

EXPRESS LETTER**Surface layer Nd isotopic composition of ferromanganese crusts collected from the Takuyo-Daigo Seamount reflects ambient seawater**HIROSHI AMAKAWA,^{1*} AKIRA USUI,² KOICHI IJIMA¹ and KATSUHIKO SUZUKI¹¹Project Team for Development of New-generation Research Protocol for Submarine Resources, Japan Agency for Marine-Earth Science Technology (JAMSTEC), 2-15, Natsushima-cho, Yokosuka-shi, Kanagawa 237-0061, Japan²Department of Geology, Kochi University, 2-5-1, Akebono-cho, Kochi-shi, Kochi 780-8520, Japan*(Received October 5, 2016; Accepted December 10, 2016; Online published January 13, 2017)*

The neodymium (Nd) isotopic composition of the surface layers of eleven ferromanganese crust samples collected from the Takuyo-Daigo Seamount (northwest Pacific Ocean) was determined. This is the first systematic study of the Nd isotopic composition of ferromanganese crusts collected by remotely operated vehicles (ROVs) from a single seamount over water depths of 1000–5400 m, representing intermediate to deep water masses in the ocean.

We found that the depth profile of ferromanganese crusts is similar to the vertical seawater profile reported for a station close to the seamount. This similarity suggests that Nd in the surface layer of the ferromanganese crust is directly supplied by ambient seawater and reflects the oceanic water mass structure in the region. These samples are suitable for determining time-series Nd isotopic data to study past ocean circulation of intermediate to deep water masses in the northern Pacific.

Keywords: ferromanganese (Fe-Mn) crust, Nd isotopic composition, seawater, Takuyo-Daigo Seamount, remotely operated vehicle (ROV)

INTRODUCTION

Ferromanganese (Fe-Mn) crusts are chemical precipitates that are widely distributed on the ocean floor, including on topographic highs such as seamounts. They form on substrates, such as silicate rocks, fish teeth and debris, and lithified sediment, at a growth rate of 1–10 mm/Ma (Hein *et al.*, 2000). The chemical composition of hydrogenously formed Fe-Mn crusts is believed to directly reflect that of seawater because it is normally free from sedimentary diagenetic influences, which disturb the original record. This is quite different from Fe-Mn nodules formed on/in sediment, which are strongly subjected to diagenetic perturbation (Frank *et al.*, 1999). Therefore, a 10-cm-thick Fe-Mn crust potentially records an undisturbed record of seawater chemical composition spanning the past 10 to 100 Ma (Hein *et al.*, 2000). Many researchers have tried to derive chemical compositions of seawater in the past by measuring various radiogenic isotopes, such as Be, Pb, Nd, Os, and Sr, on Fe-Mn crusts (Frank, 2002 and references therein). Among these radiogenic isotopes, Nd and Pb isotopic compositions are not homogenized in

the ocean due to the shorter residence times of Nd (300–500 yr; Amakawa *et al.*, 2009) and Pb (50–200 yr; Osborne *et al.*, 2014) compared with global ocean mixing (~1500 yr; Amakawa *et al.*, 2009). Therefore, time-series data of Nd and Pb isotopic compositions could be used to describe past ocean circulation changes triggered by paleogeographic events, such as the closing of the Panama gateway (Burton *et al.*, 1997) or Indonesian seaway (van de Flierdt *et al.*, 2004), or changes in continental dust flux (Ling *et al.*, 2005). So far, however, the Fe-Mn crust samples used for those studies were exclusively collected by dredging, which drags a metal net along the seafloor or seamount slope (Tokumaru *et al.*, 2015). One of the critical drawbacks of this technique is that the real sampling depths are unknown. This information is essential for identifying which water masses overlie the samples (and are in contact with the seafloor) and complicate further (paleo)oceanographic interpretations. Additionally, *in-situ* deep-sea camera observations have revealed that Fe-Mn crusts frequently separate from their substrates, such as a seamount flank, and then are in direct contact with the sediment, which might cause diagenetic perturbation. To extract undisturbed seawater geochemical information from Fe-Mn crusts, their occurrence should be monitored and checked during sampling to avoid recovering samples inappropriate for research.

