

Original Article

Wakefieldite-(Nd), a New Neodymium Vanadate Mineral in the Arase Stratiform Ferromanganese Deposit, Kochi Prefecture, Japan

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Abstract

Wakefieldite-(Nd), NdVO₄, is a new mineral found from the Arase stratiform ferromanganese deposit in Kochi Prefecture, Shikoku Island, Japan. It is the Nd-dominant analogue of wakefieldite-(Y) and wakefieldite-(Ce). The ferromanganese ore specimen mainly consists of hematite and caryopilite, and wakefieldite-(Nd) is typically enclosed in caryopilite. Wakefieldite-(Nd) is tetragonal, *I*4₁/*amd*, *a* = 7.338(16) Å, *c* = 6.509(19) Å, *V* = 350.5(18) Å³, *Z* = 4. The four strongest lines in the X-ray diffraction pattern [*d*(Å), *I*/*I*₀, *hkl*] using a Gandolfi camera are (3.67, 100, 200); (2.74, 51, 112); (4.84, 27, 101) and (1.89, 25, 312). Chemical composition of wakefieldite-(Nd) are V₂O₃ 35.25, As₂O₃ 0.93, SiO₂ 0.14, MnO 1.45, Fe₂O₃ 0.41, Y₂O₃ 2.87, La₂O₃ 7.61, Ce₂O₃ 7.37, Pr₂O₃ 6.04, Nd₂O₃ 26.79, Sm₂O₃ 4.41, Eu₂O₃ 1.36, Gd₂O₃ 3.41, Tb₂O₃ 0.22, Dy₂O₃ 1.41, Er₂O₃ 0.10, total 99.77 wt.%. The empirical formula is (Nd_{0.403}La_{0.118}Ce_{0.114}Pr_{0.093}Y_{0.064}Sm_{0.064}Mn_{0.052}Gd_{0.048}Eu_{0.020}Dy_{0.019}Fe_{0.013}Tb_{0.003}Er_{0.001})_{1.012}(V_{0.981}As_{0.020}Si_{0.006})_{1.007}O₄ on the basis of O = 4. The calculated density is 4.782 g/cm³.

Microtexture and co-existing relationship between wakefieldite-(Nd) and caryopilite suggest that recrystallization and dehydration of Fe- and Mn-oxyhydroxide led to the generation of hematite, caryopilite, rhodochrosite and wakefieldite-(Nd) by the metamorphism during the accretion of the host unit of the Arase deposit. Chondrite-normalized REE pattern of the host ferromanganese ore, which is regarded as oceanic metalliferous sediment in origin, shows negative Ce anomaly. Chemical composition of wakefieldite-(Nd) reflects Ce-depleted bulk composition of REE-enriched ferromanganese ore.

Keywords: Arase, Japan, rare earth, stratiform ferromanganese deposit, wakefieldite-(Nd).

1. Introduction

Stratiform ferromanganese ores within accretionary complexes in Japan commonly have 900–2260 ppm of total rare earth elements (REE) as whole-rock composition (Kato *et al.*, 2005a, b; Moriyama *et al.*, 2007). These total REE concentrations of ferromanganese ores are an

order of magnitude more than those of the upper continental crust (e.g. Taylor & McLennan, 1985; Rudnick & Gao, 2003). In spite of high REE concentration, no REE-bearing minerals have been described from the stratiform ferromanganese ores. We discovered a new Nd-dominant vanadate mineral, wakefieldite-(Nd), in the REE-enriched ferromanganese ore sample collected

Received 17 June 2010. Accepted for publication 4 October 2010.

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from the Arase deposit, Kochi Prefecture, Shikoku Island of Japan.

Wakefieldite-(Nd) was approved by the International Mineralogical Association (IMA), Commission on New Minerals, Nomenclature and Classification (CNMNC), #2008-032. The mineral is named according to the Levinson nomenclature for rare earth minerals, as the Nd-dominant analogue of wakefieldite-(Y) and wakefieldite-(Ce). The wakefieldite-(Nd) is found in the ferromanganese ore specimen from the Arase deposit, which is deposited in the Geological Museum of the Geological Survey of Japan, AIST. This ore specimen was donated by Dr Toyofumi Yoshimura (Endo & Bunno, 2000). The specimen number of this specimen had been labeled "GSJ D39505" as an ore specimen when the new mineral proposal was submitted, however, the wakefieldite-(Nd)-bearing ore specimen is newly labeled "GSJ M41500" as a mineral type specimen in the Geological Museum of the Geological Survey of Japan.

