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Russian Geology and Geophysics 57 (2016) 1465–1476

RUSSIAN GEOLOGY AND GEOPHYSICS

www.elsevier.com/locate/rgg

Composition and parageneses of massive pyrolusite from the deep-water basin of the Sea of Japan

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Received 26 March 2015; received in revised form 23 December 2015; accepted 29 January 2016

Abstract

Hard fragments (crushed only by a hammer) of manganese deposits differing strongly in appearance from the regional ferromanganese crusts were sampled from depths of 3500–3200 m during the dredging of an unnamed seamount in the Central Basin of the Sea of Japan. Their surface has a black carbonaceous coating; after its removal, the crusts become steel-gray. The specific weight of these crust fragments is 3.35 g/cm^3, whereas the regional crusts have a specific weight of <2 g/cm^3. X-ray diffraction analysis showed that the sampled fragments consist of pure pyrolusite. There are also fragments of crusts formed by todorokite and birnessite. All pyrolusite samples have an abnormally high content of Mn (up to 63%). The Mn/Fe ratio reaches 9016. The conclusion is drawn that the manganese crusts formed on this seamount are of hydrothermal genesis.

Keywords: ferromanganese crusts; pyrolusite; birnessite; todorokite; Sea of Japan

Introduction

Pyrolusite is widespread on the Earth's surface as natural highest manganese oxide. It is deposited in sea and lake littorals in oxic conditions, often forming commercial accumulations. Sedimentary manganese deposits form from colloid solutions supplied with river waters and coagulating in sea littorals. Their coagulation is favored by dissolved mineral salts serving as electrolytes. In the surface oxidation zone, all Mn minerals pass into pyrolusite, which forms pseudomorphs after them. Hydrothermal pyrolusite deposits are very rare (Betekhtin, 1950).

In deep zones of the World Ocean, vernadite, birnessite, todorokite, buserite, and asbolan-buserite are major Mn minerals in ferromanganese crusts and in nodules formed by iron and manganese oxides with high impurities of clay and terrigenous minerals. Other Mn minerals, including pyrolusite, are scarce and minor (Baturin, 1993; Bazilevskaya, 2007; Mel'nikov, 2005).

In 2011, during voyage 58 on the *Akademik M.A. Lavrentiev* r/v, geological sampling from an unnamed seamount in the east of the Japanese (Central) Basin of the Sea of Japan was carried out (Fig. 1). During the dredging of the western slope of the seamount, a large number of fragments of ferromanganese deposits (FMD), mostly crusts, was sampled. Among them were fragments of hard heavy FMD with black carbonaceous coating, differing strongly from ore crusts of the marginal seas of the northwestern Pacific.

Methods

The FMD samples were studied by mineralogical and physicochemical methods. The mineral composition of ferromanganese crusts was examined on a DRON-2 X-ray diffractometer. The density of samples was determined by hydrostatic weighing of dry nonparaffinaceous samples at a VLTE-2100 balance.

The contents of major and trace elements in FMD were measured by ICP-AES at the Center for Common Use, Vladivostok, using an iCAP 6500Duo (Thermo Scientific Corporation, US) spectrometer. The LOI and SiO_2 contents were determined by the gravimetric method. All analyses were carried out on weighted samples dried at 105 ºC. The relative standard deviation of results for matrix elements does not exceed 4–5%, and that for trace elements is given in Table 1. These data were obtained by 11 independent analyses of the Russian standard ferromanganese crust sample GSO 5376-90 (OOPE 604) (Zarubina et al., 2014).

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1068-7971/$ - see front matter
http://dx.doi.org/10.1016/j.rgg.2016.09.003