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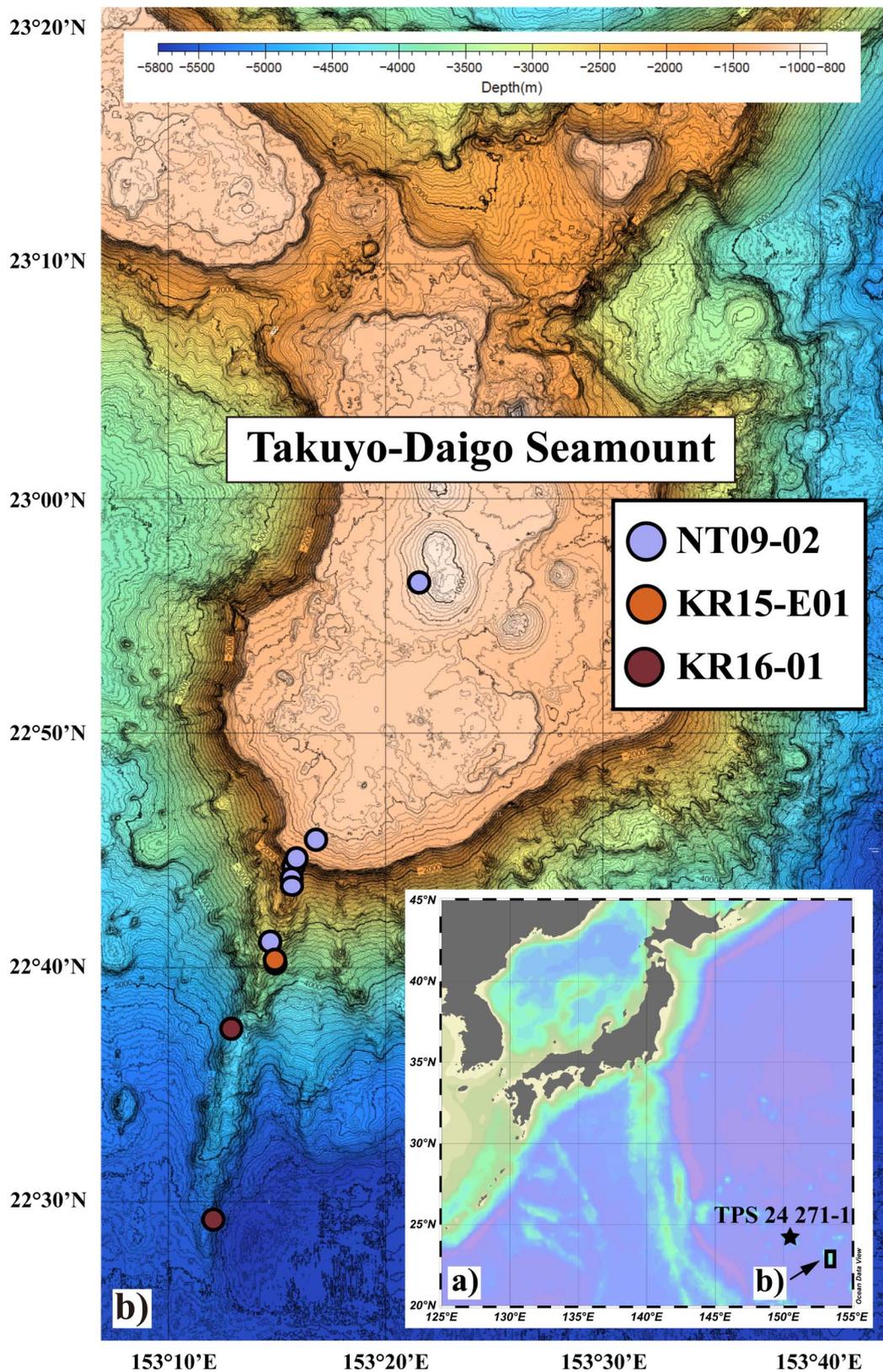


Fig. 1. a) Location of the Takuyo-Daigo Seamount. The location of Station TPS 24 271-1, where seawater Nd isotope data are available, is also plotted. b) Detailed topography of the Takuyo-Daigo Seamount with sampling locations of the Fe-Mn crusts recovered by ROV during each of the three research cruises (NT09-02, KR15-E01, KR16-01).

