



# Article Semi-Quantitative Analyses of Ferromanganese Nodules from the Pacific Ocean Using Synchrotron X-ray Powder Diffraction

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**Abstract:** The geochemistry and mineralogy of Mn nodules offer crucial insights into the origins, environmental changes, and distribution of abyssal resources. However, the conventional laboratory X-ray diffractometer, usually employed for semi-quantitative analysis of mineral composition in Mn nodules, often fails to sufficiently detect minor phases due to beam flux limitations and high background signals. In this study, we investigated differences in manganate composition, even when comprising around 1% of the phase fraction, in two manganese nodules (KC-8 and KODOS-10) using high-resolution synchrotron X-ray diffraction. The Mn/Fe ratios of KC-8 and KODOS-10 were 1.32 and 6.24, respectively, indicating that KC-8 and KODOS-10 were predominantly formed in hydrogenetic and diagenetic environments. Both samples contained quartz, vernadite, buserite, and feldspar. Todorokite and illite were exclusively observed in KODOS-10. In KC-8, the phase fractions of vernadite and buserite among manganates ranged from 94(5)%–100(4)% and 6(1)%–0%, respectively. However, in KODOS-10, the fractions of vernadite, buserite, and todorokite ranged from 47(1)%–56(2)%, 33.6(4)%–40.1(3)%, and 10(3)%–16.3(8)%, respectively.

**Keywords:** manganese nodule; western and eastern Pacific Oceans; synchrotron X-ray; geochemistry; mineralogy

# 1. Introduction

Manganese (Mn) nodules, which are primarily composed of ferromanganese oxides, are metal-contained minerals found in deep-sea environments. These nodules have received significant economic interest owing to the abundance of metals contained within such as Ni, Cu, and Co and the recent increase in demand for secondary batteries as a component of electric vehicles [1–3]. They exhibit widespread distribution across the Pacific and Indian Oceans, alongside various marine environments globally, including the Atlantic and Arctic Oceans, as well as the Baltic Sea [4–15]. Previous studies on Mn nodules have mainly focused on their morphological, structural, and geochemical characteristics [7,16,17], and mineral composition. However, minor ferromanganese oxides are often inadequately observed due to limitations of conventional laboratory X-ray diffractometers (LXRD), including restricted beam flux, suboptimal resolution, and low signal-to-background ratio.

This study aimed to comprehensively analyze manganese oxide minerals within Mn nodules obtained from the Magellan Seamount in the southwestern Pacific Ocean. For this purpose, synchrotron-based X-ray diffraction (SXRD) at the Pohang Accelerator



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Laboratory (PAL) was employed. The objective was to achieve a semi-quantitative and detailed understanding of mineral compositions.

Synchrotron X-ray diffraction (SXRD) stands out in providing highly precise information about crystallized materials. While its setup resembles that of laboratory X-ray diffraction (LXRD), SXRD boasts a significantly brighter beam—approximately 100 million times brighter than its laboratory-based counterpart—alongside tunable monochromatic wavelengths and enhanced collimation. Consequently, SXRD significantly enhances phase identification and quantitative analysis of minor materials [18,19]. Since the late 1900s, synchrotron techniques such as X-ray microdiffraction ( $\mu$ XRD), X-ray fluorescence (XRF), extended X-ray absorption fine structure (EXAFS), and transmission X-ray microscopy (TXM) have been utilized to examine manganese nodules from both soil and deep-sea environments. These techniques enable researchers to discern the spatial distribution of minerals at a microscale, explore microbiological contributions, and track compositional changes within heterogeneous (micro-) nodules during their formation [20–25].