Wakefieldite-(Y) was first described in pegmatite near Wakefield Lake, Quebec, Canada (Miles *et al.*, 1971). Wakefieldite-(Ce) was found in silicified limestone with other vanadate minerals from Kusu, Congo (Deliens & Piret, 1977; Baudracco-Gritti *et al.*, 1987), quartz vein from Tifernite, Morocco, zeolite-calcite veinlet within porphyritic trachyte from Yellow Lake, British Columbia, Canada (Howard *et al.*, 1995), and pegmatitic vein in Mt. Gee, South Australia (Bakker & Elburg, 2006). The wakefieldite-(La) was discovered from Glücksstern mine, Friedrichroda, Germany (Witzke *et al.*, 2008), the type locality of some new vanadate minerals such as gottlobite and vésigniéite (Guillemin, 1955; Witzke *et al.*, 2008).

The purpose of this paper is to describe the new mineral, wakefieldite-(Nd), from the Arase ferromanganese deposit, and discuss its genetic environment.

2. Geological setting of ferromanganese deposit in Shikoku

The Shikoku Island of Japan is composed of accretionary complexes of various formation ages. These are the Kurosegawa belt including the Permian accretionary complex, Jurassic Chichibu belt, Jurassic Mino-Tamba belt, Jurassic to Cretaceous Mikabu belt, Cretaceous Sambagawa metamorphic belt, and Cretaceous to Tertiary Northern and Southern Shimanto belt (Isozaki, 1996; Sudo & Murao, 2004) (Fig. 1). Stratiform manganese and ferromanganese deposits occur within the Chichibu, Kurosegawa and Northern Shimanto belts

(Fig. 1a). The representative ferromanganese deposits such as the Kunimiyama, Takagawa, Shobu and Toyama occur in the Chichibu belt, and the Nanatsubuchi and Arase deposits in the Kurosegawa belt (Yoshimura, 1969). These deposits were mined until the 1960s.

The Kurosegawa belt is composed of the Shirakidani and Shingai Formations (Suyari, 1961; Isozaki, 1985, 1986; Isozaki & Itaya, 1990; Wakita *et al.*, 2007). These formations consist mainly of mudstone and sandstone, and include occasionally basalt, volcanoclastite, limestone and chert (Suyari, 1961; Isozaki, 1985). The metamorphic mineral assemblage of pumpellyite, prehnite, chlorite and epidote without actinolite in basalts in the Shirakidani and Shingai Formations indicates that these units underwent prehnite-pumpellyite facies metamorphism (Isozaki, 1986). Suyari (1961) and Isozaki (1986) reported late Carboniferous to late Permian radiolarian and fusulinid fossils from the Shirakidani and Shingai Formations.

The Arase ferromanganese deposit immediately overlies basalt and underlies limestone in the Shirakidani Formation as a 60 m-long stratiform orebody elongated in NE-SW direction (Yoshimura, 1969).

3. Analytical procedure

Mineral composition of wakefieldite-(Nd) was analyzed using a JEOL JXA-8800 M WDS electron microprobe analyzer (EPMA; JEOL, Tokyo, Japan) at the National Museum of Nature and Science, Japan. The operating conditions included a beam diameter of 2 μm , 15 kV and 20 nA probe current, and standard ZAF correction. Powder X-ray diffraction data of wakefieldite-(Nd) and other constituent minerals were obtained using a Gandolfi camera with 114.6 mm in diameter and employing Ni-filtered $\text{CuK}\alpha$ radiation at the National Museum of Nature and Science. The powder X-ray diffraction patterns without and with a Si-standard material (National Bureau of Standards as abbreviated NBS hereafter, #640b) on the surface of the sample fragment were recorded on imaging plates and processed with a Fuji BAS-2500 bio-imaging analyzer (Fuji, Tokyo, Japan) and with a computer program by Nakamuta (1999).

Raman spectra of the minerals were obtained using a HORIBA LabRam HR800 Raman microscope system (HORIBA, Kyoto, Japan) at the Geological Survey of Japan, which also includes a monochromator, a filter system and a charge coupled device. Raman spectra

