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# Compositional Variations and Genesis of Sandy-Gravel Ferromanganese Deposits from the Yōmei Guyot (Holes 431, 431A DSDP), Emperor Ridge

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**Abstract:** This research presents results characterizing the mineral and chemical composition of ferromanganese (Fe-Mn) deposits from Yōmei Guyot (Holes 431 and 431A), recovered during the Deep-Sea Drilling Project (DSDP) Leg 55 R/V "Glomar Challenger". The Fe-Mn deposits are represented by sandy-gravel clasts. The mineral composition and bulk concentration of major and minor elements, as well as the distribution of rare earth elements and yttrium patterns in mineral fractions of Fe-Mn samples, showed that the deposits are composed of fragments of Fe-Mn hydrogenetic crusts and diagenetic nodules. The morphology of Fe-Mn clasts from Holes 431 and 431A DSDP, as well as a comparison with growth conditions of Fe-Mn deposits from N-W Pacific Guyots, allowed us to establish a Late Pliocene age for the formation of this Fe-Mn placer from Yōmei Guyot. Accumulations of ferromanganese clasts in a sedimentary unit led us to classify this geological body as a new mineral resource of the World Ocean.

Keywords: Fe-Mn placer; mineralogy; geochemistry; phase analysis; Yōmei Guyot; Emperor Ridge

## 1. Introduction

### 1.1. Background

Three genetic types of ferromanganese (Fe-Mn) deposits are widely distributed and have been studied in detail in the World Ocean. These are hydrogenetic crusts, hydrogenetic and diagenetic nodules, and hydrothermal deposits, each are distinguished based on the type of aqueous fluid from which the Fe-Mn (oxyhydr)oxides precipitate [1].

Ferromanganese (cobalt-rich) crusts are composed of Fe oxyhydroxide and Mn oxide, which precipitate directly from cold, ambient ocean water onto solid rock substrates. A wide variety of metals such as Co, Ti, Mn, Ni, Pt, Zr, Nb, Te, Bi, Mo, W, Th, as well as rare earth elements and yttrium (REY) are sorbed from ocean water onto those two main mineral phases (Fe oxyhydroxide and Mn oxide) [1–3].

Ferromanganese nodules are composed of Fe oxyhydroxide and Mn oxide and form by hydrogenetic and diagenetic precipitation onto a hard nucleus on the surface of soft sediment. Diagenetic precipitation occurs from sediment pore fluids consisting of ocean water modified by chemical reactions within the sediment column. Diagenesis may take place under oxic or suboxic conditions, with the boundary generally defined as a 5  $\mu$ M oxygen concentration. Mixed origin Fe–Mn nodules are more common than either of the end-member types. Ferromanganese nodules have gained



recognition as potential resources for a wide variety of elements such as Ni, Cu, Co, Mn, Mo, and Li [1–3].

Hydrothermal manganese and iron deposits occur near hot-spot volcanoes, submarine arc volcanoes, and less commonly at spreading centers [1]. These are generally either pure Fe oxyhydroxide or pure Mn oxide deposits, and form either within the sediment column or at the seabed from ascending fluids. These deposits are not usually crusts but rather stratabound layers that are distinctly different in texture and composition from crusts. If the hydrothermal fluids enter the water column, then Mn colloids progressively sorb metals from ocean water; the Fe–Mn crust forms rapidly and exhibits a hydrogenetic composition. Near the vent sites, the crusts are classified as mixed hydrogenetic–hydrothermal crust deposits. Hydrothermal Fe deposits contain low concentrations of minor metals, whereas, hydrothermal Mn deposits may have high concentrations of one or more of Mo, Li, Cr, Zn, and Ni [1–3].

These three genetic types of Fe-Mn (oxyhydr)oxide deposits are characterized by differing distributions of rare earth elements with yttrium (REY) in bulk samples [1,4], as well as in the main mineral phases [5–7].

Various factors cause ferromanganese deposits in the marine environments to be destroyed and redeposited. Intensive bottom water currents around seamounts and guyots can cause the erosion of hydrogenous crusts and the movement of fragments down the slopes, leading to post-deposition in depressions. These conditions cause the formation of breccia lenses/layers. They might form either the substrate for new crusts. For example, ancient (cretaceous) clastic phosphatized layers are substrate for younger layered hydrogenic crusts of the Marshall, Magellan, and other Pacific Guyots [8,9]. Opposite, clastic Fe-Mn deposit can cover laminated ones. For instance, 16 cm thick hydrogenous crust covered by 25 cm thick Fe-Mn breccia on the South Tasman Rise [10].

Nodules are also subject to substance destruction, with post-depositional changes in deeper parts (>2 mm) having been observed. These are believed to be caused by post-depositional dehydration [11,12]. Older nodule fragments can serve as nuclei for newly formed nodules [3].

Hydrothermal Mn breccias occur on the volcanic slopes in back-arc basins [13], island arcs [14], and hot spots [15]. They form due to a number of reasons including the formation of calderas [16].

The largest known deposit of Fe-Mn fragments is located at the top of the Yōmei Guyot of the Emperor Ridge. It was recovered by two drilled holes during the 55th cruise of the R/V Glomar Challenger [17], and studied by the participants of that cruise. The deposit was cored at a depth of 17 mbsf and contains unconsolidated Fe-Mn fragments, 80–90% of which range in size from gravel to sand; the mineral composition was studied using X-ray diffraction methods [17]. Ferromanganese crusts are represented by amorphous oxyhydroxides and weakly crystallized todorokite [17]. The contents of major elements in five samples and trace elements in three Fe-Mn samples were determined using the arc spectrometry and ARL quantometry methods [17]. The Fe content varies from 3.8 to 6.4%, and that of Mn varies from 3.9 to 10.7%. The average Fe is 5.1% and average Mn is 8.0%. Twelve trace elements (Sr, Ba, V, Ni, Co, Cr, B, Zn, Ga, Cu, Pb, and Sn) were analyzed.

The chemical and mineral composition of Fe-Mn fragments reflect the authigenic formation, and Fe-Mn oxides formed with the occasional inputs of hydrothermal fluids caused by a halmyrolysis of volcanic material in cold deep-water oxidative conditions [17]; i.e., the deposit has a hydrothermal-hydrogenous genesis.

Based on these results, additional assessments of the exploitation potential of Fe-Mn deposits at the Yōmei and Nintoku Guyots were carried out during the 9th cruise of R/V "Geologist Peter Antropov" by "Dalmorgeologiya" in 1990. The geological and geophysical studies included subbottom acoustic profiling, bathymetric surveying, sampling with a clamshell sediment sampler equipped with a camera, and sampling with a cylindrical dredge. The mineral composition of 22 Fe-Mn samples from Yōmei Guyot was studied using X-ray diffraction (XRD) methods. A content of 27 elements and losses on ignition of 18 Fe-Mn samples were determined by a number of methods: Mn by potentiometric titration; Si, Ti, Al, Ca, Na, K, P, and losses on ignition (LOI) using X-ray fluorescencespectroscopy

(XRF); Fe, Ni, Cu, and Co determinations by atomic absorption; and Ba, Pb, Sr, Zn, Mo, Zr, La, Ce, Nd, Sm, Eu, Nb, W, As, and Sb determinations using X-ray radiometric and neutron activation analysis [18].

These investigations showed that the ferromanganese deposits are composed of vernadite and 10Å manganate with minor occurrence of 7Å manganate. The average content of Mn is 21.9%, that of Fe is 12.9%, and the average sum total of Ni, Cu, and Co is 0.98%. The concentrations of other elements are also slightly different from the average composition of crusts from the Pacific Seamounts [18]. These values are higher than those in the ferromanganese core samples (431 and 431A DSDP) [17]. Closest to Yōmei Guyot, Nintoku Guyot lies at similar water depths and is characterized by the absence of the deposit cover. Due to these features, M. Melnikov [18] suggested that in the Fe-Mn deposits of the Yōmei Guyot, hydrothermal genesis was predominant and hydrogenous input had a lesser influence.