Mn nodules can be classified into hydrogenetic- and diagenetic-origin, based on their metal precipitation processes, and exhibit variations in structure, chemical composition, and mineralogy during growth [5,26]. Generally, hydrogenetic nodules exhibit smooth surface textures, laminated structures, lower Mn/Fe ratios (<2.5), and higher contents of Co, Ce, Te, and Pt [5,27]. In contrast, diagenetic nodules exhibit rough surfaces, porous structures, higher Mn/Fe ratios (Mn/Fe ratio > 2.5), higher Li, Ni, Cu, and Ca contents, and lower Ce/Th and Ce/U ratios [4,12,26,28]. However, the mineral composition of Mn nodules has not been fully elucidated, although it is expected to vary depending on the growth process. An illustrative example lies in the Fe-Mn nodules atop the tabletops of the Magellan Seamounts, which are linked with Co-rich Fe-Mn crusts. These nodules exhibit distinct layers—an inner core surrounded by Fe- and Mn-rich layers—where the nuclei display varying Mn/Fe ratios, signaling potential diagenetic processes during the initial stages of nodule formation [7].

The mineral compositions of Mn nodules, particularly the abundances of the four manganese oxide minerals (todorokite, birnessite, buserite, and vernadite [17,29]), are difficult to determine due to their small particle sizes (0.01–0.1  $\mu$ m) and low crystallinity, which prevents accurate analysis using conventional X-ray quantification methods. The chemical formulas of todorokite ((Na,Ca,K,Ba,Sr)<sub>1-x</sub>(Mn,Mg,Al)<sub>6</sub>O<sub>12</sub>·3-4H<sub>2</sub>O), birnessite ((Na,Ca,K)<sub>0.6</sub>(Mn<sup>4+</sup>,Mn<sup>3+</sup>)<sub>2</sub>O<sub>4</sub>·1.5H<sub>2</sub>O), vernadite ((Mn,Fe,Ca,Na)(O,OH)<sub>2</sub>·nH<sub>2</sub>O), and buserite (Na<sub>4</sub>Mn<sub>14</sub>O<sub>27</sub>·21H<sub>2</sub>O)) are similar. This similarity makes it challenging to differentiate them based on chemical composition, particularly through cation exchange within their structures. As a result, many previous studies on Mn nodules have provided only qualitative results for entire nodule samples or rough indications of the abundance of each mineral based on X-ray diffraction analysis graphs [27,30,31]. This study attempted to identify the minor mineral constituents in Mn nodules from the eastern and western Pacific Oceans and compare their chemical compositions. In cases where conventional quantitative analysis was challenging (i.e., for oxide minerals such as manganese oxides), we employed high-resolution data obtained through synchrotron X-ray diffraction analysis to perform semi-quantitative analysis. Through conducting this fundamental research, the advantages of high-resolution synchrotron X-ray diffraction analysis and additional applications of Mn mineral analysis are demonstrated.

## 2. Materials and Methods

# 2.1. Samples

A Manganese nodule (KC-8\_EBS01\_75, KC-8) used in this study was obtained using an epibenthic sledge from Korean Cluster-8 (KC-8, 149°34.786′ E, 17°06.125′ N, 1616 m below sea level, mbsl) of the Magellan Seamount in the Western Pacific Ocean during the R/V Isabu Expedition conducted by the Korea Institute of Ocean Science and Technology (KIOST) in 2021. Another manganese nodule (KODOS-10-2\_BC\_05, KODOS-10) was collected using a box core from the Clarion-Clipperton fracture zone (CCZ) of the eastern Pacific Ocean (131°39.796' W, 10°09.340' N, 5119 mbsl) during the R/V Onnuri Expedition in 2010 (Figures 1 and 2).



**Figure 1.** Sampling location of Mn nodules from the Western (KC-8) and Eastern (KODOS-10) Pacific Oceans.



**Figure 2.** Deep Sea Camera (DSC) image of ferromanganese nodules (black dots) on tabletop of the KC-8 seamount in the Magellan Seamount Cluster.

A total of two Fe-Mn nodules with different shapes (KC-8: spherical and KODOS-10: semi-spherical) were selected for mineralogical and geochemical analyses (Figure 1). The collected samples were broken with a hammer and ground to a bulk powder using a ball

mill (PM400, Retsch; 200 rpm, 60 min) to prepare a homogeneous sample. In total, we prepared five samples of each nodule for semi-quantification analysis.