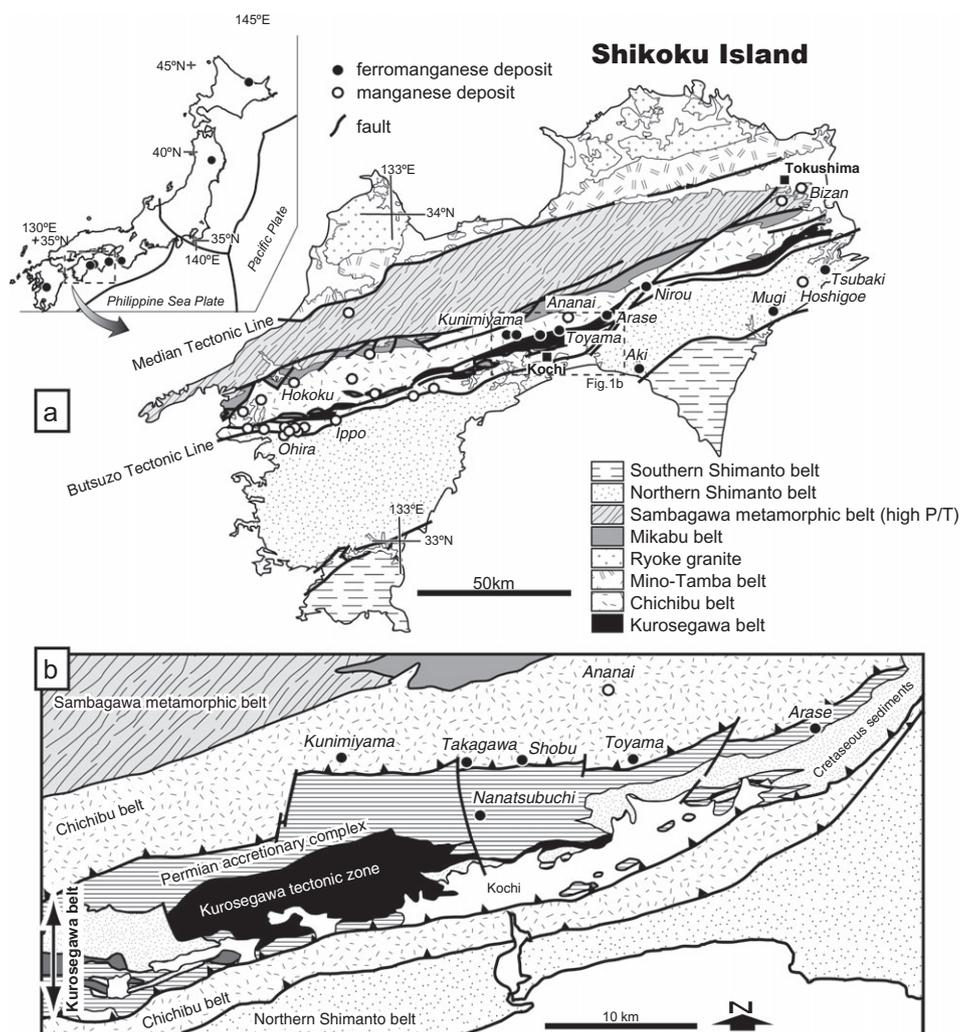


Fig. 1 (a) Geological map of the Shikoku Island, Japan with distribution of stratiform manganese and ferromanganese deposits (Yoshimura, 1969; Sudo & Murao, 2004). (b) Geological map of central Shikoku (Isozaki & Itaya, 1990).

were excited by an Ar laser (514 nm) at a resolution of 0.56 cm^{-1} in the range between 200 and 1500 cm^{-1} .

Whole-rock major and trace element compositions of ore specimens were obtained using an inductively coupled plasma mass spectrometer (ICP-MS) at Activation Laboratories Ltd, Canada.

4. Sample description

The ferromanganese ore specimen GSJ M41500 is massive in texture and black to reddish brown in color. It consists of hematite, caryopilite, calcite, rhodochrosite and wakefieldite-(Nd). Laminated texture

composed of hematite, caryopilite and elongated rhodochrosite is observed under reflected microscope. Dark orange colored caryopilite occurs as lenses parallel to the lamination (Fig. 2c). Wakefieldite-(Nd) grains occur within caryopilite, and do not exceed $20 \mu\text{m}$ in size (Fig. 2e).

4.1 Physical and optical properties of wakefieldite-(Nd)

Most physical and optical properties of wakefieldite-(Nd) such as cleavage, hardness and density were not determined because of small grain size. Crystals of wakefieldite-(Nd) generally form anhedral

