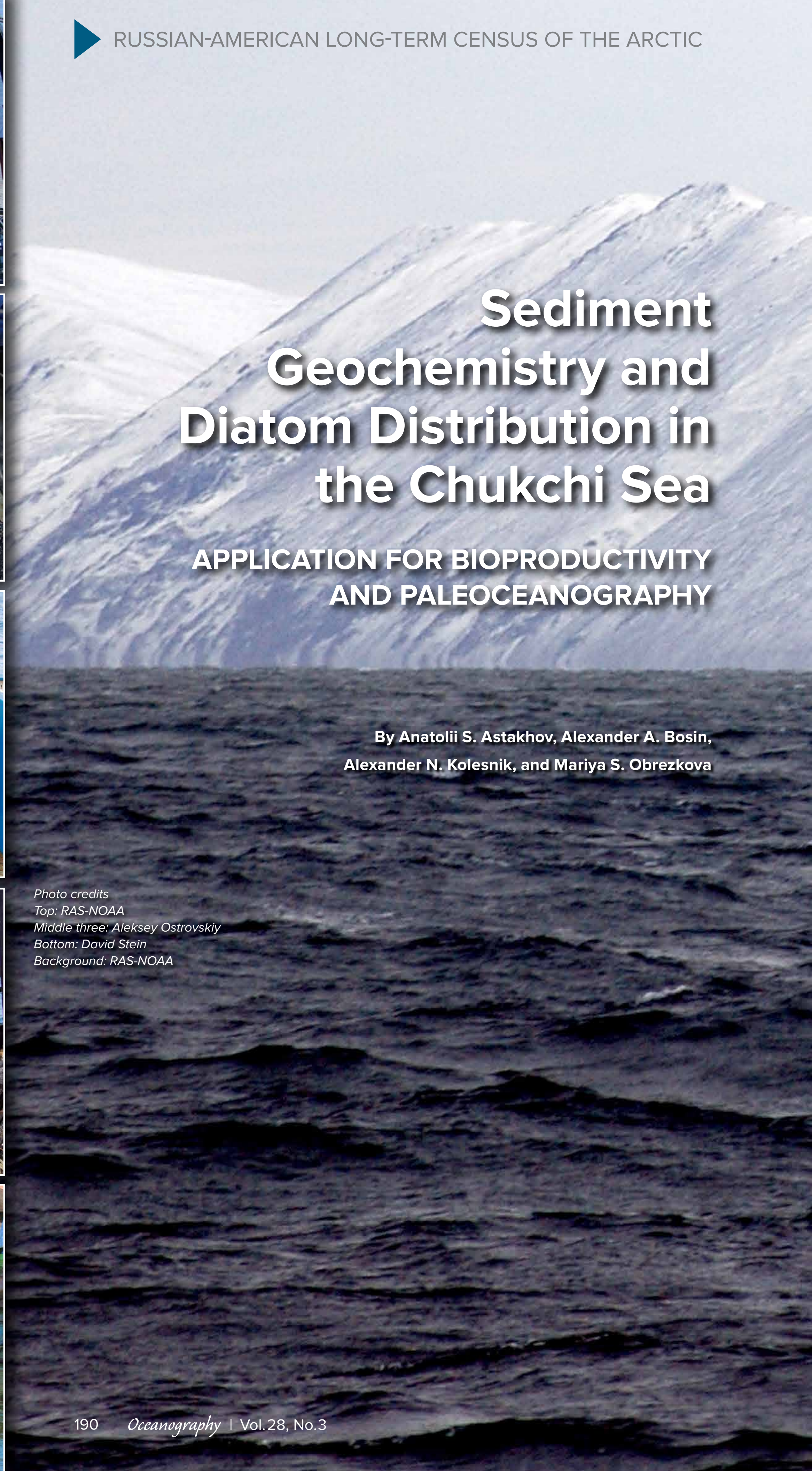

Sediment Geochemistry and Diatom Distribution in the Chukchi Sea

APPLICATION FOR BIOPRODUCTIVITY AND PALEOCEANOGRAPHY

By Anatolii S. Astakhov, Alexander A. Bosin, Alexander N. Kolesnik, and Mariya S. Obrezkova

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ABSTRACT. One goal of the first decade of the Russian-American Long-term Census of the Arctic (RUSALCA) program was to characterize benthic composition in the Chukchi and East Siberian Seas in order to understand the geological history of productivity and paleoclimatological changes in this region. To this end, our team analyzed total chemical composition; content of biogenic elements including organic carbon, opal, and chlorin; and the distribution and species composition of the diatom thanatocoenosis in surface sediment samples. Increased calcium content (Ca/Al > 0.22) and dominance of the diatoms *Paralia sulcata* and *Thalassiosira nordenskioeldii* indicate transport pathways of warm Pacific water within the Chukchi Sea. Areas of greatest ice cover are characterized by sediments with low calcium content (Ca/Al < 0.15) and the presence of strontium, and dominance of the diatom *Thalassiosira antarctica*. Distributions of elements produced by phytoplankton such as opal, chlorin, and organic carbon are less informative as indicators of water masses, bioproductivity, and ice conditions because the phytoplankton are transported by currents and they accumulate in seafloor depressions. On the Chukchi Sea shelf, these depressions usually coincide with neotectonic structures. Specific sedimentation environments within the graben-rift system of the Chukchi Sea may be created by hydrothermal vents and cold seeps, where hydrochemical conditions promote preservation of biogenic remains in the sediment and anomalous accumulation of many metals (Fe, Mn, Mo, V, Zn, Ni, Ag, Hg).

INTRODUCTION

The Arctic is a key region for the study of the global consequences of Pacific Arctic climate change. It is hypothesized that the observed sea ice loss and changes in ocean mixing and weather patterns in the Arctic also affect Northern Hemisphere weather and climate (Crane, 2005; Keigwin et al., 2006; Kaufman et al., 2009; Cohen et al., 2013; Walsh, 2013). Investigation of past climate changes allows us to understand the mechanisms and trends in these processes and to construct models of future climate variations. Unfortunately, instrumental measurements cover only the last 60–100 years, a time period that is insufficient to take into account major climate change cycles. To obtain more reliable results requires using climate change proxies that permit reconstruction of the paleoenvironment over much longer time periods. Sediment cores contain the most continuous archives of paleoenvironmental changes, so they are essential for these reconstructions. Such reconstructions for the East Siberian Sea shelf are complicated because of the paucity and poor preservation of biological remains, including the carbonates, which are needed for paleoproductivity and paleoenvironment studies in deeper parts of the Arctic Ocean (Polyak et al., 2004; de Vernal et al., 2005). The possibilities of using other proxies, such as siliceous microfossils and lithological and geochemical information from the sediments, were lacking prior to the Russian-American Long-term Census of the Arctic (RUSALCA) program.

The geochemistry of recent sediments in the Chukchi Sea has much in common with those in the other Arctic seas owing to their predominantly terrigenous origin under conditions of low runoff and low sedimentation rates (Kosheleva and Yashin, 1999; Viscosi-Shirley et al., 2003; Astakhov et al., 2013a). Unlike the other marginal seas of the Arctic Ocean, the Chukchi Sea is characterized by locally high primary productivity. As a result, the fine-grained sediments in the southern part of the sea have a high content of biogenic opal. Benthic productivity is also very high in some areas (Grebmeier et al., 2006). These observations are often explained by the spread of warm Pacific waters through Bering Strait (Figure 1). Unlike the East Siberian Sea where old terrestrial organic carbon dominates in the sediments, the Chukchi Sea is characterized by the abundance of organic remains of marine origin (Grebmeier et al., 2006; Vetrov et al., 2008). Preservation of biogenic elements and microfossils in shelf sediments depends not only on phytoplankton and benthic productivity but also on conditions that include sediment composition, seafloor relief, sedimentation rate, and geological structure (Figure 1). Local depressions and gas and hydrothermal fluxes on the seafloor are common in areas with active geological processes, and they lead to increased anoxic bottom conditions that better preserve organic remains in sediments (Pedersen and Calvert, 1990; McKay and Pedersen, 2008; Astakhov et al., 2010, 2013a).