Dehydrated samples were prepared by heating at ca. 90 °C for 12 h in air-dried condition to distinguish buserite and todorokite which have same basal reflection at 10 Å before dehydration of the buserite. We checked XRD patterns right after cooling down samples and checked again after 5 h. We found that the diffraction pattern was the same; therefore, we concluded the sample had not rehydrated during our measurement. Thermally stable buserite (buserite-II) as well as Mg-rich buserite has basal reflection of 9.6–9.7 Å. After examining our diffraction data, we could observe diffracted peak around not 9.6–9.7 Å but 10 Å. Also, basal peak was not broad, and no shoulder peak at 10 Å was detected. Therefore, we concluded that buserite-II might not exist, and the proportion of this mineral is negligible in our samples [32–35].

#### 2.2. Chemical Analysis

The compacted bulk samples were placed on a carbon tape and coated with platinum for chemical analyses. The chemical compositions were observed via energy-dispersive X-ray spectroscopy (EDS) using a ZEISS Gemini 500 (ZEISS, Oberkochen, Baden-Württemberg, Germany) field-emission scanning electron microscope (FE-SEM) at Pusan National University. EDS analyses were performed at an acceleration voltage of 15 kV and an 8.5 mm working distance. The stoichiometry of elements in each sample was averaged by ten area scans (Table 1). The analysis results were plotted in a (Cu + Ni)-Fe-Mn ternary diagram, which was divided into hydrogenetic and diagenetic origins (Figure 3).

#### 2.3. Synchrotron X-ray Powder Diffraction

High-resolution synchrotron X-ray powder diffraction data of the selected samples were measured at the 9 B beamline of the Pohang Accelerator Laboratory (PAL). The incident X-rays were vertically collimated using a mirror and monochromatized to wavelengths of 1.5419(1) or 1.5225(1) Å using a double-crystal Si(111) monochromator. The detector arm of the vertical scan diffractometer comprised six sets of Soller slits, flat Ge(111) crystal analyzers, anti-scatter baffles, and scintillation detectors, with each set separated by 20°. Each sample of ca. 0.2 g powder was prepared using the flat plate side loading method to avoid the preferred orientation, and the sample was then rotated approximately normal to the surface during the measurement to increase the sampling quality. Step scanning was performed at room temperature from 7° to 121° in two-theta with increments of 0.005° and 2° of overlap with the next detector bank. The samples were exposed for 4 s at each step to increase the degree of normalization of the diffracted beam intensity.

#### 2.4. Phase Identification and Semi-Quantitative Analysis

A qualitative phase analysis of the minerals in the samples was performed using the Match!3 program (Crystal Impact, Bonn, Germany). The background curves were determined manually and graphically. For phase identification, the second-derivative method was used to search for Bragg's peaks [36]. The "PDF-2" and "crystal open" mineral databases were used.

A semi-quantitative analysis of the selected manganate minerals was conducted by calculating the areas of the selected peaks [37,38]. The full width at half maximum (FWHM) of each peak was calculated using the profile fitting method to determine the integrated peak area for quantitative phase fraction analysis. The results of the qualitative and quantitative phase analyses are summarized in Tables 2 and 3, respectively, with error values indicated in parentheses.

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Location	Elements (%)										Mn/Fe			
	Mn	Fe	Si	Al	Mg	Ca	Na	K	C1	Ti	Со	Ni	Cu	
KC-8	34.3 (1)	26.0 (1)	10.9 (1)	4.4 (1)	5.0 (1)	4.2 (1)	8.5 (1)	0.9 (1)	2.0 (1)	1.7 (1)	1.2 (1)	0.8 (1)		1.32
KODOS-10	40.0 (1)	6.4 (1)	17.8 (1)	7.2 (1)	6.1 (1)	2.3 (1)	10.2 (1)	1.9 (1)	1.8 (1)	0.6 (1)		1.6 (1)	4.1 (1)	6.24
Southern Pacific Ocean <sup>a</sup>	16.1	16.1	7.3	3.0	1.3	2.0	1.8	0.9						1.00
Indian Ocean <sup>b</sup>	24.4	7.1	10.0	2.9	1.7	1.9	1.1	0.2						3.42
East Siberian Sea <sup>c</sup>	49.9	2.2	5.5	2.8	1.8	1.5	2.5	2.0						22.6

3. Results and Discussion

Table 1. Chemical compositions of bulk samples of Mn nodules. Errors are in parentheses.