Thus, Fe-Mn deposits in hole sediments and on the surface of solid host rock at the Yōmei Guyot have a combination of hydrothermal and hydrogenous genesis [17,18]. However, more recent studies indicate the hydrogenic genesis of Fe-Mn deposits from the Pacific Ocean guyots [2,3]. Here, to clarify the genesis of the Yōmei Guyot Fe-Mn deposits, we determined the mineral and chemical compositions of 431 and 431A DSDP core samples using ICP-AES and ICP-MS analyses of both the bulk samples and the main mineral phases. The metal distributions within the mineral phases were estimated using the sequential leaching of 4 mineral phases: I—easily leachable adsorbed cations and carbonates; II—Mn-oxide; III—Fe-oxyhydroxide; and IV—residual components [19]. The distribution of trace elements [20] and REY [7] in the mineral phases of hydrothermal and hydrogenous crusts strongly reflects their genesis. In addition, the fragmented Fe-Mn deposits of Yōmei Guyot might be identified as another type of Fe-Mn marine deposit. However, a different type name has not yet been proposed distinguishing it from hydrogenous crusts of seamounts and guyots, hydrogenic and diagenetic nodules of abyssal basins, and hydrothermal crusts of underwater volcanoes. Finally, we studied the deposition factors in shelf mineral placers in order to select criteria for the genetic identification of deep-sea Fe-Mn fragmented deposits.

#### 1.2. Geological Setting

Geological and geophysical surveys of Yōmei Guyot were carried out during the cruise of Lee8-76-NP by R/V "S.P. Lee" in 1976 [21], cruise 55 by R/V "Glomar Challenger" in 1977 [22], and cruise 9 by R/V "Geologist Peter Antropov" in 1990 [18,23]. Yōmei Guyot is located on the same basement as Nintoku Guyot: both guyots are part of the central Emperor Ridge (Figure 1). The size of the Yōmei Guyot base at 3500 m depth is  $80 \times 65$  km, and the top is located at 890 m depth. The guyot has a conical shape with well-defined northwest and northeast spurs. The summit has steep southern and shallow northern slopes with a size of  $40 \times 30$  km at 1500 m depth. The surface has abrasion outcrops, terraces, small hills, and hollows.

The top of the Yōmei Guyot and most of its slopes have been swept clean of sediments (Figure 2a) and are covered by Fe-Mn crusts and pavements with sparse nodules lying on them. The densest Fe-Mn deposits form a narrow submeridional zone (more than 30 kg/m<sup>2</sup>) (Figure 2b). Crust growth proceeded in at least three stages [18] and had an episodic pattern. The absence of sediments at the guyot top is probably caused by high velocities of bottom water currents. This is also reflected in the smooth, polished surface of Fe-Mn deposits and volcanic rocks, as well as in the unidirectional inclination of filtering hydrobionts, which were identified by underwater photos. Four sites with a negative bottom relief were found (Figure 2a), where the thickness of the deposited detrital (mostly redeposited) material and biogenic rocks is up to 50 m. Two holes (431 and 431A DSDP) were drilled at one of these sites. In the lower parts of the guyot slopes, and on the basement slopes, the sediment thickness increases sharply with increasing ocean depth.



**Figure 1.** Scheme location of Yōmei Guyot and other seamounts and Yōmei Guyot bathymetry [24] with location of Holes 431 and 431A DSDP (insert). YG—Yōmei Guyot, DG—Detroit Guyot, GG—Govorov Guyot, SG—Seth Guyot, ZG—Zubov Guyot, DB—Derugin Basin, KT—Kashevarov Trough, ZC—Zonne Chain, BV—Belyaevsky Volcano.



**Figure 2.** Sedimentary sheath thickness (**a**) and ferromanganese deposits location (**b**) within the Yōmei Guyot [18,22]: 1—acoustic background, 2—location of Fe-Mn deposits, 3—area with maximum thickness of Fe-Mn deposits, 4—seismic reflection track lines, 5—clamshell sediment sampler stations and their numbers, 6—dredge stations and their numbers, 7—DSDP Holes, 8—isopachs (m); 9—isobaths (m).

#### 2. Materials and Methods

Thirteen samples of Fe-Mn fragments from 431 and 431A DSDP holes were studied. The sampling intervals are presented in Table 1 and Figures 3 and 4.

Hole	Core	Section	Interval, cm	Code		
			40-50	YM-01		
		1-1	70–80	YM-02		
431	1		110-120	YM-03		
			140-150	YM-04		
		1-2	0–10	YM-05		
			30–40	YM-06		
		1-1	110–112	YM-09		
	1		140–145	YM-10		
431A		1-2	5–7	YM-11		
			30–32	YM-12		
	_		25–27	YM-18		
	2	2-2	42–44	YM-19		
			53–55	YM-20		

Table 1. Sampling interval in 431 and 431A DSDP Holes from Yomei Guyot.

X-ray diffraction was carried out using a MiniFlex II diffractometer (Rigaku Corporation, Tokyo, Japan) with CuK $\alpha$  radiation. The voltage on the X-ray tube was 30 kV, and the tube current was 15 mA. The scanning speed was 1° 2 $\theta$ /min. The scan angle ranged from 2.5° to 60°. The diffractometer was also equipped with a selectively absorbing Ni filter to suppress K $\beta$  lines. The ICDD 2010 database was used for mineral identification.

The chemical composition was determined by using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) (Ti, Al, Fe, Mn, Mg, Ca, Na, K, and P), the Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)(Li, Be, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb, Mo, Cd, Cs, Ba, Hf, Ta, W, Tl, Pb, Th, U and rare-earth elements), and the gravimetric method (Si).

ICP-AES was performed on an ICAP6500 Duo spectrometer (Thermo Electron Corporation, Waltham, MA, USA), which was calibrated using a multi-element certified ICP Multi Element Standard IV (Merck, Germany) solution. ICP-MS was carried out on an Agilent 7700 × quadrupole mass spectrometer (Tokyo, Japan). The OOPE 601 and OOPE 602 standard samples of the Fe-Mn nodules were analyzed to assess the accuracy.

Acid dissolution using a mixture of concentrated HF,  $HNO_3$ , and  $HClO_4(1:5:1)$  was used to determine the bulk element contents of studied samples.

We used sequential leaching to study the distribution of elements in the mineral phases of Fe-Mn crusts [19,20,25,26].

The sequential leaching procedure used in our experiments included the following stages:

Phase I—leaching of 1 g of powdered sample with acetate buffer (CH<sub>3</sub>COOH (1 N) + CH<sub>3</sub>COONa·3H<sub>2</sub>O (1 N), pH = 5) for 5 h at 25 °C at a 1:50 reagent ratio. This led to the extraction of Ca carbonates and related elements, and to the release of sorbed ions. The solution was filtered, mineralized in a microwave using concentrated HNO<sub>3</sub> and analyzed by ICP-AES and ICP-MS. The residue was washed with Type I deionized water, dried, and used in further leaching.



**Figure 3.** Fragments of Fe-Mn deposits from Hole 431 DSDP and sampling interval location (core photo from [27].



Figure 4. Fragments of Fe-Mn deposits from Hole 431A DSDP and sampling interval location (core photo from [27].

Phase II—extraction of Mn and related elements by 0.1 M hydroxylamine hydrochloride solution (pH = 2) for 24 h at 25 °C at a 1:100 sample/reagent ratio. The solution was filtered by filter paper (3–5  $\mu$ m), the hydroxylamine in the solution was decomposed using concentrated HNO<sub>3</sub> and heating (170 °C), and after evaporation, the precipitate was dissolved in 5% HNO<sub>3</sub>. Solutions were analyzed using ICP-AES and ICP-MS. To complete Mn extraction, the hydroxylamine concentration was increased to 0.5 M, as suggested in [26]. Time intervals of 3 min and 24 h were chosen to determine the optimal leaching time. In both cases, the degree of leaching of Mn was the same, but with an increase in Fe dissolution during 24 h leaching. A final Mn extraction scheme included leaching with a 0.5 M solution of hydroxylamine over 3 min. After phase I, the ratio of the sample/reagent was 1:100. The solution was filtered, the hydroxylamine in the solution was decomposed using concentrated HNO<sub>3</sub> and heating, and after evaporation the precipitate was dissolved in 5% HNO<sub>3</sub>. Solutions were analyzed using ICP-AES and ICP-MS. After phase II, the residue was washed, dried, and left for further leaching.

