

Michitoshiite-(Cu), a new Ge-containing platinum-group mineral from Kumamoto Prefecture, Japan

Takahiro Tanaka¹, Tadashi Shinmachi², Kota Kataoka³ and Daisuke Nishio-Hamane^{3*}

¹ Nittetsu mining, Chiyoda-ku, Tokyo 100–8377, Japan

² Ozato, Ichki-Kushikino, Kagoshima 899–2103, Japan

³ Institute for Solid State Physics, the University of Tokyo, Kashiwa, Chiba 277–8581, Japan

*Author for correspondence: hamane@issp.u-tokyo.ac.jp

Abstract Michitoshiite-(Cu) is a new Ge-containing platinum-group mineral discovered from the Haraigawa, Misato machi, Kumamoto Prefecture, Japan. It is named in honor of Michitoshi Miyahisa (1928–1983), a former professor of the Ehime University. Michitoshiite-(Cu) occurs mainly as the outermost layer of the nub consisting of cuprorhodsite in association with the isoferroplatinum-based grain. The grain of michitoshiite is anhedral shape up to 5 μm in size. It is opaque with a metallic luster and shows silver-gray color on the surface of nub. In reflected light, michitoshiite-(Cu) shows pale gray color with brownish tint. The Mohs hardness is 5 determined using synthetic compound. The density is 10.78 g/cm^3 calculated from the empirical formulae and the unit cell volume. The empirical formula based on 2 apfu is $(\text{Rh}_{0.95}\text{Pt}_{0.03}\text{Ir}_{0.01})_{\Sigma 0.99}[(\text{Cu}_{0.36}\text{Fe}_{0.24})_{\Sigma 0.60}\text{Ge}_{0.41}]_{\Sigma 1.01}$, and the simplified formulae is $\text{Rh}[(\text{Cu},\text{Fe}),\text{Ge}]$. Powder X-ray diffraction pattern was indexed as a cubic $Pm\bar{3}m$ (#221) with the lattice parameters $a = 2.9771(11) \text{ \AA}$ and $V = 26.39(3) \text{ \AA}^3$ ($Z = 1$). Based on the relationship between the composition and crystal structure by the synthetic experiment, michitoshiite-(Cu) is defined to be a mineral species with the composition of $\text{Rh}(\text{Cu}_{1-x}\text{Ge}_x)$ $0 < x \leq 0.5$ and the *bcc*-based structures.

Key words: michitoshiite-(Cu), platinum-group mineral, CsCl-type structure, Haraigawa, Kumamoto Prefecture

Introduction

Platinum-group minerals (PGM) are currently a large group of nearly 170 species, of which only two PGM containing Ge: marathonite $\text{Pd}_{25}\text{Ge}_9$ and palladogermanide Pd_2Ge (McDonald *et al.*, 2021). Ge is a rare element in the mantle, and so there is little opportunity to encounter the platinum-group elements (PGE), which is primarily located in the mantle. So far, no minerals containing Rh and Ge have been found. However, we recently discovered an unknown mineral containing Rh and Ge from a placer PGM deposit found in Haraigawa, Misato machi, Kumamoto Prefecture, Japan (Nishio-Hamane *et al.*, 2019). The mineral was initially reported as an unknown mineral with a composition of $\text{Rh}(\text{Ge},\text{Cu},\text{Fe})$, while as a result of our investigation, it was revealed to be a new mineral of the CsCl-type structure with $\text{Rh}[(\text{Cu},\text{Fe}),\text{Ge}]$ composition. Its crystal structure can be described by an order-disorder relationship based on the body-

tered cubic (*bcc*) structure, as discussed latter.