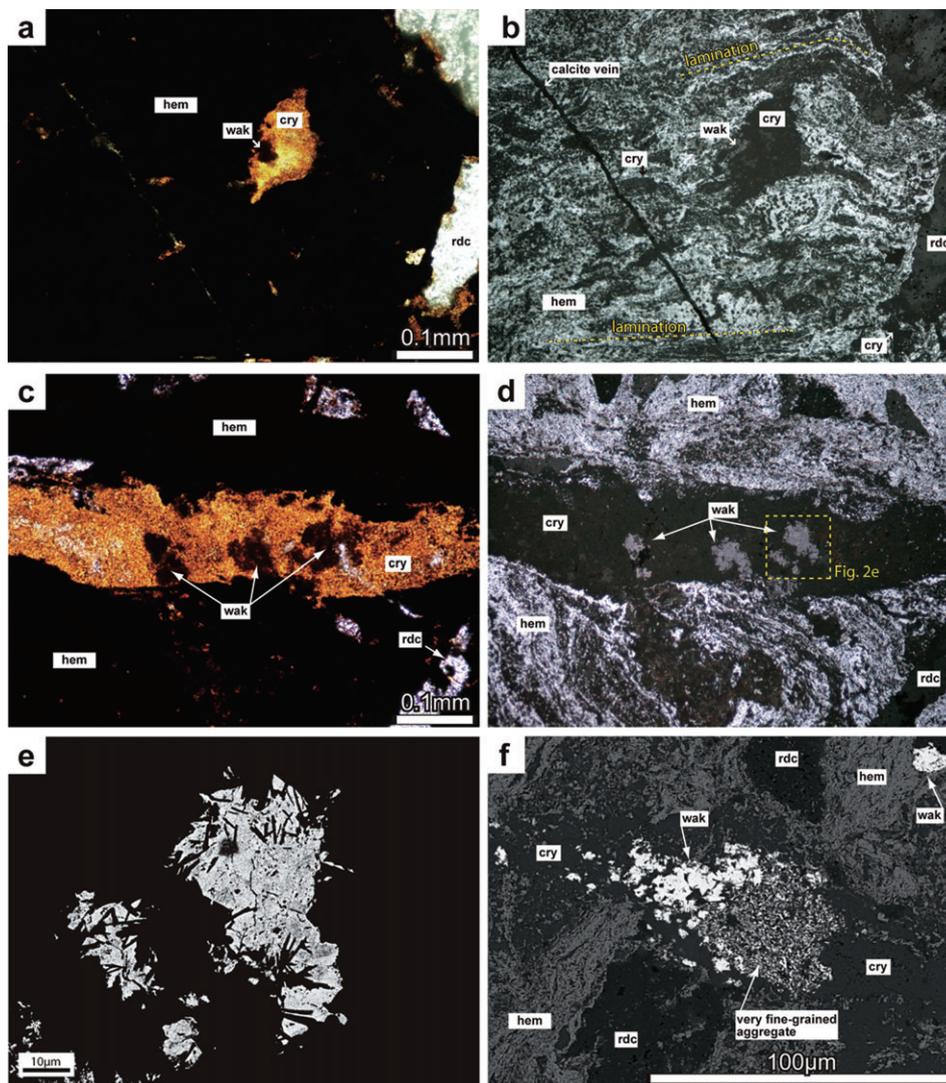


Fig. 2 Photomicrographs of wakefieldite-(Nd) (IMA2008-031) in the stratiform ferromanganese ore specimen (GSJ M41500) from the Arase deposit, Kochi Prefecture, central Shikoku, Japan. (a) Occurrence of caryopilite and wakefieldite-(Nd) under microscope (plane-polarized light). Lens-shape caryopilite enclosing fine-grained wakefieldite-(Nd) aggregate. (b) Micro texture of ferromanganese ore specimen of Figure 2a and occurrence of caryopilite and wakefieldite-(Nd) with calcite vein under reflected microscope. Laminated texture composed of hematite is often disturbed by lens-shape caryopilite and rhodochrosite. (c) Ferromanganese ore consisting of hematite, caryopilite, rhodochrosite, and wakefieldite-(Nd). Wakefieldite-(Nd) occurs within orange color caryopilite (plane-polarized light). (d) Reflection image of Figure 2c. Reflection color of wakefieldite-(Nd) is slightly dark gray. (e) Back-scatter electron image of wakefieldite-(Nd) grain in Figure 2d. (f) SEM image of wakefieldite-(Nd) and very fine-grained aggregate of wakefieldite-(Nd) and caryopilite, enclosed in caryopilite. cry: caryopilite, hem: hematite, rdc: rhodochrosite, wak: wakefieldite-(Nd).

fine-grained aggregates in the sample (Fig. 2e,f), and rarely show columnar euhedral shape. Wakefieldite-(Nd) is colorless or slightly reddish pink in thin section, however, it is difficult to identify color because of fine-grained aggregates (Fig. 2a,c). Color of wakefieldite-

(Nd) is dark gray under plane-reflected light microscope (Fig. 2), and weak reflection pleochroism and anisotropy are observed. The calculated density is 4.782 g cm^{-3} based on the empirical chemical formula and lattice parameters.

Table 1 Chemical composition of wakefieldite-(Nd) from the Arase ferromanganese ore specimen by electron microprobe (GSJ M41500)

	wt.% avg.	Range	1 σ	Cation	
La ₂ O ₃	7.61	4.87–11.38	2.58	La	0.118
Ce ₂ O ₃	7.37	4.25–11.12	2.34	Ce	0.114
Pr ₂ O ₃	6.04	5.22–7.83	0.89	Pr	0.093
Nd ₂ O ₃	26.79	21.86–30.81	2.86	Nd	0.403
Sm ₂ O ₃	4.41	3.06–5.66	1.08	Sm	0.064
Eu ₂ O ₃	1.36	0.96–1.98	0.35	Eu	0.020
Gd ₂ O ₃	3.41	2.26–4.97	1.08	Gd	0.048
Tb ₂ O ₃	0.22	0–0.47	0.15	Tb	0.003
Dy ₂ O ₃	1.41	0.61–2.25	0.58	Dy	0.019
Er ₂ O ₃	0.10	0–0.23	0.09	Er	0.001
Y ₂ O ₃	2.87	1.11–4.53	1.26	Y	0.064
MnO	1.45	0.67–1.93	0.48	Mn	0.052
Fe ₂ O ₃	0.41	0–0.95	0.31	Fe	0.013
				<i>sum = 1.011</i>	
V ₂ O ₅	35.25	34.34–36.12	0.66	V	0.981
As ₂ O ₅	0.93	0.71–1.24	0.18	As	0.020
SiO ₂	0.14	0.10–0.21	0.04	Si	0.006
				<i>sum = 1.007</i>	
Total	99.77				