Phase III—extraction of Fe-hydroxides using a mixture of 0.2 M oxalic acid and ammonium oxalate (pH = 3.5) for 12 h at 25 °C at a 1:175 sample/reagent ratio. The solution was evaporated to form wet salts and concentrated HNO<sub>3</sub> was added to destroy the organic matrix. After evaporation, the residue was dissolved in 5% HNO<sub>3</sub>. The obtained solutions were analyzed using ICP-AES and ICP-MS.

Phase IV—the solid residue from the previous stages, presented by aluminosilicates, together with the filter (filter paper) were ignited at T = 600 °C in a muffle furnace. Then, the residue was digested in Teflon bombs using a mixture of HF, HNO<sub>3</sub>, and HClO<sub>4</sub>(1:5:0.5) with heat (170 °C) applied to the wet salts, which were diluted by 2% HNO<sub>3</sub> to volume 25 mL. Solutions were analyzed using ICP-AES and ICP-MS.

Analyses were performed at the Center for Collective Use of the Far Eastern Geological Institute of the Far Eastern Branch of the Russian Academy of Sciences, Vladivostok, Russia.

#### 3. Results

Ferromanganese deposits recovered from the DSDP 431 and 431A holes are represented mainly by sharp-edged fragments and, more rarely, by slightly rounded fragments (Figures 3 and 4). The structure is usually massive or, less often, laminar. The sediment is mostly characterized by an anthracite luster (85%), but some parts have a dull luster.

The size of the Fe-Mn fragments is in the range of sandy gravel and varies from 1 to 27 mm, gradually increasing to the core bottom: ranging from 4 to 15 mm (middle size) in the 431 core and from 3 to 20 mm in the 431A.

The mineral composition of the studied samples is represented predominantly by vernadite ( $\delta$ -MnO<sub>2</sub>). However, 10Å and 7Å manganates were determined in YM-12 and YM-20 samples from the 431A hole. Accessory minerals include quartz, plagioclase, and smectite.

The bulk chemical composition of 431 and 431A DSDP samples is shown in Table 2. A ternary plot of Fe:Mn:(Co + Ni + Cu) × 10 (Bonatti diagram [28], Figure 5) shows that most of the studied samples fall within the hydrogenic crusts field, however, YM-12 and YM-20 samples are located beyond the field limit. Manganese, Si, K, Mg, Li, Cr, Sb, and Ba are enriched and Fe, Ti, P, Be, Se, Sr, Zr, Mo, Nb, Ta, Hf, Tl, Pb, Th, U, and REY declined in the YM-12 and YM-20 samples. The contents of other elements such as Al, Ca, Sc, V and W do not vary.

We also studied the mineral and chemical composition of the YM-12 and YM-20 samples to determine the reason for differential element accumulation. The sample 431-5 from the YM-05 interval of the 431 DSDP hole has maximum sums of Co, Ni, Cu, and  $\Sigma$ REY of 10,963 ppm and 3042 ppm, respectively (Table 2), which are typical for hydrogenous crusts [2], therefore it was selected as a main group. We chose the 431A-12 sample from the YM-12 interval of the 431A hole as a representative sample of the contrast group. It is enriched in Mn (31.38%) and Cr (14.4 ppm), as is typical for hydrothermal deposits [2]. Karpoff et al. (1980) [17] and Melnikov (1993) [18] suggested hydrothermal influence at the Yōmei Guyot. We studied the REY distribution in the main mineral phases of the 431-5 and 431A-12 samples to assess whether this was true. The REY pattern distribution in manganese

and iron mineral phases of hydrothermal-hydrogenetic deposits has a peculiarity. The Mn phase inherits the composition of the initial hydrothermal fluid and has an extremely small  $\Sigma$ REY. The Fe phase approaches the REY pattern distribution seen in hydrogenetic Fe-Mn crusts of guyots and has increased by an amount of REY [7].

The mineral composition of the 431-5 sample is composed of vernadite ( $\delta$ -MnO<sub>2</sub>), and sample 431A-12 contains 10Å and 7Å manganates. Table 3 presents the chemical composition of these two samples in comparison with the Fe-Mn crusts from the different regions of the Pacific Ocean. The Mn and Fe contents in the 431-5 sample from the Yōmei Guyot are 28.89% and 15.57%, respectively, and in 431A-12, they are 34.96% and 8.76%, respectively. The differences are observed in the major elements (Si, Al, Ti, K, and P), trace elements (Li, Be, Cr, As, Sr, Nb, Mo, Ba, Ta, Tl, Pb, Th, and U), and REY. Some chemical elements have similar values (Sc, Ga, Cd) or exhibit slight variations (V, Co, Ni, Cu, and Zn).

Table 4 shows the distribution (concentration (ppm) and percentage (%)) of the main elements (Ca, Mn, Fe, Si and Al) and REY in the mineral phases of the Yōmei Guyot Fe-Mn deposits.

Phase I (easily leached cations and carbonates) contains about 2/3 of Ca (70.66% and 68.46% in 431-5 and 431A-12 samples, respectively). The Mn, Fe, Si, and Al contents are extremely small. The  $\Sigma$ REY does not exceed 0.44% (431-5) and 1.31% (431A-12) (Table 4). The minimum Ce content varies from 0.01–0.09% and the maximum Y concentration is in a range from 2.79–4.60%. Moreover, the highest concentrations are observed from Sm to Dy.

Mn oxides (Phase II) contain most of the Mn (97.76% and 98.18% in 431-5 and 431A-12, respectively), and 28.78% (431-5) and 26.94% (431A-12) of Ca. Fe, Si and Al contents in phase II are similar to the values of Phase I. 57.32% (431-5) and 53.45% (431A-12) of La were released with the Mn fraction (Table 4). The  $\Sigma$ REY is 41.31% for 431-5 and 39.73% for 431A-12.

Phase III (Fe (oxyhydr)oxides) dissolves 88.88% (431-5) and 69.16% (431A-12) of Fe together with 99.05% (431-5) and 92.51% (431A-12) of P. The distribution of REY is different in phase III. 431-5 samples have depleted levels of REY compared to 431A-12 (Table 4). The REY concentrations in both samples increase from light to heavy with the maximum Lu content (Table 4). The REY accumulation in Fe phase dominates the Mn phase, starting from Tm in sample 431-5 and from Ce in sample 431A-12. The  $\Sigma$ REY are 10.43 (431-5) and 43.14% (431A-12).

Phase IV (the residual aluminosilicates) contains the bulk of Si and Al: in 431-5 they are 85.77 and 46.81%, respectively; in 431A-12, they are 94.77 and 72.31%, respectively. Other element contents are low, except for K. The  $\Sigma$ REY in sample 431-5 reached 47.82%. Eu had the maximum content, of 69.77%. Sample 431A-12 is characterized by a moderate accumulation of REY, 15.65% with the maximum content of Sm, 24.8%



**Figure 5.** Fe-Mn deposits from Yōmei Guyot on the Mn-Fe-(Cu+Co+Ni) × 10 ternary diagram [28]. 1—samples composed by vernadite; 2—samples composed by 10Å and 7Å manganates (Table 2).