Tectonic processes in the Chukchi Sea are thought to be dominated by a Cenozoic episode of rifting and crustal stretching that created en echelon rift structures (Shipilov et al., 1989). A study of the onshore Chukotka graben revealed late Cenozoic volcanism and numerous hydrothermal vents that discharge water with temperatures of up to 97°C (Polyak et al., 2010; Figure 1). This graben extends into Herald Valley and the shelf edge of the Chukchi Sea in the north (Shipilov et al., 1989; Alekseev, 2004). Analysis of the focal mechanisms of the largest earthquakes and seismo-tectonic dislocations verifies recent rifting at the eastern Chukchi Peninsula (Fujita et al., 2002). The activity within the northward-trending graben–rift system on the Chukchi Shelf is manifested by seismicity seaward of the eastern Chukchi Peninsula. The graben structures follow the bottom topography. There are also some indications of gas plumes in Herald Valley (Leif Anderson, University of Gothenburg, *pers. comm.*, 2015), suggesting some thermogenic venting of methane (see Alekseev, 2004; Yashin and Kim, 2007; Matveeva et al., 2015, in this issue). The Chukchi Sea's graben-rift system is bounded to the north by the Cenozoic Charlie rift basin (Figure 1). Their geological relationships are unknown due to a lack of knowledge of the regional geology (Astakhov et al., 2013a).

The overall focus of this study was to reveal sedimentary indicators of climate change based both on the investigation of phytoplankton-produced biogenic elements in Chukchi Sea sediments and on the study of the chemical composition of the sediments. More specifically, we seek to find the answers to the following questions:

- How does biogenic sedimentation affect the distribution of major and trace elements in the bottom sediments of the Chukchi Sea?
- How does the sedimentation of biogenic matter (organic carbon, opal, chlorin) produced by phytoplankton with silica shells and buried in surface sediments of the Chukchi Sea reflect changes in primary production and ice conditions?
- How much does the species composition of diatom thanatocoenoses in Chukchi Sea sediment characterize the water masses and the ice regime?
- How do specific geodynamic conditions of the graben-rift system influence the accumulation of biogenic matter in sediment?
- Which geochemical and micropaleontological sediment indices can be used to determine changes in paleoceanographic conditions (water mass, bioproductivity, and ice) on the Pacific Arctic shelves?

MATERIAL AND METHODS

Sediment samples were obtained from the Chukchi Sea shelf using box corers, grabs, and hydraulic corers during cruises on the Russian research vessels *Professor Khromov* and *Sever* in the framework of the RUSALCA project in 2004, 2006, 2009, and 2012. Additional samples used in this investigation were obtained from other projects (Figure 2).

For analysis of biogenic content and total chemistry, sediment samples were powdered to <0.063 mm particle size in an agate mortar. We used the standard procedure outlined in Astakhov et al. (2013a) to determine concentrations of organic carbon, biogenic opal, and major and trace elements. The chlorin content in the samples was determined using the standard procedure as outlined in Bosin et al. (2010). Grain size was measured by the Laser Particle Sizer Analysette 22. Preparation of the samples for diatom analysis was done according to the standard technique and, due to the low diatom content, all samples were treated with the heavy liquid (CdI_2+KI) with a specific gravity of 2.6 g (Tsoy et al., 2009; Obrezkova et al., 2014).

Samples obtained from other institutes and researchers were processed by the same techniques. Most of these analytical results, including grain size and chemical composition, have been previously published (Astakhov et al., 2010, 2013a,b). New results and previously published data (Feder et al., 1994; Viscosi-Shirley et al., 2003) were used for the construction of each chemical element distribution map and for statistical analysis of geochemical data (Figure 2).

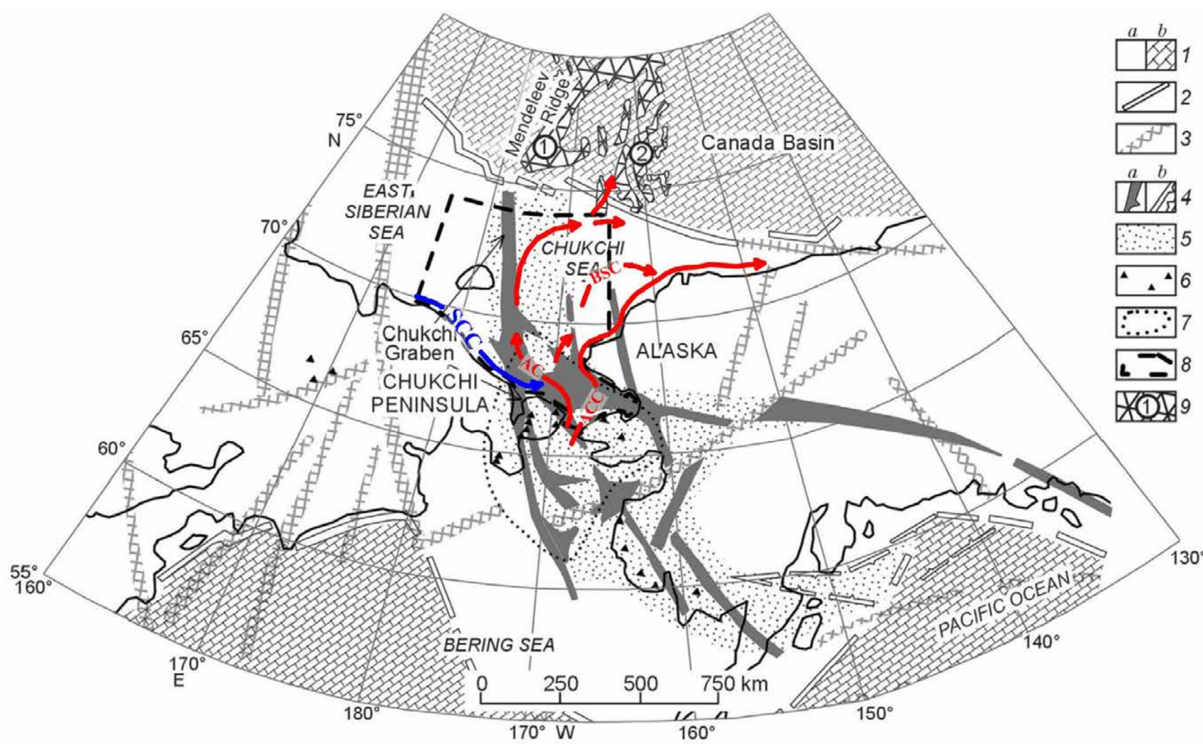

FIGURE 1. Location of the study area and the graben-rift system of the Chukchi Sea at the intersection of the Arctic and Pacific transitional zones (Shipilov et al., 1989). Geology symbols in the legend: 1 = areas with continental and subcontinental (*a*) oceanic and (*b*) suboceanic crust; 2 = continental flexure; 3 = largest belts of transtensional faults; 4 = extensional faults (*a* = Chukchi-Bering Sea and Alaskan graben-rift systems; *b* = rift zone of the Gulf of Alaska); 5 = areas of immediate interaction (displacement-detachment) between transitional zones; 6 = areas of Cenozoic volcanism outside island arc systems (Polyak et al., 2010); 7 = zone of recent crustal extension (Levi et al., 2009); 8 = bounds of study area; 9 = Cenozoic rift basins (① = Charlie, ② = Northwind). Arrows show the major warm (red) and cold (blue) water currents of the Chukchi Sea (Grebmeier, 2012): SCC = Siberian Coastal Current, ACC = Alaska Coastal Current, BSC = Bering Shelf Water (Current), AC = Anadyr Current (Bering Sea Water).

RESULTS

General Sediment Chemical Composition

The major element composition of Chukchi Sea sediments (Figure 3) is related to grain size (Figure 4), with the separation of terrigenous materials by mineral content occurring during their transport by currents (Viscosi-Shirley et al., 2003; Astakhov et al., 2013a). Sand and sandy silt sediments are characterized by high Si content (Figure 3). Clayey sediments are enriched in Al and Fe, which is typical for terrigenous sediment (Viscosi-Shirley et al., 2003).