This new mineral is named michitoshiite-(Cu) in honor of former professor Michitoshi Miyahisa (1928–1983) of the Ehime University, who contributed greatly to the advancement of mineralogy, petrology and economic geology in Japan through his research on many ore deposits in Kyushu. He once focused on Ge as a resource and studied Ge-bearing minerals from Kyushu (e.g, Kinoshita and Miyahisa, 1953). The suffix of mineral name represents Cu-dominant character. Mineral and name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA2019-029a). The type specimen of michitoshiite-(Cu) has been deposited at the National Museum of Nature and Science, Tsukuba, Japan, specimen number NSM-46298 (holotype) and NSM-46299 (cotype). This paper includes a description of new mineral and the observations for the synthetic compounds made to determine the crystal structure.

Occurrence

The PGM placer deposit where the michitoshiite-(Cu) was found is located at Haraigawa, Misato machi, Kumamoto Prefecture, Japan (32°34'50"N 130°47'59"E). Most of the PGM placer is composed of the isoferroplatinum-based grains, and the grain surface is often altered to tulameenite or tetraferroplatinum. Such isoferroplatinum-based grains are characterized by many inclusions and nubs (Nishio-Hamane *et al.*, 2019). The nubs consist mainly of laurite, erlichmanite, cuprorhodsite, ferrotorreyweiserite, and shiranuiite. Nishio-Hamane *et al.* (2024) demonstrated that the cuprorhodsite- and shiranuiite-based nub originates from bowieite, which is the second most common inclusions of the isoferroplatinum-based grains. Ferrotorreyweiserite may also derived from bowieite, because it occurs as the nub and has the Rh-dominant character as same as cuprorhodsite and shiranuiite. Michitoshiite-(Cu) occurs in association with the cuprorhodsite-, ferrotorreyweiserite-, or shiranuiite-based nubs.

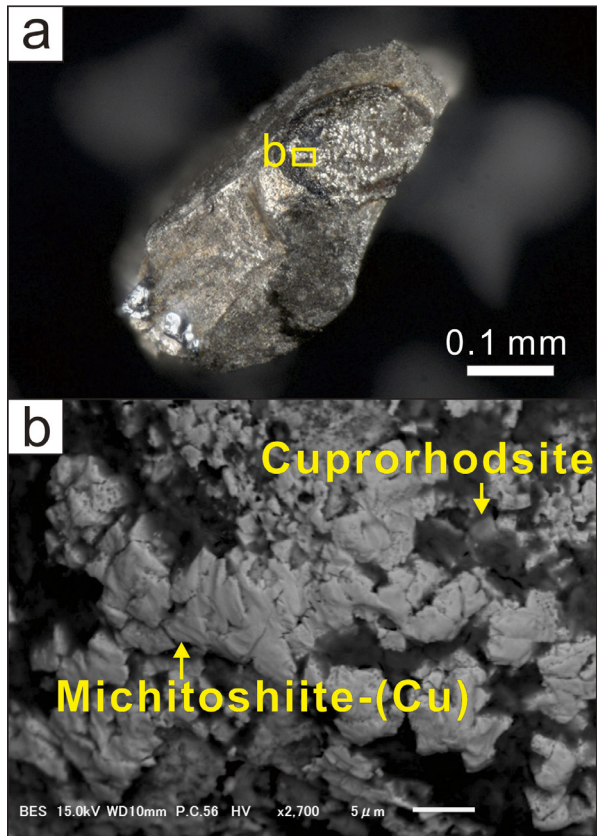


Fig. 1. The representative occurrence of michitoshiite-(Cu) (a). Michitoshiite-(Cu) forms the outermost layer of the cuprorhodsite-based nub in association with the isoferroplatinum-based grain (b).

Fig. 1 shows representative occurrence of michitoshiite-(Cu). In its most common occurrence, michitoshiite-(Cu) forms the outermost layer of the cuprorhodsite-based nub associated with isoferroplatinum-based grain. It rarely occurs as a component inside the nub in association with cuprorhodsite, ferrotorreyweiserite, or shiranuiite. Fig. 2 shows the coexistence of michitoshiite-(Cu) and ferrotorreyweiserite. In this type of the occurrence, michitoshiite-(Cu) occurs along the crack in the aggregate. Nishio-Hamane *et al.* (2019, 2024) reported similar mixture occurrence of michitoshiite-(Cu) and cuprorhodsite or shiranuiite. Since Ge is not contained in the isoferroplatinum-based grain and its inclusions, it must have come from an external source.

