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https://doi.org/10.5109/1543613

出版情報：九州大學理學部紀要 : Series D, Geology. 15 (1), pp.73-78, 1964-06-25. Faculty of Science, Kyushu University
バージョン：
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Mem. Fac. Sci., Kyushu Univ., Ser. D, Geology, Vol. XV, No. 1,
pp. 73-78, 1 text-fig, 3 tables, plates 7-8, May 31, 1964

A new vanadium garnet, $(Mn, Ca)_3V_2Si_3O_{12}$, from the Yamato mine, Amami Islands, Japan

By

Hitoshi MOMOI

Abstract

A vanadium garnet has been found from a manganese ore deposit of the Yamato mine in the Palaeozoic formation of Amami Ōshima Island. The garnet forms dull greenish aggregates impregnated in the rhodonite ore and associates with some rare minerals, such as roscoelite and "haradaite." The garnet is yellowish green in thin section, usually isotropic. Refractive index, 1.855 ± 0.005. Specific gravity, 3.91 at 18°C. Cell dimension, $a_0 = 11.9743$ Å. Chemical composition: SiO_2 35.76, TiO_2 0.11, Al_2O_3 1.96, Fe_2O_3 1.13, V_2O_3 24.90, FeO tr., MnO 15.92, MgO 0.08, CaO 19.28, Na_2O 0.25, K_2O 0.04, H_2O^+ 0.54, H_2O^- 0.10, total 100.07 wt. %. Chemical formula is $(Ca_{1.79}Mn_{1.17}Mg_{0.01}Na_{0.04})_{3.01}(V'''_{1.72}Al'''_{0.20}Fe'''_{0.07}Ti_{0.01})_{2.00}Si_{3.00}O_{12.00}$. The Yamato garnet is composed of two kinds of garnet molecule $Mn_3V_2Si_3O_{12}$ and $Ca_3V_2Si_3O_{12}$. It reveals the existence of a new manganese-calcium series in vanadium garnet group.

Introduction

Manganese ore deposits of the Yamato mine were studied by Professor T. YOSHIMURA (1940-41, 1952 and later), who found in 1957 a peculiar green impregnation in the rhodonite ore and observed uvarovite-like garnet grains and fuchsite-like mica flakes under the microscope. The author, afterwards, found that they contain vanadium as a main component. These minerals have been confirmed to be a manganoan vanadium garnet, a manganoan roscoelite, and haradaite. This paper is a description of the manganoan vanadium garnet. Reports on the latter two minerals are now in preparation respectively.

Well-known vanadium minerals belong to vanadium oxides, vanadates, and their hydrates. Vanadium silicate minerals are also known, such as roscoelite, ardennite, and vanadium garnet. The vanadium garnet molecule was at first proposed by BADALOV (1951, 1952), who had described a vanadium-bearing garnet which contained 4.52 wt.% of vanadium trioxide (C in Table 1). His garnet was green in color, its central portion being darker. It was found in a contact zone of quartz veins with black vanadium-bearing quartz-graphite hornfelses.

Recently, a new mineral name, goldmanite, was proposed for the calcium-vanadium garnet.* Accordingly, the Yamato garnet may well be called "man-

Read at the annual meeting of the Mineralogical Society of Japan in June, 1962; Manuscript received October 31, 1963.

* By private communication from Prof. Takeo WATANABE to Prof. Toyofumi YOSHIMURA.

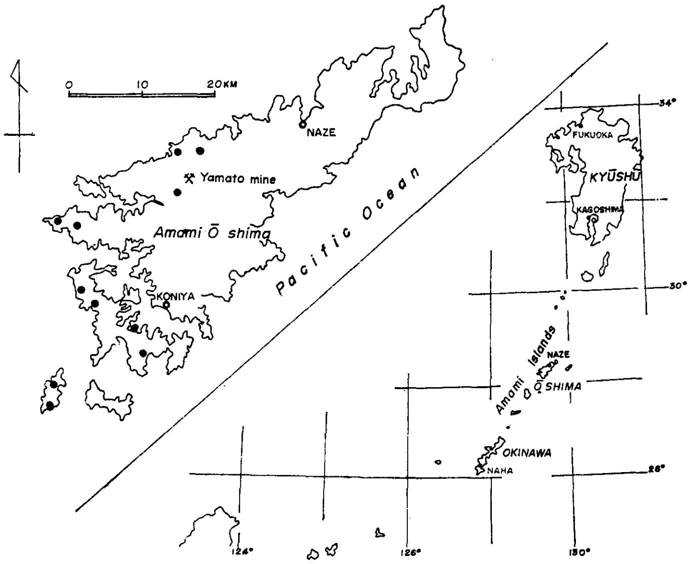

Fig. 1. Location of the Yamato mine, Kagoshima Prefecture, Japan. Solid circles are manganese deposits.

ganoan goldmanite."