<sup>a</sup> Hein et al., 2013 [39], <sup>b</sup> Jauhari and Pattan, 2000, Pattan et al., 2001, Baturin and Dubinchuk, 2010, Pattan and Parthiban, 2011, Balaram et al., 2006 [40–44], <sup>c</sup> Yu et al., 2020 [38].

The chemical analysis results of two bulk powder samples, KC-8 and KODOS-10, are presented in Table 1. In the KC-8 sample, the most abundant element was Mn, accounting for 34.3% of the atomic fraction, followed by Fe (26.0%), Si (10.9%), Na (8.5%), Mg (5.0%), Al (4.4%), Ca (4.2%), and K (0.9%). In contrast, KODOS-10 showed Mn as the predominant element at 40.0%, followed by Si (17.8%), Na (10.2%), Al (7.2%), Fe (6.4%), Mg (6.1%), Ca (2.3%), and K (1.9%). The presence of Si and Al, albeit lower than Mn, suggests the coexistence of aluminosilicate minerals as minor phases. This implies the inflow of dissolved mineral sources or their presence on the sediment surface. The coexistence of these minerals with Mn and Fe may contribute to their potential dilution. Notably, the Fe content differed significantly between the two samples; KC-8 comprised 26.0% Fe, while KODOS-10 contained 6.4% Fe. Consequently, the Mn/Fe ratios were 1.32 for KC-8 and 6.24 for KODOS-10. These ratios are commonly utilized to differentiate between the two genetic formation origins of Mn nodules. Hydrogenetic and diagenetic formation is assumed when the ratio is below or above 5.0, respectively [45]. The Mn/Fe ratios observed in Mn nodules from the Southern Pacific Ocean, Indian Ocean, and East Siberian Sea were 1.00, 3.42, and 22.6, respectively (Table 1). These findings suggest that the nodules from the Southern Pacific Ocean and Indian Ocean were predominantly formed through hydrogenetic processes, while those from the East Siberian Sea originated primarily through diagenesis [2,38,39].

Figure 3 shows a (Cu + Ni)-Fe-Mn ternary diagram of Mn nodules from the Magellan Seamounts in the western Pacific Ocean [7]. The western Pacific Magellan Seamount cluster, formed around 120 million years ago during the Cretaceous period, and subsequently displaced northwest due to tectonic movements, offers ideal conditions for the development of Co-rich Fe-Mn crusts owing to its low sedimentation rate ( $0.4-4 \text{ mm}/10^3 \text{ years}$ ) and obstruction of bottom currents by the seamounts [1]. In our previous results, we observed a transition from early diagenetic to hydrogenetic conditions, indicated by inner-to-outer part chemical variations (depicted as grey symbols). Additionally, the presence of todorokite primarily in the inner part, accompanied by high Mn/Fe ratios reaching up to 3.71, signifies the nodule's exposure to diagenetic conditions during the initial stages of its formation. Subsequently, a shift in origin occurred at the tabletop of the seamount. Therefore, considering these findings, the KC-8 sample obtained from the same seamount is also deemed a mixed-type nodule, showcasing a similar evolutionary pattern in its formation as observed in previous analyses [7].



**Figure 3.** Ternary diagrams of Fe-Mn-(Cu + Ni) system to differentiate the genetic origins of the ferromanganese nodules. Grey and black colored symbols represent the results of our previous and present studies, respectively [7].

Manganese nodules within the Clarion-Clipperton Zone (CCZ) in the Pacific Ocean are commonly classified as mixed-type nodules, yet their primary formations exhibit distinct differences. For instance, nodules sourced from Cook Island within the CCZ's southeastern Pacific Ocean region are primarily formed through hydrogenetic precipitation. These nodules exhibit lower Mn/Fe ratios, approximately around one, signifying a hydrogenetic origin. In contrast, nodules from the northeastern CCZ region are characterized by a higher Mn/Fe ratio of approximately five, indicating that their composition is richer in diagenetic components. These differences underscore the diverse origins and predominant formations of manganese nodules within various regions of the CCZ [39,46].