Table 1. Nd isotopic composition for the surface of the ferromanganese crusts from the Takuyo-Daigo Seamount

Sample No.	Cruise No.	Water depth [m]	Latitude	Longitude	Sample treatment	$^{143}\text{Nd}/^{144}\text{Nd}^a$	ϵ_{Nd}^b	Internal error	External error ^c	Reported error ^d
HPD#959-R07	NT09-02	1019	22°56.501' N	153°21.592' E	1.0M HCl+H ₂ O ₂	0.512485 ± 0.000010	-2.98	0.20	0.27	0.27
					2.5M HCl	0.512492 ± 0.000015	-2.85	0.30	0.24	0.39
HPD#957-R11	NT09-02	1252	22°45.485' N	153°16.759' E	2.5M HCl	0.512493 ± 0.000015	-2.82	0.30	0.24	0.38
HPD#956-R15	NT09-02	1440	22°44.601' N	153°15.991' E	1.0M HCl+H ₂ O ₂	0.512486 ± 0.000011	-2.97	0.21	0.26	0.26
HPD#956-R09	NT09-02	1626	22°44.390' N	153°15.846' E	1.0M HCl+H ₂ O ₂	0.512477 ± 0.000009	-3.15	0.18	0.08	0.20
HPD#955-R12	NT09-02	1937	22°43.858' N	153°15.652' E	2.5M HCl	0.512468 ± 0.000014	-3.32	0.27	0.35	0.35
HPD#955-R09	NT09-02	2008	22°43.546' N	153°15.716' E	1.0M HCl+H ₂ O ₂	0.512464 ± 0.000009	-3.40	0.17	0.08	0.19
					2.5M HCl	0.512468 ± 0.000017	-3.33	0.34	0.13	0.36
HPD#953-R15	NT09-02	2892	22°41.098' N	153°14.672' E	2.5M HCl	0.512458 ± 0.000010	-3.51	0.19	0.24	0.24
KAIKO#646-R03	KR15-E01	3357	22°40.363' N	153°14.903' E	1.0M HCl+H ₂ O ₂	0.512445 ± 0.000011	-3.77	0.22	0.27	0.27
					2.5M HCl	0.512442 ± 0.000008	-3.82	0.16	0.35	0.35
KAIKO#646-R01	KR15-E01	3472	22°40.255' N	153°14.956' E	2.5M HCl	0.512442 ± 0.000013	-3.83	0.26	0.35	0.35
KAIKO#684-R05	KR16-01	4441	22°37.410' N	153°12.942' E	1.0M HCl+H ₂ O ₂	0.512416 ± 0.000010	-4.33	0.20	0.08	0.21
KAIKO#683-R05	KR16-01	5385	22°29.186' N	153°12.079' E	1.0M HCl+H ₂ O ₂	0.512387 ± 0.000013	-4.89	0.25	0.08	0.26
NOD-P-1 ^e	Reference material ^f				1.0M HCl+H ₂ O ₂	0.512437 ± 0.000012				

^a Errors are $2\sigma_m$ (internal errors).

^b $\epsilon_{\text{Nd}} = ((^{143}\text{Nd}/^{144}\text{Nd})_{\text{sample}}/0.512638 - 1) \times 10^4$.

^c Errors are based on 2 standard deviation of repeated analyses of standard solutions.

^d Errors are typically 2σ external error of standard solutions analyzed during the analytical sessions. If the internal errors are larger than the external errors, propagated errors are reported.

^e Errors are 2 standard deviation of repeated analyses ($n = 4$).

^f USGS Fe-Mn nodule reference material from the Pacific Ocean (see text for details).

