Distribution Ti in Mineral Fractions of Ferromanganese Deposits From the N-W Pacific

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Abstract. The research is presents results of titanium concentrations in mineral fractions of ferromanganese deposit deferent genesis formed in N-W Pacific active and stable tectonic settings. The obtained data are shown that the distribution of titanium in the mineral fractions of the FMD from the N-W Pacific is an additional criterion for their genetic classification. The potential ores of the Magellan seamounts Guyots contain 2.6 million tons of easily recovered titanium, which brings them closer to the reserves of titanomagnetite placers of the coastal strip of the marginal seas of the Far East of Russia Federation.

1. Introduction
Titanium, manganese and chromium are critical ferrous metals according to the doctrine of the economic development of Russia's mineral resource base (Bortnikov et al., 2016). All known titanium terrestrial deposits are composed of oxide minerals. The largest Ti deposit in the World is confined to the Yaregskoi fossil (Devonian) placer of leucoxene close to Southern Timan. The proven reserve of this deposit is tens of millions of tonnes of ore account for about 50% of Russia's total reserves (Ivanova, 2002). In the Far East of Russia, quaternary titanomagnetite placers are known in the coastal belts of the west of the Tatar Strait, the Kuril Islands, Kamchatka and several other places. Forecasted titanium resources in these placers are estimated in the first million tonnes (Andreev, 2014). The presence of fine fractions of titanium minerals in deep sediments and ferromanganese deposits (FMD) is considered a criterion for a terrestrial source.

The titanium is delivered to the global ocean as dissolved and suspended forms by river and atmospheric (eolian, pyroclastic) flow. However, the amount of titanium added annually from the continent (0.12 million tons) does not agree with the data on the annual accumulation of titanium in oceanic sediments (2.12 million tons). This deficit (2 million tons per year) is supplemented by the hydrothermal fluids (Kurnosov, 1986).

Marine FMD of different genesis contain variable amounts of titanium. The maximum content is characteristic of hydrogenous cobalt-rich crusts and decreases consecutively to diagenetic nodules and reaches a minimum in hydrothermal crusts. The average titanium content in the hydrogenetic FMD of the central Pacific varies close to 1%. This high concentration of titanium was the basis for considering it as a potential source of strategic metal. The Ti content in the hydrogenic crusts of the tropical zone of the northern Pacific is 1.27% on average and begins to decrease as the continent approaches 0.96% in the FMD of the Marshall Islands (Bau et al., 1996).
A study was carried out on the distribution of titanium in the main (four) mineral fractions of FMD in the central equatorial Pacific (Hein, Koschinsky, 2014). It has been established that in hydrogenic FMD the main value of titanium is concentrated in the hydrous Fe oxide fraction, with a minor amount in the residual fraction. Diagenetic and hydrothermal samples of FMD show the maximum values of titanium content in the residual fraction, and in the hydrous Fe oxide fraction it is very small. These facts made it possible to suggest that titanium, realized in the hydrous Fe oxide fraction, represents a discrete (separate) hydrogenic titanium phase, probably Ti(OH)₄ (Hein, Koschinsky, 2014). The distribution of titanium in the mineral fractions of various genetic types of FMD in the North-West Pacific is not known. This message is devoted to solving this issue.

2. Materials and methods

Samples for the study were selected from sediments and FMD of the main genetic types draged from various morphostructures of the seabed of back-arc basins and close areas of the North West Pacific. Modern sediments were recovered from the Derugin Basin of the Sea of Okhotsk, hydrothermal Fe crusts (ochers, umbers) from the slopes of the local basin of the Philippine Sea, hydrothermal manganese crusts from the underwater Belyaevsky Volcano in the Sea of Japan, hydrogenogenic ferromanganese crusts from the underwater Volcano 1 (Zonne Ridge) and the tectonic mountain in the Kashevarov Trough in the Sea of Okhotsk and, in addition, cobalt-rich crusts of Detroit and Yomei Guyots (the northern closure and the central part of the Imperial Range, respectively), Seth (western end of Markus-Wake), Magellan and Marshall Islands, and diagenetic nodules from Deriugin Basin and Yomei Guyot. The study of the distribution of titanium in the mineral fractions (easily leachable adsorbed cations and carbonates - 1 phase, manganese oxides - 2 phase, iron hydroxides - 3 phase and residual - 4 phase) was carried out by sequential selective leaching on the ICAP6500 Duo spectrometer (Thermo Electron Corporation, USA) in Central Committee of the Far Eastern Geological Institute of the Far Eastern Branch of the Russian Academy of Sciences (Mikhailik et al., 2017).