Michitoshiite-(Cu) on the surface of the nub shows a silver-gray color and pale gray with brown-

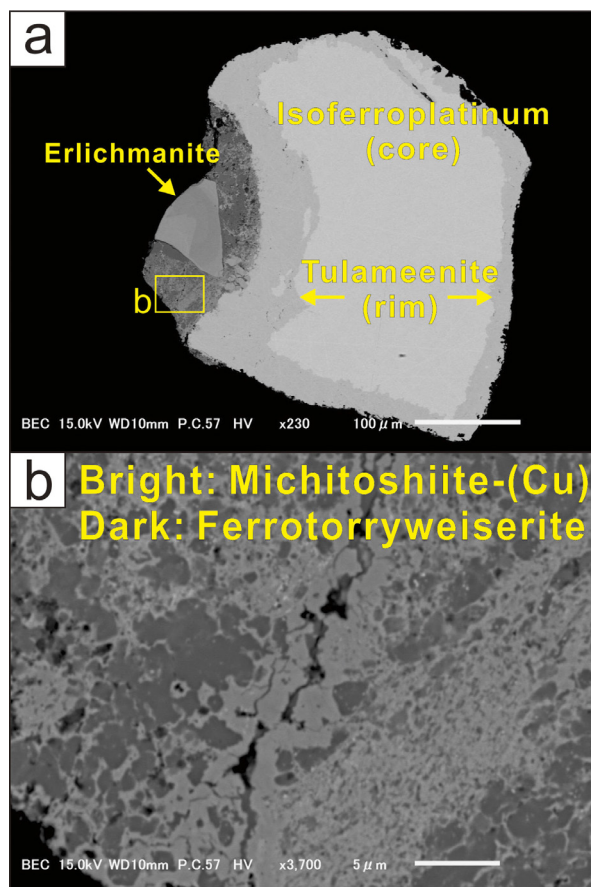


Fig. 2. Back-scattered electron images of a polished plane for the occurrence of michitoshiite-(Cu). The isoferroplatinum-based grain covered with tulameenite has the nub consisting of erlichmanite, michitoshiite-(Cu), and ferrotorreyweiserite (a). The nub, excluding erlichmanite, consists of the mixture of michitoshiite-(Cu) and ferrotorreyweiserite (b).

ish tint in reflected light. It is fine anhedral grains up to 5 μm on the nub. The Mohs hardness obtained using synthetic analogue is 5. The calculated density is 5.78 $\text{g}\cdot\text{cm}^{-3}$ from the empirical formula and powder X-ray diffraction (XRD) data. Other physical and optical properties could not be determined due to the small grain size.

Chemical composition

Chemical analyses were conducted using a scanning electron microscope (JEOL IT-100) equipped with an energy dispersive X-ray spectroscopy attachment operated at 15 kV and 0.8 nA with a 1 μm beam diameter. The ZAF method was used for data correction. The standards employed in these analyses were comprised of pure elements (Fe, Cu, Ge, Rh, Ir and Pt). The analytical results are given in Table 1. The empirical formula calculated on the basis of 2 apfu is $(\text{Rh}_{0.95}\text{Pt}_{0.03}\text{Ir}_{0.01})_{\Sigma 0.99}[(\text{Cu}_{0.36}\text{Fe}_{0.24})_{\Sigma 0.60}\text{Ge}_{0.41}]_{\Sigma 1.01}$. The simplified formula is $\text{Rh}[(\text{Cu,Fe),Ge}]$.