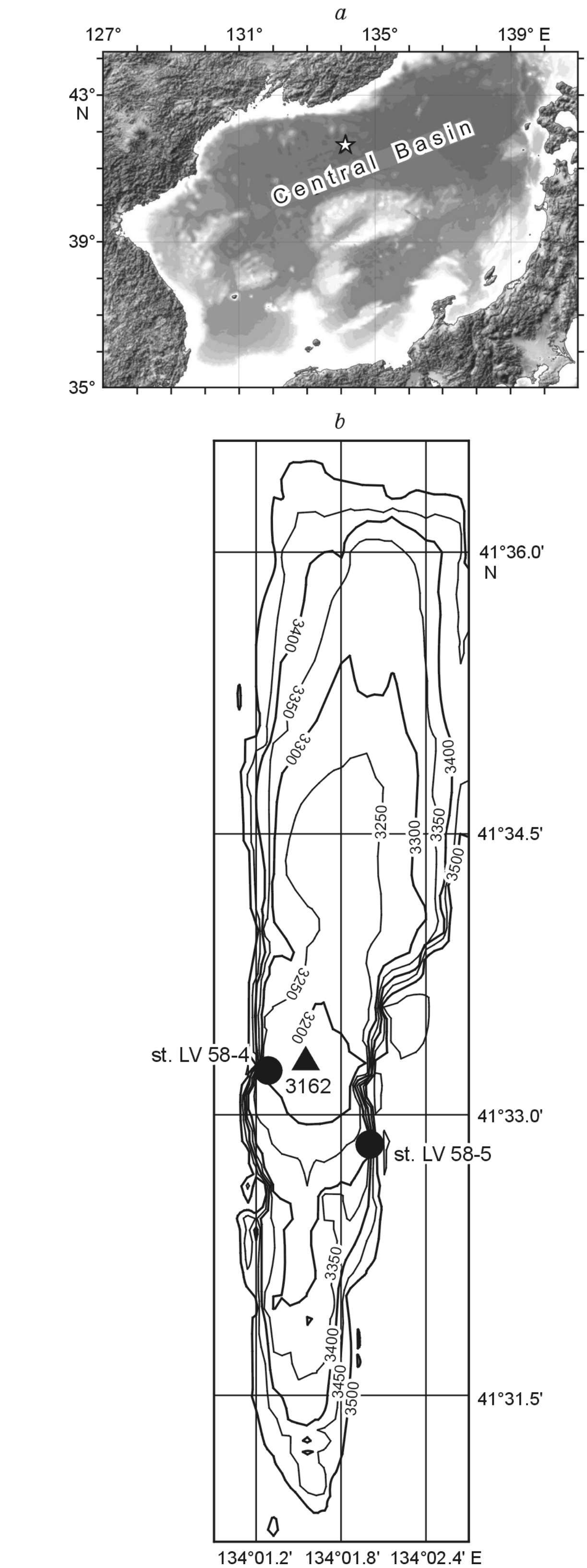

Fig. 1. Location (*a*) and topography (*b*) of the unnamed seamount in the Central Basin of the Sea of Japan (from data of voyage 58 on the *Akademik M.A. Lavrentiev* r/v).

The microstructure and stages of ore deposition were elucidated by studying the polished sections of ferromanganese crusts on a JXA-8100 (JEOL, Japan) microprobe with three wave spectrometers equipped with an INCAx–sight (OXFORD Instruments, England) energy dispersive spectrometer at the Center for Common Use, Vladivostok. Polished sections were prepared using organic-based diamond pastes free of impurities amounting to ≤0.01 wt.% (detection limit of the microprobe).

Geologic structure of the unnamed seamount

The unnamed seamount in the Japanese (Central) Basin of the Sea of Japan was discovered by the staff of the Pacific Oceanological Institute, Vladivostok, during seismic works performed in the course of voyage 7 on the *Professor Gagarinskii* r/v (Karnaukh et al., 2007). In 2011, during voyage 58 on the *Akademik M.A. Lavrentiev* r/v, bathymetric survey and geological sampling (dredging) of the slopes of this seamount were performed to study its size and structure (S"edin et al., 2014). The research showed that the seamount extends to ~10.5 km strictly in the N–S direction and is well expressed along the 3500 m isobath (Fig. 1). In the northern part, the width of the seamount at the foot is ~2.2 km, and in the southern part it is ~1.2 km. The peak is localized at a depth of 3350–3300 m. It is virtually a plateau, with a gentle uplift at the center, reaching depths of <3200 m (minimum depth is 3162 m). A distinct shallow-depth (relative depth of

Table 1. Element contents (ppm) in the GSO 5376-90 (OOPE 604) standard ore crust sample

Element	Determined (n = 11)	S	S_1	Certified
Cu	1319 ± 52	77	5.8	1300 ± 100
Ni	3263 ± 151	226	6.9	3400 ± 200
Co	2738 ± 162	241	8.8	2700 ± 100
Zn	553.9 ± 32.8	48.9	8.8	600 ± 50
Pb	1049 ± 53	79	7.5	1050 ± 50
As	140.4 ± 19.0	28.3	20.0	140 ± 30
Mo	350.3 ± 16.3	25.2	7.2	350 ± 30
W	51.98 ± 2.86	4.25	8.1	
Cr	59.43 ± 3.46	5.15	8.7	67 ± 8
V	566.3 ± 27.4	40.9	7.2	540 ± 60
Ba	1599 ± 33	49	3.1	1600 ± 200
Sr	1099 ± 54	81	7.4	1100 ± 100
Li	20.10 ± 2.03	3.03	15.0	19
Rb	19.10 ± 1.40	2.09	11.0	19 ± 3
Cs	0.80 ± 0.04	0.06	7.9	–
U	6.71 ± 0.45	0.67	10.0	6 ± 2
Zr	512.2 ± 18.7	27.8	5.4	550 ± 40

Note. n, Number of independent analyses; S, root-mean-square deviation; S_1, relative root-mean-square deviation ($S_1 = S \cdot 100 \pm \%$). Data were borrowed from Zarubina et al. (2014).