Occurrences

The Yamato mine is an only working manganese mine in the Amami-Ōshima Island, north of the Okinawa Island. The location map of the mine is drawn in Figure 1. The ore deposits are found developed in the Paleozoic formation which consists of bedded chert, black shale, schalstein, and diabase. The deposit is massive, and the main constituent minerals of the ores are rhodonite, braunite, and rhodochrosite. Besides them, the following are found as ore and gangue minerals: bementite, manganese axinite, spessartine, pyrophanite, hematite, pyrite, chalcopyrite, molybdenite, malachite, manganoan roscoelite, manganoan goldmanite, haradaite, manganoan calcite, barite, antigolite, albite, and quartz. Vanadium minerals occurred in the marginal portion of a small pocket, which was protrusive to the upper hanging wall from the main ore body. Near the boundary between the ore and wall rock, we find in places veinlets of sulphide minerals, which continue to green mineral veinlets and patches in the rhodonite ore. Green veinlets, consisting mainly of haradaite and roscoelite, are also found sometimes crossing the green impregnations. The vanadium garnet is found in both of the green parts.

The green aggregate has therefore two kinds of mineral assemblage: (1) rhodonite, roscoelite, goldmanite, and quartz; (2) roscoelite, goldmanite, rhodochrosite, quartz and haradaite. In the veinlet which traverses the wall rock, we find the third assemblage: (3) goldmanite, haradaite, roscoelite, barite, and quartz. The garnet in a vein is commonly euhedral and includes fine-grained quartz in its core.

Physical properties

Color of the vanadium garnet is dull dark green in massive aggregate and pale greenish yellow in thin section. Goldmanite-quartz-rhodonite aggregate shows light green mass color. Grain size of the impregnated granular garnet is 0.01-0.03 mm., and that of well-grown one imbedded in rhodonite or antigorite mass is 0.5-1.0 mm. It is optically isotropic, but rarely shows optical anomaly separated into 3 or 4 sectors. The euhedral crystal is a dodecahedral type and shows commonly hexagonal and rarely square outline in section. Refractive index is 1.855±0.005 (immersion method, with sodium light). Specific gravity is 3.91 at 18°C (pycnometer method using carbontetrachloride). Calculated density is 3.97_7.

Chemical analysis

Material for chemical analyses was crushed, silk-screened (150-200 mesh),

Table 1. Chemical compositions of the vanadium garnets

	A	B	C
SiO_2	35.76	41.54	39.16
TiO_2	0.11	0.09	—
Al_2O_3	1.93	1.54	16.39
V_2O_3	24.90	22.94	4.52
Fe_2O_3	1.13	1.15**	3.13**
FeO	tr.	—	—
MnO	15.92	14.40	—
MgO	0.08	0.12	3.30
CaO	19.28	17.11	31.96
Na_2O	0.25	0.27	—
K_2O	0.04	0.05	—
H_2O^+	0.54*	0.52***	—
H_2O^-	0.10	0.10***	—
CO_2	—	0.00***	—
Cr_2O_3	—	—	1.01
Total	100.07	99.83	99.47

* Ignition loss. ** Total iron. *** Analyzed by the Elementary Chemical Analysis Center, Kyushu University.

A. Manganoan goldmanite from the Yamato mine, with less one wt. % impurity of quartz. Analyst H. MOMOI.

B. Ditto, with about 10 wt. % impurity of quartz. Analyst H. MOMOI

C. Vanadian garnet from Zapiski Vsesoyuz (BADALOV, 1951).

Table 2. Chemical composition and atomic ratios of manganoan goldmanite excluded impurity of quartz, from the Yamato mine, Kagoshima Prefecture ("A" in Table 1)