The stacked synchrotron X-ray diffraction patterns are shown in Figure 4, and the phase identification results are summarized in Table 2. Diffraction peaks belonging to quartz (SiO<sub>2</sub>), buserite (Na<sub>4</sub>Mn<sub>14</sub>O<sub>27</sub>·21H<sub>2</sub>O), and vernadite ((Mn,Fe,Ca,Na)(O,OH)<sub>2</sub>·nH<sub>2</sub>O) were predominant, and feldspar such as anorthite (Ca[Si,Al]<sub>2</sub>O<sub>8</sub>) was present as minor a constituent in all samples. Todorokite ((Na,Ca,K,Ba,Sr)<sub>1-x</sub>(Mn,Mg,Al)<sub>6</sub>O<sub>12</sub>·3–4H<sub>2</sub>O), birnessite ((Na,Ca,K)<sub>0.6</sub>(Mn<sup>4+</sup>,Mn<sup>3+</sup>)<sub>2</sub>O<sub>4</sub>·1.5H<sub>2</sub>O) and illite (K<sub>0.65</sub>Al<sub>2.0</sub>(Al<sub>0.65</sub>Si<sub>3.35</sub>O<sub>10</sub>)(OH)<sub>2</sub>) were observed only in the KODOS-10 sample. According to Park et al., todorokite can be included in KC-8 sample as nuclei. However, we did not find todorokite in this work because the fraction of todorokite in the bulk powder sample was too low to be observed by X-ray diffraction [7]. The peak intensity of vernadite (observed at 36.5° in two-theta, coexisting with buserite) appears notably higher in KC-8 compared to KODOS-10. This disparity suggests that vernadite is predominantly formed in a hydrogenetic environment, primarily through the direct precipitation of Fe oxyhydroxide. This higher intensity in KC-8 implies a greater prevalence of hydrogenetic conditions favoring vernadite formation.



T: Todorokite, B: Buserite, DB: Dehydrated Busserite, Bir: Birnessite, I: Illite, F: Feldspar, Q: Quartz, V: Vernadite

**Figure 4.** Stacked synchrotron X-ray powder diffraction patterns of the KC-8 and KODOS-10 samples. **Table 2.** Phase identification results of KC-8 and KODOS-10.

KC-8	KODOS-10
Quartz	Quartz
Feldspar Buscrito	Feldspar
Vernadite	Buserite
vernadice	Vernadite
	Birnessite
	Illite

In the case of KODOS-10, even after heating, a distinct peak at 9° persisted, identified as originating from todorokite. The notable presence of this peak aligns with the high Mn/Fe ratio (6.24), indicative of its formation primarily under diagenetic conditions. The composition of Mn nodules predominantly comprises todorokite, buserite, birnessite, and vernadite. These findings align consistently with earlier mineralogical studies conducted in the CCZ region, highlighting similar mineralogical compositions such as Fe-vernadite, todorokite, feroxyhyte, quartz, feldspar, and clay minerals [27]. They are mainly composed of manganate minerals such as 10 Å manganate minerals (e.g., 10 Å vernadite, todorokite, and buserite) and 7 Å manganate minerals (e.g., 7 Å vernadite and birnessite) [47,48].

The manganese layers in these minerals are formed by  $MnO_6$  octahedra interconnected through shared edges. Buserite, birnessite, and vernadite fall into the category of phyllomanganates, while todorokite belongs to tectomanganates. Buserite shares a similar framework with birnessite, allowing its Mn layer to readily expand or collapse based on the cation and hydration levels within its interlayers. Typically, the d-spacing of the Mn-layers (d(001)) in buserite measures around 10 Å, observed at a peak of 9° two-theta, and decreases to 7 Å at a peak of 12° two-theta when partially dehydrated to a hydration level akin to birnessite. The inflexible pore size of todorokite also measures around 10 Å, reflected in its (001) peak, similar in size and interlayer distance to buserite. Consequently, both todorokite and buserite exhibit their d(001) peak at the same two-theta (9°) in our samples. To achieve precise quantitative analysis and differentiate between todorokite and buserite, all samples underwent heating at 90 °C to partially dehydrate buserite and separate its (001) peak from the todorokite peak. For KC-8, the peak at 9° completely shifted to 12° after heating, indicating the exclusive presence of buserite in this sample. However, in KODOS-10, the intensity at 9° decreased while the peak at 12° increased after heating, indicating the coexistence of todorokite and buserite.