Table 2. Bulk chemical composition of the 431 and 431A DSDP Holes Fe-Mn deposits	
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	Hole 431 DSDP Hole 431A DSDP												
Liement –	YM-01	YM-02	YM-03	YM-04	YM-05	YM-06	YM-09	YM-10	YM-11	YM-12	YM-18	YM-19	YM-20
							%						
Si	2.10	2.15	2.61	2.05	1.54	1.59	3.36	4.11	3.59	5.09	1.82	2.57	3.36
Al	0.37	0.37	0.50	0.33	0.29	0.23	0.39	0.44	0.48	0.64	0.25	0.51	0.41
Ca	2.68	2.70	2.53	2.60	2.78	2.70	2.49	2.34	2.23	1.46	2.80	2.60	1.71
Fe	13.04	13.83	13.87	14.15	13.68	13.71	12.35	12.84	12.96	10.54	14.75	15.68	10.26
K Ma	0.48	0.48	0.54	0.46	0.50	0.46	0.56	0.65	0.64	0.97	0.41	0.41	0.84
Mg	1.11	1.10	1.14	1.10	1.14	1.17	1.20	1.42	1.21	1.00	1.11 27.12	1.34	1.48
Na	27.07	21.07	27.00	20.40	29.45	27.83	20.85	3.36	2.38	1.83	2 52	24.23	2 13
P	0.38	0.40	0.48	0.40	0.39	0.41	0.39	0.35	0.38	0.24	0.38	0.48	0.22
Ti	0.75	0.72	0.70	0.66	0.72	0.68	0.70	0.62	0.71	0.24	0.64	0.60	0.38
LOI	18.10	17.60	19.60	20.40	19.40	21.60	20.80	20.90	19.80	16.20	20.30	21.00	19.00
	ppm												
Li	3.33	3.09	8.84	2.58	1.8	1.28	4.81	6.1	4.91	6.84	2.47	11	25.5
Be	3.24	3.41	3	3.26	3.06	3.13	2.55	2.64	2.98	1.99	2.85	3.39	1.89
Sc	5.36	5.43	5.61	5.44	5.73	5.39	4.75	4.75	4.98	4.41	5.20	6.23	5.73
V	756	768	745	761	828	773	621	583	568	522	780	703	629
Cr	4.34	4.85	7.42	3.00	3.38	7.52	4.65	1.22	10.1	14.4	2.84 4012	6.67 4142	9.67 2720
Ni	4343 5275	4210 5052	5215	4227	4327 5771	5042	3995	4203 3625	4043	3335	4013	4143 5431	4588
Cu	566	521	608	495	665	383	490	459	488	282	348	507	-587
Zn	638	597	624	540	651	532	703	716	744	910	479	646	1109
Ga	36.8	32.1	33	31.6	35.1	31.4	32.2	29.5	31	26.7	32.1	29.3	27.8
As	238	252	221	240	236	244	169	158	169	104	235	251	122
Rb	4.35	4.35	5.03	3.85	3.88	3.24	5.46	6.3	6.36	14.8	2.86	3.37	9.72
Sr	1481	1482	1440	1471	1537	1496	1483	1372	1403	945	1512	1350	1203
Y	149	157	161	163	154	162	100	94	106	66	166	174	95
Zr	419	413	447	424	439	396	409	366	386	178	360	421	357
Nb	41.9	40.3	36.9	35.5	38.8	38.2	37.8	31.6	34.9 679	12.5	31.8	28.2	19
Cd	4.62	5.02	923 5.97	979 4 54	5 12	4.62	6.22	55	61	447 5.43	3 75	4 40	491 7 37
Cs	0.17	0.17	0.19	0.11	0.12	0.1	0.22	0.28	0.27	0.86	0.12	0.14	0.46
Ba	1836	1551	1644	1423	1736	1345	3019	3060	2772	4362	1343	1143	5645
La	232	235	230	238	223	257	173	166	178	81	254	217	110
Ce	2185	2000	1795	1911	2145	1894	2008	1654	1771	429	1790	1289	619
Pr	53.9	53.4	51.4	53.5	53.1	60.1	39.8	36.4	39.9	16.7	55.2	49.6	21.3
Nd	224	225	219	228	222	252	165	151	167	71	232	215	93
Sm	49.1	48.7	48.5	50.6	48.8	55.7	36.1	33.6	36.5	15.6	50.6	47.6	20.2
Eu C-l	11.6	11.8	11.8	12.1	11.8	13.0	8.8 40.2	8.1	8.8 10 1	4	12.2	11.4 50.2	5.5 27.0
Ga Th	00.4 7.83	65.7 8.02	64 8.02	65.2 8.26	04.0 7 96	09.1 9.02	49.3 5.81	44.8 5 39	40.1 5 78	20.4 2.65	04.2 8 27	39.3 7 79	27.9 3.63
Dv	44.1	45.4	46.3	46.9	45.4	51.4	32.3	29.5	32.5	15.9	47.8	45.1	22.4
Ho	8.55	9.03	9.21	9.34	8.76	9.96	6.27	5.79	6.41	3.27	9.55	8.84	4.7
Er	24.9	26.5	27.2	27.4	25.7	28.8	18.2	17.1	18.6	10	28.1	25.7	13.7
Tm	3.56	3.83	3.84	3.89	3.78	4.22	2.66	2.48	2.59	1.41	3.97	3.66	1.91
Yb	23.9	25.1	25.6	25.8	24.2	27.6	17.5	16.4	17.8	9.7	26.2	23.4	13.8
Lu	3.54	3.78	3.75	3.95	3.67	4.11	2.62	2.41	2.68	1.47	3.90	3.42	2.07
Hf	7.25	7.04	7.12	5.91	7.21	6.40	6.75	5.88	6.74	2.65	4.80	5.17	5.54
Ta	0.39	0.39	0.35	0.28	0.39	0.42	0.3	0.31	0.41	0.09	0.28	0.26	0.17
VV TI	141	139	135	141	165	133	107	97	94 26	74	139	97 107	93 16
11 Ph	100	2051	∠0ð 1990	2068	192	205 2261	50 1761	24 1561	∠0 1678	13 773	203 1990	127 1935	10
Th	27.7	2001	28.3	32.0	27.2	22.01	27.4	24.7	25.1	7.7	26.5	34.9	12.9
U	13.3	14.1	14.2	14.3	14.4	14.4	11.4	10.1	10.2	6.2	13.7	12.7	7.8
$\Sigma$ REY	3087	2919	2705	2847	3042	2898	2666	2267	2442	748	2752	2181	1054

Note: LOI—loss on ignition.

