HYDROCHEMICAL STRUCTURE OF THE JAPAN/EAST SEA IN SUMMER 1999

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Introduction

Hydrochemical properties of sea water allow better understanding of hydrophysical processes such as gas exchange on air/seawater interface, circulation and convection, behavior of the mesoscale structures like eddies. Hydrochemical parameters are often used as connective tissue between biological and physical processes. In some cases they can also indicate geological processes on sea floor.

Some hydrochemical properties of the Japan/East Sea have been studied (Kim *et al.*, 1992; Chen *et al.*, 1995; Chen *et al.*, 1996; Kim, 1997; Tishchenko *et al.*, 1998; Riser *et al.*, 1999; Oh *et al.*, 1999). Except oxygen, the hydrochemical parameters (nutrients, pH, alkalinity) of the Japan/East Sea are still not well investigated. Oceanographic survey of the Japan/East Sea was carried out in June-August, 1999 by R/V "Roger Revelle" and "Professor Khromov". The hydrochemical and CTD data (dissolved oxygen, nutrients, pH and alkalinity) were collected for 200 stations along with CTD hydrographic data. Scheme of the stations is presented in Fig. 1. Our consideration will be focused on general scope of features of the hydrochemical structure of the Japan/East Sea.
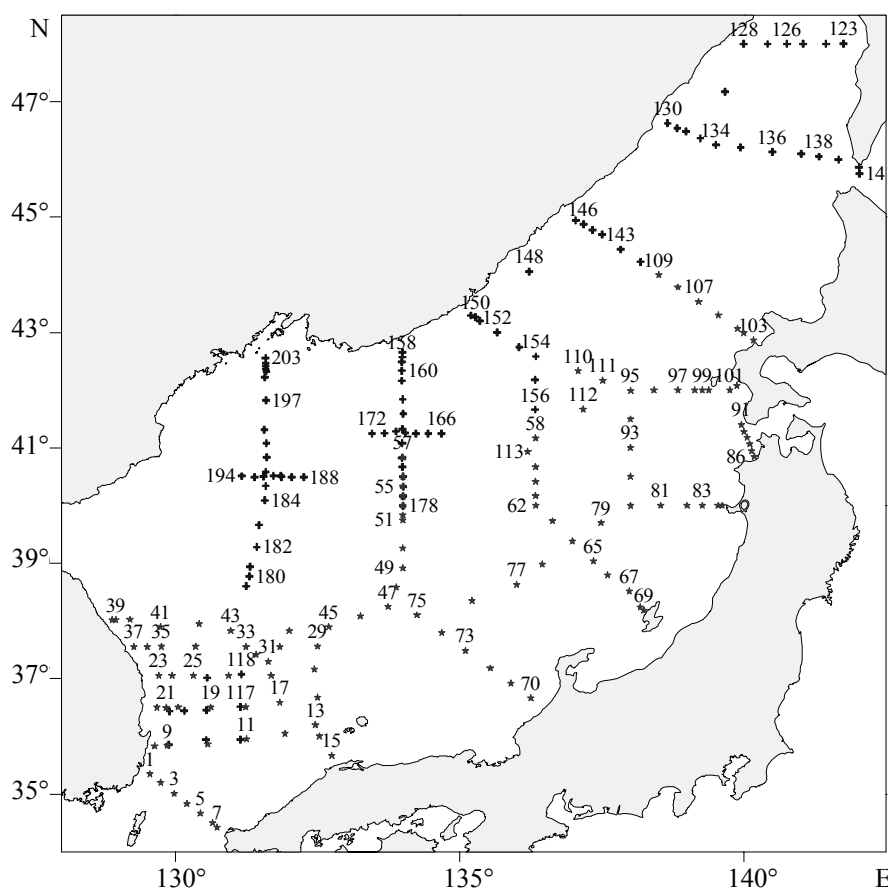

Fig. 1. Scheme of the stations of the R/V "Roger Revelle" (June 24 – July 17, 1999) and Professor Khromov (July 22 – August 13, 1999)

Methods and Data

A sample from each Niskin bottle has been analyzed on dissolved oxygen and nutrients (nitrate, nitrite, silicate, and phosphate) using equipment provided by Ocean Data Facility of Scripps Institution of Oceanography. Oxygen was run using a Dosimat UV-endpoint detection automatic titration system. Estimated from replicates precision of oxygen analysis was generally good to 0.05 ml/l. Nutrients were measured using a Technicon AA-II CFA system with a PC based acquisition system. Estimated from replicates precision of these data was generally good to about 1% of the measured values. Equipment for total alkalinity (TA) and pH was provided by the Pacific Oceanological Institute (Professor Andrew Dickson kindly lent thermostat). As a rule fifteen bottles have been analyzed on pH and TA for each station. TA was measured by means of Brujewicz's method (Brujewicz, 1944). Determination of TA is direct colorimetric titration by hydrochloric acid in an open system using a mixed indicator (methylene blue and methyl red). The titration is carried out under flow of CO_2-free air (or nitrogen). The change of the sample color from green to light-pink at the equivalence point is detected visually. The acid (~0.02 N) was daily standardized by Dickson's CRM. Estimated precision was about 0.2% ($4 \sim 5$ $\mu mol\,kg^{-1}$). pH measurements were carried out by potentiometric method using electrochemical cell without liquid junction (Tishchenko and Pavlova, 1999). Uncertainty of the pH_T measurements was about ± 0.004 pH unit. Dissolved inorganic carbon (DIC), CO_2 partial pressure (pCO_2) have been calculated from measured pH and TA by generally accepted method (Millero, 1995).

Results and Discussion

For establishment of main features of the hydrochemical structure of the Japan/East Sea on a large-scale, we mapped chemical fields on isopycnal surfaces σ_θ=27.10, σ_θ=27.27, σ_θ=27.31, and σ_θ=27.34. Choice of these isopycnal surfaces is stipulated by features of the oxygen and salinity profiles in northern part of the sea (Fig. 2 and Table 1).