Groups of elements were determined by correlating grain size and chemical composition (Table 1). The sand fraction consists of detritus where quartz dominance correlates with Si, and coarse silt with Ca, Ti, Sr, Cd. Fine silt and clay fractions (<0.01 mm) consist of clay minerals, including Al, K, Fe, and many trace elements. Some elements such as Mn, P, Cu, and Ni have no significant correlations with grain size compositions.

Biogenic sedimentation is traced by the distribution of Ca (Figure 3), and some elements (Sr, Cd) included in biogenic carbon remain. The correlation coefficient of the content of Ca and Sr, for example, was 0.62 for a set of over 300 samples. They are represented by fragments of foraminifera shells (Table 1), which is typical for the deep Arctic Ocean (Polyak et al., 2004).

The distribution of Mn and to some extent Fe indicates seafloor redox conditions. Maxima in Mn content are found in oxidized sediments from the Pacific Arctic basins and in some regions of the outer shelf (Astakhov et al., 2013b). This is also typical for Fe, but the Fe-enriched content of the finest sediment fraction affects its distribution (Figure 3). Many trace elements (Co, Cr, Pb, V, Y, Yb, Zn, Zr, and Mo) also tend to accumulate in clay-size sediments and correlate with the clay fraction (Table 1). Amorphous iron sulfides with increased concentration of Mo, V, Zn, Cr, and Ag are found in sediments that accumulated in anoxic and euxinic conditions.

In general, sediments collected from depressions in the graben–rift system are characterized by their small grain size and nutrient richness, and they contain Fe (Figure 3), trace metals, sulfophiles, and siderophiles (Astakhov et al., 2013b) that settled in anoxic conditions.

Biogenic Sediment Chemistry

Analyses of organic matter produced by phytoplankton and buried in sediments (biogenic opal, chlorophyll, organic carbon) provide excellent proxies for determining paleoceanographic conditions and marine primary production (Keigwin et al., 2006; Gorbarenko et al., 2014). In the Chukchi Sea, the distribution of paleoproductivity indicators in the sediments found on the seafloor, including types of diatoms (Figure 5), is strongly connected with warm water masses that arrive through Bering Strait. But this correlation is slightly distorted by the deposition of diatom frustules (the silicified cell walls of a diatoms) preliminarily processed by zooplankton and easily transported by currents for a significant distance before becoming buried in sediments. Diatom remains accumulate in seafloor depressions, or currents transport them to the outer shelf and the Arctic basin. According to Grebmeier et al. (2006), up to 20% of the export production during summer is moved off the Chukchi Sea shelf into the Canada Basin in this way.

Biogenic matter produced by phytoplankton is absent in sediments in areas with strong near-bottom currents, such as Bering Strait and the adjoining part of Kotzebue Bay, and on the sandy Herald and Hanna Shoals. High biogenic opal content is typical for Herald Valley, in flat depressions of the South Chukchi basin, and for parts of the outer shelf influenced by warm Pacific waters. The greatest biogenic element content and

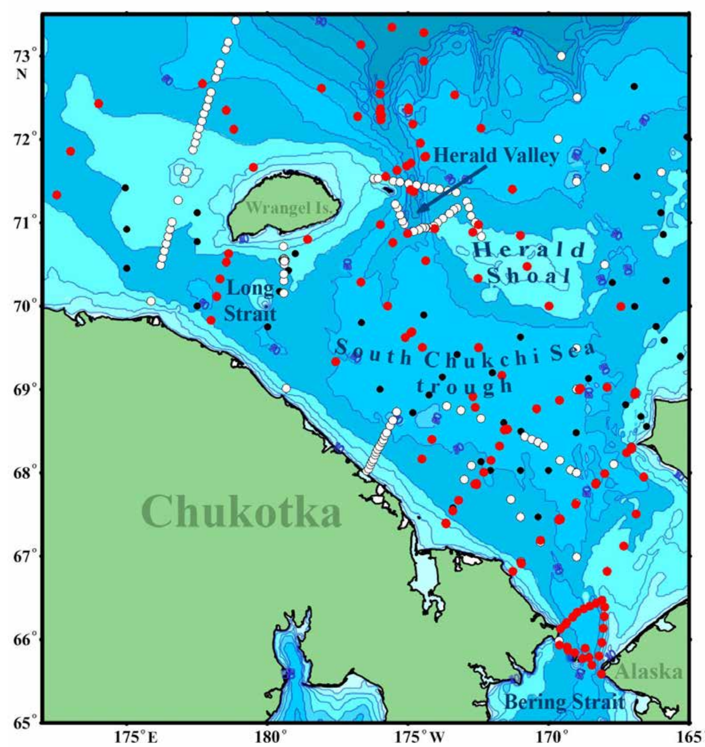

FIGURE 2. Map of the survey area and location of sediment collection stations. Red circles = Russian-American Long-term Census of the Arctic (RUSALCA) geological stations, white circles = stations from other expeditions and studied by the authors (Astakhov et al., 2010, 2013a,b), black circles = previously published data (Feder et al., 1994; Viscosi-Shirley et al., 2003).

diatom abundance is found in the frontal zone between the warm northward-flowing Anadyr Water (which imports additional biogenic elements and stimulates intense phytoplankton growth off of Chukotka) and the much colder southward-flowing Siberian Coastal Current (Figure 5). The average position of the 50% ice concentration line for September during 1979–1983 in Figure 5 allows us to estimate the influence of relatively warm Pacific water on sea ice conditions of the Chukchi Sea before the recent climate warming.

Sea ice conditions (type, duration, and extent) also control the distribution of biogenic elements; accordingly, they are the main factor influencing the Chukchi Sea's bioproductivity (Grebmeier, 2012). High concentrations of diatoms, biogenic opal, and chlorin accumulate in areas with prolonged ice-free periods. The distribution of organic carbon in sediments is complicated by an admixture of more