Floment	431-5	431A-12	ΤK	DB	PB	ZC	GG	GZ	GS	GD	VB
Liement -						%					
Si	2.37	5.25	7.93	12.3	4.82	12.38	2.48	4.82	4.53	3.21	0.68
Al	0.37	0.72	1.93	2.88	1.5	2.14	0.45	1.25	1.13	0.31	0.34
Ca	2.80	1.23	1.36	2.56	1.82	1.97	2.63	2.94	2.84	2.71	1.51
Fe	15.57	8.76	5.79	1.28	6.12	17.20	18.36	18.52	13.35	16.85	4.01
Κ	0.51	1.21	1.30	1.05	0.81	0.71	0.46	0.67	0.65	0.45	0.93
Mg	1.15	1.96	1.47	1.04	1.71	0.83	1.19	1.01	1.06	1.08	1.29
Mn	28.89	34.96	32.48	31.7	34.2	15.33	25.48	22.97	25.11	28.70	52.90
Na	1.95	1.62	1.61	3.02	2.65	2.35	1.92	1.67	1.95	2.04	2.48
Р	0.47	0.15	0.15	0.04	0.15	0.32	0.40	0.29	0.27	0.40	0.02
Ti	0.75	0.12	0.19	0.1	0.16	0.37	1.35	1.29	1.06	0.84	0.058
LOI	19.29	16.11	11.67	11.3	16.20	10.21	21.41	16.25	13.42	14.34	14.07
						ppm					
Li	3.20	19.5	30.1	285	311	3.12	0.99	2.19	0.56	1.61	843
Be	3.67	1.34	1.39	0.5	1.4	2.76	5.29	5.33	2.41	4.31	0.23
Sc	5.62	5.16	4.27	3.94	7.58	9.55	16.4	9.44	5.45	7.71	1.03
V	802	617	606	258	431	427	815	637	449	734	266
Cr	0.68	17.10	16.7	16.2	16	13.1	2.1	9.58	21.7	13.9	8.21
Co	3708	4654	559	47.1	475	671	5876	5414	4719	3828	187
Ni	4561	3139	5885	821	13,008	2422	4162	4165	6227	5130	729
Cu	373	611	1477	74.9	5988	310	1026	1340	856	809	93
Zn	531	810	986	608	1845	419	643	639	537	609	243
Ga	6.77	5.24	14.7	13.1	31.7	10	16.6	5.61	9.09	10.9	19.1
As	310	87.5	110	20.1	n.d.	214	264	215	152	245	47
Sr	1597	968	952	466	687	1030	1815	1564	1244	1805	989
Y	178	53.7	78.4	18.2	69	130	202	165	111	178	14.8
Zr	455	145	154	23.2	325	456	523	746	386	541	7.7
Nb	43.9	7.97	10.8	1.4	13.2	26.7	47.9	73.3	47.7	47.2	1.09
Mo	1044 5 20	435	752	363	547	350	649	452	379	712	285
Ca Pa	5.29 1.492	0.01 0007	23.1	2680	10.0	3.33 1102	3.74 1654	3.80 1742	4.95	5.8 1012	7.3
Da	201	66.2	102	2000	60	104	240	275	1011	204	0495 141
La	1005	100.5	510	14.9	00 110	194 722	1058	275	10 <del>4</del> 1116	304 1925	14.1 20.2
Dr.	1995 66 5	199	22 5	2.68	110	733 51.4	77.2	547	20.0	74.1	20.3
Nd	266	13 55 4	23.5	5.00 16.1	63	213	296	04.7 210	164	212	2.7 11 7
Sm	58.3	12.1	21.6	3.4	14	46.8	290 61	47.1	34.3	70	23
E11	13.2	2 92	5 37	0.89	3.87	40.0 11 1	15.1	10.8	8 37	16.4	0.61
Cd	58.9	13.3	23.8	4.02	15.6	11.1	68.9	47.9	38.8	72.6	29
Th	9.84	2.14	3.89	0.62	2.52	7.64	10	8.08	5.96	11.4	0.43
Dv	55.5	12.6	23.7	4.02	15.8	43.6	55.5	43.4	34.5	61.3	2.8
Ho	11	2.66	4.75	0.59	3.42	8.18	11.1	9	6.84	11.7	0.54
Er	32.6	7.82	14.2	1.86	9.8	23.7	30.8	25.8	19.9	33.5	1.7
Tm	4.64	1.15	2.09	0.25	1.49	3.24	4.32	3.79	2.83	5.03	0.21
Yb	29.9	7.6	14	2.4	10.3	21.6	27	22.9	18.9	32	1.5
Lu	4.51	1.18	2.16	0.37	1.61	3.25	3.98	3.47	2.79	4.78	0.21
Hf	5.78	1.64	1.95	0.08	4.74	8.37	6.11	12.6	6.77	6.15	0.05
Та	0.36	0.08	0.2	0.01	0.23	0.31	0.6	0.94	0.68	0.33	0.06
W	139.5	95.7	136	112	75	57.3	89.8	71.7	70.9	128	21
T1	192.2	9.47	71.2	12.5	129	71.7	167	163	159	56.3	3.4
Pb	2274	446	405	7.37	121	597	1571	1349	1371	1847	15.9
Th	29.6	6.19	7.35	1.57	6.9	48.3	16.5	11.9	28.8	23.3	0.41
U	15	4.28	5.27	7.19	4.28	9.39	13	11.8	9.19	15.4	6.4
ΣREY	3074	451	931	97	401	1540	2270	1912	1788	3013	76.8
Ce/Ce*	3.31	1.56	2.39	0.78	0.82	1.69	1.49	1.83	3.00	2.80	0.76
Y <sub>SN</sub> /Ho <sub>SN</sub>	0.57	0.71	0.58	1.09	0.71	0.56	0.64	0.65	0.57	0.54	0.97

**Table 3.** Bulk chemical composition of the samples 431-5 µ431A-12 compare with Fe-Mn deposits from different geological settings.

**Note:** LOI—loss on ignition; n.d.—not detected; TK—Kashevarov Trough [29]; DB—Derugin Basin: our unpublished data; PB—Peru Basin [30]; ZC—Sonne Chain [31]; GG—Govorov Guyot [32]; GZ—Zubov Guyot: our unpublished data; CS - Seth Guyot [33]; GD—Detroit Guyot [34]; VB—Belyaevsky underwater volcano [35]; Ce/Ce\*—cerium anomaly.

	431-5													
Element	Fraction I		Fraction II		Fraction III		Fraction IV		Σ	Bulk	R			
	ppm	%	ppm	%	ppm	%	ppm	%	ppm	ppm	%			
Si	398	1.68	198	0.84	2775	11.71	20,325	85.77	23,697	23,697	100			
Ti	0.95	0.02	32.2	0.51	6118	81.95	171	2.71	6323	7466	85			
Al	18.5	0.53	262	7.47	1589	42.97	1646	46.82	3517	3699	95			
Fe	2.26	0.00	16,484	10.72	136,616	87.76	602	0.39	153,705	155,666	99			
Mn	20.4	0.01	275.312	97.76	5924	2.05	372	0.13	281,630	288,925	97			
Mø	7911	78.63	1715	17.05	252	2.20	181	1.81	10.061	11,495	88			
Ca	17 900	70.66	7289	28.78	40	0.14	101	0.41	25 333	27 966	91			
Na	n a	n a	16.076	96.98	9.62	0.11	490	2.96	16 577	19 519	85			
K	3330	66.25	110,070	23.88	18.0	0.05	471	0.30	5018	5112	98			
R D	16.0	0.35	E 7	25.00	10.9	0.57	17.2	9.39	4104	4729	90			
Г У	10.0	0.4	3.7	0.14	4154	07.00	17.5	0.41	4194	4750	100			
Ŷ	5.25	2.79	98.9	52.54	44.6	25.10	39.5	20.98	188	178	106			
La	1.81	0.64	162	57.32	19.5	6.69	99.2	35.13	282	291	97			
Ce	0.20	0.01	793	40.90	172	8.64	973	50.20	1938	1995	97			
Pr	0.42	0.66	23.8	37.38	5.03	7.56	34.4	54.05	63.6	66.5	96			
Nd	2.28	0.88	91	35.02	19	7.14	148	56.79	260	266	98			
Sm	0.73	1.20	15.9	26.16	5.13	8.79	39.1	64.22	60.9	58.3	104			
Eu	0.17	1.05	3.36	21.03	1.3	9.88	11.1	69.77	15.9	13.2	121			
Gd	0.85	1.23	17.6	25.56	6.15	10.45	44.3	64.29	69	58.9	117			
Th	0.12	1 27	2 76	29.40	1 49	15.18	5.02	53 44	94	9.84	96			
Dv	0.12	1.26	14.9	29.10	11 1	20.09	24.6	47.93	51.4	55.5	93			
Бу Цо	0.05	1.20	2 27	21.22	2 68	20.07	4 25	41 74	10.4	11	04			
F.,	0.15	1.29	0.20	21.52	2.00	24.24	4.55	41./4	20.7	22 (	7 <del>1</del> 01			
Er	0.55	1.17	9.30	31.52	9.35	28.72	10.7	35.83	29.7	32.0	91			
Im	0.04	0.92	1.28	29.38	1.76	37.91	1.27	29.19	4.35	4.64	94			
Yb	0.24	0.87	7.40	27.20	12.9	43.22	6.66	24.49	27.2	29.9	91			
Lu	0.04	0.99	1.20	29.06	1.97	43.65	0.91	22.12	4.12	4.51	91			
$\Sigma$ REY	13.3	0.44	1245	41.31	314	10.22	1441	47.82	3014	3074	98			
Ce/Ce*	0.05		2.87		4.00		3.77		3.34	3.31				
Y <sub>SN</sub> /Ho <sub>SN</sub>	1.43		1.07		0.59		0.32		0.64	0.57				
						431A-12								
Si	<d.l.< td=""><td>n.a.</td><td>173</td><td>0.33</td><td>2569</td><td>4.90</td><td>49,745</td><td>94.77</td><td>52,489</td><td>52,489</td><td>100</td></d.l.<>	n.a.	173	0.33	2569	4.90	49,745	94.77	52,489	52,489	100			
Ti	0.49	0.05	43.9	4.28	692	67.44	289	28.23	1026	1186	86			
Al	23.7	0.35	261	3.89	1579	23.45	4870	72.31	6735	7163	94			
Fe	3.25	0.00	6758	7.80	59,954	69.17	19,964	23.03	86.680	87,583	99			
Mn	626	0.19	329,141	98.18	5213	1.56	264	0.08	335,246	349.576	96			
Mø	5527	29.45	8906	47 46	737	3.93	3595	19.16	18 766	19 550	96			
<u>6</u> Са	7312	68 46	2877	26.94	52.9	0.50	437	4 10	10,681	12 345	20 87			
Ca Na	n 2	n 2	1/ /10	20.94 06.40	J∠.9 D6 D	0.50	509	3 10	14 054	16 167	07 07			
ind V	11.a. 2210	11.d. 27 10	1200	10.44	212	2.05	2250	0.40 01.07	10 202	10,107	74 05			
N D	3310	32.19	4399	42.79	515 1075	3.05	2239	Z1.9/	10,282	12,000	65			
ľ	19.6	1.69	7.99	0.69	1075	92.52	59.3	5.10	1162	1504	- 11			
Y	2.36	4.60	24.3	47.31	23	44.78	1.7	3.31	51.3	53.7	95			
La	0.55	0.97	30.1	53.45	17.6	31.23	8.07	14.35	56.2	66.3	85			
Ce	0.15	0.09	66.4	39.05	72.1	42.46	31.3	18.40	170	199	85			
Pr	0.12	1.17	3.74	35.62	4.32	41.19	2.31	22.02	10.5	13	81			
Nd	0.71	1.53	12.9	27.87	22.1	47.78	10.5	22.83	46.2	55.4	84			
Sm	0.22	2.10	2.94	27.40	4.91	45.71	2.66	24.80	10.7	12.1	88			
Eu	0.06	2.62	0.68	30.68	1.11	49.81	0.38	16.89	2.23	2.92	76			
Gd	0.31	3.09	3.24	32.51	4.9	49.18	1.52	15.21	9.97	13.3	75			
Tb	0.04	2.43	0.52	30.90	0.91	53.87	0.22	12.80	1.69	2.14	79			
Dv	0.23	2.37	3	30.89	5.63	58.04	0.84	8 70	9 70	12.6	77			
Ho	0.05	2.07	0.69	33.36	1 21	58 09	0.12	6 11	2.08	2 66	79			
гю Е	0.05	2.40	1.07	22.04	2 4	60.00	0.13	1 54	2.00 5.07	2.00	70			
Eľ Tm	0.14	2.2ð 1.90	1.7/	02.94 21 74	3.0 0.5/	62.27	0.27	4.00	0.97	7.0Z	70			
1 m	0.02	1.80	0.28	31./4	0.56	03.27	0.03	3.18	0.88	1.15	/6			
YD	0.10	1.68	1.7	29.60	3.79	66.01	0.16	2.72	5.75	7.6	76			
Lu	0.02	1.90	0.29	31.52	0.58	64.03	0.02	2.55	0.90	1.18	77			
$\Sigma$ REY	5.07	1.32	153	39.73	166	43.29	60.1	15.65	384	451	85			
Ce/Ce*	0.13		1.38		1.91		1.66		1.61	1.56				