Table 1

Characteristics of isopycnal layers

N	Layer	P, db	θ, °C	S, psu	σ_θ	O_2, μM/kg
1	O_2 max – S min	186	2.965	34.035	27.11	283.8
2	O_2 max – S min	184	1.378	34.066	27.27	292.1
3	S max	337	0.904	34.075	27.31	165.0
4	O_2 max	904	0.847	34.068	27.34	221.4

Note: O_2 max – S min – first type of dissolved oxygen maximum related with Japan/East Sea Intermediate Water.

O_2 max – S min – first type of dissolved oxygen maximum related with Japan/East Sea Intermediate Water.

S max – layer of the salinity maximum in the northern part of the Japan/East Sea.

O_2 max – weak deep dissolved oxygen maximum in the northern part of the Japan/East Sea.

Isopycnals σ_θ=27.10 and σ_θ=27.27 (Fig. 2a, b) are considered as mean values of potential densities for two types of subsurface oxygen maximum and salinity minimum (Japan/East Sea Intermediate Water). The layers with higher values of temperature (σ_θ=27.10) were situated in the east part of the sea on periphery of large anticyclonic eddy with center on 40.5°N, 131.5°E and near Yamato Bank. The second type of colder layers with maximum of oxygen (σ_θ=27.27) was observed near Yamato Bank and in the area of the Tsushima Current near Tsugaru Strait (40-42°N). Probably, these layers are formed on the subarctic front in winter by means of convection and subduction (Senjyu, 1999). In the northern part of the Japan/East Sea high salinity values exceeding 34.07 have been found in the intermediate layer (Fig. 2c, d). The potential density of core of the layer varied from 27.27 to 27.32 of σ_θ with mean value around 27.31 σ_θ. This water appeared between fresh upper layer and less salty Deep Water as modified "remnant" of subtropical origin surface water. Characteristics of this layer change in wide range. Therefore intermediate salinity maximum is not a separate water mass with one region of formation.
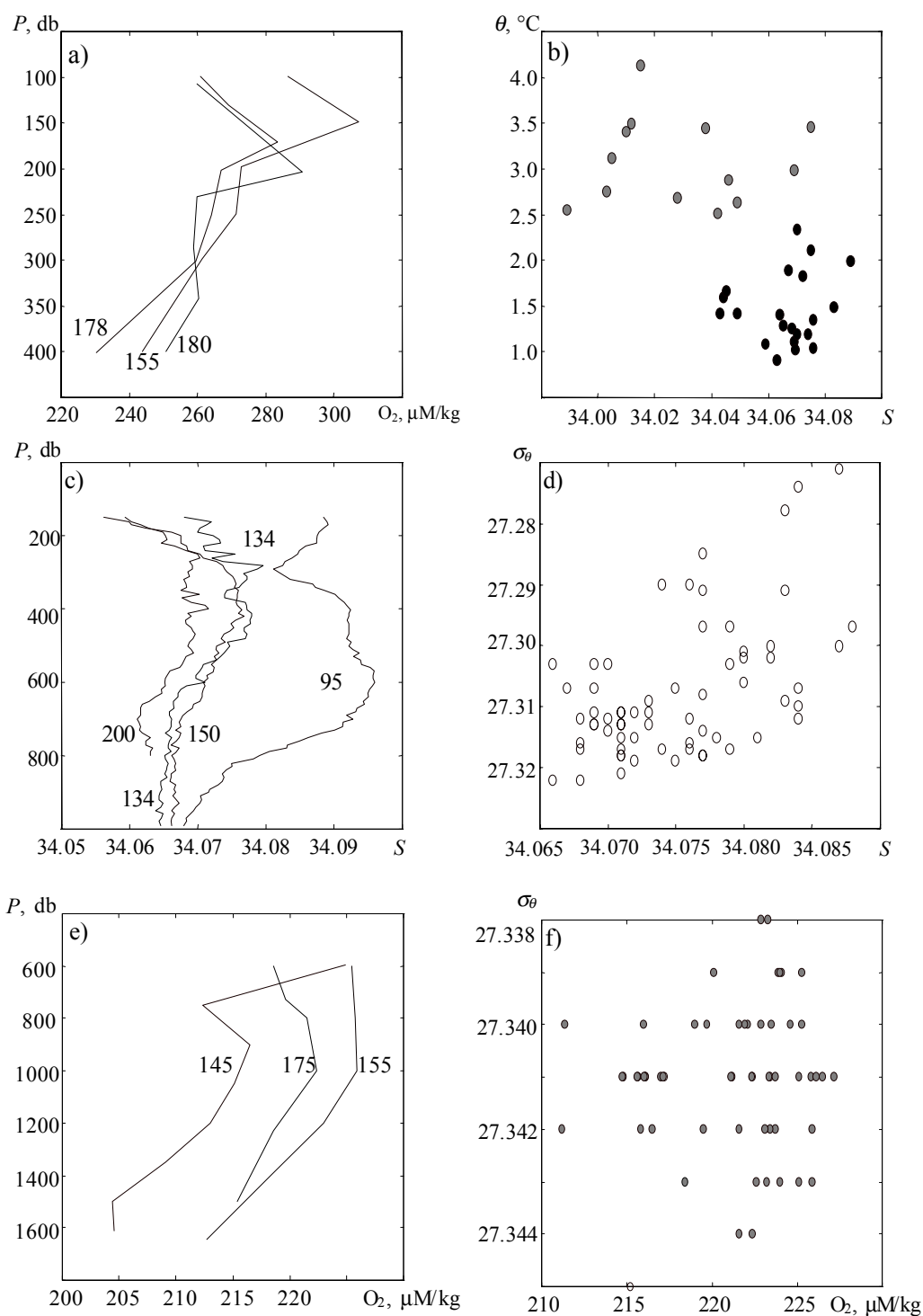
Fig. 2. Profiles of dissolved oxygen (a) and potential temperature-salinity diagram (b) for intermediate water. Profiles of salinity (c) and potential density-salinity diagram (d) for salinity maximum in the north part of the sea. Profiles of dissolved oxygen (e) and potential density-dissolved oxygen diagram (f) for weak oxygen maximum in the upper part of the deep water (north part of the sea)