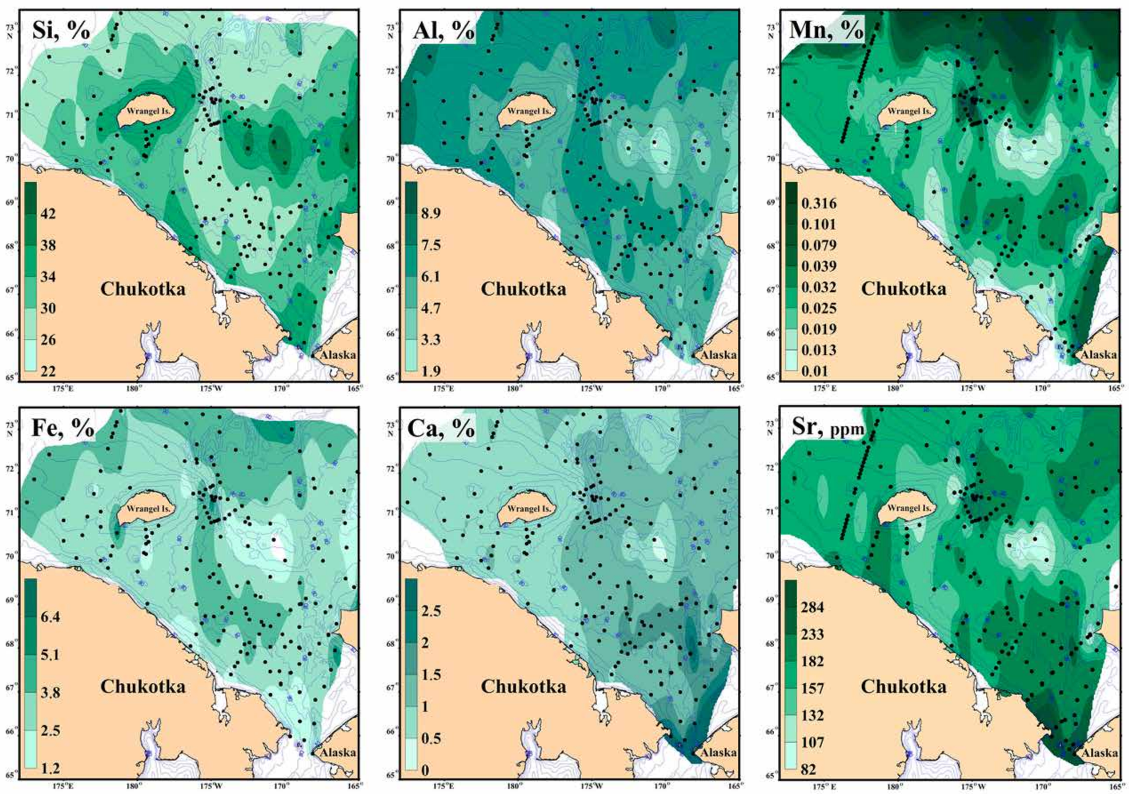

FIGURE 3. Examples of distribution of the chemical elements in the surface sediments of the Chukchi Sea. The Si and Al distributions demonstrate the influence of sediment grain size and, accordingly, bottom relief. Mn indicates influence of bottom relief; Fe, combined influence of grain-size and bottom relief; and Ca and Sr, influence of biogenic sedimentation (Table 1).

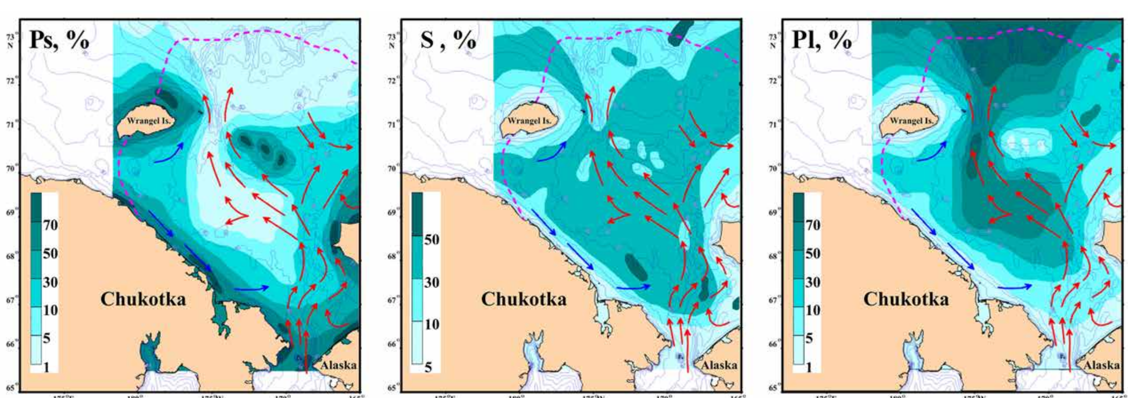

FIGURE 4. Map of particle size distribution of surface sediments of the Chukchi Sea modified after Shuisky and Ogorodnikov (1981). Grain size fraction (see Table 1): Ps = >0.1 mm, S (S_1+S_2) = 0.1–0.01 mm, Pl = <0.01 mm. Red and blue arrows show the warm and cold currents, respectively (Coachman et al., 1975); dashed pink line is the average position of the 50% ice concentration line for September during 1979–1983 (Frolov, 2008).

ancient carbon (Grebmeier et al., 2006; Vetrov et al., 2008) and benthic organic matter, including microbial carbon (Ivanov et al., 2010).

Diatom Assemblages

In the surface sediment samples, 166 diatom species belonging to 63 genera were identified. The most diverse genera are *Navicula*, *Chaetoceros*, and *Thalassiosira* (Figure 6). It should be noted that redeposited extinct Cenozoic species such as *Actinocyclus ingens* Rattray, *Neodenticula kamtschatica* (Zabelina) Akiba et Yanagisawa, and *Pyxidicula zabelinae* (Jousé) Makarova et Moiseeva were found in the surface sediment samples as well. Cluster analysis of the diatom distribution in surface sediments revealed that the stations sampled divided into two contrasting provinces: eastern (cluster A) and western (cluster B) parts of the Chukchi Sea, which are, in turn, subdivided into smaller groupings. Each cluster is characterized by a specific diatom assemblage (Table 2).

The maximal concentrations by percentages of planktonic sublittoral species (*Odontella aurita* (Lyngbye) Agardh [up to 30%]) were found in sandy sediments of Herald Shoal (cluster A1; Figure 7a), but usually its concentration in Arctic Sea sediments doesn't exceed 5%. This species was probably eroded from older deposits, as it is typically found in river deltas and in sea areas with low salinity (Hendey, 1964).

Sublittoral and benthic diatoms (cluster A2) are composed mainly of *Paralia sulcata* Cleve (up to 83%), which dominate in the eastern part of the Chukchi Sea (Figure 7b). The distribution of *P. sulcata* in the thanatocoenosis of the southern part of the Chukchi Sea correlates with freshened waters of the Alaska Coastal Current (ACC; Woodgate and Aagaard, 2005) and coincides with the sublittoral assemblage marked out by Polyakova (1997). The sporadic occurrence of freshwater diatoms (e.g., *Amphora libyca, Caloneis bacillum, Tabellaria flocculosa*) can be explained by the influence of river runoff from Alaska's western coast (Polyakova, 1997; Obrezkova et al., 2014).

The diatom assemblage in the southwestern area (cluster B1) is characterized by planktonic algae, with neritic *Thalassiosira nordenskioeldii* Cleve dominating (up to 55%; Figure 7c). This species grows near the marginal ice edge during periods of ice melting, and it is indicative of the highly productive Bering Sea water masses (von Quillfeldt et al., 2003). This "ice" assemblage contains high content (up to 7%) of such warm-water species as *Thalassionema nitzschioides* (Grunow) Mereschkowsky, *Coscinodiscus asteromphalus* Ehrenberg, and *Shionodiscus oestrupii* (Ostenfeld) Alverson, Kang et Theriot, indicating Pacific waters.

Neritic cold-water *Thalassiosira antarctica* Comber (Figure 7d) dominates (up to 53%) in the western and northern parts of the Chukchi Sea (cluster B2-1).

The maximal concentration of cryophilic species (*Fragilariopsis oceanica* (Cleve) Hasle, *Fr. cylindrus* (Grunow) Krieger, *Fossula arctica* Hasle, Syvertsen et von Quillfeldt) is found north of Bering Strait (cluster B2-2-a, Figure 7e). Such indicators of warm Pacific waters

TABLE 1. Cross-correlation coefficients of element content, grain-size composition (S_1, S_2, Pl)*, and biogenic elements in Chukchi Sea sediments.

	S_1	S_2	Pl	Chlorin	Diatoms	Opal	OC
S_2	–0.13						
Pl	–0.30	–0.10					
Chlorin	–0.29	**0.22**	0.38				
Diatoms	0.00	0.09	–0.39	0.20			
Opal	0.15	–0.10	**0.87**	–	–		
OC	–0.46	0.13	**0.50**	**0.68**	–0.02	**0.75**	
Si	**0.26**	–0.20	–0.65	–0.33	0.03	0.01	–0.60
Ti	–0.09	**0.28**	**0.53**	0.18	0.24	0.18	**0.24**
Al	–0.13	0.18	**0.58**	0.07	0.20	–0.08	**0.46**
Fe	–0.27	0.17	**0.49**	0.15	0.01	0.00	**0.38**
Mn	–0.03	0.12	0.02	–0.18	–0.15	–0.26	0
Mg	–0.24	**0.29**	**0.57**	**0.32**	–0.05	0.01	**0.6**
Ca	–0.02	**0.27**	0.18	–0.02	–0.07	–0.19	–0.10
K	–0.16	0.01	**0.31**	–0.05	–0.02	–	**0.24**
Ba	–0.09	–0.20	**0.37**	–0.09	0.15	**0.32**	0
Co	–0.19	0.16	**0.24**	–0.16	0.15	–0.33	–0.2
Cr	–0.32	**0.25**	**0.37**	**0.24**	0.21	0.05	**0.33**
Cu	–0.14	–0.10	–0.24	–0.25	**0.33**	–0.41	**0.22**
Ni	–0.29	0.12	–0.14	–0.01	0.04	–0.55	0.06
Pb	–0.06	0.11	**0.32**	–0.13	–0.14	0.12	**0.48**
Sr	0.03	**0.30**	0.12	0.05	0.08	0.08	0
V	–0.15	**0.27**	**0.47**	**0.19**	–0.08	–0.08	**0.58**
Y	–0.08	0	**0.63**	0.06	**0.35**	–0.23	0
Yb	–0.26	0.01	**0.55**	–0.06	**0.38**	–0.21	–0.10
Zn	–0.25	0.16	**0.55**	0.19	0.03	0.23	**0.62**
Zr	–0.04	0.04	**0.59**	0.18	0.11	–0.13	0.12
La	–0.10	–0.20	**0.38**	–0.13	0.21	–0.29	–0.20
Mo	–0.17	–0.10	**0.57**	–0.11	0.01	–	**0.46**
Cd	–0.15	**0.23**	0.05	**0.38**	–0.23	–	0
Hg	–0.47	–0.20	**0.34**	**0.25**	0.07	–0.27	**0.29**