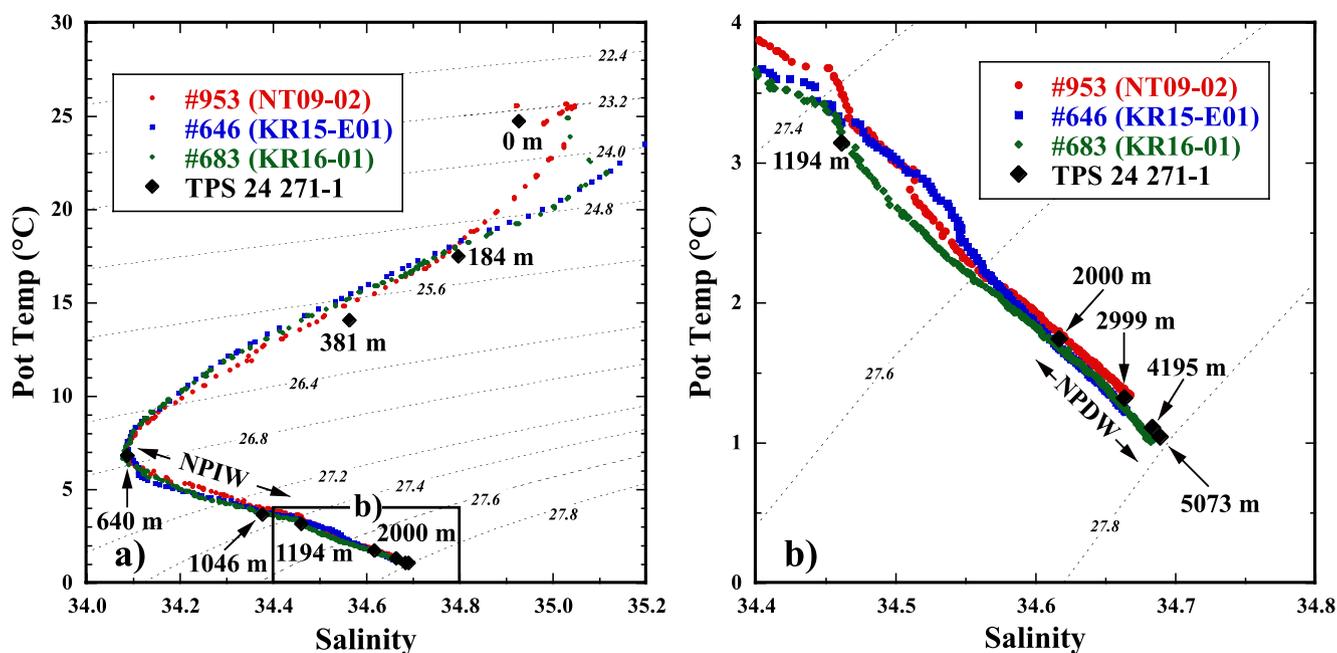


Fig. 2. θ - S diagrams of ROV-based and TPS 24 271-1 water column data. The ROV data were obtained by CTD profilers during each of the three research cruises (NT09-02, KR15-E01, KR16-01). TPS 24 271-1 data are from Piepgras and Jacobsen (1988). The data from greater water depths are enlarged in (b). The potential density curves ($\sigma_\theta = 22.4$ – 27.8) are also shown.

Fortunately, recent progress in the use of remotely operated vehicles (ROVs) enables us to collect appropriate Fe-Mn crust samples by allowing *in-situ* monitoring of water depth and crust occurrence. However, only a few recent studies have reported trace element isotopic compositions of Fe-Mn crusts sampled by ROV (U: Goto *et al.*, 2014; Os: Tokumaru *et al.*, 2015). Thus, we report here the first record of surface layer (outermost 0–1 mm) Nd isotopic composition of Fe-Mn crusts collected by ROV from various water depths (1000–5400 m) along the Takuyo-Daigo Seamount (northwest Pacific), and compare our data with seawater Nd data previously reported for a nearby station. The sampling depths correspond to intermediate to deep water masses in the northwest Pacific, which allows us to reconstruct changes water mass circulation.

SAMPLING LOCATION AND METHODS

The Takuyo-Daigo Seamount is located in the northwest Pacific, ~1900 km from Honshu Island, Japan (Fig. 1a). Several ROV dives confirmed that Fe-Mn crusts ubiquitously occur along the southwest ridge of the seamount at water depths ranging from 900 m to 5500 m (Fig. 1b). The Fe-Mn crust samples were collected during three cruises with ROVs: *RV Natsushima* NT09-02 Leg 2 (8–24 February 2009), equipped with ROV *Hyper-Dolphin*; *RV Kairei* KR15-E01 (3–13 February 2015) and KR16-

01 Leg 1 (9–19 January 2016), both equipped with ROV *Kaiko*. Fe-Mn crust samples were collected by a ROV manipulator (Supplementary Fig. S1) with/without a rotator cutter. The video of the ROV sampling is available on the following link: “http://www.jamstec.go.jp/e/about/press_release/20160209/”. Very recently, Usui *et al.* (in press) have determined the growth rates of 2.3 to 3.5 mm/Ma for several Fe-Mn crusts from the Takuyo-Daigo Seamount using $^{10}\text{Be}/^9\text{Be}$ dating method. This implies that an 1 mm of surface layer crust sample from this area corresponds to a period of 0.29 to 0.43 Ma.