Figs. 3 and 4 show distribution of oxygen and silicate concentrations on isopycnal surfaces. For comparison, we plotted maps of these parameters on different horizontal levels (Figs. 5 and 6). The same maps have been fulfilled for all hydrochemical properties. Because of fields of different chemical tracers have a similar behavior, therefore, here we demonstrate the maps of oxygen and silicate concentrations, only. Hydrochemical properties distribution shows (Fig. 3, 4, σ_θ =27.31) two areas with oxygen maximum and silicate minimum. The first of them was located approximately in the central part of Japan

Basin cyclonic gyre, second - in western part of cold sector. Apparently, it means that this isopycnal was ventilated in these two zones in previous winter. The zone located to the south of Vladivostok (41°-42°N) is known as area of formation of the upper portion of the Deep Water (Senjyu and Sudo, 1994). The second zone between warm and salty waters of the Tsushima Current and cold and fresh Liman Current was also considered as an area deep water masses formation (R/V "Vityaz" report, 1953). Convection can be the basic process of ventilation of this layer. In the first zone convection is caused by intensive winter cooling and evaporation. In the second zone the most probable source of convection is cooling of salty Tsushima Current waters which enter the cold sector as meanders, jets or eddies (Ponomarev *et al.*, 1996). For most of the stations within the Japan Basin a weak maximum of oxygen concentration have been revealed at potential densities 27.338÷27.345 (mean value is about 27.34 σ_θ). At separate stations (for example, St. 155) this layer appears as oxystad.
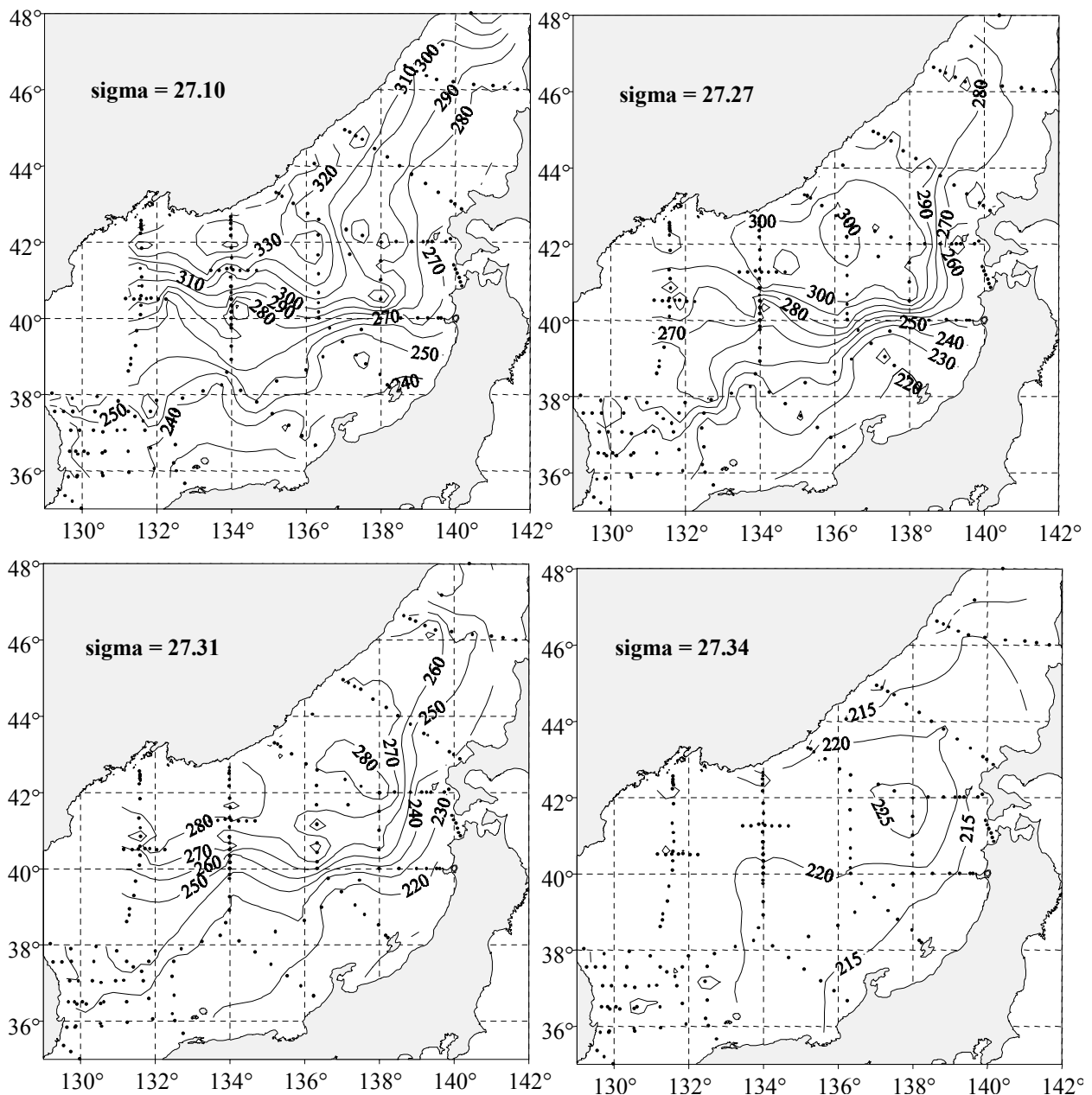