Number of cations are calculated on the basis of 4 oxygens.

4.2 Chemical composition of wakefieldite-(Nd)

The results of the electron microprobe analysis are given in Table 1. The chemical composition leads to an empirical formula as (Nd_{0.403}La_{0.118}Ce_{0.114}Pr_{0.093}Y_{0.064}Sm_{0.064}Mn_{0.052}Gd_{0.048}Eu_{0.020}Dy_{0.019}Fe_{0.013}Tb_{0.003}Er_{0.001})_{1.012}(V_{0.981}As_{0.020}Si_{0.006})_{1.007}O₄ on the basis of O = 4. The simplified formula is (Nd,La,Ce,Pr)(V,As)O₄, and the ideal formula is NdVO₄, which requires Nd₂O₃ 64.91 wt.% and V₂O₅ 35.09 wt.%. No O-H stretching Raman spectrum was observed between 3000 and 3500 cm⁻¹ in wakefieldite-(Nd).

4.3 Crystallography

Single crystal studies were not carried out due to the small size. The powder X-ray diffraction data of wakefieldite-(Nd) are given in Table 2 with reference data of wakefieldite-(Ce) (Deliens & Piret, 1977), wakefieldite-(Y) (Miles *et al.*, 1971) and La-dominant wakefieldite-(Ce) (IMA89-035a), as well as synthetic NdVO₄ (ICDD #15-769) (National Bureau of Standards, 1966), CeVO₄ (ICDD #12-757) (National Bureau of Standards, 1962) and YVO₄ (ICDD #17-341) (National Bureau of Standards, 1965). Wakefieldite-(Nd) is tetragonal with space group *I4₁/amd*. The unit cell parameters, refined from the powder X-ray diffraction data with the Si-standard material using a computer

Table 2 Crystallography and X-ray powder-diffraction data for wakefieldite-(Nd) from the Arase deposit (GSJ M41500), and reference data of wakefieldite minerals and synthetic rare earth vanadates

<i>a</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)	<i>Z</i>	Wakefieldite-(Nd)†		NdVO ₄ ‡		Wakefieldite-(La)§		Wakefieldite-(Ce)¶		Wakefieldite-(Y)‡‡		YVO ₄ §§	
				<i>d</i> _{meas}	<i>d</i> _{calc.}										
101	27	4.84	4	4.87	4.835	2	4.906	7.41	7.35	4.89	4.89	4.74	4.711	8	4.711
200	100	3.67	100	3.67	3.664	100	3.707	6.50	6.56	3.68	3.68	3.56	3.559	100	3.559
211	7	2.92	12	2.93	2.921	5	2.939	356.8(6)	4	2.933	2.933	2.83	2.831	2	2.831
112	51	2.74	70	2.76	2.732	10	2.759			2.766	2.766	2.66	2.668	46	2.668
220	11	2.60	20	2.59	2.590	7	2.623			2.594	2.594	2.51	2.518	12	2.518
202	4	2.42	6	2.43	2.419	3	2.447					2.35	2.357	6	2.357
301	9	2.29	16	2.29	2.284	5	2.309			2.291	2.291	2.21	2.220	12	2.220
103	14	2.09	10	2.08	2.059	5	2.088			2.086	2.086	2.01	2.012	5	2.012
321			12	1.938	1.938	4	1.902			1.941	1.941	1.881	1.884	6	1.884
312	25	1.886	55	1.889	1.881	19	1.853			1.891	1.891	1.824	1.830	46	1.830
400	7	1.838	16	1.835	1.833	3	1.811			1.833	1.833	1.774	1.780	13	1.780

†This study, ‡ICDD #15-769, §Witzke *et al.* (2008), ¶Deliens and Piret (1977), ††Miles *et al.* (1971), †††ICDD #17-341.

