Conditions of the accumulation of organic matter and metals in the bottom sediments of the Chukchi Sea

A.S. Astakhov a,*, E.A. Gusev b,c, A.N. Kolesnik a, R.B. Shakirov a

a V.I. Ilichev Pacific Oceanological Institute, Far Eastern Branch of the Russian Academy of Sciences, ul. Baltiiskaya 43, Vladivostok, 690041, Russia
b VNIIOkeangeologiya, named after I.S. Gramberg, Angliiskii pr. 2, St. Petersburg, 190121, Russia
c Saint Petersburg State University, Faculty of Geography and Geo-Ecology, Vasil’evskii Ostrov, 10 Liniya 33–35, St. Petersburg, 199178, Russia

Received 6 June 2012; accepted 18 October 2012

Abstract

The chemical composition of bottom sediments in the Chukchi and, partly, East Siberian Seas was studied. In the south and west of the Chukchi Sea, a zone has been detected with the accumulation of sediments rich in organic carbon, an increased background content and anomalies of sulfophile metals (Mo, Zn, Hg, Ag, Au), iron-group metals (V, Ni, Co), and some PGE (Ru, Pt). This zone is confined to the neotectonic active system of rift troughs extending from the Bering Strait and eastern Chukchi Peninsula to the continental slope, where it is bounded by the Cenozoic Charlie rift basin of the Canadian hollow. The geochemical features of the carbon-enriched sediments evidence that they formed under oxygen-deficient conditions and, sometimes, in suboxic and anoxic environments near endogenic water and gas sources. The high carbon and metal contents suggest that the very fine-grained sediments in the rift troughs of the Chukchi Sea are a possible analog of some types of ancient highly carbonateous sediments belonging to black shales.

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Keywords: sedimentation; organic carbon; metals; rifting; black shales; Chukchi Sea

Introduction

Nowadays, one of the most discussed questions in geological publications is the relationship of tectonic processes with short oceanic anoxic events accompanied by the accumulation of organic-enriched sediments (black shales). This relationship is evident in geologic time, because the main oceanic anoxic events are observed in rifting epochs with attendant spreading, trap, and island-arc volcanism (Khan and Polyakova, 2010). The principal cause of these events is presumed to be an increase in the primary biologic productivity owing to volcanic and hydrothermal activity. Most of the present-day anoxic basins of normal salinity, with persistent hydrogen sulfide contamination, are also localized within active geologic structures: rift zones, island arcs, and Alpine-folded backarc basins and internal basins (Kholodov, 2002). Studies of the last decade cite volcanism as a factor usually preceding the formation of anoxic basins and the accumulation of black shales (Jones and Jenkyns, 2001; Khan and Polyakova, 2010; Larson and Erba, 1999). The overprinting of other paleo-oceanologic and paleoclimatic events is important. In many recent works, researchers point out the increased carbon dioxide content of the atmosphere. This increase is accompanied by the greenhouse effect and corresponding increase in the temperature of waters, which reduces their oxygen saturation (Larson and Erba, 1999). Massive destabilization of gas hydrates in bottom sediments is presumed to be the cause of past global anoxic events (Hesselbo et al., 2000) and a mechanism of the tectonic initiation of anoxia. The anoxic character of bottom waters (Jones and Jenkyns, 2001), intense supply of organic matter (Pedersen and Calvert, 1990), and low sedimentation rate (Yudovich and Ketris, 1988) are cited by many authors as the principal factors of the formation of individual black shales, regardless of geodynamic settings.

The principles of geodynamic control over the formation of ancient black shales need testing on recent sediments. This could be possible owing to the presence of recent sea basins with the above factors of geodynamic control over the formation of anoxic basins. The problem is that direct comparison is impossible for most of the compositional parameters of sediments in recent anoxic basins and black shales, because many of the mineralogic and geochemical characteristics of the latter depend on postdepositional
changes. Besides that, present-day anoxic basins are small and incomparable in the rate of organic-matter accumulation with typical black-shale basins, especially in the Mesozoic, when the climatic conditions (greenhouse climate) differed dramatically. This indicates that the syndepositional analogs of only some types of ancient carbonateous sediments, which formed mainly in geodynamically active zones, can be now distinguished. Nevertheless, there are successful comparisons between carbon-enriched sediments from ancient and recent basins in some parameters (Astakhov et al., 2010a; Brumsack, 2006; Tyson and Pearson, 1991).

We selected the Chukchi Sea (Fig. 1) to study the effect of the above-mentioned geologic processes on the accumulation of organic matter and metals in the very fine-grained sediments of tectonically conditioned recent basins as well as to draw comparisons with the background sediments and the sediments of ancient and present-day anoxic basins. Sediments enriched in planktonic organic matter (Grebmeier et al., 2006) and precious metals (Astakhov et al., 2010a, b) are observed here within local basins formed by the Late Cenozoic activity of a graben–rift system. The bottom waters show a seasonal oxygen deficiency (Frolov, 2008), and the sediments are enriched in biogenic silica along with organic carbon (Astakhov et al., 2010b). These sediments were previously compared to the Perman–Triassic black shales of northwestern Russia in formation conditions and some geochemical characteristics (Astakhov et al., 2010a).

Samples of surficial bottom sediments were taken with dredgers and gravity corers during the cruises on board the RV Professor Khromov (2009), the RV Akademik M.A. Lavrentyev (2008), and the seagoing tug Shuya (2006) (Fig. 2). The sample preparation, sample analysis, and data processing were carried out by the previously tested technique (Astakhov et al., 2013), and the analytical results are presented at http://chukchi-sea.poi.dvo.ru/tables.php. Also, we used the previously published data on the chemical composition of the Chukchi Sea sediments (Astakhov et al., 2010b, 2013; Feder et al., 1994; Viscosi-Shirley et al., 2003).

