

A Vanadium-bearing Spessartine from Itaga, Kanuma City, Tochigi Prefecture, Japan

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Abstract A grey yellow spessartine of contact metamorphic origin from Itaga, Kanuma City, Tochigi Prefecture, contains 0.21 to 0.87 wt. % of V_2O_5 , yielding the empirical formula $(Mn_{2.63}Ca_{0.20}Fe_{0.07}^{2+})_{\Sigma 2.99}(Al_{1.85}Fe_{0.08}^{3+}V_{0.06}^{3+})_{\Sigma 1.99}(Si_{2.98}Ti_{0.03})_{\Sigma 3.01}O_{12.00}$ for the most vanadium-rich point. The grain analysed is discontinuously rimmed with a spessartine-grossular solid solution with the formula $(Mn_{1.56}Ca_{1.48})_{\Sigma 3.04}(Al_{1.01}Fe_{0.03}^{3+}V_{0.02}^{3+})_{\Sigma 1.96}(Si_{2.04}Fe_{0.05}^{3+}Ti_{0.01})_{\Sigma 3.00}O_{11.96}$. The material represents an example of concentration of vanadium in a manganese silicate ore without forming any independent mineral of vanadium, which was concentrated therein prior to the metamorphism. The garnet occurs as isolated trapezohedra in an aggregate of blady rhodonite, which involves an aggregate of siegenite and cobaltite, the former proving a lower concentration of arsenic.

Introduction

In Japanese bedded manganese ore deposits the occurrence of vanadium in garnet is uniquely known at the Yamato mine, Kagoshima, Prefecture, where manganoo goldmanite, manganoo roscoelite (MOMOI, 1964), and haradaite (WATANABE *et al.*, 1982) are also reported. Except for this locality, all the vanadium carriers therein are not manganese minerals but such barium- or strontium-vanadium silicates as suzukiite (MATSUBARA *et al.*, 1982), nagashimalite (MATSUBARA & KATO, 1980) and haradaite (WATANABE *et al.*, 1982), and a vanadium-bearing aegirine (NAKAI *et al.*, 1976). The present material represents an example of camouflaged occurrence of vanadium by aluminum in a manganese ore mineral formed under a moderate grade of contact metamorphism. A brief discussion is added to compare other vanadium carriers related to bedded manganese ore deposits in Japan.

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Description of the Studied Material

The locality is a quarry for paving materials operated by Taiyo Mining Company for more than 10 years. It is located about 800 meters west of Itaga Station, Nikko Line, Tobu Railway Company, or Itaga, Kanuma City, Tochigi Prefecture (Fig. 1).

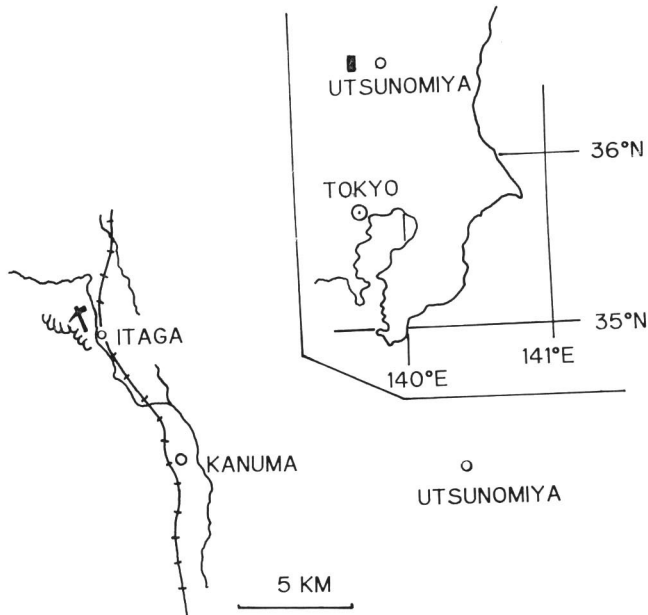


Fig. 1. The index map of the quarry near Itaga, Kanuma City, Tochigi Prefecture, Japan.