	Recalculated wt. %	Molecular ratio	Atomic ratio 0=12.00		
SiO_2	35.09	5843	Si	3.004	
TiO_2	0.11	14	Ti	0.007	2.002
Al_2O_3	1.98	194	Al'''	0.199	
V_2O_3	25.13	1676	V'''	1.723	
Fe_2O_3	1.14	71	Fe'''	0.073	
MnO	16.07	2266	Mn	1.165	3.005
MgO	0.08	20	Mg	0.010	
CaO	19.47	3472	Ca	1.785	
Na_2O	0.25	40	Na	0.041	
K_2O	0.04	4	K	0.004	
H_2O^+	0.54				
H_2O^-	0.16				
Total	(100.00)				

and passed through the Frantz Isodynamic separator. After treating in thallus formate solution, it was washed by 2% dilute hydrochloric acid. The final sample, however, contained quartz inclusion less than one per cent. The chemical analyses were made for four portions of the powdered samples; (1) Total vanadium oxide, a part of alumina, and silicas were extracted by warm water after alkali-fusion. The residue was used for determination of manganese oxide, total iron, a part of alumina, lime and magnesia (common gravimetric method). The filtrate was, after excluding silica, separated to alumina and vanadium oxide by the cupferron precipitation and total vanadium oxide was weighed. (2) Vanadium trioxide and ferrous iron were determined by permanganate titration from the solution treated with hydrofluoric and sulphuric acids. After reduction by sulphurous anhydride, the titration was repeated. (3) Alkalies were determined by flame photometric method. (4) Carbon dioxide and water were analyzed by Mr. M. SHIDO of the Elementary Chemical Analysis Center, Kyushu University. The results of analyses are given in Table 1. The chemical formula was calculated on the basis of twelve oxygens as shown in Table 2. It shows a good agreement with the ideal formula, $(Ca,Mn)_3V_2Si_3O_{12}$.

X-ray powder study

X-ray powder pattern of the garnet was obtained by a Shimadzu X-ray diffractometer with filtered Fe Kα and Cu Kα radiations. The experimental conditions were: 30 KV, 10 mA, time constant 5.0 seconds, scanning speed $\frac{1}{4}$ degree 2θ per minute, slits 3-2-0.2 mm. The readings of diffraction angles were corrected with an internal standard of silicon or quartz. Unit cell dimension

Table 3. X-ray powder data of manganoan goldmanite from the Yamato mine, Kagoshima Prefecture, Japan
(Filtered CuKα radiation, λ=1.54050 Å)

I	2θ deg.	$d_{obs.}$ (Å)	$d_{calc.}$ (Å)	hkl
55	29.81	2.9946	2.9936	400
100	33.43	2.6781	2.6775	420
6	35.14	2.5516	2.5529	332
72	36.73	2.4446	2.4442	422
21	38.28	2.3492	2.3483	501; 431
23	41.26	2.1861	2.1862	521
34	46.73	1.9422	1.9425	611; 532
9	48.00	1.8937	1.8933	620
13	52.92	1.7287	1.7284	444
40	55.26	1.6609	1.6605	640
75	57.55	1.6001	1.6002	642
15	61.93	1.4970	1.4968	800
17	70.25	1.3388	1.3388	840
19	72.28	1.3060	1.3065	843
13	74.27	1.2760	1.2765	664
6	79.13	1.2093	1.2096	941; 853; 770
15	87.65	1.1123	1.1118	10, 4, 0; 864
15	89.64	1.0927	1.0931	10, 4, 2

is a_0=11.9743 Å. The dimensions calculated according to the formula of BERTAUT and FORRAT (1957) are 12.019 Å for $Ca_3V_2Si_3O_{12}$ and 11.767 Å for $Mn_3V_2Si_3O_{12}$, provided ionic radius of vanadium is 0.65 Å (after GOLDSCHMIDT).

Acknowledgment

I express my sincere thanks to Professor Toyofumi YOSHIMURA of Kyushu University for his guidance during this work and offering the precious samples and reading the manuscript. Thanks are due to Professor Takeo WATANABE of the University of Tokyo for the valuable suggestion as to vanadium minerals, to Dr. Haruo SHIROZU of Kyushu University for his valuable discussions and reading the manuscript, to Dr. Jun ITO of the University of Tokyo at that time for the suggestions as to the chemical analysis of vanadium, to Dr. Masaru YAMAGUCHI of Kyushu University for his kind advices as to spectrochemical analysis, and to Dr. Mayumi YOSHINAGA of Kyushu University for his much advices. This work was partly indebted to the Grant in Aid for Scientific Researches from the Department of Education of Japan.