Station TPS 24 271-1, where a vertical profile of seawater Nd isotopic composition has been reported (Piepgras and Jacobsen, 1988), is located close to the Takuyo-Daigo Seamount (Fig. 1a).

ANALYTICAL METHODS

We selected Fe-Mn crust samples with intact and undisturbed surfaces for Nd isotopic analysis (Tokumaru *et al.*, 2015). In the laboratory, the topmost surface (<1 mm thick) of each Fe-Mn crust was carefully scraped with a ceramic knife. The sample was leached with either 2.5 M HCl (Ling *et al.*, 2005) or 1M HCl with H_2O_2 (Amakawa *et al.*, 1996), and the leachate was pipetted and transferred to a Teflon-coated vessel. The leachate was subsequently diluted with MilliQ water to ~0.5 M HCl and stored in a polyethylene plastic bottle. An aliquot was taken, evapo-

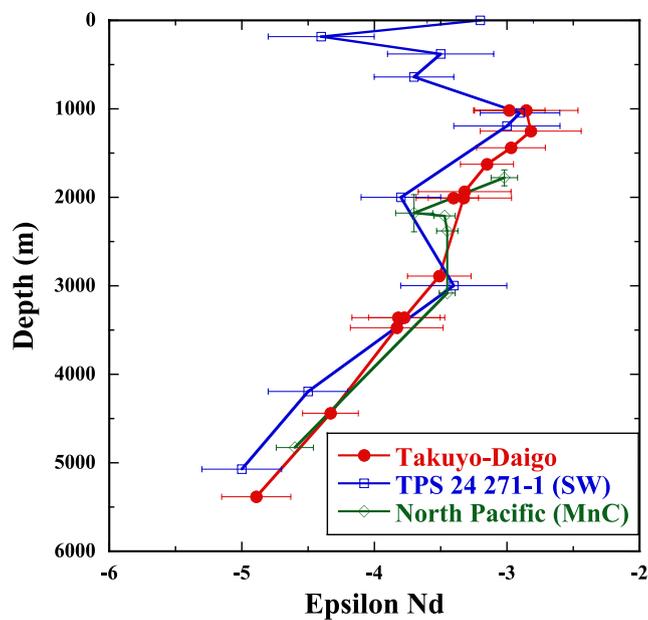


Fig. 3. The profile of Nd isotopic compositions from Fe-Mn crust surface layers collected from the Takuyo-Daigo Seamount. The vertical seawater profile from TPS 24 271-1 (Piepgras and Jacobsen, 1988), and previously reported data (Ling *et al.*, 1997, 2005) are also plotted.

rated and then dissolved in 0.25 M HCl. This solution was loaded onto an Ln Resin column (LN-C50-A, Eichrom Technologies, Inc.) to separate and purify Nd (Amakawa *et al.*, 2009; Scher and Delaney, 2010; Huang *et al.*, 2012). Major elements and La were eluted with 4.5 ml of 0.25 M HCl, and then the Nd fraction was subsequently collected by elution of 10 ml of 0.25 M HCl. The solution was passed through a Pre-filter Resin column (PF-B100-A, Eichrom Technologies, Inc.) to remove organic matter, and was repeatedly treated with HClO₄ and HNO₃ to completely decompose any residual organic matter. The purified Nd fraction was finally dissolved in 5% HNO₃.

The Nd isotopic composition was determined with a multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS; NEPTUNE Plus, Thermo Fisher Scientific K.K.), housed at the Japan Agency for Marine-Earth Science and Technology (JAMSTEC). The MC-ICP-MS has eight movable and one fixed central Faraday cups and was operated in low-resolution mode ($M/\Delta M = 400$) and at a radio frequency power of 1200 W. A dry introduction system (desolvating nebulizer; CETAC ARIDUS II) with a sample solution uptake rate of 100 $\mu\text{l}/\text{min}$ was used. Detailed instrumental settings are described in Supplementary Table S1.