OC = organic carbon; Bold = significant positive correlations with $p < 0.05$. Dash = no data.

* S_1, S_2, Pl are grain-size fractions according to the Russian classification (Likht et al., 1994). They generally correspond with ISO 14688-1:2002 standard fractions as: Ps (Figure 4) = coarse and medium sand (0.1–1.0 mm). S_1 = fine sand (0.1–0.05 mm). S_2 = coarse silt (0.05–0.01 mm). Pl = fine silt and clay (<0.01 mm).

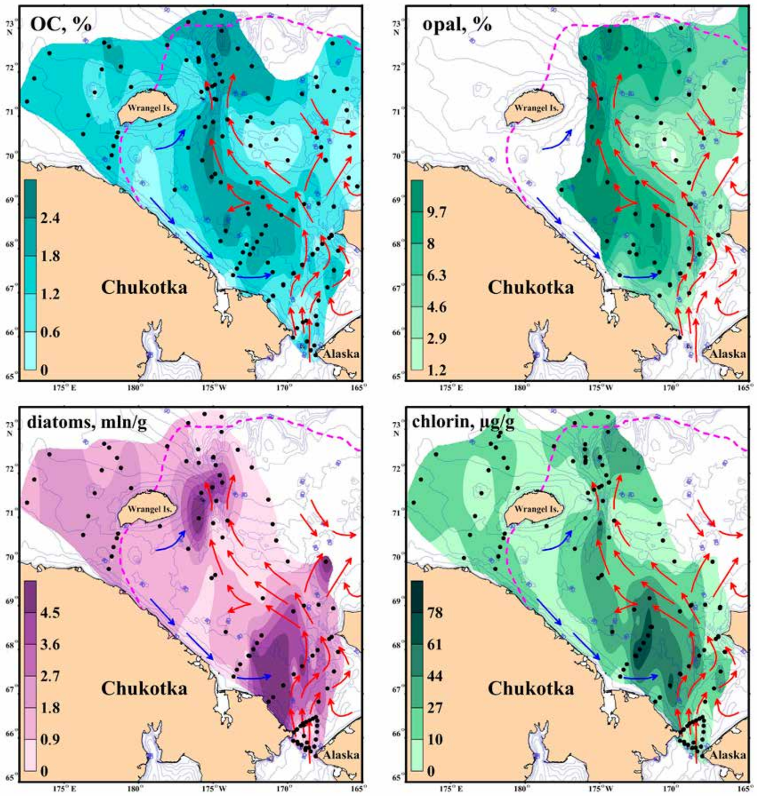

FIGURE 5. Content of biogenic elements and diatom frustules in surface bottom sediments of the Chukchi Sea. Red and blue arrows show the warm and cold currents, respectively (Coachman et al., 1975). The dashed pink line denotes the average position of the 50% ice concentration line for September during 1979–1983 (Frolov, 2008).

as *Paralia sulcata* and *Thalassiosira nordenskioeldii* are also appreciable members of this assemblage. *Pauliella taeniata* is also present in this area and can be an indicator of early phytoplankton spring bloom (Sukhanova et al., 2009), but frustules were observed sporadically in sediments as a result of their dissolution in Chukchi Sea waters.

The diatom assemblage related to the Herald Valley sediments (cluster B2-2b) consists of two species typical for both western cold-water and eastern warm-water areas *(Paralia sulcata, Thalassiosira antarctica*), with *Chaetoceros* species dominating (up to 54%; Figure 7f). Generally, these species are indicative of highly productive and Fe-rich surface waters (Ren et al., 2014). Additional oceanic diatom species, amounting to as much as 12% of the total diatom flora, found in the Chukchi Sea include *Coscinodiscus oculus-iridis* (Ehrenberg) Ehrenberg, *Rhizosolenia hebetate* Bailey, *Actinocyclus curvatulus* Janisch, *Thalassiothrix longissima* Cleve et Grunow, *Coscinodiscus radiatus* Ehrenberg, and *Thalassiosira eccentrica* (Ehrenberg) Cleve.