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Hitoshi MOMOI

A New Vandium Garnet from the YAMATO Mine

Plates 7–8

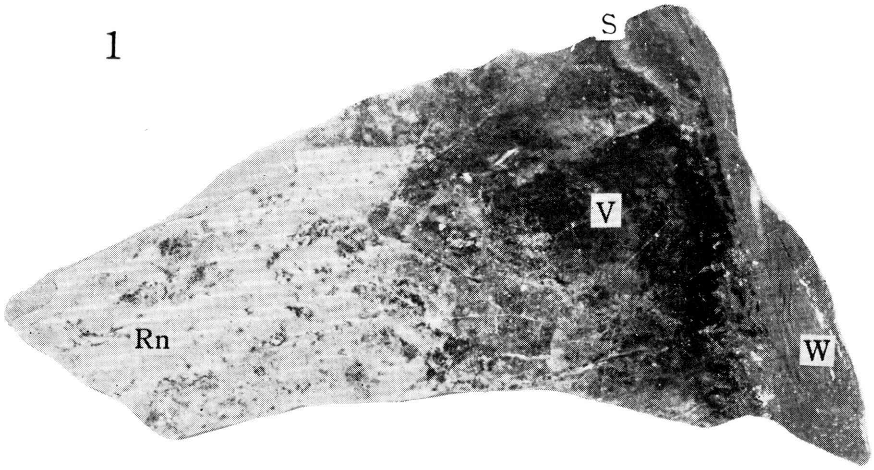
Plate 7

Explanation of Plate 7

Figs. 1–3. Photographs of the vanadium minerals from the Yamato mine, Kagoshima Prefecture.

1. Polished hand specimen showing the green vanadium minerals (V) (vanadium garnet and manganoan roscoelite) impregnated from slate (W) into pink rhodonite (Rn) and showing a sulphide veinlet (S) intruded into the boundary between ore and wall rock.
2. Vanadium garnet (G) having the vein-like form at the margin of haradaite (H) vein cutting rhodonite (P), and carbonate (C) veinlet crossing them. Open nicols.
3. Haradaite (H), vanadium garnet (G), euhedral rhodonite (P), and rhodochro- (C). Open nicols.

Photos by H. Momoi



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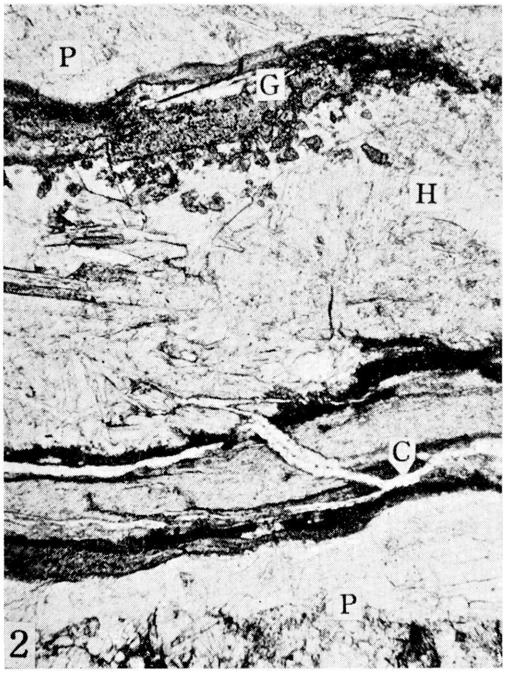

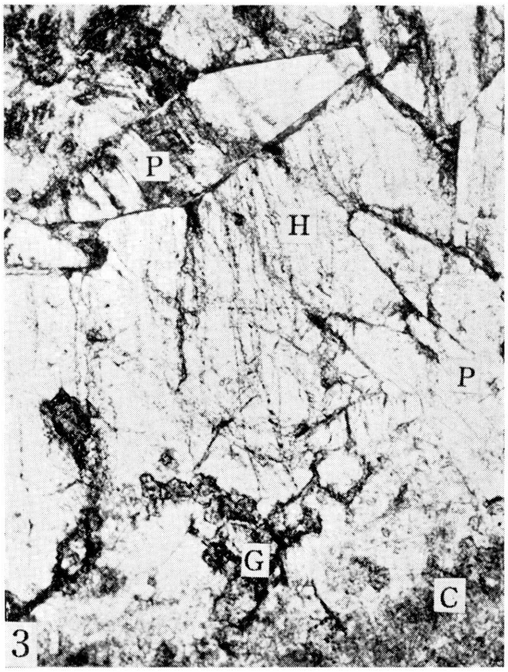

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H. Momoi: A new vanadium garnet from the Yamato mine