X-ray crystallography

Single-crystal XRD analysis for michitoshiite-(Cu) could not be performed due to the small grain sizes. Therefore, a micro-XRD technique was employed using a Rigaku Ultrax18 diffractometer with $\text{CrK}\alpha$ radiation operated at 40 kV and 200 mA. This instrument incorporated a 100 μm collimator equipped with a curved position sensitive proportional counter and an oscillating sample stage. Fig. 3 shows the powder XRD pattern for michitoshiite-(Cu) shown in Fig. 1. Although the diffractions of michitoshiite-(Cu) and cuprorhodsite appear in the X-ray profile due to their occurrence, five distinct peaks from michitoshiite-(Cu) were obtained. Table

Table 1. Chemical composition of michitoshiite-(Cu).

	wt% (n = 5)		apfu	
	average.	range.		
Rh	57.13	54.31–59.80	Rh	0.95
Ir	0.92	0.06–2.40	Ir	0.03
Pt	3.68	1.15–5.79	Pt	0.01
Cu	13.52	12.88–13.82	Σ	0.99
Fe	7.82	7.01–9.12		
Ge	17.24	15.65–18.26	Cu	0.36
Total	100.31		Fe	0.24
			Ge	0.41
			Σ	1.01

2 summarizes the diffraction data for michitoshiite-(Cu). The XRD peaks can be indexed as the cubic $Pm\bar{3}m$ (#221) with the lattice parameters $a = 2.9771(11)\text{\AA}$ and $V = 26.39(3)\text{\AA}^3$ ($Z = 1$). The five lines of michitoshiite-(Cu) in the powder XRD pattern [d in \AA (I/I_0) hkl] are 2.103 (100) 110, 1.717 (3) 111, 1.487 (15) 200, 1.332 (6) 210, and 1.216 (70) 211.

Discussion

Structure of michitoshiite-(Cu)

In the RhCu-RhFe-RhGe system, each end-member compound has a different structure: a face-centered cubic (fcc) structure for RhCu , the CsCl -type structure for RhFe , and a MnP -type structure for RhGe . On the other hand, the structure of the solid solution in the RhCu-RhFe-RhGe system has not been investigated so far. In particular, the CsCl -type structure with a certain composition links to the disordered bcc - and the complete ordered Heuser-type structures, considering the order-disorder relationship (Fig. 4). However, since natural samples were very limited, this issue was addressed by synthetic experiments. Table 3 summarize the

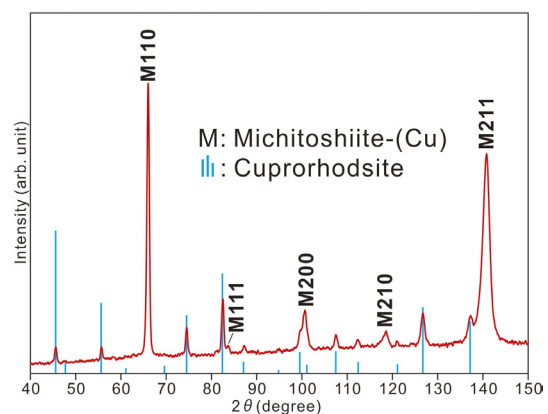


Fig. 3. X-ray diffraction pattern ($\text{CrK}\alpha$ radiation) of michitoshiite-(Cu).

Table 2. X-ray powder diffraction data (d in \AA) for michitoshiite-(Cu).