**Geologic conditions and sedimentation peculiarities**

The geodynamic settings and manifestations of present-day geologic activity in the Chukchi Sea are roughly determined by a zone of recent crustal stretching (Fig. 1), distinguished along with two zones in northeastern Asia (Laptev Sea and Baikal zones) (Levi et al., 2009). This results in the recent activity of a graben–rift system of Mesozoic–Early Cenozoic near-N–S and near-E–W rift structures (Fig. 1) (Polyak et al., 2010; Shipilov et al., 1989; Timofeev et al., 2012). The system resembles that of pull-apart basins. The best known neotectonic structure in this system is the “Chukchi graben” (Alekseev, 2002; Shipilov et al., 1989), which extends from the eastern Chukchi Peninsula in the south to the Herald Trench and the shelf edge of the Chukchi Sea in the north. This graben with thick Cretaceous–Cenozoic sediments has experienced activity accompanied by basaltic volcanism and hydrothermal processes as a part of the graben–rift system in the Neogene–Quaternary (Cheshko et al., 2004; Polyak et al., 2010). Its studied onshore part in the eastern Chukchi Peninsula (Kolyuchin–Mechigment zone) hosts Late Cenozoic volcanics and numerous hydrothermal vents with a discharging-water temperature of up to 97 °C (Cheshko et al., 2004; Smirnov, 2012). The hydrothermal vents in this zone differ from those on the Chukchi Peninsula in the composition of gases with abundant evidence for mantle components (Polyak et al., 2010). Also, this zone contains epicenters of numerous shallow-focus earthquakes of low amplitude (Imaev et al., 2000). Analysis of the focal mechanisms of the largest earthquakes and seismotectonic dislocations revealed a present-day rift zone on the eastern Chukchi Peninsula (Fujita et al., 2002). The recent activity of the graben–rift system within the Chukchi Sea is manifested in the seismicity to seaward of the eastern Chukchi Peninsula and in the bottom topography, which fully reflects the position of the major basins. Geophysical data suggest the presence of volcanics in the sedimentary cover (Shipilov et al., 1989), whereas the seismoacoustic profiles within Herald Shoal show near-N–S faults which dislocate the recent cover (Gusev et al., 2009). Indirect evidence includes the intense methane supply within some structures of the graben–rift system to the surficial bottom sediments, pore water, and seawater (Alekseev, 2002; Yashin and Kim, 2007) as well as very high rate of methane production (up to 4410 nL/dm$^3$ day) and sulfate reduction (up to 2590 µgS/dm$^3$ day) at low organic-carbon content (Lein et al., 2007). The graben–rift system of the Chukchi Sea is bounded in the north by the Cenozoic Charlie rift basin, but their relationships are unknown because of the poor knowledge of the region.

The geochemistry of recent sedimentation in the Chukchi Sea has much in common with that in the other Arctic seas owing to its predominantly terrigenous origin under conditions of low runoff and low sedimentation rate. Unlike the other marginal seas of the Arctic Ocean, the Chukchi Sea is characterized by the locally high biologic productivity of phytoplankton. As a result, the very fine-grained sediments in the southern segment of the sea have a high content of biogenic silica, and the biologic productivity of benthos is very high in some areas (Grebmeier et al., 2006). These facts are often explained by the spread of warm Pacific waters through the Bering Strait (Grebmeier et al., 2006). Judging by the content of amorphous silica, diatom content is 5–12% on the entire leveled surface of the South Chukchi Plain. Also, this area is marked by a high content of organic carbon (Astakhov et al., 2013; Kosheleva and Yashin, 1999). Unlike the East Siberian Sea with predominant terrigenous organic matter in the sediments, the Chukchi Sea is characterized by the predominance of marine planktonic organic matter (Grebmeier et al., 2006; Vetrov et al., 2008). All the above facts make the Chukchi Sea very similar to some tectonically conditioned black-shale basins of the past, whose sediments have a low organic-matter content. Therefore, this paper is aimed at (1) the study of the distribution of organic matter and metals with respect to the neotectonic
position of bottom areas, (2) definition of the causes why the sediments are locally enriched in them, and (3) comparison with sediments from ancient and recent anoxic basins.

Results and discussion

Biogenic components of the sediments. The distribution of biogenic components in the bottom sediments of the Chukchi Sea has features specific to all the Arctic seas and only to this sea. The first one is a low content of biogenic carbonates, typical of the Arctic shelf seas. Our data on inorganic-carbon content and the available literature data on its distribution (Astakhov et al., 2013; Lein et al., 2007) in the surficial sediment layer indicate almost absent biogenic carbonate sedimentation in the Chukchi Sea. The surficial sediments and the Upper Quaternary marine sediments stripped by the gravity coring and drilling (Gusev et al., 2009; Lein et al., 2007) contain no more than tenths of a percent carbonate (total) carbon. On the other hand, benthic and planktonic communities, including carbonate-shelled organisms, are highly productive (Grebmeier et al., 2006). This inconsistency might be due to the dissolution of carbonate biogenic remnants in bottom waters or on the seabed, as is typical of high-latitude basin shelves.