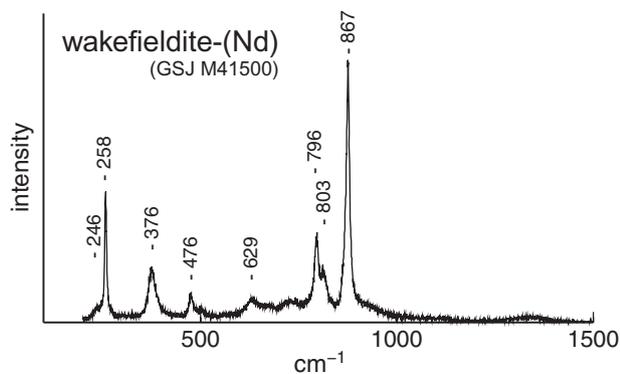


Fig. 3 Raman spectra of wakefieldite-(Nd) in the Arase ferromanganese ore (GSJ M41500) from Kochi Prefecture, Japan.

program by Toraya (1993), are; $a = 7.338(16) \text{ \AA}$, $c = 6.509(19) \text{ \AA}$, $V = 350.5(18) \text{ \AA}^3$, and $Z = 4$.

Figure 3 exhibits Raman spectrum of wakefieldite-(Nd). The Raman peaks of wakefieldite-(Nd) and wakefieldite-(Ce) presented by the RRUFF project database (<http://rruff.info/>) (RRUFF ID: D060176 and D060542) and synthetic NdVO_4 , CeVO_4 and YVO_4 (Au *et al.*, 1996; Au & Zhang, 1997) are tabulated in Table 3. The Raman spectrum of wakefieldite-(Nd) shows three strong peaks at 780–880 cm^{-1} and weak to moderate peaks at 200–500 cm^{-1} . The Raman spectrum of wakefieldite-(Nd) in ferromanganese ore is consistent with those of wakefieldite-(Ce) by the RRUFF project database. The Raman peaks of wakefieldite-(Nd) are also similar to those of synthetic NdVO_4 (Au & Zhang, 1997) at 380, 480, 800, 810 and 870 cm^{-1} .

4.4 Whole-rock composition

Representative whole-rock major and trace element compositions of the Arase ferromanganese specimen (GSJ M41500) are shown in Table 4. The sample consists of Fe, Mn, Si, and Ca as major constituents with trace amounts of V, Ni, Zn, As, Y and REE. It mainly consists of Fe and Mn, and Mn/Fe ratio of the ore is 0.9 (Fig. 4a). Chondrite-normalized REE pattern of the Arase ferromanganese ore (Fig. 4b) shows LREE enrichment ($\text{La}_N/\text{Yb}_N = 8.7$: the subscript N indicating that all elements are normalized to the Chondrite values) and negative Ce anomaly ($2\text{Ce}_N/(\text{La}_N + \text{Pr}_N) = 0.22$). Whole-rock compositions of ferromanganese ore sample (GSJ D39514) from the Kunimiyama deposit in the Chichibu belt, located about 40 km east of the Arase deposit (Fig. 1), are also shown in Table 4 for comparison (Fig. 4).

5. Genetic environment of wakefieldite-(Nd) in ferromanganese ore

The Shirakidani Formation, which contains the Arase ferromanganese orebody, comprises Permian limestone blocks, Permian chert and basaltic rocks in sandstone and mudstone matrix. Isozaki (1986, 1996) suggested that seamounts with reef limestone collapsed prior to the subduction and the Shirakidani Formation contains mechanically mixed limestone–basalt and pelagic sediment–basalt blocks in terrigenous clastics during the accretionary event. The Arase orebody occurs between footwall pillow basalt lava and hanging wall limestone (Yoshimura, 1969), indicating that the orebody was deposited on submarine basalt lavas.

The Arase ferromanganese ore sample is high in Fe_2O_3 , MnO and V concentrations (Table 4). Geochemical data of the Arase and Kunimiyama ore samples plot consistently within the field of submarine-hydrothermal deposits as metalliferous sediment on a geochemical discrimination diagram (Bonatti *et al.*, 1972) (Fig. 4a). The Chondrite-normalized REE patterns of the Arase and Kunimiyama ore samples are consistent with those of hydrothermal metalliferous sediments on East Pacific Rise (EPR) with negative Ce anomaly rather than hydrogenous ferromanganese crust with positive Ce anomaly (Barrett & Jarvis, 1988; Hein *et al.*, 2005; Kato *et al.*, 2005a) (Fig. 4b). Major and trace element compositions of the Arase ore suggest that the deposit was formed by precipitation of Fe- and Mn-oxyhydroxides from hydrothermal solutions associated with submarine magmatic activities (Gurvich, 2006). Geochemical composition of the Arase ore is comparable to the Kunimiyama ore, which is immediately underlain Mid-Ocean Ridge (MOR) type basalt and overlaid by red chert (Sawamura & Yoshinaga, 1953; Nozaki *et al.*, 2005; Kato *et al.*, 2005a) (Fig. 4b).