I_{meas}	d_{meas}	d_{calc}	hkl
—	—	2.977	100
100	2.103	2.105	110
3	1.717	1.719	111
15	1.487	1.489	200
6	1.332	1.331	210
70	1.216	1.215	211

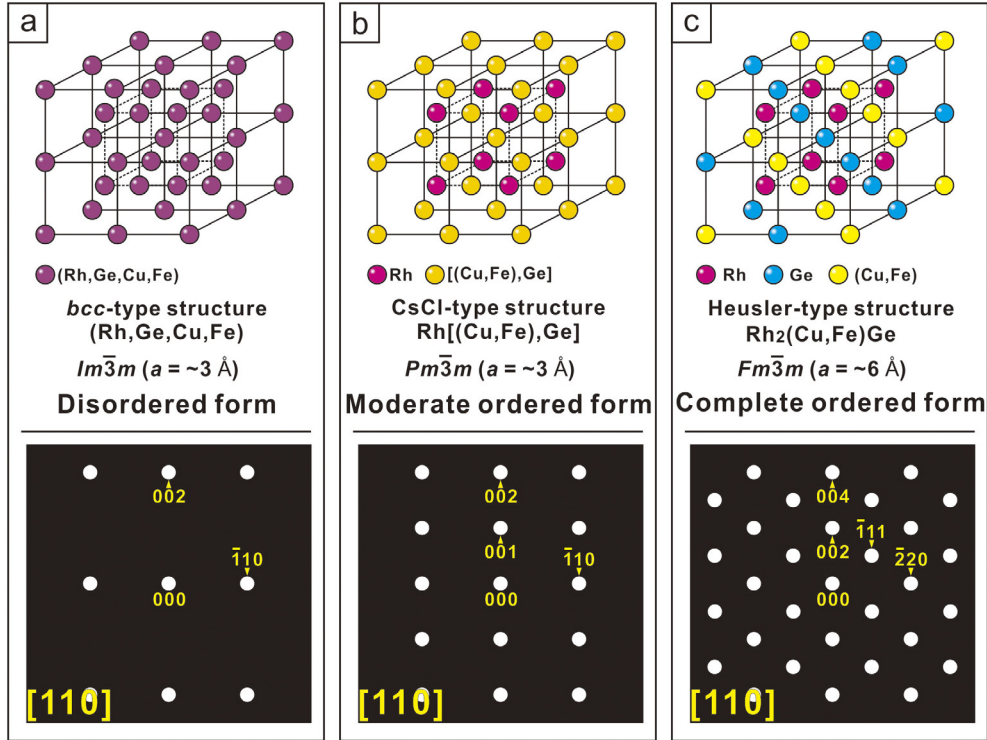


Fig. 4. The view of possible structure types for michitoshiite-(Cu) and the simulated electron diffraction images from [110]: the *bcc*- (a), the *CsCl*- (b), and the Heusler-type structures (c). Those structures are topologically equivalent as polymorphism in an order-disorder relationship and can be distinguished in the electron diffraction patterns from [110].

Table 3. Results of synthetic experiments.

Composition	Structure type	Unit cell parameter (Space group)	Structure formula	Reference
RhCu	<i>fcc</i>	$a = 3.73 \text{ \AA} (Fm\bar{3}m)$	$(Rh_{0.5}Cu_{0.5})_{\Sigma 1}$	Luo and Duwez (1964)
RhFe	<i>CsCl</i>	$a = 2.998 \text{ \AA} (Pm\bar{3}m)$	RhFe	Zsoldos (1967)
RhGe	<i>MnP</i>	$a = 5.44, b = 7.57, c = 4.00 \text{ \AA} (Pnam)$	RhGe	Geller (1955)
RhCu _{0.6} Fe _{0.4}	<i>fcc</i>	$a = 3.779(2) \text{ \AA} (Fm\bar{3}m)$	$(Rh_{0.5}Cu_{0.3}Fe_{0.2})_{\Sigma 1}$	This study
RhGe _{0.4} Cu _{0.35} Fe _{0.25}	<i>CsCl</i>	$a = 2.969(4) \text{ \AA} (Pm\bar{3}m)$	$Rh[(Cu_{0.35}Fe_{0.25})_{\Sigma 0.6}Ge_{0.4}]_{\Sigma 1}$	This study
RhGe _{0.5} Cu _{0.25} Fe _{0.25}	Heusler	$a = 5.9660(7) \text{ \AA} (Fm\bar{3}m)$	$Rh_2(Cu_{0.5}Fe_{0.5})_{\Sigma 1}Ge$	This study
RhCu _{0.6} Ge _{0.4}	Heusler	$a = 5.9618(9) \text{ \AA} (Fm\bar{3}m)$	$Rh_2Cu(Ge_{0.8}Cu_{0.2})_{\Sigma 1}$	This study

phases in the RhCu–RhFe–RhGe system confirmed by this study and references. The compounds used in this study were synthesized by mixing the metals and then heating them at 1050°C under vacuum for 72 hours.