The distribution of organic carbon shows a distinct zone of increased contents in the southern and western Chukchi Sea, which can be marked off by isoline 2% $C_{org}$ (Fig. 3). Also, increased contents were detected at some points north of Wrangel Island and in the strip directed strictly to the north of the Bering Strait. The available data on the content of amorphous silica in the southern segment of the sea (Astakhov et al., 2010b, 2013) show a good amorphous silica–organic carbon correlation (0.79 for 56 samples) (Fig. 4). This presupposes the supply of organic carbon to the sediments together with diatoms, and the high $C_{org}$ contents might be due to an increase in the primary productivity of this area or to the removal of biogenic debris from the surrounding bottom areas by currents. The heavy isotopic composition of organic carbon from the sediments of this zone also indicates the predominance of planktonic organic matter in its formation (Grebmeier et al., 2006; Vetrov et al., 2008). Also, organic carbon contents of >2% are observed in some samples from the East Siberian Sea, northwest of Wrangel Island (Fig. 3). However, the light isotopic composition of organic carbon in these areas indicates the predominance of terrigenous organic matter, supplied by the thermal abrasion of the continental coasts, isles, and submarine shoals (Vetrov et al., 2008). For example, high organic-carbon contents (up to 3.5%) are observed in the Pliocene–Pleistocene alluvial and littoral-marine sediments of the borehole drilled near Wrangel Island (Gusev et al., 2009).

Areas with high $C_{org}$ and $SiO_2_{amorph}$ contents of the Chukchi Sea sediments coincide with the major structures of...
the graben–rift system (Fig. 1), which might be caused by different factors. First, the neotectonic structures of the graben–rift system determine the present-day shelf topography such as the presence of depressions and valleys, including the existence of the Bering Strait. The main branches of the current from the Bering Strait spread in these seabed depressions, bringing warm waters rich in biogenic debris. These waters increase the primary productivity of the waters and, correspondingly, the supply of organic carbon and amorphous silica to the seabed. On the other hand, the above-mentioned morphostructures, which are depressed seabed areas, are covered with the most fine-grained sediments, in which organic debris accumulates, including that from the surrounding rises. The area is characterized by a significant positive correlation between the contents of <0.01 mm fractions and organic carbon, but the very wide scatter of the points (Fig. 4).
is indicative of an effect on organic-carbon accumulation and other processes.

One of such factors might be endogenic fluids supplied from the crust to bottom sediments and bottom waters in active fault zones. They can increase the micro- and macrobenthos productivity and primary productivity by the supply of Si, P, Fe, and other elements participating in planktonic biochemical processes. The above-mentioned morphostructures are characterized by intense microbial activity (Ivanov et al., 2010; Lein et al., 2007) and areas of very high macrobenthos productivity (Grebmeier et al., 2006).

Thus, the high organic-carbon contents of the bottom sediments in the narrow zone coinciding with some structures of the graben–rift system are produced by several causes: (1) increased primary productivity owing to the supply of biogenic-rich Pacific waters; (2) the presence of closed depressions and hollows in the shelf, to which fine-grained sediments, including planktonic debris, are removed; and (3) the presence of endogenic water and gas vents increasing the benthic and planktonic productivity. Predominantly allochthonous organic matter is removed from rivers or older Quaternary sediments eroded on the shore or seabed to the westernmost Chukchi Sea and the East Siberian Sea (Fig. 3).

**Total chemical composition of the sediments.** A field study and microscopic examinations show that all the bottom sediment samples are terrigenous, with an insignificant admixture of biogenic material. Their grain size varies from coarse sands to pelites. The distribution of their types over the area is consistent with available maps of bottom sediments (Kosheleva and Yashin, 1999). The sands are common in the littoral shelf and on Herald and Hanna Shoals. The pelite covers the outer shelf, the continental slope, and the entire deep-water part of the study area. A considerable part of the shelf is covered with mixed, predominantly silty sediments admixed with very fine-grained clay as well as ice-laid sand, gravel, and pebbles.

Most of the shelves of the Chukchi and East Siberian Seas are covered with reduced gray, dark gray, or black sediments. The most dark-colored varieties are observed in the Herald Trench and at almost all the stations in the East Siberian Sea. Also, a smell of hydrogen sulfide and compacted lumps of black sediments with a high content of amorphous iron sulfides (pyrite) are observed here at many stations. Oxidized brown and gray-brown sediments, typical of the entire deep-water part of the Arctic Ocean, appear only near the shelf edge.

Average contents of chemical elements and the statistical parameters of their distribution are shown in Table 1. As compared with the average crustal abundance (Wedepohl, 1995), the Chukchi Sea sediments are enriched in Ag, Mo, Zn, P, V, Ba, and Si. Also, they are dramatically enriched in Au compared to the average content in clays and shales (Wedepohl, 1995). On the other hand, the Chukchi Sea sediments are considerably depleted in Au with respect to
background contents in ancient black shales (Yudovich and Ketris, 1988, Table 5) but have the same contents of most of the studied major and trace elements (Mn, P, Co, Cr, V, Cu, Zn, Pb, Sr, Yb, Y, La, Ti, Zr). The average contents of Mo, Ag, Cd, and Ni in the Chukchi Sea sediments are lower than the lower limit of background contents in ancient black shales.

The data obtained on the chemical composition, organic-carbon content, and grain size of the sediments were summarized by statistical processing in the STATISTICA 8 standard software: correlation, R-mode factor (Fig. 5), and Q-mode factor analyses. The results of the analyses were used to explain the relations between metals and their groups as well as with the sediment lithology.

The data obtained confirm the dependence of the chemical composition of sediments on their grain size, which was observed for marine terrigenous sedimentation, e.g., in the Chukchi Sea (Astakhov et al., 2008, 2013; Viscosi-Shirley et al., 2003). Grain size reflects mainly the sediment mineralogy—the ratio of the clayey (pelitic) to clastic (sandy-silty) components of terrigenous sediments. Areas of sandy and sandy-silty sediments are marked by high Si content (Fig. 6). They are made up of clastic terrigenous material, predominantly quartz. This is also evidenced by a positive correlation (0.26) of Si with the content of the coarse silty fraction and a negative one with the contents of pelitic and fine silty fractions. Silica is isolated on the diagram in the spaces of the first and second R-factors (Fig. 5A).