**Table 4.** Concentration and percentage (%) of major elements and rare earth elements and yttrium (REY) (ppm) in 431 and 431A DSDP Holes Fe-Mn deposits as well as recovery elements (R) during leaching experiment.

Note: <d.l.—below detection limit; n.A.—not analyzed; **bold**—maximum concentration element in fraction; Ce/Ce\*—cerium anomaly.

0.46

0.67

0.87

0.71

1.25

Y<sub>SN</sub>/Ho<sub>SN</sub>

1.67

#### 4. Discussion

Most of the samples from the 431 and 431A DSDP cores of Yōmei Guyot contain vernadite ( $\delta$ -MnO<sub>2</sub>), indicating a hydrogenous component, and two samples of the 431A core include hydrothermal and diagenetic 10Å and 7Å manganates [2]). This is consistent with previous studies of Fe-Mn fragments from the Yōmei Guyot core [17] and crusts and nodules from the guyot top [18]. However, X-ray diffraction methods do not allow determination of 10Å manganate minerals due to overlapping of the diffraction peaks of todorokite, asbolan, buserite-I, buserite-II, mixed-layer phases of asbolan-buserite-I, buserite-I-buserite-II, and buserite-I-"defective lithiophorite" [36]. In total, 7Å-manganate is represented by hydrothermal and diagenetic birnessite [2]. The repeated XRD results are consistent with the vernadite composition of 431-5 and with the presence of 10Å manganate and birnessite in the samples from 431A-2. As we used different fragments from the same stratigraphic hole intervals for the repeated X-ray diffraction analyses, the mineral composition indicates that the Fe-Mn fragments in the YM-05 and YM-12 intervals probably came from the same sources (Table 1). Thus, the vernadite-containing fragments reveal the hydrogenous component, and the 10Å manganate and birnessite-bearing intervals reflect either hydrothermal or diagenetic genesis.

A ternary Bonatti plot of Fe:Mn:  $(Co + Ni + Cu) \times 10$  of 431-5 and 431A-12 samples is shown in Figure 6. The 431-5 sample falls near the hydrogenous Fe-Mn crusts of the Marshall, Magellan, and Markus-Wake Seamounts, whichare located close to the Detroit Guyot of the Emperor Ridge. The 431A-12 sample is located near the hydrogenous crusts of the Okhotsk seamounts field, which are characterized by high content of allothigenic input [29]. In the Figure 6, the diagenetic Peru Basin nodules and hydrothermal crust from the Japan Sea are placed at a distance from the Yōmei Guyot samples. This proves the hydrogenous geneses of both studied samples.



**Figure 6.** Plot of Pacific Fe-Mn deposits of different genesis on the Mn-Fe-(Cu+Co+Ni)  $\times$  10 ternary diagram [28]. 1—sandy-gravel Fe-Mn fragments from the Yōmei Guyot (Holes 431, 431A) (Table 3); 2—Fe-Mn crust from the Kashevarov Trough, the Sea of Okhotsk, [29]; 3—Fe-Mn nodules from the Peru Basin, [30]; 4—Fe-Mn crust from the Seth Guyot, Markus-Wake cluster, [33]; 5—Fe-Mn crust from the Detroit Guyot, Emperor Ridge, [34]; 6—Fe-Mn crust from the Belyaevsky Volcano, the Sea of Japan, [35]. Our unpublished data: 7—Fe-Mn crust from the Zubov Guyot, Marshall Island cluster; 8—Fe-Mn crust from the Govorov Guyot, Magellan Seamounts [32]; 9—Fe-Mn crust from the Zonne Chain, the Sea of Okhotsk, [31].

However, the main (from Si, Ti to P, and LOI) elemental composition of the 431-5 and 431A-12 samples differ significantly. The 431-5 element contents are similar to those of crusts from NW Pacific Ocean and those of the 431A-12 sample are identical to diagenetic nodules of the Peru Basin (Table 3). The latter form in a high-bioproductivity environment, that produces suboxic conditions [37] and

indicates the diagenetic geneses of samples. In contrast, the Co (4654 ppm), Ni (3139 ppm), and Cu (611 ppm) contents in 431A-12 fragment is the same as that in the hydrogenous crusts of the NW Pacific Ocean (Co—3733 ppm, Ni—3495 ppm, Cu—1074 ppm), which differs significantly from the diagenetic nodules of the Peru Basin (Co - 475 ppm, Ni—13010 ppm, Cu—5988 ppm). The high Co and Ni contents of the latter is attributed to the presence of Cu<sup>2+</sup> and Ni<sup>2+</sup> in available vacancies within 10Å manganate [30]. The elemental distribution in the 431A-12 sample is possibly related to the combined hydrogenous and diagenetic genesis. The pore fluids are a source of Ni, Cu and Co is sorbed from ocean water [30].