In order to investigate the crystal structure of michitoshiite-(Cu) with empirical formulae, two compounds were prepared: RhGe_{0.4}Cu_{0.35}Fe_{0.25} and RhGe_{0.5}Cu_{0.25}Fe_{0.25}. Powder XRD patterns indicated that these were either the *CsCl*-type or the Heusler-type structures, but it was not possible to determine which one due to the low diffraction intensity of the criterion peak. Therefore, further investigation was carried out using a transmission electron microscope (JEOL JEM-2100), because the distinction between the *CsCl*-type and the Heusler-type structures is obvious by electron diffraction from [110] (Fig. 4).

On the other hand, since the diffraction intensity used as the criterion was weak, the data was recorded by long exposure time (30 seconds) using an imaging plate to ensure reliable detection. Fig. 5 shows the electron diffraction from [110] for two samples. The RhGe_{0.4}Cu_{0.35}Fe_{0.25} compound can be indexed as the *CsCl*-type structure, and thus the structure formula is defined to be $Rh[(Cu_{0.35}Fe_{0.25})_{\Sigma 0.6}Ge_{0.4}]_{\Sigma 1}$. The RhGe_{0.5}Cu_{0.25}Fe_{0.25} compound shows the Heusler-type structure, indicating the structure formula of $Rh_2(Cu_{0.5}Fe_{0.5})_{\Sigma 1}Ge$. Although the compositional differences between the two compounds were very slight, they crystallized in different structures. Since michitoshiite-(Cu), $(Rh_{0.95}Pt_{0.03}Ir_{0.01})_{\Sigma 0.99}[(Cu_{0.36}Fe_{0.24})_{\Sigma 0.60}Ge_{0.41}]_{\Sigma 1.01}$, is almost identical to $Rh[(Cu_{0.35}Fe_{0.25})_{\Sigma 0.6}Ge_{0.4}]_{\Sigma 1}$, it should have the *CsCl*-type structure.