The enrichment of the sediments in Al, Mg, and, partly, Fe and K depends on the content of pelitic (clayey) material in the sediments, which is typical of terrigenous sedimentation (Astakhov et al., 1995; Viscosi-Shirley et al., 2003). These elements are essential in hydromica (Al, K), chlorite, kaolinite (Al), and smectite (Fe, Mg). The distribution of Mn and, partly, Fe (Fig. 6) is influenced by the accumulation of authigenic minerals (sulfides, oxides) of iron and manganese in the very fine-grained sediments of geologically active areas (Astakhov et al., 2008, 2010b).

Variations in the Ca content of the sediments depend mainly on the biogenic-carbonate admixture. Judging by its correlation with the fine silty fraction of the sediments, this admixture consists of foraminifer shells, which is also typical of deep-water areas in the Arctic Ocean (Astakhov et al., 2013). The sediments near the Bering Strait are also enriched in Ca (Fig. 6) owing to the supply of warm and biogenic-rich Pacific waters (Fig. 2).
Table 1. Average contents of chemical elements in the Chukchi Sea bottom sediments, statistical parameters of their distribution, and concentration coefficients ($k_i$) as compared with clarkes (in bold)

<table>
<thead>
<tr>
<th>Element</th>
<th>Unit</th>
<th>Content</th>
<th>Average</th>
<th>Standard Dev. ($\delta$)</th>
<th>Average for sedimentary rocks (Vinogradov, 1962)</th>
<th>Crustal average (Wedepohl, 1995)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>max</td>
<td>min</td>
<td>$\delta$</td>
<td>content $k_i$</td>
<td>content $k_i$</td>
</tr>
<tr>
<td>Si</td>
<td>%</td>
<td>46.30</td>
<td>24.99</td>
<td>3.67</td>
<td>23.8 1.32</td>
<td>28.80 1.09</td>
</tr>
<tr>
<td>Ti</td>
<td>%</td>
<td>0.49</td>
<td>0.14</td>
<td>0.06</td>
<td>0.45 0.76</td>
<td>0.40 0.86</td>
</tr>
<tr>
<td>Al</td>
<td>%</td>
<td>8.98</td>
<td>1.60</td>
<td>5.80</td>
<td>10.45 0.56</td>
<td>7.96 0.73</td>
</tr>
<tr>
<td>Fe</td>
<td>%</td>
<td>9.42</td>
<td>0.70</td>
<td>3.58</td>
<td>3.33 1.07</td>
<td>4.32 0.83</td>
</tr>
<tr>
<td>Mn</td>
<td>%</td>
<td>2.45</td>
<td>0.01</td>
<td>0.07</td>
<td>0.23 0.97</td>
<td>0.97 0.91</td>
</tr>
<tr>
<td>Mg</td>
<td>%</td>
<td>2.80</td>
<td>0.30</td>
<td>1.26</td>
<td>1.34 0.94</td>
<td>2.20 0.57</td>
</tr>
<tr>
<td>Ca</td>
<td>%</td>
<td>10.1</td>
<td>0.44</td>
<td>1.23</td>
<td>2.53 0.48</td>
<td>3.85 0.32</td>
</tr>
<tr>
<td>K</td>
<td>%</td>
<td>2.66</td>
<td>0.98</td>
<td>1.71</td>
<td>2.28 0.75</td>
<td>2.14 0.80</td>
</tr>
<tr>
<td>Na</td>
<td>%</td>
<td>2.99</td>
<td>1.05</td>
<td>2.09**</td>
<td>0.66 3.17</td>
<td>2.36 0.89</td>
</tr>
<tr>
<td>P</td>
<td>%</td>
<td>0.35</td>
<td>0.04</td>
<td>0.11</td>
<td>0.08 1.40</td>
<td>0.08 1.42</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>%</td>
<td>13.52</td>
<td>0.20</td>
<td>5.97</td>
<td>––  ––</td>
<td>––  ––</td>
</tr>
<tr>
<td>Corg</td>
<td>%</td>
<td>2.57</td>
<td>0.06</td>
<td>1.25</td>
<td>––  ––</td>
<td>––  ––</td>
</tr>
<tr>
<td>Ba</td>
<td>ppm</td>
<td>1055</td>
<td>106</td>
<td>666</td>
<td>800 0.83</td>
<td>584 1.14</td>
</tr>
<tr>
<td>Cd</td>
<td>ppm</td>
<td>0.83</td>
<td>0.08</td>
<td>0.21</td>
<td>0.13 1.62</td>
<td>0.1 2.10</td>
</tr>
<tr>
<td>Co</td>
<td>ppm</td>
<td>151</td>
<td>1</td>
<td>17</td>
<td>20 0.86</td>
<td>24 0.71</td>
</tr>
<tr>
<td>Cr</td>
<td>ppm</td>
<td>141</td>
<td>10</td>
<td>74</td>
<td>100 0.74</td>
<td>126 0.58</td>
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<td>Cu</td>
<td>ppm</td>
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<td>53</td>
<td>57 0.93</td>
<td>25 2.12</td>
</tr>
<tr>
<td>Ni</td>
<td>ppm</td>
<td>101</td>
<td>0.2</td>
<td>30</td>
<td>95 0.32</td>
<td>56 0.54</td>
</tr>
<tr>
<td>Pb</td>
<td>ppm</td>
<td>102</td>
<td>2</td>
<td>12</td>
<td>20 0.58</td>
<td>15 0.78</td>
</tr>
<tr>
<td>Sr</td>
<td>ppm</td>
<td>475</td>
<td>101</td>
<td>182</td>
<td>450 0.41</td>
<td>333 0.55</td>
</tr>
<tr>
<td>V</td>
<td>ppm</td>
<td>277</td>
<td>31</td>
<td>113</td>
<td>130 0.87</td>
<td>98 1.16</td>
</tr>
<tr>
<td>Y</td>
<td>ppm</td>
<td>31</td>
<td>8</td>
<td>17</td>
<td>30 0.56</td>
<td>24 0.71</td>
</tr>
<tr>
<td>Yb</td>
<td>ppm</td>
<td>13</td>
<td>1</td>
<td>2</td>
<td>3 0.70</td>
<td>2 1.05</td>
</tr>
<tr>
<td>Zn</td>
<td>ppm</td>
<td>186</td>
<td>20</td>
<td>88</td>
<td>80 1.10</td>
<td>65 1.36</td>
</tr>
<tr>
<td>Zr</td>
<td>ppm</td>
<td>134</td>
<td>29</td>
<td>73</td>
<td>200 0.37</td>
<td>203 0.36</td>
</tr>
<tr>
<td>La</td>
<td>ppm</td>
<td>37</td>
<td>10</td>
<td>23</td>
<td>40 0.57</td>
<td>30 0.76</td>
</tr>
<tr>
<td>Mo</td>
<td>ppm</td>
<td>10</td>
<td>0.5</td>
<td>2</td>
<td>2 0.91</td>
<td>1.1 1.66</td>
</tr>
<tr>
<td>Ag*</td>
<td>ppm</td>
<td>1.57</td>
<td>0.05</td>
<td>0.17</td>
<td>0.1 1.70</td>
<td>0.07 2.57</td>
</tr>
<tr>
<td>Au*</td>
<td>ppb</td>
<td>14</td>
<td>1</td>
<td>4</td>
<td>3 4.01</td>
<td>2.5 1.60</td>
</tr>
<tr>
<td>Pt*</td>
<td>ppb</td>
<td>106</td>
<td>12</td>
<td>40</td>
<td>22 ––</td>
<td>––  ––</td>
</tr>
<tr>
<td>Os*</td>
<td>ppb</td>
<td>2.11</td>
<td>0.07</td>
<td>0.61</td>
<td>––  ––</td>
<td>––  ––</td>
</tr>
<tr>
<td>Ir*</td>
<td>ppb</td>
<td>1.91</td>
<td>0.04</td>
<td>0.56</td>
<td>––  ––</td>
<td>––  ––</td>
</tr>
<tr>
<td>Ru*</td>
<td>ppb</td>
<td>28.0</td>
<td>1.3</td>
<td>6.7</td>
<td>5.7 ––</td>
<td>––  ––</td>
</tr>
<tr>
<td>Hg</td>
<td>ppb</td>
<td>90</td>
<td>6</td>
<td>30</td>
<td>400 0.07</td>
<td>10 3.00</td>
</tr>
</tbody>
</table>