The Ba/Ti ratio in Fe-Mn deposits reflects their genesis. The Ba/Ti value of 62 is interpreted as evidence of hydrothermal input [35,38–41] and 0.22 is typical for the hydrogenous crusts of the northern Pacific Ocean [30]. The Ba/Ti ratio of hydrogenous crusts from back-arc basins with high bioproductivity such as the Kashevarov Trough of the Okhotsk Sea increases up to 5.22 [29] and in diagenetic nodules varies from 1.97 in the Peru Basin [30] to 2.76 in the Deryugin Basin of the Okhotsk Sea [31]. The Ba/Ti ratio in the 431-5 sample of the Yōmei Guyot is 0.20 and the closest value to this is that of the hydrogenous crusts of the Pacific Guyots. In the "contrasting" 431A-12 sample, the Ba/Ti ratio is 6.91, reflecting an additional supply of Ba, probably due to a high bioproductivity.

Hydrothermal deposits have an enriched Li content (from 148 to 1188 ppm) [42]. The Li content in diagenetic nodules is less (95.4–318.7 ppm) and is depleted in hydrogenous crusts (1.18–5.68 ppm) [43]. The Li content in mixed types, such as hydrothermal/hydrogenous and hydrogenous/diagenetic, varies from 2.4 to 62 ppm [42]. The Li value in the 431-5 sample is 3.20 ppm reflecting a hydrogenous component and is higher in sample 431A-12 (19.5 ppm), which probably corresponds to it having had a mixed input.

Thallium is a redox-sensitive trace element oxidized on the surface of Fe-Mn oxyhydroxides. Since hydrogenous crusts contain higher amounts of Tl (155 ppm in the North Pacific Prime Zone) in comparison with deep-water diagenetic nodules (129 ppm in the Peru Basin) [2]. The Tl content in the 431-5 sample is 192.2 ppm, slightly higher than in the hydrogenous crusts of the Marshall (163 ppm), Magellan (167 ppm), and other Pacific Guyots (Table 3). It reflects Tl precipitation in oxic conditions. The Tl content in the 431A-12 sample is significantly less (9.47 ppm) and is comparable to shallow-water diagenetic Fe-Mn nodules of the Baltic Sea, which vary from 5.35 to 19.5 ppm, hydrothermal crusts, which vary from 0.68–44.0 ppm, and mixed hydrothermal and hydrogenous Fe-Mn crusts, which vary from 7.00–9.48 ppm [44]. We suggest that Tl in the 431A-12 sample has a hydrothermal or hydrothermal/hydrogenous genesis and its accumulation probably occurred in the local suboxic conditions. Yōmei Guyot crusts formed in deep-sea conditions (1000 m or more) [17,45].

REY are sensitive to changes in redox conditions [46]. Hydrogenous Fe-Mn crusts are enriched in REY up to 1682 ppm on average, with an Nd content of 162 ppm. Diagenetic nodules have a mean REY content of about 349 ppm and Nd concentration of 58 ppm. Hydrothermal deposits contain minimal content of REY (29.8 ppm) and Nd (5.2 ppm) [1]. The distribution of PAAS normalized REY (McLennan, 1989) contents of three of these genetic types are different (Figure 7a). The  $\Sigma$ REY and Nd content in the 431-5 sample from the Yōmei Guyot are 3074 ppm and 266 ppm, respectively (Table 3), reflecting their hydrogenous geneses. The amounts of REY and Nd in sample 431A-12 are 451 ppm and 55.4 ppm, respectively, indicating their diagenetic formation. The PAAS normalized REY [47] contents of 431-5 and 431A-12 samples from the Yōmei Guyot show a similar fractionation of bulk composition (Figure 7b). Moreover, the REY distribution of hydrogenous crusts in Figure 7a is the same as the 431-5 sample in Figure 7b. The REY distribution excluding Ce content of the 431A-12 sample is similar to that of diagenetic nodules (Figure 7a). The Ce behavior closely corresponds to that in hydrogenous geneses and the 431A-12 sample possibly corresponds to the diagenetic influence but with features typical for seamounts.



**Figure 7.** Shale-normalized (PAAS after [47]) REY patterns of Fe-Mn deposits of differing genesis (a) and Fe-Mn sandy-gravel deposits from the Holes 431 and 431A cores from the Yōmei Guyot (b). 1—Hydrogenetic Fe-Mn crusts; 2—hydrogenetic Fe-Mn nodules; 3—non-phosphorous Fe-Mn crusts; 4—digenetic Fe-Mn nodules; 5—hydrothermal Fe-Mn deposits; 6—sample 431-5; 7—sample 431A-12; 8—distribution limits REY patterns after Table 2.

The chemical composition of representative samples from the 431 and 431A DSDP holes of the Yōmei Guyot indicates the hydrogenous origin of the 431-5 sample and the undeterminable hydrothermal or diagenetic genesis of the 431A-12 sample. The study of REY distribution in the mineral phases is the most useful method for studying the samples' geneses. For example, the REY distribution in the Mn phase of hydrothermal crusts differs significantly from those of the hydrogenous and diagenetic geneses and from the Fe phases of all genetic types [6,7,48,49].

The sequential leaching of 431-5 and 431A-12 samples of Yōmei Guyot helps to determine their geneses. Since Phase I is depleted by REY, PAAS normalized contents on a logarithmic scale are inconvenient to use, and we instead use normalized values on an arithmetic scale (Figure 8). The REY from Sm to Dy are enriched in samples with a maximum value of Gd, which is typical for seawater, and, accordingly, for hydrogenous Fe-Mn crusts [50]. A negative Ce anomaly in seawater is formed because Ce can take a tetravalent state and is easily hydrolyzed and scavenged onto Fe–Mn oxides/hydroxides and clay particles [51]. A negative Ce anomaly indicates oxic conditions because a positive Ce anomaly in the extraction of highly mobile REY indicates a reduced environment of precipitation [37,52]. The REY contents of leached Phase I from sample 431-5 falls near the boundary between the logarithmic high-latitude and equatorial Fe-Mn Pacific crusts, and those of the 431A-12 sample are similar to ring-like diagenetic Fe-Mn nodules from the Deryugin Basin.



**Figure 8.** Shale-normalized (PAAS after [47]) REY patterns of Fe-Mn deposits of differing genesis in fraction I: 1—hydrothermal Fe-Mn deposits from the Sea of Japan, [7]; 2—hydrogenetic Fe-Mn crusts from the North Pacific, [48]; 3—Fe-Mn crusts from the Central Pacific (our unpublished data); 4—phosphatized Fe-Mn crusts from the Central Pacific (our unpublished data); 5—diagenetic ring-like Fe-Mn nodule from the Sea of Okhotsk, [52]; 6—sample 431-5; 7—sample 431A-12.

The REY content in Phase II is illustrated using a logarithmic scale (Figure 9), because normalized concentrations of different genetic types of Fe-Mn deposits and their sources such as seawater and hydrothermal fluid differ by orders of magnitude. We combined the REY distribution fields of high-latitude and equatorial Fe-Mn crusts from the Pacific Ocean as one logarithmic "Fe-Mn crusts from Pacific Ocean" field because of overlapping. The hydrothermal deposits are characterized by extremely low REY contents and an Eu concentration below the detection limit, reflecting their deposition from a low-temperature fluid [53]. Their formation near high-temperature fluids would lead to Euaccumulation [7]. Hydrogenous crusts are enriched in REY and have a positive Ce anomaly (Figure 9). Graphs of most ancient phosphatized Fe-Mn crust layers and diagenetic nodules fall in-between. Phosphatized layers of Phase II show high REY contents and positive Ce and negative Y anomalies due to dissolution, restructuring, and secondary enrichment caused by environmental changes [2]. Diagenetic nodules from the Sea of Okhotsk are depleted in REY and have clearly defined positive Y and poor Ce and Gd anomalies [2]. The REY distribution of the 431-5 sample coincides with the hydrogenous crusts and nodules reflecting element sorption from bottom waters in phase II (Figure 9). The REY distribution pattern of the 431A-12 sample is similar to that of diagenetic nodules from the Sea of Okhotsk and indicates the deposition of Phase II from pore waters. The significant difference in REY content between the 431A-12 sample and the diagenetic nodules of the Sea of Okhotsk is associated with the higher growth rate of the latter.