Fig. 3. Distribution of the dissolved oxygen on isopycnal surfaces: 27.21, 27.27, 27.31 and 27.34
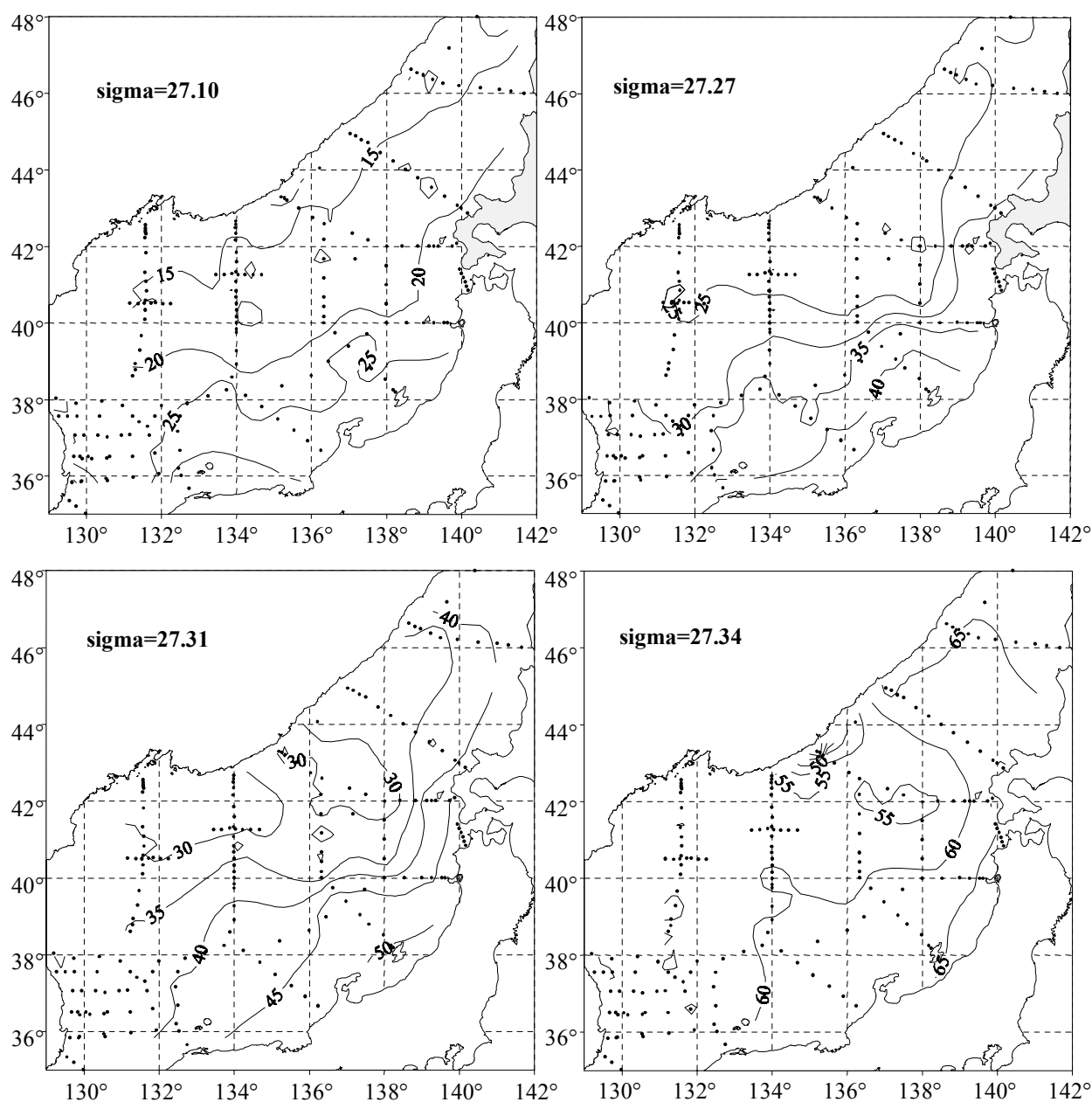
Fig. 4. Distribution of the inorganic silicate on isopycnal surfaces 27.21, 27.27, 27.31 and 27.34

The significant anomalies (increase of oxygen and decrease of silicate concentrations) in chemical fields have been found at 500 and 1000 m (Figs. 5, 6). The anomalies located around φ=40.5°N, λ=132°E and φ=41.26°N, λ=134°E practically disappeared on isopycnal surfaces 27.31 σ_θ and 27.34 σ_θ (Figs. 3, 4). In other words, they are caused by strong dynamic processes which result in deepening of isopycnal surfaces. We suggest, that anticyclonic eddies produce these anomalies. The suggestion is supported by infrared images obtained from NOAA satellites on 08/07/99 and 08/10/99 and sections presented on Fig. 8.

The anomaly located around φ=42°N, λ=138°E we call as vertical mixing area. It is revealed on different levels and isopycnal surfaces (27.31 and 27.34 σ_θ) as well. Existence of the feature on both, horizontal levels and isopycnal surfaces is evidence of diapycnal mixing. Mechanism of diapycnal mixing also can include other processes mentioned above: (1) heat exchange between two waters (warm/saline and the cold/fresh) results in contrary moving of them which gives mixing; (2) mixing forms more dense water due to volume contraction (cabbeling); (3) dense parcels spreading into deep layers which have neutral buoyancy (Tishchenko *et al.*, 2001).

Another important feature of nutrients and oxygen distributions on isopycnal surfaces is that,