* After (Astakhov et al., 2010b).
** The values are overestimated because of the high water saturation of the silts.

The correlation and factor analyses (Fig. 4) show that many trace elements (Co, Cr, Pb, V, Y, Yb, Zn, Zr, Mo) also accumulate in very fine-grained sediments, as is typical of terrigenous sediments containing different concentrators: clayey minerals, organic matter, iron and manganese hydroxides, and finely dispersed iron sulfides (Astakhov et al., 1995; McMurtry et al., 1991). The distribution of some trace elements (Sr, Cd, Pb) in the fine silty fraction, like that of Ca, depends on the biogenic-carbonate admixture. Like Mn, a group of trace elements (Cu, Ni, La, Ag, Co), as well as Au and Pt (Astakhov et al., 2010b), shows no correlation with the contents of size fractions and organic carbon. Their high
contents in very fine-grained sediments in some areas were previously explained by local hydrochemical conditions (Astakhov et al., 2008, 2010a).

**Multielement geochemical associations.** The factor analysis illustrates the above-mentioned dependence of the contents of many major and trace elements on the grain size of the sediments. The diagram (Fig. 5A) shows three groups of elements concentrated in different grain-size types of sediments and correlating with certain size fractions. Coarseness decreases in the same direction: coarse silt–fine silt–pelite. Silicon is isolated as a typical element of sandy sediments showing a significant positive correlation only with coarse silt. A large group of elements enriching very fine-grained sediments is isolated in the upper and right parts of the diagram (large positive values of factors 1 and 2). They show a good mutual correlation and a significant positive correlation with the content of the pelite fraction. This group is tentatively divided into two multielement associations, typical of the clastic (Ti–Y–Yb–Zr–La) and clayey-authigenic (Al–Mg–Fe–Zn–V–Mo–C\textsubscript{org}) components of the pelite fraction. Also, a group of elements is distinguished with near-zero values of factors 1 and 2. It comprises elements correlating with the content of fine silt (Ca, Sr), not correlating with the size fractions (Mn, Ni), and correlating with the content of the pelite fraction but having a close paragenetic relationship with other elements of this group (Mn–Co–Cr–Ni; Ca–Sr–Pb in biogenic carbonates).

Differences in chemical composition related to the predominance of clayey or clastic terrigenous material and manifested in their grain-size composition were eliminated by normalization to Al, which is often used in geochemical studies of sediments (McKay and Pedersen, 2008). Correlation and R-mode factor analyses were performed for the matrix including element/Al ratios in each sample. Their results are generalized in Fig. 5B. The diagram shows three multielement associations with the chemical elements showing almost linear relationships or significant correlations as well as lithochemical assignment. Association I (Si–La–Ba–Y–Zr–Ti–Yb) is due to compositional variations in terrigenous matter, whereas association II (Ca–Mg–Sr–Pb) is determined by the presence of biogenic carbonates in the sediment.