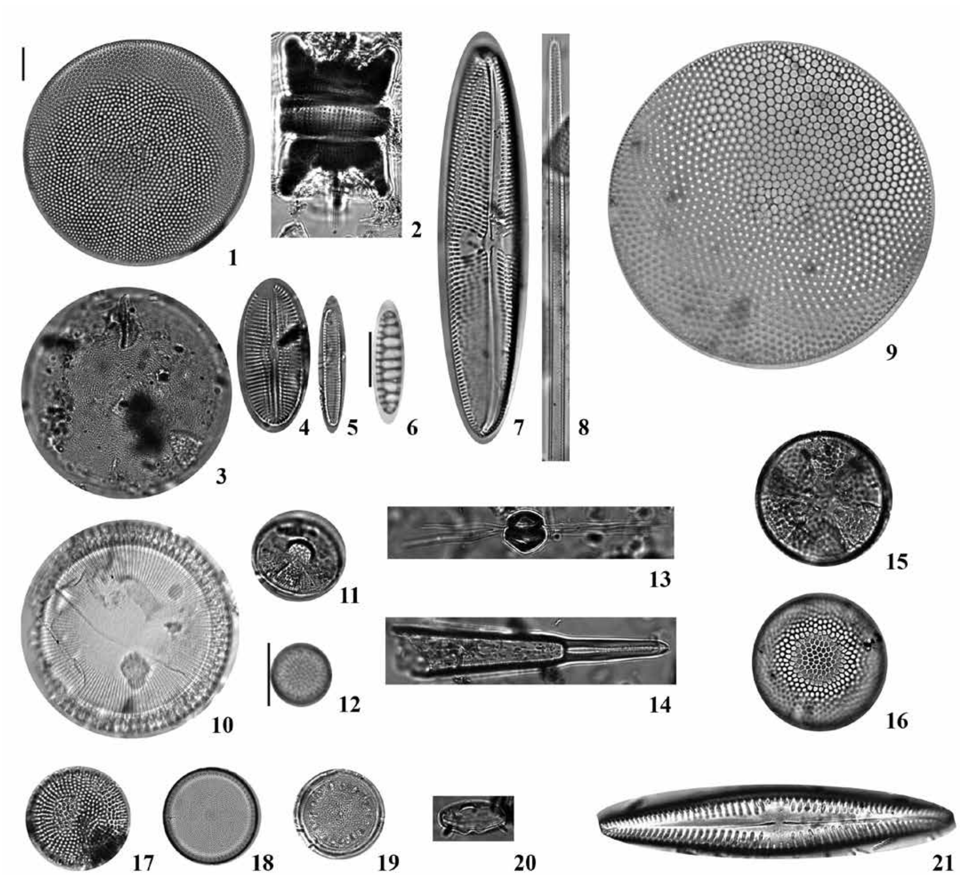

FIGURE 6. Typical diatoms found in Chukchi Sea sediments. 1 = *Actinocyclus curvatulus* Janisch. 2 = *Odontella aurita* (Lyngbye) Agardh. 3 = *Porosira glacialis* (Grunow) Jorgensen. 4 = *Diploneis smithii* (Brebisson) Cleve. 5 = *Fragilariopsis oceanica* (Cleve) Hasle. 6 = *Neodenticula kamtschatica* (Zabelina) Akiba et Yanagisawa. 7 = *Trachyneis aspera* var. *intermedia* (Grunow) Cleve. 8 = *Thalassiothrix longissima* Cleve et Grunow. 9 = *Coscinodiscus oculus iridis* Ehrenberg. 10 = *Paralia sulcata* (Ehrenberg) Cleve. 11 = *Bacterosira bathyomphala* (Cleve) Syversten et Hasle. 12 = *Detonula confervacea* (Cleve) Gran. 13 = *Chaetoceros furcellatus* Bailey. 14 = *Rhizosolenia hebetata* Bailey. 15 = *Actinoptychus senarius* (Ehrenberg) Ehrenberg. 16 = *Thalassiosira antarctica* Comber. 17 = *T. hyperborea* (Grunow) Hasle. 18 = *T. hyalina* (Grunow) Gran. 19 = *T. nordenskioeldii* Cleve. 20 = *Ch. debilis* Cleve. 21 = *Navicula peregrina* (Ehrenberg) Kützing. 1, 8, 9, 14 = oceanic. 2, 3, 5, 11–13, 15–20 = neritic. 4, 7, 21 = benthic. 6 = extinct. 10 = sublittoral. Scale bar in the top left is 10 μm.

DISCUSSION

Diatom species thanatocoenosis dominates in the sediment we studied. The selective solubility of diatoms leads to the formation of peculiar assemblages in sediments, featuring the absence of some typical biocoenosis species and the relative abundance of others that are better preserved in sediments (Jousé, 1962). *Bacterosira bathyomphala, Pauliella taeniata*, and *Chaetoceros socialis* are the dominant plankton in the Chukchi Sea (Sergeeva et al., 2010), but their content in sediments seldom exceeds 10%. Nevertheless, the diatom assemblages found in the sediments reliably reflect the main oceanography and ice conditions of the Chukchi Sea and can be used to reconstruct the paleoenvironment. The data on diatoms collected from sediments and biogenic elements produced by phytoplankton are evidence of the redistribution of planktogenic matter by currents and their accumulation in the finest sediment fraction.

To normalize the influence that grain size has on chemical composition, we used a standard Al normalization method to determine chemical composition (McKay and Pedersen, 2008). Figure 8 presents the correlation and R-factor analysis for normalized element data. Groups of elements with linear or significant correlations are combined into three poly-elemental associations. Association I

TABLE 2. Clusters determined in Chukchi Sea surface sediments by mean content (%) of dominant diatom species (bold text).

	A		B			
				B2		
					B2-2	
Dominant Species	**A1**	**A2**	**B1**	**B2-1**	**B2-2a**	**B2-2b**
Chaetoceros species	2.3	6.6	9.8	15.3	12.8	**20.0**
Cryophilic group	7.0	8.2	14.1	7.6	**24.3**	7.3
Odontella aurita	**27.3**	1.4	3.6	0.7	2.4	1.8
Paralia sulcata	16.3	**53.3**	4.7	11.5	17.2	**20.1**
Thalassiosira antarctica	18.3	6.5	12.8	**41.5**	11.6	**22.5**
Thalassiosira nordenskieoldii	0.3	2.0	**39.8**	2.0	11.8	5.7

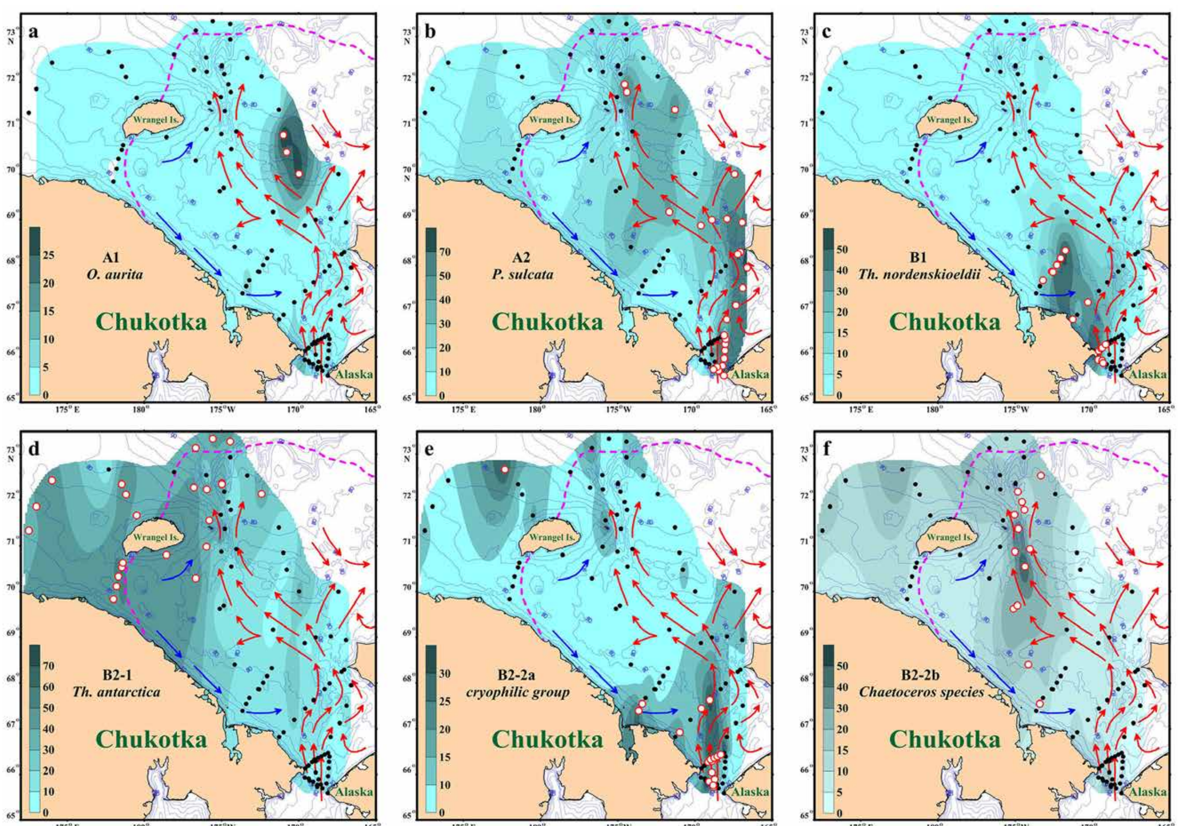

FIGURE 7. Distributions of the diatom dominant species (%) and their assemblages (clusters) in the surface sediments of the Chukchi Sea: (a) *Odontella aurita* and cluster A1; (b) *Paralia sulcata* and cluster A2; (c) *Thalassiosira nordenskioeldii* and cluster B1; (d) *Thalassiosira antarctica* and cluster B2-1; (e) cryophilic species and cluster B2-2a; (f) *Chaetoceros* species and cluster B2-2b. Red and blue arrows show warm and cold currents, respectively (Coachman et al., 1975). The dashed pink line is the average position of the 50% ice concentration line for September during 1979–1983 (Frolov, 2008). White-filled red circles indicate stations where the designated cluster was dominant. Black dots are all other stations.

(Si-La-Ba-Y-Zr-Ti-Yb) is related to the variation of clastic minerals in sediment. Association II (Ca-Mg-Sr-Pb) is determined by the abundance of biogenic carbonate in sediment. Association III (Fe, Mn, and other trace elements) is defined by the presence of oxides and sulfides of the diagenetic minerals Fe and Mn, which accumulate certain trace metals.