nutrients concentrations are increasing and oxygen concentrations are decreasing towards the southeastern part of the Japan/East Sea. It looks as if the "age" of water grows along isopycnal surfaces in the given direction. Explanation of the phenomena is that the isopycnal surfaces are deepening in this direction (Fig.8). Owing to smooth changing of the nutrients concentrations it is not easy to distinguish polar front between south and north parts of the
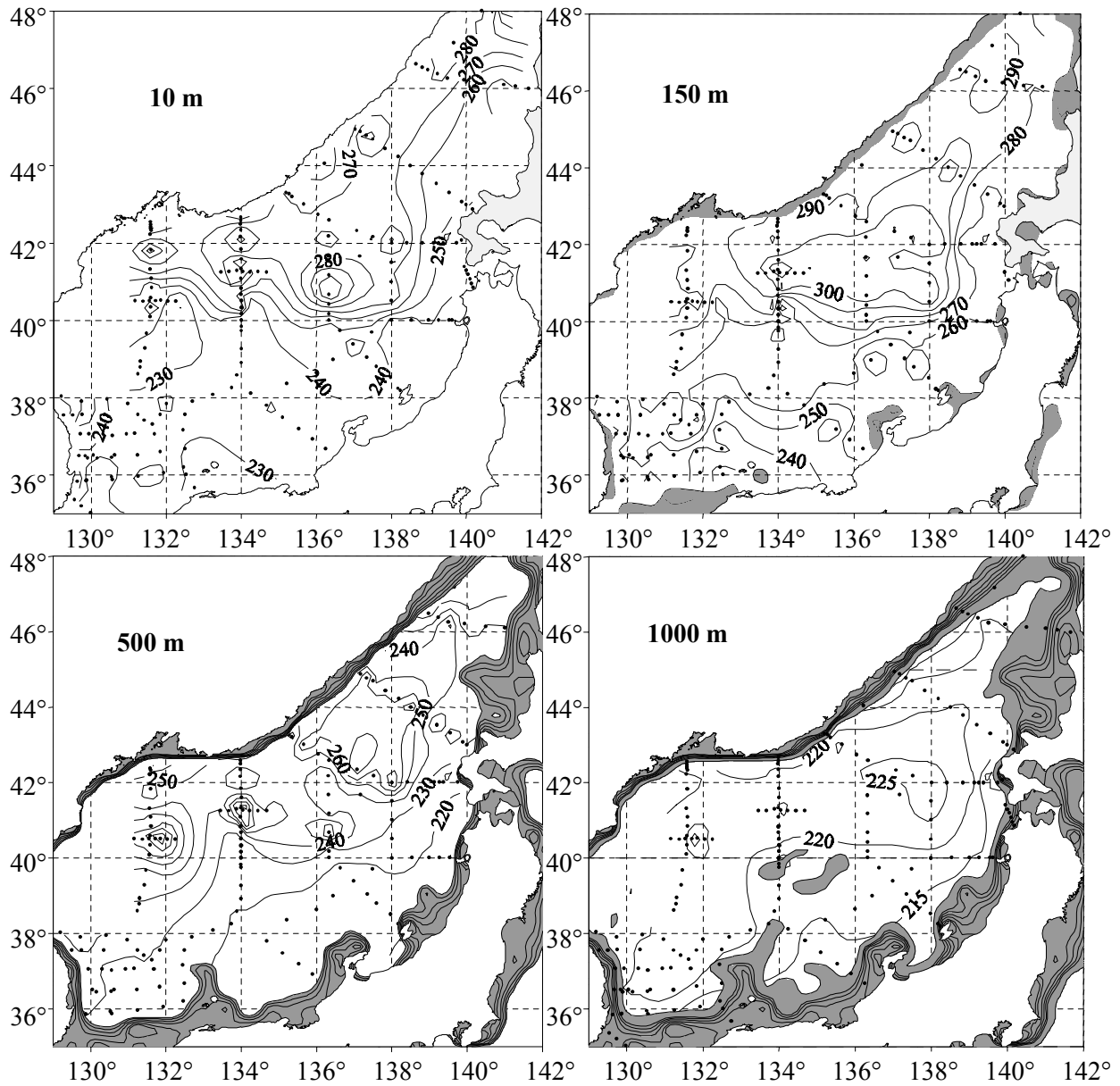

Fig. 5. Distribution of dissolved oxygen (μmol/kg) at 10 m, 150 m, 500 m and 1000 m depth