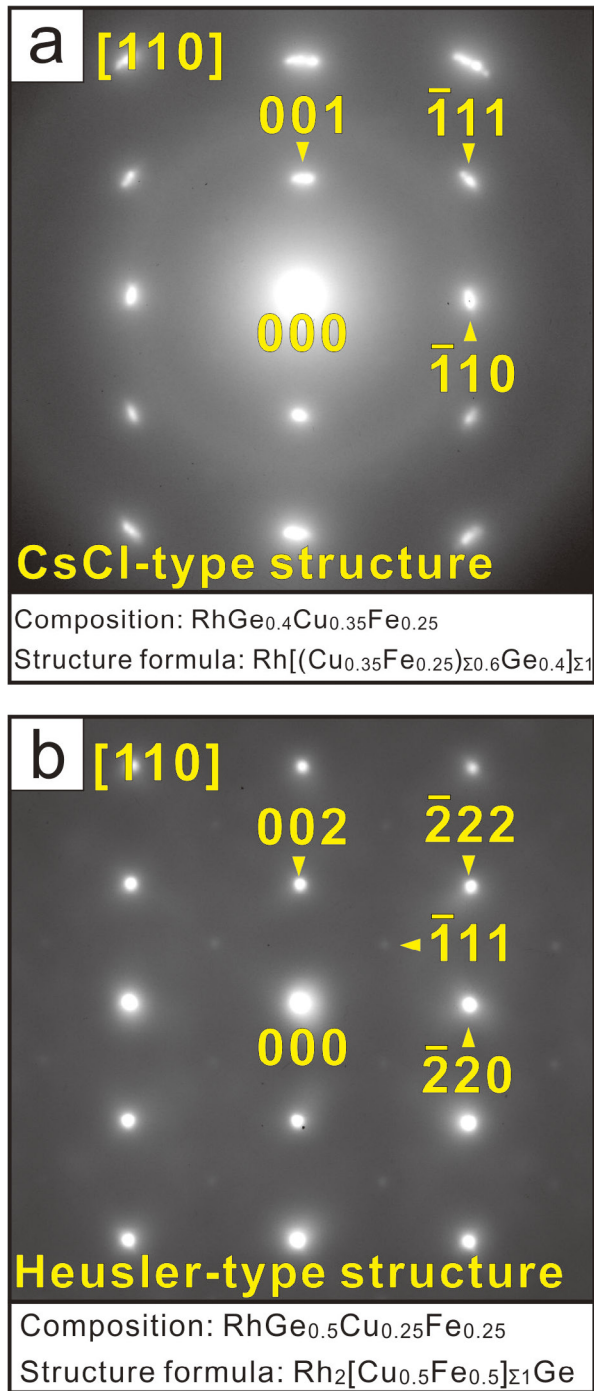


Fig. 5. Selected area electron diffraction patterns for $\text{RhGe}_{0.4}\text{Cu}_{0.35}\text{Fe}_{0.25}$ (a) and $\text{RhGe}_{0.5}\text{Cu}_{0.25}\text{Fe}_{0.25}$ (b). The former can be indexed as the CsCl-type structure with $a = 2.969 \text{ \AA}$ ($Pm\bar{3}m$) of the $\text{Rh}[(\text{Cu}_{0.35}\text{Fe}_{0.25})_{\Sigma 0.6}\text{Ge}_{0.4}]$ formula, while the latter is the Heusler-type structure with $a = 5.9660 \text{ \AA}$ ($Fm\bar{3}m$) of the $\text{Rh}_2(\text{Cu}_{0.5}\text{Fe}_{0.5})_{\Sigma 1}\text{Ge}$ formula.

Definition of michitoshiite-(Cu) in the RhCu–RhFe–RhGe system

Fig. 6 summarized the composition area of michitoshiite-(Cu) in the RhCu–RhFe–RhGe system. Considering the atomic combination and structure relationship (Table 3), the compositional area of

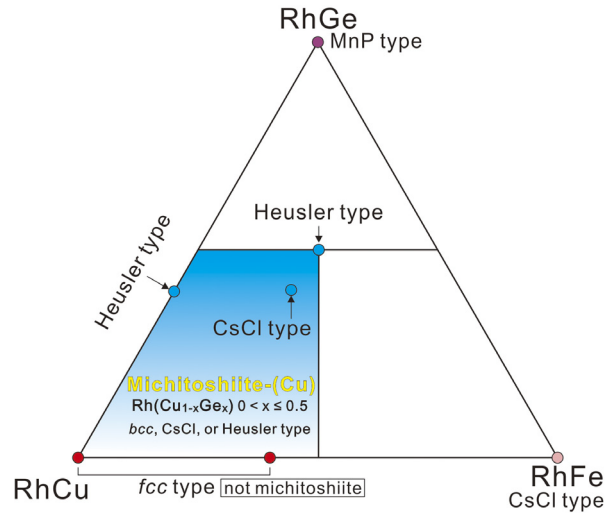


Fig. 6. The composition area of michitoshiite-(Cu) in the RhCu–RhFe–RhGe system based on the experimental results.