Modern metalliferous sediment near the EPR is mainly composed of Fe- and Mn-oxyhydroxides and Fe-smectite minerals, and these materials are the prevalent carriers of the trace elements such as V and REE in metalliferous sediments (Gurvich, 2006). On the other hand, hematite and caryopillite are dominant phases in both the Arase and Kunimiyama ferromanganese ores. Hematite was probably formed by dehydration during the accretion rather than diagenetic process on the seafloor because of absence of hematite in the core sample of metalliferous sediments at EPR (Bodei *et al.*, 2008). Laminated texture by foliated hematite, caryopillite and rhodochrosite is occasionally disturbed by wakefieldite-(Nd)-enclosed caryopillite

Table 3 Raman spectra of wakefieldite-(Nd), wakefieldite-(Ce) and synthetic CeVO₄, NdVO₄ and YVO₄

Wakefieldite-(Nd) [†] Arase, SW Japan	NdVO ₄ [‡] synthetic	Wakefieldite-(Ce) [§] North Balacko, Canada	Wakefieldite-(Ce) [¶] Yellow Lake, Canada	CeVO ₄ ^{††} synthetic	YVO ₄ ^{†††} synthetic	Assignment
	148 s	122 w		120 s 148 vs 202 m	122 m 150 w	
246 w		227 w	228 w			REE-O vibration
258 s		269 vw	260 m	244 m	280 vs 320 vs 398 vs	REE-O vibration REE-O vibration REE-O vibration
376 m	386 w 408 vw	374 m	376 m			
476 m	476 vw 528 vw	465 w	466 w	482 w	422 s 494 m	REE-O vibration
629 w	706 w				662 w	V2O5 (<i>impurity</i>)
796 s	798 m	785 s	785 m			vibration of VO ₄ group
803 m	812 m	798 m	798 m			vibration of VO ₄ group
867 vs	874 s	862 vs	862 vs		820 w 842 w 896 s	vibration of VO ₄ group
	1000 m			1012 vw	1090 s	V2O5 (<i>impurity</i>)

[†]This study, [‡]Au and Zhang (1997), ^{††}Au *et al.* (1996).

[§]RRUFF ID = D060176 (<http://rruff.info/wakefieldite/>display=default/R060176).

[¶]RRUFF ID = D060542 (<http://rruff.info/wakefieldite/>display=default/R060542).

Raman spectra of wakefieldite-(Ce) was determined by RRUFF project database (<http://rruff.info/>).

Table 4 Whole-rock compositions of the Arase and Kunimiyama ferromanganese ore samples in central Shikoku, Japan

Deposit	GSJ ID	Major element (wt.%)														Trace element (ppm)							
		Fe ₂ O ₃	MnO	SiO ₂	CaO	V	As	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	ΣREE
Arase	GSJ M41500	39	33.1	16.4	1.78	1413	265	422	656	296	146	582	126	31	138	21	110	20	60	8.5	54	8.1	2256
Kunimiyama	GSJ D39514	38.1	28.8	14.4	5.19	1417	340	330	506	303	121	485	110	27	119	18	96	17	50	7.1	44	6.5	1910