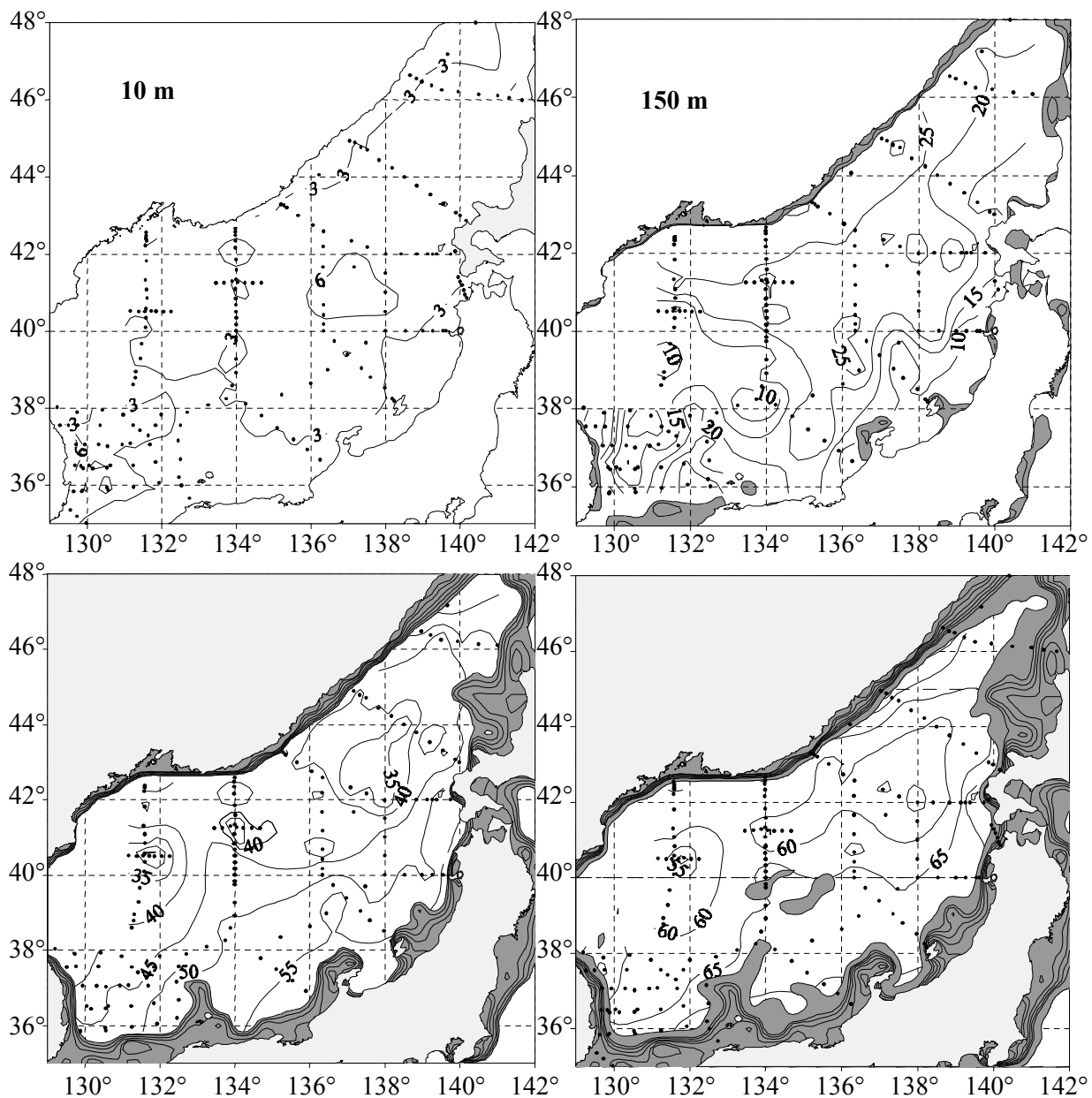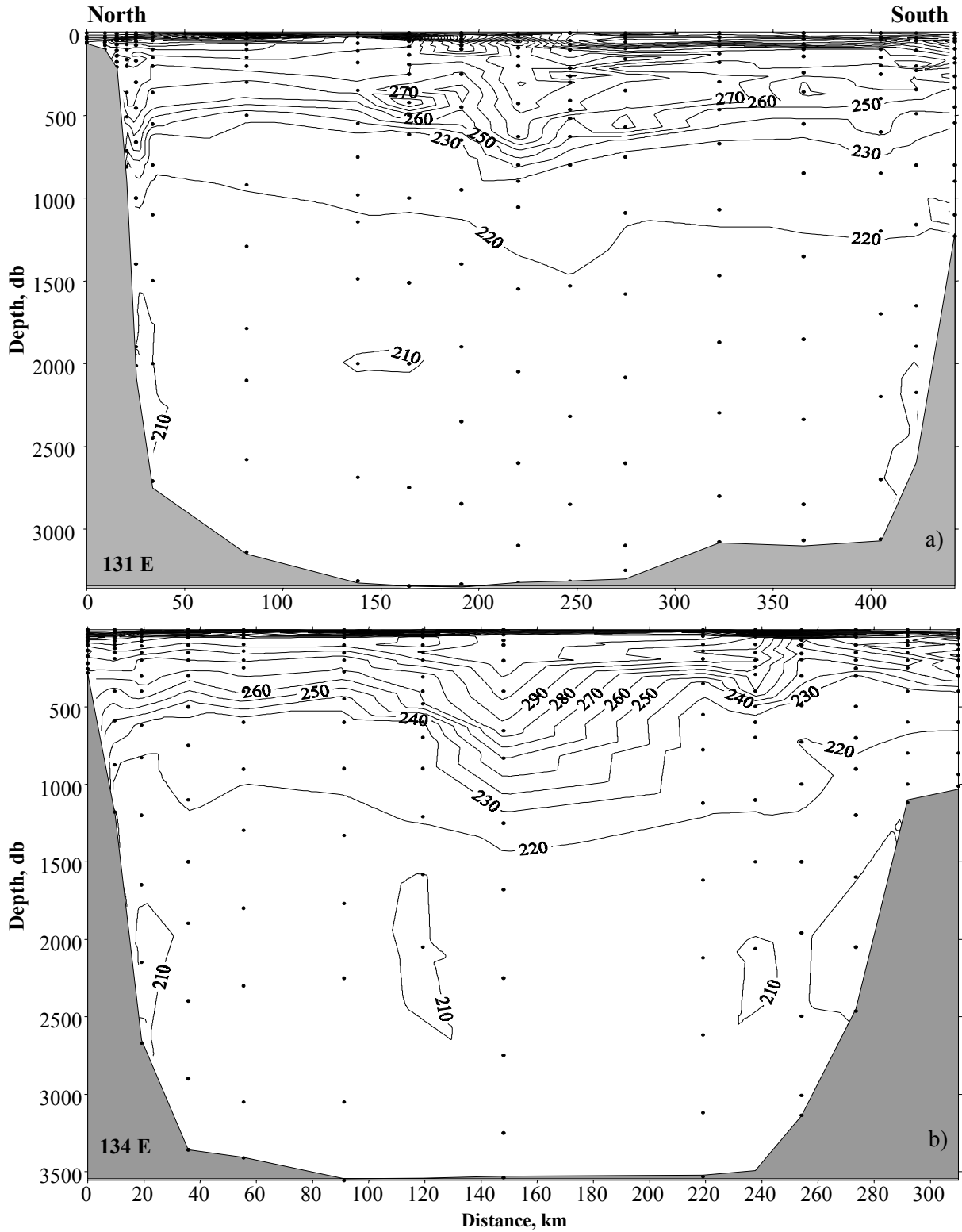*Fig. 6. Distribution of inorganic silicate (μmol/kg) at 10 m, 150 m, 500 m and 1000 m depth*