Measured $^{143}\text{Nd}/^{144}\text{Nd}$ ratios were exponentially normalized to $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$. A standard-sample

bracketing method was employed to correct the raw values using 20 ppb of the solution standards JNdi-1 (certified value = 0.512115; Tanaka *et al.*, 2000) or La Jolla (certified value = 0.511858; Lugmair *et al.*, 1983). Nd isotopic composition is expressed in epsilon (ϵ) notation (see Table 1 for definition). Errors are two standard deviations (2σ , 2SD) of the external uncertainty of repeated standard analysis, or propagated uncertainty, if two standard deviations of the mean ($2\sigma_m$) is larger than the 2SD. Normally, 2SD of the standard over one session (one day) ranges from 0.13 to 0.35 in epsilon units.

We also analyzed the Nd isotopic composition of United States Geological Survey (USGS) reference material (NOD-P-1), which is a Fe-Mn nodule sample from the Pacific Ocean. The average of repeated analyses of NOD-P-1 is 0.512437 ± 0.000012 ($n = 4$; Table 1), which is identical to the previously reported average value (0.512432 ± 0.000014 , $n = 9$) (Foster and Vance, 2006; Huang *et al.*, 2012).

The surface layers of four samples (HPD#959-R07, HPD#956-R15, HPD#956-R09, and HPD#955-R12; Table 1) were previously studied for U (Goto *et al.*, 2014) or Os (Tokumaru *et al.*, 2015) isotopic compositions.

RESULTS AND DISCUSSION

θ -S diagrams from the Takuyo-Daigo Seamount and reference seawater station

Hydrographic data obtained by conductivity, temperature, and depth (CTD) profilers on the ROVs are plotted on θ -S diagrams (Fig. 2), together with the data from seawater station TPS 24 271-1 (Piepgras and Jacobsen, 1988). The CTD profilers were an SBE9plus (NT09-02) and an SBE-49 FastCAT (KR15-E01 and KR16-01); all were from Sea-Bird Electronics, Inc. We did not plot all of the related dive data from the ROVs because the CTD data were reproducible within each research cruise. Although some discrepancies are observed between ROV data and TPS 24 271-1 data at shallow water depths, they show similar plots below 1000 m. This implies that the water mass structure below 1000 m is similar for the Takuyo-Daigo Seamount and TPS 24 271-1.

North Pacific Intermediate Water (NPIW) occupies depths between 610–1130 m (σ_θ (potential density) = 26.6–27.4; Amakawa *et al.*, 2009), as shown by a characteristic salinity minimum at ~ 660 m ($S = \sim 34.1$; Fig. 2a). North Pacific Deep Water (NPDW) is present between 1950–5400 m ($S = 34.6$ – 34.7 , $\sigma_\theta = 27.6$ – 27.8 ; Fig. 2b, Amakawa *et al.*, 2009).

Nd isotopic composition of Fe-Mn crust surface layers

As a quality control step, we compared data obtained by two leaching methods performed on three samples, and found that both methods yielded almost the same data

within analytical error (Table 1). This indicates that we can directly compare data irrespective of the leaching method used.

The Nd isotopic composition of the surface layer of Fe-Mn crusts is plotted as a sampling depth profile in Fig. 3, together with the Nd seawater vertical profile from TPS 24 271-1. The previously reported data from Fe-Mn crust surface layers in the North Pacific are also shown (Ling *et al.*, 1997, 2005). The results show a gradual decrease in Nd isotopic composition of the Fe-Mn crust samples from shallow water depths ($\epsilon_{\text{Nd}} = -2.85$ at 1019 m) to deep ($\epsilon_{\text{Nd}} = -4.89$ at 5385 m), which mimics the seawater data reported for TPS 24 271-1 (Fig. 3). Between 1000 m and 3000 m, the Fe-Mn crust and seawater data show the same values within error. Although there are some differences below 3000 m, both data are almost identical when errors are considered.