Association III (Fe, Mn, and some trace elements) is the most interesting for our studies. It is determined by the presence of minerals (oxides or sulfides) of iron and manganese, which accumulate trace elements. A considerable part of iron and manganese is contained in clastic and clayey silicates, so that the closest correlations in this association are typical of V and sulfophile elements (Zn, Mo). Iron and manganese show significantly worse correlations with them, each other, and organic carbon (Fig. 5B). Organic carbon (C\textsubscript{org}/Al) does not belong to any of the above associations, because it shows significant positive correlations with elements of both association II and association III (Fig. 5B). The elements of biogenic carbonates (in this case, Ca, Mg, Sr, Pb) must correlate with organic carbon, because they are all supplied to the sediments together in biogenic debris of planktonic organisms. The correlation of C\textsubscript{org} with elements of association III (Hg, V, Mo, Zn, Cr) needs additional explanations.

All these elements are believed to be deposited from an aqueous medium by iron and manganese hydroxides or organic matter. Their accumulation rate largely depends on the concentration of metals in water. Therefore, they can enrich bottom sediments near hydrothermal vents and in other peculiar hydrochemical conditions producing their increased contents for various reasons. Their behavior is different in

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**Fig. 5. Results of the R-mode factor analysis of the chemical composition of the Chukchi Sea samples with varimax rotation: diagrams in the space of the first and second R-factors for the contents of elements and size fractions (A) and Al-normalized element contents (B). Circles mark off elements showing a significant positive correlation with organic-carbon content or C\textsubscript{org}/Al, and lines indicate the most significant correlations (solid, >0.7; dashed, 0.6–0.7). I–III, multielement associations.**
Fig. 6. Major-element contents (%) of the Chukchi Sea bottom sediments. Dots show the sampling sites.
background concentrations in seawater. Mercury and zinc are thought to be deposited from the water column predominantly by planktonic organic matter, including accumulation in the bottom sediments of water basins together with diatoms (Ellwood and Hunter, 2000). This determines their correlation with organic matter in the bottom sediments of the Chukchi Sea. Intense V accumulation in recent and ancient sea basins is typical of anoxic conditions and especially basins with hydrogen sulfide contamination (Kholodov, 2002; Kholodov and Nedumov, 1991). Vanadium accumulates in the sediments mainly in the trivalent form. It coexists with elements of close geochemical properties (Mo, Ni, Cr, Co, Ag).

**Possible anoxia and role of geodynamic settings.** The available data on the hydrochemistry of natural waters (Fig. 2A) indicate that areas with seasonal or year-round oxygen deficiency in the bottom waters of the Chukchi Sea coexist with a high oxygen content, typical of the Arctic Ocean (Frolov, 2008). The measured oxygen contents in these areas are high (4–6 nL/L), much higher than those in typical anoxic or even suboxic conditions (Tyson and Pearson, 1991). However, these are minimum values for the Arctic Ocean, with its low water temperatures and high oxygenation. Anoxic conditions are presumed to appear in limited areas under the effect of additional factors within these zones. The existence of anoxia and hydrogen sulfide environments at the same background contents in the bottom waters of Buor-Khaya Bay (Laptev Sea) (Frolov, 2008) is, most likely, stimulated by abnormally high methane flows from the bottom sediments to the bottom water. According to Ya.E. Yudovich and M.P. Ketris (1988), hydrogen sulfide (euxinic) environments are a variety of anoxic ones and can exist only under permanent supply of hydrogen sulfide from the underlying sediments. Typical hydrogen sulfide conditions are not characteristic of the Chukchi Sea, judging by the low (<0.017) Mo/Mn coefficient in the bottom sediments (Fig. 4), whose values of more than 0.02 indicate hydrogen sulfide contamination (Kholodov and Nedumov, 1991). On the other hand, the values of this coefficient are high enough, especially in very fine-grained sediments enriched in organic carbon (Fig. 4), for suboxic or anoxic conditions in local areas.

Episodic existence of suboxic or even anoxic bottom waters in areas of seasonal waters with a decreased oxygen content (Fig. 2) is evidenced by increased V, Mo, and Zn contents of the sediments in the outer shelf and on the South Chukchi Plain (Fig. 7). These are typical elements of anoxic environments, which coexist and correlate with organic carbon (Fig. 5B). The correlation is considerably worse for Fe, Mn, Ni, and especially Co, whose distribution is governed by some more factors (enrichment in heavy minerals from sandy sediments, hydrothermal activity, early diageneric redistribution).

As pointed out above, gas and water vents of different origins are known or predicted in the Chukchi Sea shelf. Shows of hydrocarbon gases are mapped here from bottom-water anomalies, some of which are quite stable and revealed by repeated mapping (Alekseev, 2002; Yashin and Kim, 2007). Hydrothermal vents are predicted from their existence in the onshore parts of the structures which extend in the shelf. The best known of them is the Chukchi graben, which extends from the eastern Chukchi Peninsula to the Herald Trench and outer shelf (Fig. 1). It is marked off everywhere by local depressions with sediments enriched in organic carbon (Fig. 3), Fe, Mg (Fig. 6), Zn, V, Mo, and, locally, Ni and Cr (Fig. 7). As shown by Astakhov et al. (2010b), this local structure is characterized by increased Ag and Ru contents. The latter, the only one of the studied precious metals, shows a significant positive correlation with organic carbon. Thus, organic matter and sulfophile metals accumulate within the local neotectonic structure with the formation of anomalous contents, as is typical of anoxic and even hydrogen sulfide environments.