The semi-quantitative analysis results of the phase fractions of the selected manganate minerals (buserite, vernadite, and todorokite) based on comparing selected peak area are shown in Figure 5 and summarized in Table 3. The manganate in the KC-8 consisted mostly of vernadite, ranging from 94(5)%–100(4)%, and trace amounts of buserite, ranging from 6(1)%–0%. In contrast, while vernadite was still a major manganate in the KODOS-10, ranging from 47(1)%-56(2)%, the phase fractions of buserite and todorokite increased from 33.6(4)%-40.1(3)% and 10(3)%-16.3(8)%, respectively. In our previous study, Mn nodules in the tabletops of the OSM-9 Magellan seamount in the western Pacific Ocean included vernadite and todorokite. Diagenesis was initially dominant, while hydrogenesis gradually became more dominant over time. However, we only observed vernadite in our XRD results, and we consequently expect that the KC-8 did not undergo diagenetic processes or was formed after hydrogenetic conditions became dominant. In the KODOS-10, the vernadite and todorokite coexist. Like most of the nodules of this area, the nodules in this study were also mixed type nodules. The observed discrepancy in the mineral composition of the KODOS-10 sample could potentially be attributed to imperfect homogenization during sample preparation or indicate notable heterogeneity within the nodules. To delve deeper into comprehending the formation process specific to KODOS-10, our forthcoming study will systematically explore variations between its inner and outer parts. This investigation will employ a range of methodologies, including an age-dating method, chemical analysis, electron micro diffraction, and X-ray diffraction measurements. By scrutinizing these differences, we aim to gain a detailed and comprehensive understanding of the developmental mechanisms underlying the KODOS-10 nodules.



**Figure 5.** Ternary diagrams of phase fraction of buserite, todorokite, and vernadite resulting from semi-quantification analysis.

Sample	No.	Todorokite	Buserite	Vernadite	Sum
	1	0	1.0(1)	99(4)	100(2)
VC 9	2	0	1(1)	99(3)	100(2)
$KC-\delta$	3	0	0	100(4)	100(4)
$(KC-8_1\_ED501_75)$	4	0	6(1)	94(5)	100(3)
	5	0	1(1)	99(3)	100(2)
	1	16.3(8)	36.7(9)	47(2)	100.0(8)
	2	10(3)	40(2)	50(2)	100(2)
(VODOS10, 2, PC, 05)	3	10.5(2)	33.6(4)	56(2)	100.1(9)
(KODO310-2_DC-03)	4	12.4(3)	39.8(5)	48(1)	100.2(6)
	5	12.6(2)	40.1(3)	47(1)	99.7(5)

**Table 3.** Phase fraction (%) of manganates in the KC-8 and the KODOS-10. Estimated standard deviation is in parentheses.