The similarity between the vertical profiles of Nd isotopic composition for Fe-Mn crusts and seawater indicates that the surface layers of the Fe-Mn crust reliably record ambient seawater, which is likely a result of the hydrogenous origin of Nd (Fig. 3). This tight link between the surface layer of Fe-Mn crusts and seawater has been already suggested in the North Pacific between 1800 m and 4800 m water depths (Ling *et al.*, 1997; Amakawa *et al.*, 2009). Previous studies have reported that seawater samples collected around 1000 m in subtropical North Pacific stations, including TPS 24 271-1, show a narrow range in Nd isotopic composition ($\epsilon_{\text{Nd}} = -4$ to -3), which is attributed to NPIW originating off the coast of Sanriku, Japan (Amakawa *et al.*, 2009 and references therein). Sample HPD#959-R07 (1019 m, $\epsilon_{\text{Nd}} = -3.0$ and -2.9) shows an ϵ_{Nd} value consistent with NPIW (Fig. 3). The average ϵ_{Nd} value of samples collected below 2000 m, corresponding to NPDW, is -3.9 ± 0.5 ($n = 8$). This value is consistent with previously estimated values for NPDW (-3.9 ± 0.7 , Amakawa *et al.*, 2009; -3.5 ± 0.5 , Fröllje *et al.*, 2016), which further highlights the close relationship between Nd isotopic compositions from Fe-Mn crusts and ambient seawater.

Previous studies on U and Os isotopic compositions using the same Fe-Mn crust samples revealed that they exhibit the same values as seawater (Goto *et al.*, 2014; Tokumaru *et al.*, 2015). The Nd data presented in this study corroborates those studies' conclusions. Additionally, variations in the vertical distribution of seawater Nd isotopic composition indicate that the Nd values from Fe-Mn crusts directly reflect the water mass structure at the sampling site.

It is interesting to note that our ϵ_{Nd} surface layer (<1 mm) profile is consistent with previously reported data for the northern Pacific Ocean (Fig. 3; Ling *et al.*, 1997, 2005). This is surprising because those samples are from a wide area ($9^{\circ}18' \text{ N}$ to $21^{\circ}45' \text{ N}$, $160^{\circ}44' \text{ E}$ to $146^{\circ}03' \text{ W}$) and most of them are located far from the Takuyo-Daigo Seamount. This implies that the seawater Nd isotopic distribution in the northwest to central Pacific is horizontally fairly homogenous below 1000 m and might have been so for 0.1 to 0.2 Ma, assuming a 2.3 to 3.5 mm/Ma growth rate (Usui *et al.*, in press) at the area and a 0.5 mm sampling depth for the surface Fe-Mn crust.

CONCLUSIONS

We found that the Nd isotopic composition of Fe-Mn crust surface layers, collected from various depths along the Takuyo-Daigo Seamount, reliably reflects seawater values. This suggests that the Fe-Mn crust samples were not disturbed by diagenetic processes, and may be suitable for the production of accurate time-series Nd isotopic data for paleoceanographic studies. One benefit to using Fe-Mn crust samples from the Takuyo-Daigo Seamount for paleoceanography is that they cover a wide water depth range at a single site. Several Nd isotopic time-series datasets have already been generated using Fe-Mn crust samples collected from various water depths in the Pacific (Fig. 3; Ling *et al.*, 1997, 2005; van de Flierdt *et al.*, 2004). However, their sampling locations are widely distributed and the heterogeneous seawater Nd isotopic distribution within the Pacific Ocean needs to be taken into consideration (Amakawa *et al.*, 2009). This problem is circumvented by using data from Fe-Mn crusts collected along a seamount ridge or flank, as demonstrated in this study. This removes complications resulting from the regional heterogeneity of water mass Nd isotopic compositions, and helps reconstructions of intermediate and deep water mass circulation. Combined with ROV sampling, single site Fe-Mn crust sampling would greatly improve the quality of radiogenic isotope time-series data and subsequent paleoceanographic studies.

Acknowledgments—We would like to thank the captains, officers and crew of the *RV Natsushima* and *RV Kairei*, and the operation teams of the ROVs *Hyper-Dolphin* and *Kaiko* for their collaboration in sampling. We also would like to thank Associate Editor Yoshiki Sohrin for handling the manuscript, and Taryn Noble and an anonymous reviewer for their useful comments. This work is funded by “Scientific research on genesis of marine resources” for “Next-generation technology for ocean resources exploration (ZIPANG in ocean),” an initiative that is part of the “Cross-ministerial Strategic Innovation Promotion Program (SIP)” of the Japanese government.

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SUPPLEMENTARY MATERIALS

URL (<http://www.terrapub.co.jp/journals/GJ/archives/data/51/MS463.pdf>)

Figure S1

Table S1