The lithological modulus (Fe + Mn)/Ti (Fig. 8), often used as an indicator of hydrothermal supply of metals to sediments, has increased values within the Chukchi graben only in local areas. The outer shelf of the Chukchi Sea contains a wider area, which is adjacent to the exposure of Cenozoic Charlie and Northwind rift structures to the continental slope. Also, local areas with an increased coefficient are distinguished in Barrow Canyon, near Pt. Hope, and south of Wrangel Island. Some of these anomalies are probably due to the concentration of magnetite and other clastic ferrous-rich minerals in the sediments.

**Anomalous metal contents.** The existence of local areas with peculiar hydrochemical conditions, including those determined by endogenic activity, might be evidenced by anomalous contents of elements (especially trace elements) of association III (Fig. 5B), which usually deposit in very fine-grained sediments from sea or pore waters. The anomalies were detected from extreme contents higher than the boundary value, which is equal to the average content of the element plus triple mean square deviation (Yudovich and Ketris, 1988). The position of stations with sediments having anomalous contents of metals of multielement association III and some precious metals is shown in Fig. 9. Among the latter, anomalous contents are formed by Ag, Ru, Au, and Pt (Fig. 9), whose distribution has been studied only in the southern Chukchi Sea (Astakhov et al., 2010b). As shown by Fig. 9, samples with anomalous metal contents are localized in three zones:

1. the northernmost part of the study area, which contains oxidized sediments and predicted extensions of the Cenozoic Charlie and Northwind rift structures to the continental slope and shelf;
2. the Chukchi graben and some other structures of the graben–rift system, in which they are associated with high organic-carbon contents;
3. sandy sediments near the northwestern coast of Alaska (Barrow zone).
Fig. 7. Contents ($10^{-7}$%) of trace elements of multielement association III in the Chukchi Sea bottom sediments.
The Barrow zone, which extends from Barrow Canyon along the continental coast of Alaska, has anomalous contents of Fe and some trace elements of association III (Co, Cr, V). These anomalies exist predominantly in sandy sediments and might be produced by the supply of clastics with a high metal content during the erosion of some geologic bodies on the coast or seabed. On the other hand, anomalies were detected in the mixed silty-sandy sediments of the South Chukchi Plain and Barrow Canyon, which suggests the existence of endogenic fluid activity. Evidently, this zone belongs to a neotectonic or, probably, older fault structure, which determines the existence of Barrow Canyon and the valley separating Herald and Hanna Shoals from the continental coast of Alaska.

Anomalies in the contents of Mn and some trace elements are observed in the oxidized very fine-grained sediments with a low organic-carbon content in the outer shelf of the Chukchi Sea, on the extension of the Cenozoic Charlie rift basin. Peculiar sedimentation conditions, probably created by the supply of endogenic fluids, were previously observed here from the major-element relationships and increased contents of many trace elements and Mn (Astakhov et al., 2008, 2013).

Most of the samples with anomalous metal contents are localized within the Chukchi graben—the part of the Chukchi Sea graben–rift system which has shown the most intense geologic activity in the Cenozoic. Anomalous metal contents are found here in very fine-grained sediments with high contents of organic carbon and biogenic silica. The shape and localization of the anomalies suggest that most of them have been produced by intense accumulation of metals from bottom or pore waters in characteristic hydrochemical conditions created by endogenic sources of different types. Hydrothermal vents can increase the metal concentration in bottom or pore waters and stimulate intense accumulation of Fe, Zn, Ni, and, maybe, Au. Vents of different types, including the most widespread cool gas vents, can create suboxic and anoxic conditions in bottom or pore waters and stimulate intense accumulation of organic carbon, Mo, V, Ag, Cd, and Ru. It is these metals that form the highest concentrations in the bottom sediments of the Chukchi Sea (Table 1). The almost ideal coincidence between the structures of the graben–rift system, sediments with a high content of organic carbon, and anomalies of different metals indicates the leading role of recent geodynamic processes in the accumulation of trace elements of association III, Ag, Ru, and Au in the Chukchi Sea bottom sediments.

There are three more anomalies northwest of the Chukchi graben, in very fine-grained sediments enriched in organic carbon (Fig. 9). The effect of endogenic sources on the sedimentation geochemistry is also evidenced by the characteristics of the host sediments and the set of chemical elements forming anomalous (Mo, Mn) and increased (Zn, Ni, V) contents. This is confirmed by the fact that a methane content 3–4 times higher than the background was observed at a station with an anomalous Mo content of bottom water (Shakirov et al., 2010). Some regional tectonic models presuppose the presence of a near-E–W rift structure which intersects, or is the extension of, the Chukchi graben (Bogdanov et al., 1995; Shipilov et al., 1989). This area also belongs to the highly promising North Chukchi petroleum basin (Kaminskii et al., 2011), and hydrocarbon pool defluidization is not precluded.

**Main factors of metal accumulation.**

The studies showed that the accumulation or organic matter and metals in the Chukchi Sea is governed by several factors.

1. Warm and biogenic-rich Pacific waters spreading through the Bering Strait, shrinking the ice coverage of the area, and stimulating the primary productivity with the accumulation of biogenic debris and some metals (C_{org}, SiO_{2amorph}, P, Ca, Mg, Sr, Pb);
2. The presence of valleys and isolated depressions in the shelf, whose very fine-grained sediments are enriched in biogenic debris and many metals with respect to more coarse-grained sediments in the surrounding areas;
3. Widespread occurrence of oxygen-deficient seasonal environments, which determines the general enrichment of the sediments in iron-group (Fe, V) and sulfophile (Ag, Mo, Zn, Cd) elements;
4. The presence of endogenic gas and water vents within the active structures of the graben–rift system, which determines:
   a. an increase in the productivity of planktonic and benthic, including microbial, communities owing to the supply of elements participating in biochemical processes (carb-
on/methane, P, Si, Fe) from the endogenic sources and accelerated accumulation of biogenic debris in the bottom sediments;

(b) more anoxic conditions and, probably, hydrogen sulfide contamination of bottom and pore waters in local areas near endogenic sources, with the formation of anomalous contents of elements typical of these conditions, including early diagenesis (Mo, Zn, V, Ni, and, probably, Ag, Ru);

(c) supply of metals from hydrothermal sources or a change produced by them in the physicochemical conditions of bottom and pore waters, with the formation of anomalous and increased contents of some elements (Fe, Mn, Au, Pt, Hg).