Fig. 7. Sections of dissolved oxygen (μmol/kg) across stations 203-195, 187-179 (a); and stations 157-164, 173-178 (b). Deepening of isolines at central parts of the sections corresponds to anticyclonic mesoscale eddies
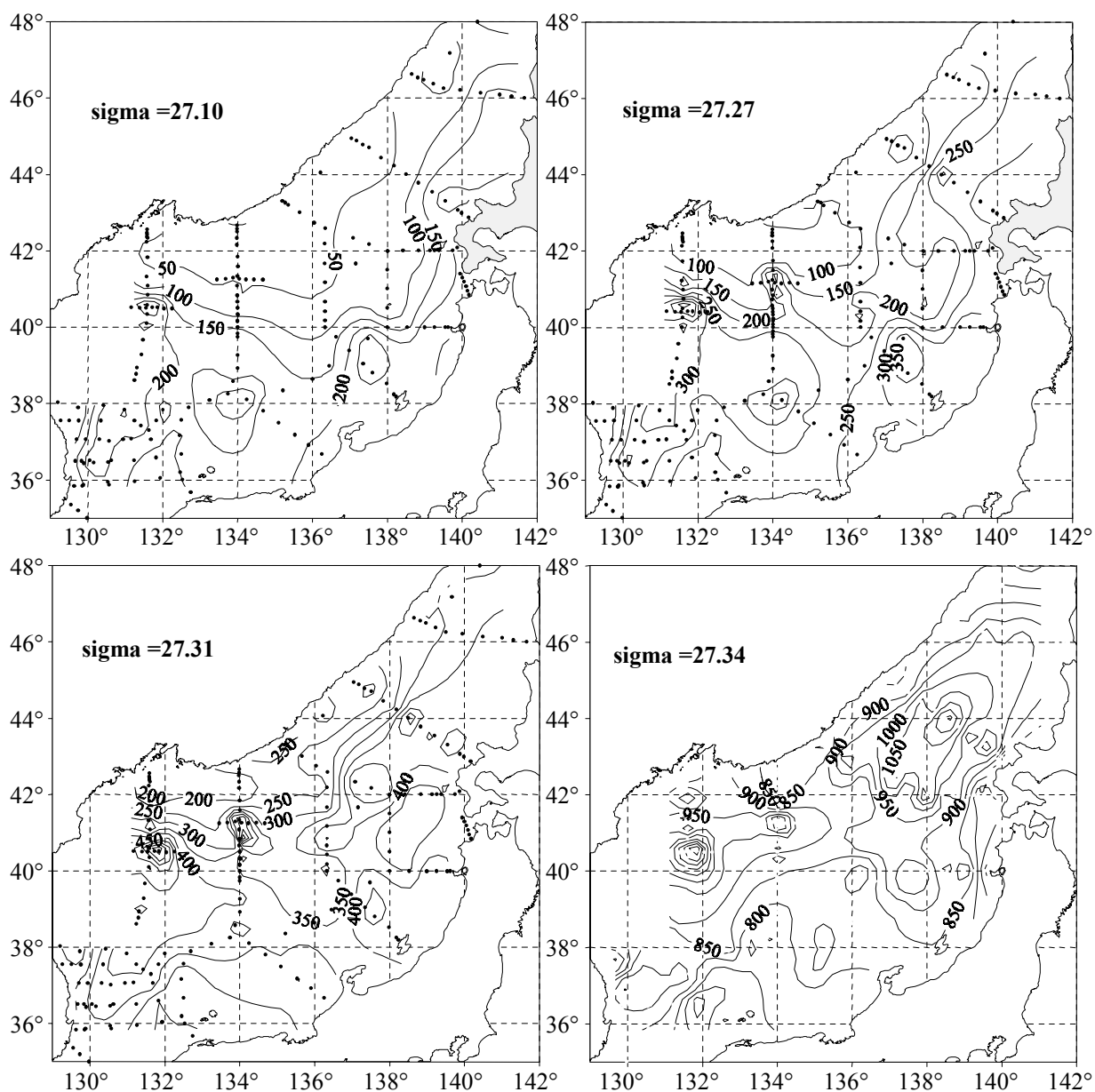
Fig. 8. Depths of the isopycnic surfaces: 27.21, 27.27, 27.31 and 27.34

Japan/East Sea by means of nutrient or carbonate system species. From all chemical parameters dissolved oxygen is the best for this task. Due to photosynthesis, nutrients are consumed from shallow levels. Concentrations of silicate decrease to less than 1 μmol/kg, phosphate – to less than 0.1 μmol/kg and nitrate concentrations reach undetectable level. However, there are anomalies of relatively high concentrations of nutrients on the shallow layers (for example, silicate on 10 m surface, Fig. 6). Nitrate and phosphate have a similar anomalies. Anomalies along coasts of South Korea can be explained by upwelling. Apparently, others are results of subsurface mixing, but nature of this is unclear.

CO_2 partial pressure have been calculated from measured pH and alkalinity using constants recommended by Millero (1995). Distribution of pCO_2 is shown on Fig. 9. The figure clearly demonstrates that most of the Japan/East Sea is sink for atmospheric CO_2. It is effect of photosynthetic activity in the summer. There are two areas around 41°N, 134°E and 41°N, 131°E where pCO_2 of surface sea water exceeds atmospheric CO_2 partial pressure, which is about 355 μatm. They are situated closely to anticyclonic eddies. Two possible processes are responsible for high pCO_2. One of them is subsurface mixing by means of eddies activity which supplies CO_2-rich water on surface. Another is heating of surface water (Tishchenko *et al.*, 1998).
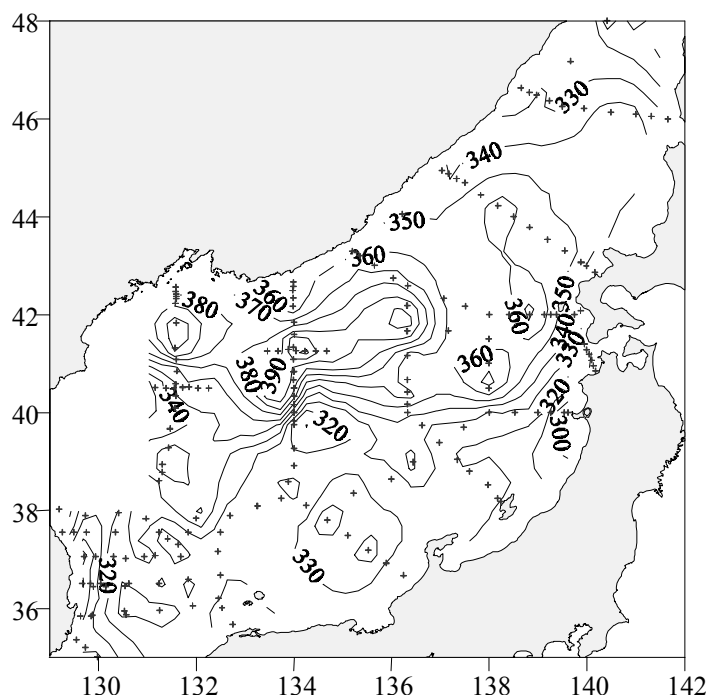
Fig. 9. Distribution of CO₂ partial pressure (µatm.) on the surface of the Japan/East Sea