Figure 6 displays the powder diffraction patterns of KC-8 and KODOS-10 using Lab-XRD and synchrotron-XRD (LXRD and SXRD), respectively, aiming to highlight differences in peak width and signal-to-background ratios. In LXRD, the background signal appears notably higher compared to SXRD. This increased background signal is typically attributed to air scattering, fluorescence, and non-crystallized sample components. SXRD benefits from an exceptionally bright beam, approximately 100 million times stronger than laboratory-sourced X-rays. It employs a Soller slit and crystal analyzer before the diffractometer to filter out noise signals and elevate the sample-to-background ratio. When utilizing SXRD, we observe distinct peaks, notably around  $12^{\circ}$  and  $18^{\circ}$  of two-theta in the KC-8 sample, enabling precise identification and semi-quantification of minor phases within the samples. A comparison of Full Width at Half Maximum (FWHM) for selected peaks is summarized in Table 4, revealing changes in peak width based on two-theta degrees when using SXRD and LXRD. While the FWHM at 9° remains similar between both XRD types, ranging from 0.53(2) to 0.59(3), the FWHM at 36.5° significantly differs, spanning 0.99(3) to 3.49(12). Moreover, the FWHM values obtained from SXRD are consistently lower than those from LXRD. The phenomenon of overlapping Bragg peaks due to emission of characteristic X-rays K $\alpha$ 1 and K $\alpha$ 2 is observed in LXRD, especially impacting semi-crystallized minerals like vernadite. This overlap, especially at high angles, may lead to errors in semi-quantitative analysis based on peak area calculations. Conversely, SXRD employs monochromatic X-rays, resulting in sharper peak widths and enabling more accurate semi-quantitative analysis.

Sampla	Maaaaaaaaaa	FWHM (°)	FWHM (°)						
Sample	Measurements	$9^\circ$ at $2\theta$	<b>12</b> °	<b>26.5</b> °	36.5°				
KC-8	Synchrotron-XRD	0.56(5)	1.75(17)	0.064(4)	0.99(3)				
	Lab-XRD	0.59(3)	-	0.089(3)	1.21(3)				
KODOS-10	Synchrotron-XRD	0.53(2)	0.33(3)	-	1.54(3)				
	Lab-XRD	0.58(6)	0.48(4)	-	3.49(12)				

Table 4. Full width at half maximum (FWHM) of selected peaks.



T : Todorokite, B : Buserite, Bir : Birnessite, I : Illite, F : Feldspar, Q : Quartz, V : Vernadite

Figure 6. Stacked plots of powder diffraction patterns using laboratory- and synchrotron-based XRD.

## 4. Conclusions

We conducted geochemical and mineralogical analyses on two bulk mixed-type Mn nodules sourced from the western and eastern Pacific Oceans. The objective was to discern differences in their genetic origins, mineral compositions, and the prevalence of various manganates. The Fe content varied between the samples, resulting in Mn/Fe ratios of 1.32 for KC-8 and 6.24 for KODOS-10. This suggests predominant influences of hydrogenetic and diagenetic conditions in the formation of KC-8 and KODOS-10, respectively. Utilizing high-resolution synchrotron X-ray diffraction (SXRD), both samples exhibited quartz, vernadite, buserite, and feldspar. However, KODOS-10 uniquely displayed birnessite and illite. Phase fractions revealed vernadite predominance above 94(5)% in KC-8, while KODOS-10 displayed a vernadite fraction ranging from 47(1)% to 56(2)%. Additionally, KODOS-10 exhibited higher proportions of buserite and todorokite, constituting 33.6(4)% to 40.1(3)%. The enhanced brightness and signal-to-background ratio of the SXRD facilitated clear observation of minor phase fractions, approximately 1%, a level not easily detected using traditional methods. Moreover, the Full Width at Half Maximum (FWHM) in SXRD was lower than that in LXRD due to differences in X-ray characteristics. We anticipate our findings will contribute fundamental insights into understanding the origin of Mn nodules in the Pacific Ocean and their distribution in seamounts. To delve deeper into nodule origins, we plan to conduct a detailed analysis of systematic differences between the inner and outer nodule sections of KODOS-10. This investigation will utilize an age-dating method, chemical analyses, electron micro diffraction, and X-ray diffraction measurements. Author Contributions: Conceptualization, J.J. and Y.L.; methodology, S.L., J.K., K.H., Y.K., K.Y., H.A., J.P. and D.S.; software, S.L., H.A. and J.P.; validation, J.K., K.H., Y.K. and K.Y.; formal analysis, S.L., H.A. and J.P.; investigation, J.J., K.Y., D.S. and Y.L.; resources, J.J.; writing—original draft preparation, J.J. and Y.L.; writing—review and editing, J.J. and Y.L.; project administration, J.J. and Y.L.; funding acquisition, J.J. All authors have read and agreed to the published version of the manuscript.

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