The above-mentioned processes are possible on the seabed only at low sedimentation rates. In the Chukchi Sea, this is due to the small area of the drainage basin and the absence of mouths of large rivers on the coast.

The presence of valleys and isolated basins in the shelf, as a consequence of the tectonic activity of the graben–rift system in the Cenozoic, reveals the leading role of geodynamic settings in the formation of very fine-grained sediments enriched in organic carbon (>2%), precious metals (Ag, Au, Pt, Ru), and metals of association III (Mo, V, Ni, Cr, Co, Fe) in the Chukchi Sea. Enrichment in these elements is typical of ancient black shales (Yudovich and Ketris, 1988, Table 5), but some metals (e.g., Au) are considerably more concentrated in the latter than in the Chukchi Sea sediments. Therefore, an important fact is the accumulation of the recent carbonaceous sediments of the Chukchi Sea within a tectonically active structure with developed fluid-dynamic processes. They are also rich in reactive components: weakly transformed organic matter, amorphous silica, and amorphous iron sulfides. All this determines the possibility of the additional supply, redistribution, and concentration of metals in the subsequent postdepositional, including hydrothermal, processes. It is not impossible that additional carbon accumulation takes place as a result of the microbial transformation of endogenic methane and carbon dioxide, as it is now observed on the geochemical barrier seawater–seabed (Ivanov et al., 2010). The existence of Pt-rich Fe–Mn concretions within the Chukchi graben was previously pointed out (Astakhov et al., 2010a). The metals contained in them can also be preserved in the sediments in the case of postdepositional transformations.

Fig. 9. Organic-carbon content (%) of the Chukchi Sea bottom sediments and location of samples with anomalous metal contents: siderophile elements, green circles (including 1, Mn, Co, Ni, Hg); chalcophile elements, yellow circles (including 2, Cd, Hg; 3, Cd, Mo); and PGE, red circles. Red ruling shows the main structures of the Meso-Cenozoic graben–rift system in the southern Chukchi Sea, after (Shipilov et al., 1989); oval, the Barrow zone; and rectangle, the Chukchi graben.
Conclusions

The Chukchi Sea bottom sediments have increased contents of Ag, Mo, Cd, Zn, Cu, P, V, Au, and Ba with respect to average ones in the crust and sedimentary rocks, as is typical of oxygen-deficient sea basins. Sediments enriched in organic carbon with respect to the background accumulate in the narrow zone of the neotectonic structure of the Chukchi graben and some other structures of the graben–rift system. They have a considerably lower Si content, increased Fe, Al, and Mg contents, and even higher contents of Mo, Zn, V, and Au. Analysis of data using multivariate statistics revealed the grain size of sediments and organic-carbon content as the main factors of the background accumulation of the above metals. A correlation of organic carbon with both biogenic elements (in this case, Ca, Mg, Sr, Pb) and metals (Hg, Mo, Zn, V, Cr) was established with the effect of grain size eliminated by normalization to Al.

Besides that, the neotectonic active structures accumulating organic-enriched bottom sediments contain points with an anomalous content of sulfophile metals, including precious ones. The geologic conditions surrounding the accumulation of organic-carbon-enriched sediments with an anomalous content of metals, as well as their lithologic and geochemical characteristics, are evidence for different causes of anomaly formation. Anomalous contents of Mo, V, Ag, and Ru are likely to form in local areas with anoxic bottom or pore waters developing near cool gas or water-gas vents. On the other hand, anomalous contents of Fe, Mn, Zn, Hg, Ni, and Au are likely to form near water (including thermal) springs supplying metals or creating favorable physicochemical conditions for various ways of metal deposition from bottom or pore waters. It is evident that biochemical processes play an important role and part of the anomalies might have been produced during early diagenesis. In turn, accelerated diagenesis might have been initiated by the same fluid sources.

Thus, bottom sediments enriched in organic matter and metals develop in the Chukchi Sea mainly owing to peculiar geodynamic settings: recent fluid activity and long-lasting crustal extension with the formation of a system of troughs (grabens), reflected in the bottom topography. Importantly, the dissolution of biogenic carbonates and the absence of intense supply of terrigenous matter are the causes of the low sedimentation rate. Favorable oceanologic conditions, including the stratification of the water column and the supply of warm Pacific waters through the Bering Strait, are a secondary and, probably, nonessential factor.

The study was supported in part by the Russian Foundation for Basic Research (grant no. 12-05-91167-GFEN_a) and the Far Eastern Branch of the Russian Academy of Sciences (grant no. 12-II-CO-07-021).

The authors thank K. Crane, G.A. Cherkashev, G.I. Ivanov, A.G. Mochalov, A.A. Merezhko, A.A. Bosin, E.A. Logvina, and D.A. Korshunov for help with the organization and execution of the fieldwork. Also, our thanks go to N.V. Zarubina, G.I. Gorbach, M.V. Ivanov, T.A. Korovin, A.A. Mar’yash, and N.V. Khurkalo for help with the analytical studies.

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