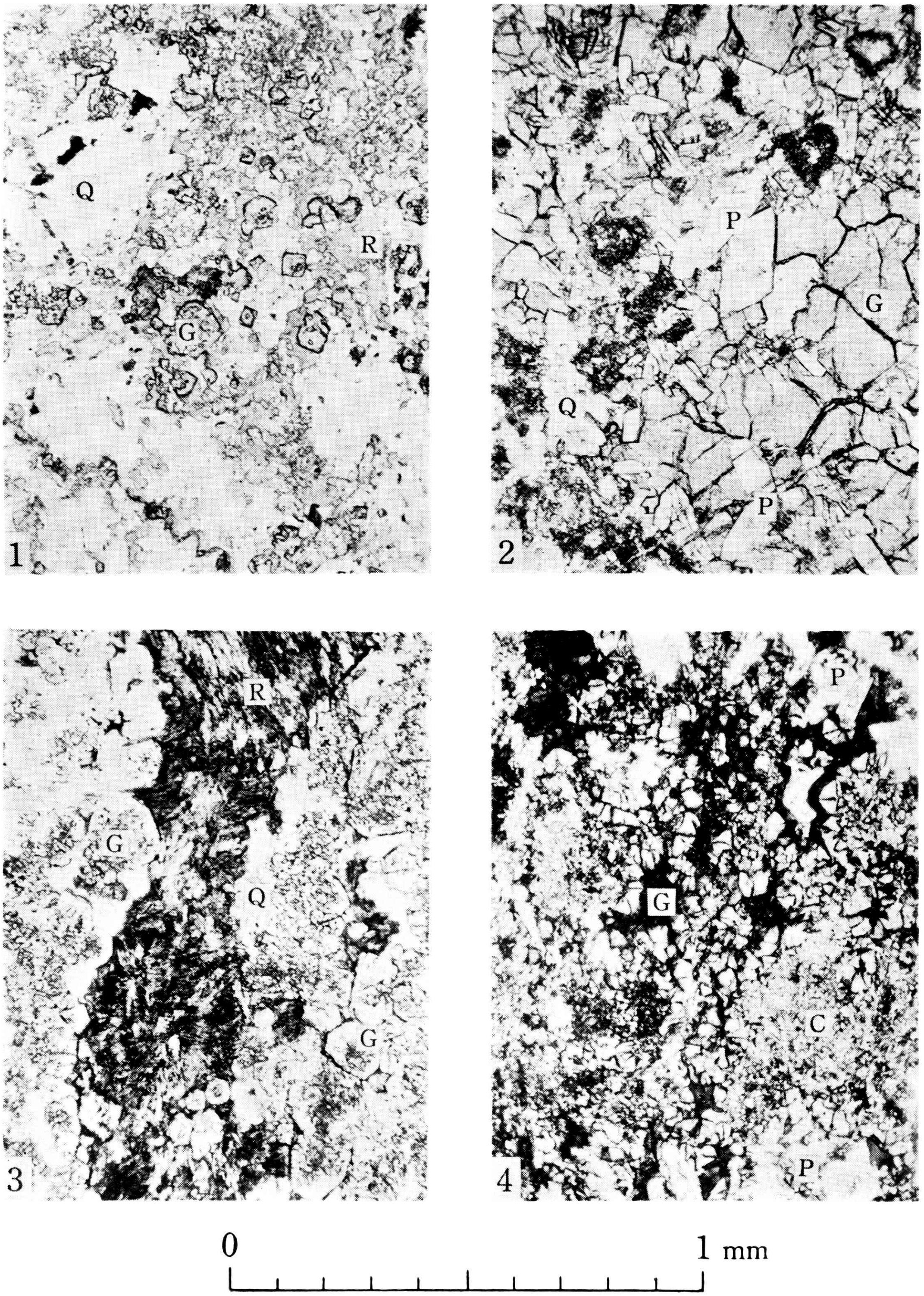
Plate 8

Explanation of Plate 8

Figs. 1–4. Photomicrographs of the vanadium minerals from the Yamato mine, Kagoshima Prefecture.

1. Vanadium garnet (G) -manganoan roscoelite (R) -quartz (Q) rock. Open nicols.
2. Anhedral vanadium garnet(G) in quartz (Q) -rhodonite (P) ore. Open nicols.
3. Manganoan roscoelite (R) vein in quartz (Q) -vanadium garnet (G) rock. Open nicols.
4. Vanadium garnet (G) showing optical anomally in rhodonite (P) -rhodochrosite (C) ore. Open nicols.

Photos by H. MOMOI.



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