3. Results and discussions

The results indicate that the first fraction is characterized by the minimum values of titanium content (hundredths and thousandths part %). The lowest values are characteristic for hydrothermal both iron and manganese differences (0.08 - 0.3 ppm). Increase is observed in hydrogenic crusts in marginal seas, as well as diagenetic nodules and biogenic-terrigenous sediments (0.11 - 0.53 ppm). And then is increased in cobalt-rich crusts of guyots as the distance from the continent (0.85-1.00 ppm) to the middle of the Pacific (1.06 - 1.53 ppm).

In the Mn oxide fraction (2), low titanium contents have also been obtained. The minimum values are determined in all hydrothermal deposits and sediments (0.04 - 6.4 ppm). Above the concentration in the hydrogenic crusts of the marginal seas (10-97 ppm) and at the guyots (6-83 ppm, and in individual layers increase to 153 ppm) are observed. High values are characteristic for diagenetic nodules (151 ppm).

In the hydrous Fe oxide fraction (3), the maximum variability in the content of titanium is observed. Hydrothermal formations (both iron and manganese) contain a minimum of titanium (1.2 - 55 ppm). A little higher than the values noted in the sediments (104 - 157 ppm), then they increase in diagenetic nodules (692 - 1193 ppm) and the marginal hydrogenic crusts (792 - 4982 ppm) and the maximum values are reached in the hydrogenic crusts from guyots 5534 - 11282 ppm).

In the residual fraction (4), the lowest titanium content is found in hydrothermal iron crusts (3.9-40 ppm), and in hydrothermal manganese crusts it is higher (68-470 ppm). Hydrogenic crusts of Yomei Guyot (170 ppm), Seth Guyot (380 ppm) and Magellan seamounts (62 - 617 ppm) are characterized by similar values. The content of titanium in the hydrogenic crusts of the marginal seas (244-1 1160 ppm) and the Marshall Islands (380-1311 ppm) is slightly higher. The amount of titanium in diagenetic nodules (290 - 1344 ppm) is the same range The maximum quantity were founded both detrital sediments (1543 - 2980 ppm) and hydrogenic Detroit Guyot crusts (2050 - 2540 ppm), located
close to the continent.

4. Conclusions
The relative distribution of titanium in the mineral fractions of FMD and detrital sediments of the N-W Pacific is shown in the figure and indicates a visible difference between these genetic types. In all hydrogenic FMD, the total amount of titanium is distributed in fraction 3 (69% on average - the marginal sea and 87% - oceanic guyots) and fraction 4 (29% and 12%, respectively). Diagenetic and hydrothermal FMD samples, as well as modern sediments, show a different distribution (figure). These data indicate that the distribution of titanium in the mineral fractions of the FMD from the N-W Pacific is an additional criterion for their genetic classification.

The dry ore reserves of cobalt-rich crusts from the five Magellan Guyots of the North Pacific Prime Zone are estimated at 337.4 million tonnes (Andreev, 2007). The ores contain 0.81% titanium (an average of 212 tests (Melnikov, 2009)). According to our data, the hydrous Fe oxide fraction of FMD Magellan Guyots is 96%. Consequently, the potential ores of the Magellan seamounts Guyots contain 2.6 million tons of easily recovered titanium, which brings them closer to the reserves of titanomagnetite placers of the coastal strip of the marginal seas of the Far East of Russia Federation.

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![Figure 1](image_url) Distribution Ti in mineral fractions of detrital sediments and ferromanganese deposits from the N-W Pacific.

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