michitoshiite-(Cu) should be distinguished in comparison with (Cu + Fe) and Ge. The composition of michitoshiite-(Cu) was dominated by Ge in the Cu–Fe–Ge system, while it is characterized by $(\text{Cu} + \text{Fe}) > \text{Ge}$ and $\text{Cu} > \text{Fe}$ compositions. Also, a small amount of Ge is probably essential to form the *bcc*-based structure in Cu-dominant area. In a synthesis experiment, the $\text{Rh}(\text{Cu}, \text{Fe})$ composition did not form the *bcc*-based structure, while $\text{Rh}(\text{Cu}, \text{Ge})$ was crystallized to the Heusler-type structure (Table 3). In conclusion, the chemical formula of michitoshiite-(Cu) is set to be $\text{Rh}(\text{Cu}_{1-x}\text{Ge}_x)$ $0 < x \leq 0.5$ as shown in Fig. 6. Since the order-disorder relationship does not separate species according to the definition of mineral species (Nickel and Grice, 1998), michitoshiite-(Cu), $\text{Rh}(\text{Cu}_{1-x}\text{Ge}_x)$ $0 < x \leq 0.5$, is considered to be the mineral species with the *bcc*-, the CsCl-type, or the Heusler-type structures.

Conclusion

This study found and described the new mineral, michitoshiite-(Cu), from the placer deposit on Haraigawa, Misato machi, Kumamoto Prefecture, Japan. It occurs mainly as the outermost layer of the nub in association with the isoferroplatinum-based grain and rarely inside nub. Cuprorhodsitite, ferrotorreyweiserite, and/or shiranuiite are accompanied with michitoshiite-(Cu). Considering the relationships between composition and crystal structure, michi-

toshiite-(Cu) is the mineral species having the composition of $\text{Rh}(\text{Cu}_{1-x}\text{Ge}_x)$ $0 < x \leq 0.5$ and the *bcc*-based structure. The type michitoshiite-(Cu) should have the CsCl-type structure.

Acknowledgement

The authors would like to thank Dr. Ritsuro Miyawaki of the National Museum of Nature and Science for advising the definition of mineral species.

References

- Geller, S. (1955) The rhodium-germanium system I. The crystal structures of Rh_2Ge , Rh_5Ge_3 and RhGe . *Acta Crystallographica*, **8**: 14–21.
- Kinoshita, K. and Miyahisa, M. (1953) Lievrite and Datolite from the Kura-uchi Obira Mine, as Germanium resource. *Journal of Mining Institute of Kyushu*, **21**: 327–334 (in Japanese with English abstract).
- Luo, H. L. and Duwez, P. (1964) Solid solutions of rhodium with copper and nickel. *Journal of the Less Common Metals*, **6**: 248–249.
- McDonald, A. M., Ames, D. E., Kjarsgaard, I. M., Cabri, L. J., Zhe, W., Ross, K. C. and Good, D. J. (2021) Marathonite, $\text{Pd}_{25}\text{Ge}_9$, and palladogermanide, Pd_2Ge , two new platinum-group minerals from the Marathon deposit, Coldwell Complex, Ontario, Canada: Descriptions, crystal-chemical considerations, and genetic implications. *The Canadian Mineralogist*, **59**: 1865–1886.
- Nishio-Hamane, D., Tanaka, T. and Shinmachi, T. (2019) Minakawaite and platinum-group minerals in the placer from the clinopyroxenite area in serpentinite mélange of Kurosegawa belt, Kumamoto Prefecture, Japan. *Journal of Mineralogical and Petrological Sciences*, **114**: 252–262.
- Nishio-Hamane, D., Tanaka, T. and Shinmachi, T. (2024) Shiranuiite, $\text{Cu}^+(\text{Rh}^{3+}\text{Rh}^{4+})\text{S}_4$, a new mineral in the thiospinel group from Kumamoto, Japan. *Journal of Mineralogical and Petrological Sciences*, **119**: in press.
- Zsoldos, L. (1967) Lattice parameter change of FeRh alloys due to antiferromagnetic-ferromagnetic transformations. *Physica Status Solidi*, **20**: 25–28.