Very important feature of the hydrochemical structure of the Japan/East Sea has been found on the section across stations 130-140 (latitude is about 46°N). Noticeable decreasing of dissolved oxygen and increasing of DIC, pCO_2 and nutrients concentrations has been found near bottom at 800÷1200 m depth along continental slope (Fig. 10). The similar pattern have been obtained in the next cruise of R/V "Professor Khromov" implemented on February 22 – March 23, 2000. Therefore, the decreasing of oxygen content and increasing of DIC, pCO_2 and nutrients concentrations are independent from the seasons. Additionally, noticeable ammonium concentrations (0.14 µmol/kg) and detectable amount of the nitrite have been found near seafloor in winter cruise of R/V "Professor Khromov" (the casts were taken to within 5 meters of the bottom of the sea). Before 200÷100 m to bottom, transmissivity declined on the stations which have such anomalies. Obviously this anomaly is connected with geological processes. The simplest explanation is that methane venting area is here. Due to early diagenesis of organic matter in the sediments, pore water becomes reached by ammonium (few mmol/kg), phosphate (few hundreds of µmol/kg), silicate (more than 1mmol/kg), TA (few tens of mmol/kg), and high CO_2 concentrations (pCO_2 is about 1 atm.) (Ingle *et al.*, 1990; Tishchenko, *et al.*, 2000b). Methane bubbling passing through sediments, draws out pore water into seawater forming continual flow of nutrients, TA and CO_2. At the same time ammonium must be oxidized to nitrate by dissolved oxygen in seawater. This reaction is going by means of microbiological activity and its intermediate product is nitrite. Additionally, oxygen would be consumed by microbiological oxidation of methane and ammonium. For checking of the hypothesis future investigations are necessary.

Our preliminary consideration of the hydrochemical structure of the Japan/East Sea can be summarized as follows.

1) Oxygen concentrations are decreasing and nutrients concentrations are increasing on isopycnal surfaces towards the southeastern part of the Japan/East Sea.

2) There are hydrochemical anomalies on horizontal surfaces which practically disappeared on isopycnal surfaces. These anomalies are produced by strong dynamic structures like mesoscale eddies.

3) There is hydrochemical anomaly located around φ=42°N, λ=138°E caused by diapycnal mixing. This area is characterized by intense vertical mixing and may be suggested as possible source of the Japan Sea Proper Water ventilation.

4) Most of the Japan/East Sea is sink for atmospheric CO_2.

5) Due to biogeochemical activity noticeable decreasing of dissolved oxygen and increasing DIC, pCO_2

and nutrients concentrations have been found near bottom at 800÷1200 m along continental slope around 46° latitude. It was suggested that methane bubbling passing through sediments, draws out pore water reached into seawater forming continual flow of nutrients, TA and CO_2 from sediments into seawater. Oxygen would be consumed by microbiological oxidation of methane and ammonium.
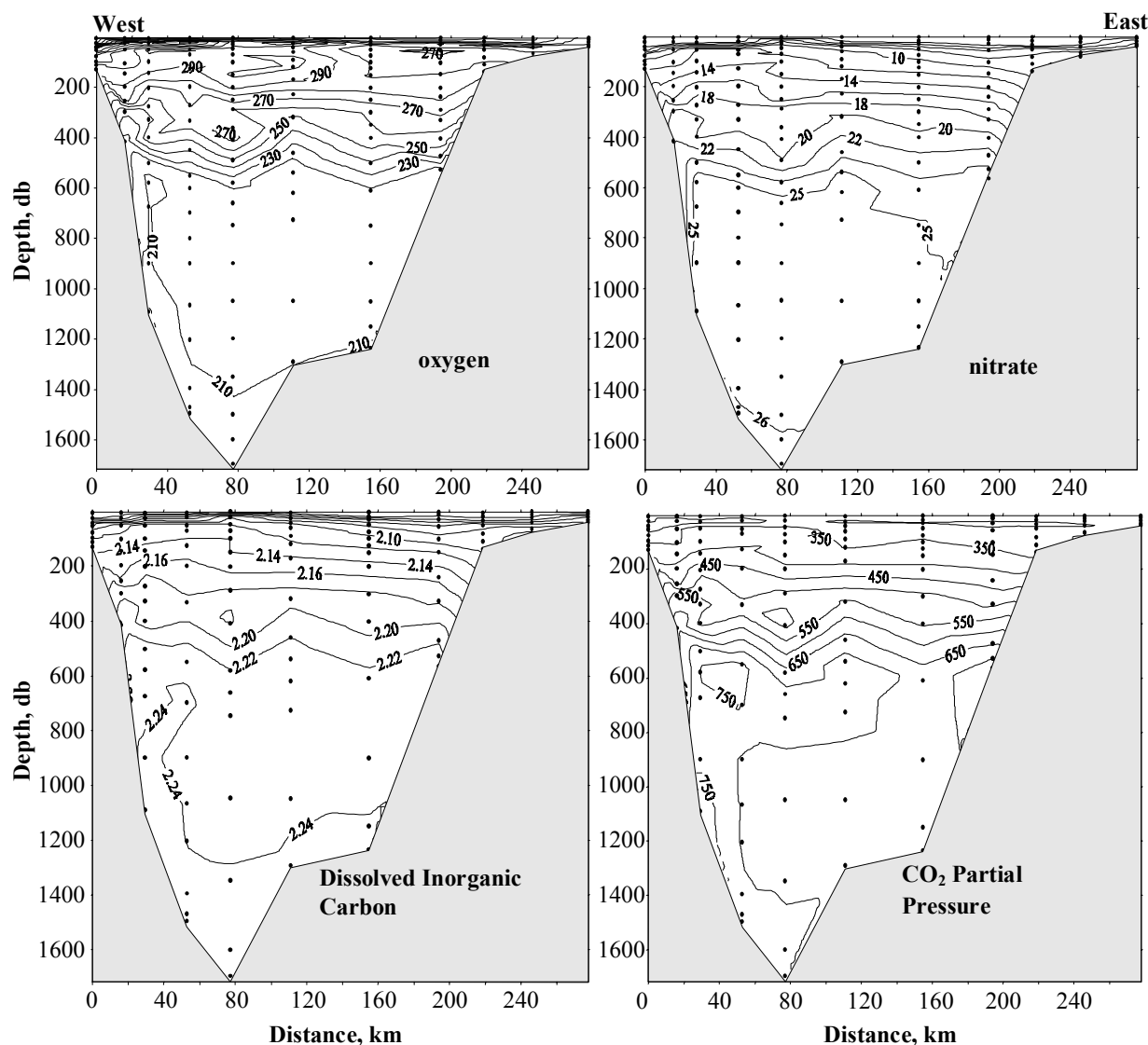

Fig. 10. Sections of oxygen (μmol/kg), nitrate (μmol/kg) concentrations and DIC (mmol/kg), pCO₂ (μatm) across stations 130-140

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