Organic carbon (OC/Al) is included in the analysis, but it is not a part of these associations, nor are biogenic opal and chlorin, because they have strong positive correlations with elements from associations II and III (Figure 8). The correlation of organic carbon from biogenic carbonate elements (Ca, Mg, Sr, Pb, in this case) is obvious because they have a common source in biogenic remains, but the connection with elements from association III (V, Mo, Zn, Cr, Hg) is more complicated. We assume that all of these elements are deposited with plankton and also with iron and manganese hydroxides. Their accumulation mainly depends on the metal concentrations in the water; accordingly, they enrich sediments in areas with specific hydrochemical conditions, such as around hydrothermal vents (Gurvich, 1998; Hsu et al., 2003). In average seawater, Zn and Hg fall out from the water mass, mainly with planktogenic organic matter that includes diatoms, and are deposited in the bottom sediments (Ellwood and Hunter, 2000). This process clearly reveals the correlation of elements from association III with organic matter in Chukchi Sea sediments. Usually, an intensive accumulation of V and metals with similar geochemical properties (Mo, Zn, Cr, Co, Ag) in marine environments is typical for anoxic conditions and especially for basins with hydrosulfuric contamination (Bürton, 1966; Helz et al., 1996). Such conditions are also favorable for organic carbon and chlorin accumulation as a result of suppressed organic matter destruction (Pedersen and Calvert, 1990; Gorbarenko et al., 2014).

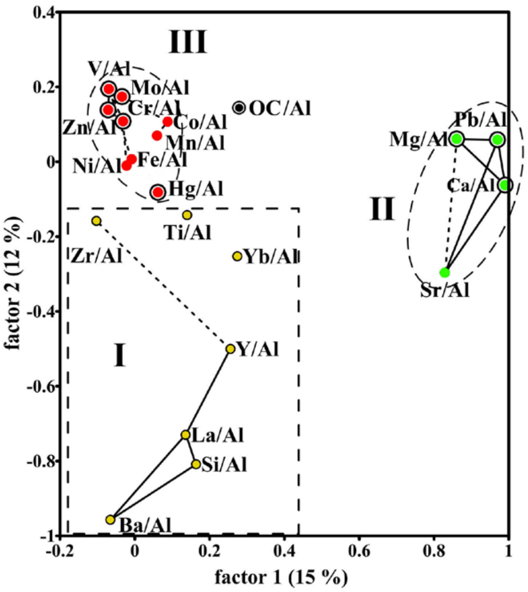

FIGURE 8. Graphical representation of the factor loadings with Varimax rotation for Al normalized contents of the chemical elements. I–III = poly-elemental associations. Black circles indicate the elements that are correlated with the Al-normalized content of organic carbon (OC/Al). Lines connect elements with the most significant correlation (solid: >0.7, dashed: 0.6–0.7).

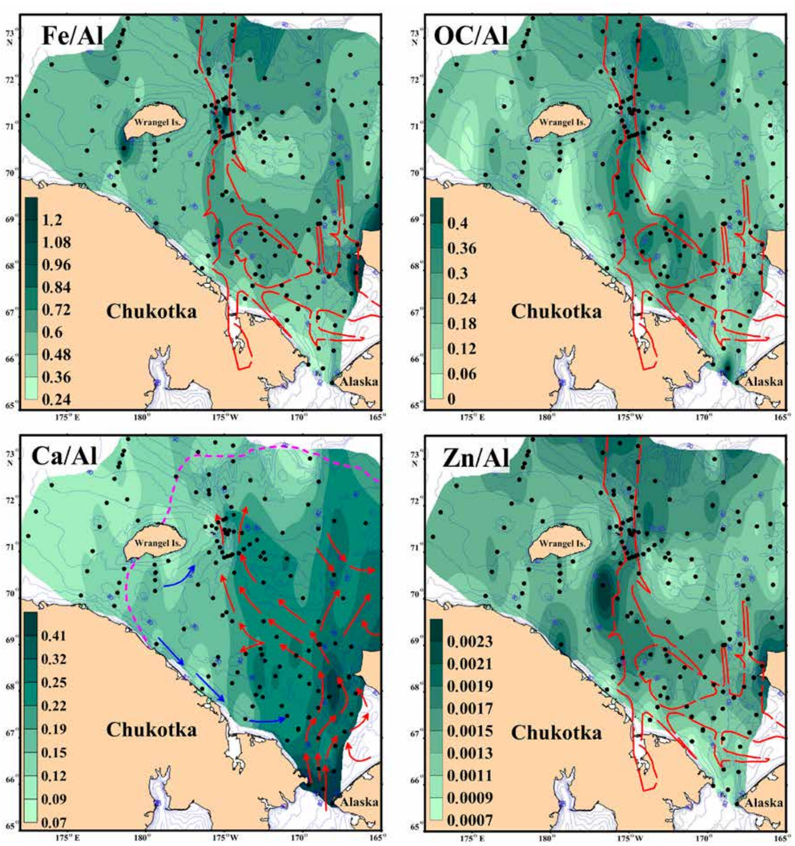

FIGURE 9. Contents of Al-normalized elements in surface sediments of the Chukchi Sea. Red and blue arrows show warm and cold currents, respectively (Coachman et al., 1975), and red dashed lines contour the main neotectonic depressions, as in Shipilov et al. (1989).

The distribution of some elements demonstrates the influence of bioproductivity and biochemical processes on sedimentation after removal of the grain-size effect by Al normalization. The normalized Ca content (Ca/Al) shows the accumulation of biogenic carbonates, and it is possible to use this for reconstructions of paleoproductivity and paleoceanological conditions, for example, to reflect the distribution of the warm water mass coming in from the Bering Sea (Figure 9). Diatom assemblages where *Paralia sulcata* or

Thalassiosira nordenskioeldii dominate also indicate similar water masses (Figure 7b,c).

Organic carbon and chlorin in the Chukchi Sea shelf sediments indicate redox conditions rather than bioproductivity, because they reflect the distribution of anoxic and euxinic conditions due to better preservation in sediments. Also, similar conditions are indicated by the number of elements such as V, Mo, and Mo/Mn as well as diatom assemblages with *Chaetoceros* dominance from cluster B2-2b (Figure 7f). The low content of biogenic opal, Ca/Al, and diatoms, and *Thalassiosira antarctica* dominance in diatom assemblages, indicates the perennial presence of sea ice.

Figure 10 shows some features of the chemical compositions of bottom sediments and the locations of the diatom thanatocoenoses that reflect the strong influence of geological processes on deposition. This is well demonstrated by the distribution of metalliferous sediments, although the reasons for their formation are different. Areas with methane vents are mostly associated with graben-rift structures. Anoxic or even euxinic conditions form in these sediments, and bottom waters favor the accumulation of Mo, Cd, V, Zn, Ag, Ru, and some other trace elements. It is assumed that the abnormal concentrations of Fe, Ni, Co, Au, Pt, and Hg in the sediments may be associated with various water or gas-water sources, including hydrothermal vents, which either import these metals or modify the physicochemical conditions of the bottom water, making them more favorable for the deposition of metals from seawater by biochemical processes (Astakhov et al., 2013b). Diatoms of the *Chaetoceros* genus, which dominate in the sediments of Herald Valley and are part of cluster B2-2b, are a very useful indicator of geodynamic conditions, perhaps due to their increased productivity in areas with aqueous sources of iron supplies.