**Figure 9.** Shale-normalized (PAAS [47]) REY patterns of Fe-Mn deposits of differing genesis in fraction II: 1—hydrothermal Fe-Mn deposits from the Sea of Japan, [7]; 2—combined data on hydrogenetic Fe-Mn crusts from the North Pacific, [48] and the Central Pacific (our unpublished data); 3—phosphatized Fe-Mn crusts from the Central Pacific (our unpublished data); 4—diagenetic ring-like Fe-Mn nodule from the Sea of Okhotsk, [52]; 5—sample 431-5; 6—sample 431A-12.

We presented the REY contents of Phase III using a logarithmic scale (Figure 10), similarly to Phase II. The hydrogenous crusts in Phase III are enriched in REY, especially in heavy REY, due to prolonged exposure to seawater [4]. Low REY concentrations are observed in hydrothermal crusts in spite of the presence of Fe hydroxides, which are important in the REY accumulation [4,7]. In addition, due to higher growth rates, there is no increase to the heavy REY concentrations [7]. The diagenetic nodules of the Sea of Okhotsk reflect similar conditions of REY accumulation. The REY distribution of phosphatized crust layers indicates the affinity of accumulation with hydrogenous crusts, but under special conditions due the presence of positive Ce and Y anomalies. Such REY distribution is consistent with possible secondary changes of hydrogenous crusts [2]. The REY distribution of the 431-5 sample corroborates the hydrogenous formation of Phase III due to similarities between its limited REY content and the mean values in hydrogenous crusts. The 431A-12 sample pattern is otherwise the same as that of diagenetic nodules of the Sea of Okhotsk, but with a higher REY content. This makes it possible to consider Phase III of the 431A-12 sample as a diagenetic.





**Figure 10.** Shale-normalized (PAAS after [47]) REY patterns of Fe-Mn deposits of differing genesis in fraction III (legend see in Figure 7).

The REY composition in the aluminosilicate phase differs between genetic types (Figure 11). Distribution plots of REY in Phase IV of samples 431-5 and 431A-12 are similar, but the metal contents differ. The REY distribution pattern of both studied samples is the identical to the hydrogenous Fe-Mn crusts of the NW Pacific crusts.



**Figure 11.** Shale-normalized (PAAS after [47]) REY patterns of Fe-Mn deposits of differing genesis in fraction IV (legend see in Figure 7).

Based on our results most of the Fe-Mn fragments from the 431 and 431A DSDP holes from the Yōmei Guyot are hydrogenous and fewer of them are diagenetic. We did not find any evidence for any Fe-Mn fragments having a hydrothermal origin.

#### 4.1. The Initiation of Growth of the Fe-Mn Deposit

Based on previous studies [17,18], sandy-gravel deposits with a high content of Fe-Mn fragments (80–90%) on the Yōmei Guyot formed during the Quaternary. Consequently, fragments of the youngest brown coal (Pliocene-Quaternary) crust layer should be presented in the bottom part of the core and porous (Miocene) and anthracite (Paleocene-Eocene) layers with Cretaceous relicts should cover it. These layers exist on all guyots in the equatorial Pacific Ocean [8,9]. The Fe-Mn crusts of the northern Pacific Ocean have a two-layer structure. They consist of a thick anthracite (130 mm) layer formed between the Late Oligocene and the beginning of the Late Pliocene, and an inconsistently covered brown-coal (18 mm) layer of the Upper Pliocene-Quaternary period [34,54]. This is the difference in the morphology of the coeval layers of high-latitude crusts from equatorial ones. Notably, the Pliocene-Quaternary brown-coal layer occurs throughout the northern hemisphere in the Pacific Ocean [8,9,54]. We did not discover any fragments of either the Pliocene-Quaternary layer or the most ancient Paleocene-Eocene layer characterized by a high P content (>0.7%, Table 2) in the 431 and 431A DSDP holes. The Fe-Mn deposit is represented only by fragments of the Miocene anthracite layer, reflecting the initiation of growth of the Yōmei Guyot Fe-Mn deposit earlier than the Quaternary period.

Fe-Mn crust growth on guyots takes place when the velocity of the bottom water currents varies from 10 to 30 cm/s [55]. With increasing current velocity crust growth stops and they start to erode. The Fe-Mn crusts on the Emperor Ridge guyots were eroding between 3.97–3.21 Myr [54]. We suggest that initial Fe-Mn crust destruction and post-deposition of sandy-gravel size Fe-Mn deposits in depressions on the Yōmei Guyot top occurred during this period. In addition, Pliocene (6–3 Myr) volcanic activity in the Pacific Ocean might have influenced the destruction of Fe-Mn deposits [56]. Growth of the brown-coal upper layer on Detroit Guyot initiated since 3.21 Myr [48,49], broadly corresponding to global events such as the initiation of northern hemisphere glaciation, the final closing of the Isthmus of Panama, decreasing activity of AABW, and an increase in eolian dust flux [54,57–59]. Thus, the destruction of Fe-Mn crusts and the post-deposition of its fragments on the Yōmei Guyot top occurred in the Late Pliocene.

#### 4.2. Genetic Type of the Sandy-Gravel Fe-Mn Deposit

Investigations into the placer deposits began in the mid-to-late XX Century and focused on the shelf areas of continental borderlands [11,60–62]. During this time, the metallogeny of shelf area placers was studied in detail, but the ocean area was poorly investigated. Only in 1993 were Fe-Mn sandy-gravel ocean seamount deposits proposed to exist with a MnO content up to 25% [23]. This was based on only a few publications [17,18].

Underwater placers on the coasts and continental margins are formed as a result of weathering of source rock, the release of the valuable component, its migration, and its accumulation [11,60–62]. The Yōmei Guyot Fe-Mn deposit has all these properties. The source rock on this Guyot was Fe-Mn crusts and nodules. The valuable component release stage on the Yōmei Guyot corresponds to the separation of Fe-Mn material from the substrate, because Fe-Mn crusts and nodules as a rock comprises the valuable component. The main mechanism of transportation was bottom water currents, and accumulation occurred in depressions. The coarse and non-rounded fragments reflect a short migration of Fe-Mn fragments. Thus, we suggest the definition of the Fe-Mn sandy-gravel deposit of the Yōmei Guyot as an oceanic petrogenic Fe-Mn placer in the vicinity of the source rocks.

#### 5. Conclusions

The 431 and 431A DSDP cores from the Yōmei Guyot contain layers bearing up to 90% Fe-Mn fragments. The average sizes of the Fe-Mn fragments decrease from 20 mm to 3 mm from the bottom of the core to the seafloor surface, reflecting a decrease in bottom water current velocities. In general, the Fe-Mn deposit is characterized as sandy-gravel.

Based on the morphology, Fe-Mn fragments are divided into two types: dense black with anthracite luster (85% of core material) and slightly porous dark gray to black with a dull luster.

The first type of fragments is composed of vernadite. The Mn content is 28.89%, Fe is 15.57%,  $\Sigma$  Co, Ni, Cu is 8642 ppm, and  $\Sigma$  REY is 3074 ppm. The chemical composition of the bulk samples and the main mineral phases reflects the hydrogenous origin of the Fe-Mn fragments. The source of these fragments was Fe-Mn crusts and pavements of the Yōmei Guyot top. The second type of fragments contains 10 Å manganate and birnessite. The average Mn content is 34.96%, Fe is 8.76%,  $\Sigma$  Co, Ni, Cu is 8404 ppm, and  $\Sigma$  REY is 451 ppm. The results show the Fe-Mn fragments of the second type have a diagenetic origin and their source is ferromanganese nodules formed in specific environments on the guyot top. In contrast to previous investigations [17,18] we did not discover a hydrothermal influence on the formation of the Fe-Mn deposits from the Yōmei Guyot.

The fragmented Fe-Mn deposits of Yomei Guyot formed between 3.97 and 3.21 Myr.

Due to the formation processes of the studied deposit, we define it as a Fe-Mn placer, a new genetic type of ocean mineral deposit.

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