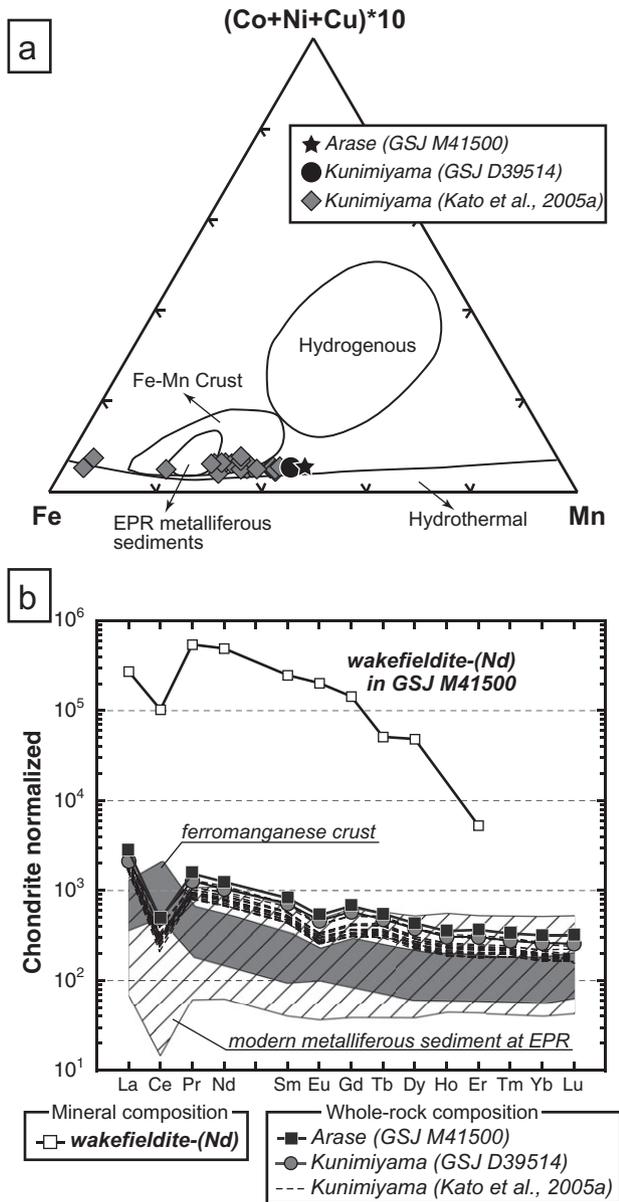


Fig. 4 (a) Whole-rock compositions of the Arase and Kunimiyama ferromanganese ores on the Mn-Fe-(Co+Ni+Cu)*10 discrimination diagram (Bonatti *et al.*, 1972). (b) Chondrite-normalized REE patterns of wakefieldite-(Nd) in GSJ M41500 determined by the electron microprobe, and those of whole-rock ferromanganese ores from the Arase (GSJ M41500) and Kunimiyama deposits measured by the ICP-MS. Gray hatch and slashed area indicate compositions of ferromanganese crusts at California (Hein *et al.*, 2005) and modern oceanic metalliferous sediments at EPR (Barrett & Jarvis, 1988), respectively.

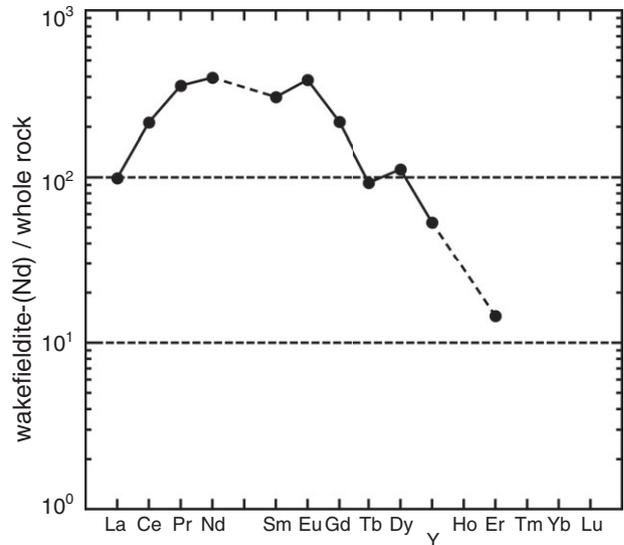


Fig. 5 REE pattern of wakefieldite-(Nd) normalized by whole-rock composition of the Arase ferromanganese ore.

(Fig. 2b). This texture suggests that caryopilite was formed at a syn- or post-hematite recrystallization stage under ductile condition. Finally, calcite veins crosscut these textures (Fig. 2b). The original sedimentary environment and the texture of ferromanganese ores at Arase suggest that wakefieldite-(Nd) was crystallized during the prehnite-pumpellyite facies metamorphic process with recrystallization of Fe- and Mn-oxyhydroxide to hematite, caryopilite, and rhodochrosite. Very fine grains of wakefieldite-(Nd) (<10 μm) are also observed from the Kunimiyama ferromanganese ore specimen (GSJ D39514). Crystallization of wakefieldite-(Nd) in the REE- and V-enriched ferromanganese ore would be common phenomena under prehnite-pumpellyite facies metamorphism.

Whole-rock compositions of modern metalliferous sediments and ferromanganese ore specimen have negative Ce anomaly (Fig. 4b) because of selective elimination of Ce from seawater under oxic conditions. This negative Ce anomaly is also reflected in the REE pattern of the wakefieldite-(Nd) (Fig. 4b). The REE pattern of wakefieldite-(Nd) normalized by whole-rock composition shows an enrichment of light to middle rare earth ions in wakefieldite-(Nd) (Fig. 5). However, La and Ce are relatively depleted in wakefieldite-(Nd) compared to other light-middle rare earth ions. This depletion is consistent with vanadate minerals with the xenotime-type structure, which are depleted in large

La ion in Kolitsch & Holtstam (2004) and Fan *et al.* (2006).

Acknowledgments

We thank Ms. M. Shigeoka, National Museum of Nature and Science, for her assistance in the electron microprobe analysis, and also Dr N. Takeno, Institute for Geo-Resources and Environment, AIST, for his support in the Laser-Raman micro-spectrometer analysis. The Geological Museum of the Geological Survey of Japan, AIST, is thanked for permission to use ore collection of the Arase deposit (GSJ M41500) and Kunimiyama deposit (GSJ D39514). We thank Dr E. L. Tongu (Council for Geoscience, South Africa) for his helpful comments on early versions of the manuscript. We also thank Professor H. Shimazaki for critical review of the manuscript. This work is partially supported by the Sasakawa Scientific Research Grant from the Japan Science Society.

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