Generally, increased organic carbon and chlorin are associated with active geological structures, while various water masses substantially affect the distribution of these elements. The effect of geological processes in the accumulation of these elements, as well as the opal, is revealed indirectly through several factors:

- Increased primary productivity around water and water-gas vents through the supply of methane, iron, and some trace elements
- Drifting of biogenic remains and their accumulation in seafloor depressions, which in the Chukchi Sea coincide with active neotectonic structures
- Better preservation of organic matter in anoxic and euxinic conditions that commonly occur in depressions within the active neotectonic structures

Figure 11 presents the specifics of the chemical composition of bottom sediments and diatom thanatocoenoses, reflecting the prevailing influence of water masses and the ice regime on sedimentation. Calcium (Ca/Al) is the best element to employ in tracing the influence of warm Pacific waters within the Arctic's ice-free area in August. The late summer ice-free zone is also delineated in the distribution of the cluster A2 diatom assemblage, in which *Thalassiosira antarctica* is scarce. Diatom assemblages in the area of significant Pacific water impact (Ca/Al > 0.22) refer to two clusters: (1) cluster A2 in Bering Shelf Water and the Alaska Coastal Current, dominated by *Paralia sulcata*, and (2) cluster B1 in Anadyr Water in the westernmost part of Bering Strait and along the Chukotka coast, dominated by *Thalassiosira nordenskioeldii*. Also, sediments in this area contain the Chukchi Sea's maximal concentrations of chlorin and siliceous remains of diatoms (Figure 5) as well as the results of benthic peak productivity (Grebmeier et al., 2006). Models of the distribution of water masses in the Chukchi Sea (Weingartner et al., 2005; Grebmeier et al., 2012) indicate that this area is where the cold East Siberian and warm Anadyr Currents come into contact, suggesting that increased primary productivity occurs along water mass fronts that complement each other and include the elements necessary for active phytoplankton growth. The Anadyr Current to the north of 68°N cannot be detected in sediment chemistry or diatom assemblages (Figure 7c), except in the area of Herald Valley with its raised content of chlorin

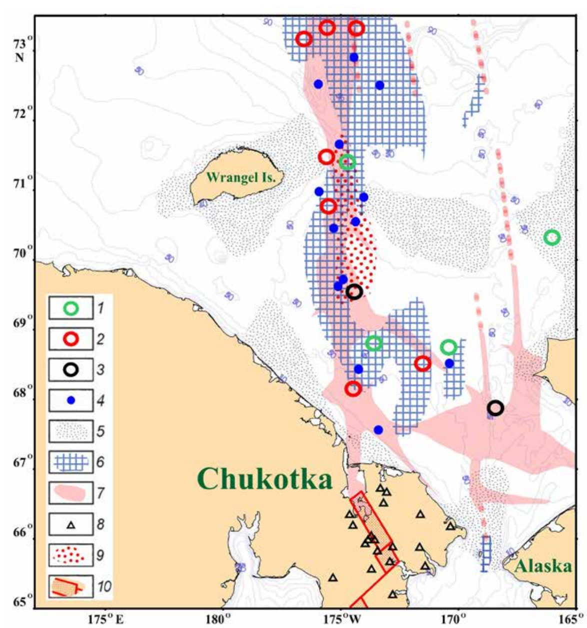

FIGURE 10. Features of the chemical composition of bottom sediments and diatom thanatocoenosis, reflecting the dominant influence of geological processes. Stations with anomalous metal content (Astakhov et al., 2013a): 1 = siderophiles (Fe, Ni, Co, Cr); 2 = sulfophiles (Mo, Cd, Zn, Ag, Au, Hg); 3 = platinum group (Pt, Ru); 4 = stations with diatom thanatocoenoses corresponding to cluster B2-2a; 5 = area of sandy sediments; 6 = increased content of organic carbon (OC/Al > 0,3); 7 = position of the graben-rift system of the Chukchi Sea (Shipilov et al., 1989); 8 = hydrothermal vents of East Chukotka (Polyak et al., 2010); 9 = zone with more than 30% concentration in sediment of the diatom genus *Chaetoceros*; 10 = current borders of the East Chukotka rift zone (Fujita et al., 2002).

and diatoms in the sediments. Better comparability between sea currents and the chemical composition of surface sediment and diatom thanatocoenoses buried in the surface sediment can be achieved using the Coachman et al. (1975) map of Chukchi Sea currents. The possible explanation for this difference is the variety of age intervals covered by instrumental measurements versus those derived from the sediments.

The Coachman et al. (1975) model is mainly based on data obtained in the mid-twentieth century, whereas the later map showing a separate Anadyr Current (Weingartner et al., 2005; Grebmeier, 2012) was developed from data collected at the end of the twentieth and beginning of the twenty-first centuries. During this period, there were substantial changes in Bering Strait water exchange (Woodgate and Aagaard, 2005) and the melting of sea ice in the Chukchi Sea, which led to new water mass patterns in the Chukchi Sea. The bottom sediments (0–2 cm of the surface layer) covered a prolonged time interval, from the first decades in the southern and southwestern parts with a high sedimentation rate (Gusev et al., 2014) to hundreds of years in the northern part of the Chukchi Sea. This may explain why there is not complete concurrence in the records of the water masses in the Chukchi Sea and the geochemical features of sediments and diatom thanatocoenoses. However, these proxies may be used as indicators of different water masses and, consequently, point to the temperature and ice regime histories of this region.

CONCLUSION

The use of paleoceanographic proxies as indicators of sea ice conditions must take into consideration the geological environment and hydrochemical conditions of near-bottom water. Our results show that intensive accumulation of biogenic components, including those produced by phytoplankton, in Pacific Arctic shelf sediments is not always suitable for use as a paleoproductivity proxy during paleoreconstructions. The distribution of biogenic opal, organic carbon, and chlorophyll-*a* derivatives is strongly influenced by current and wave transport, with a tendency to accumulate in seafloor depressions. Sediments in local hollows and depressions of the Chukchi Sea are enriched in organic matter due to better preservation of organic carbon and chlorin in anoxic conditions. These seafloor structures are formed by neotectonic processes, and anoxic conditions in this area are probably caused by methane and hydro-gas vents. The concentration of biogenic carbonates indicated by Al-normalized content of Ca and Sr is the most useful proxy for paleoceanographic reconstruction. Diatom assemblages can be considered as indicators of different types of water masses and, with additional data, can be used to reconstruct surface temperature and sea ice conditions.

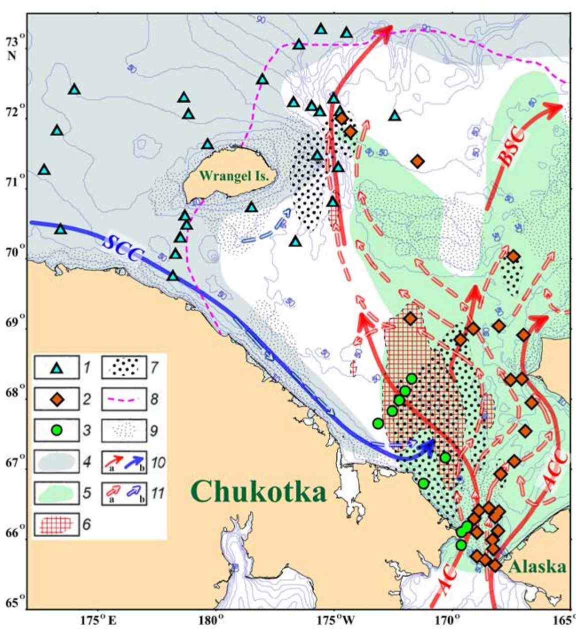

FIGURE 11. Features of the chemical composition of bottom sediments and diatom thanatocoenoses, reflecting the dominant influence of oceanographic conditions. In the legend: 1 = diatom assemblages corresponding to cluster B2-1, dominated by *Thalassiosira antarctica*; 2 = diatom assemblages corresponding to cluster A2, dominated by *Paralia sulcata*; 3 = diatom assemblage corresponding to cluster B1, dominated by *Thalassiosira nordenskioeldii*; 4 = sediment with reduced calcium content (Ca/Al < 0.15); 5 = sediment with increased calcium content (Ca/Al > 0.22); 6 = high concentration of chlorin in sediment (>44 µg g^{-1}); 7 = increased concentration of more than 2.7 million diatom frustules (the silicified cell wall of a diatom) per gram of sediments; 8 = average position of the 50% ice concentration line for September during 1979–1983 (Frolov, 2008); 9 = distribution of sandy sediments; 10 = the major warm (a) and cold (b) water currents of the Chukchi Sea (Grebmeier, 2012): SCC = Siberian Coastal Current, ACC = Alaska Coastal Current, BSC = Bering Shelf Water (Current), and AC = Anadyr Current (Bering Sea Water); 11 = the major warm (a) and cold (b) water currents of the Chukchi Sea, according to Coachman et al. (1975).

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