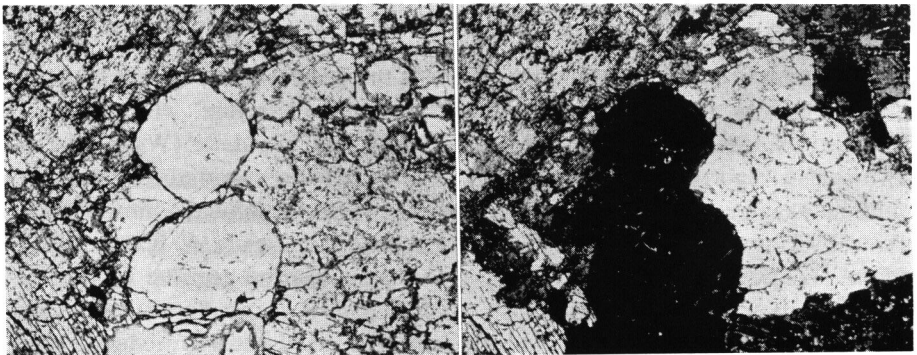


Fig. 2. Photomicrographs of trapezohedral spessartine and blady rhodonite. Field view 1.8×1.2 mm. Left; one polar, right; crossed polars.

The quarried objects are Mesozoic sedimentary rocks represented by chert with a subordinate amount of slate, which is contact metamorphosed into a cordierite hornfels in places due to granitic intrusion, its closest exposure being located about 3.5 km north of the locality (HIDEHIRA *et al.*, 1967). Within a chert bed is a lenticular ore mass dominantly composed of rhodonite with local developments of coarser-grained parts and of hydrothermal veins comprising quartz, sulphides and manganese-bearing carbonates. Beside them, minor amounts of manganooan tremolite, bustamite, helvine, pyrophanite, and hübnerite are found in rhodonite ores as macroscopic constituents.

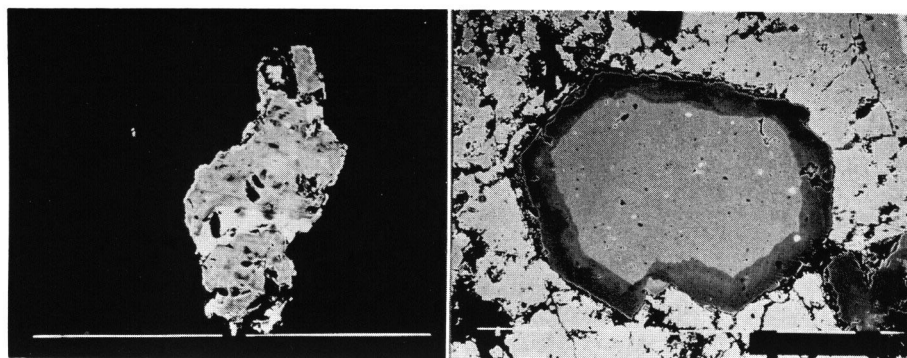


Fig. 3

Fig. 4

Fig. 3. Back-scattered electron scanning image of siegenite (gray) and cobaltite (white) in rhodonite (black). Bar indicates 100 microns.

Fig. 4. Back-scattered electron scanning image of analysed spessartine. Bar indicates 100 microns.

The sulphides include pyrite, sphalerite, pyrrhotite, chalcopyrite, galena and tetrahedrite in the order of appearance. Spessartine is found in rhodonite ores as aggregates or isolated trapezohedra reaching a half centimeter across with a better sizing. The spessartine forming aggregates is deep grey to black in colour and the individual grains are granular with lesser degree of sizing, whereas the isolated trapezohedra are idiomorphic to hypidiomorphic and grey yellow, orange to brownish orange in colour.

Under the microscope, trapezohedral spessartine grains are surrounded by rhodonite blades of a few millimeter long (Fig. 2). All of trapezohedra are discernibly zoned with thin crust, some parts of which are weakly birefringent. As stated later, the crustal part contains high CaO content.

X-ray powder diffraction pattern taken on one of the isolated grains gave $a=11.642(2)\text{\AA}$, which is for the average of whole grain and is reasonable value if unit cell edges of end members forming the spessartine are considered. The associated minerals are largely occupied by rhodonite but in the aggregate is found an irregular shaped opaque minerals of less than 0.1 millimeter long, and it is found to be aggregate of siegenite and cobaltite. The former has an outline of dodecahedral form against the latter, which also superficially coats the former (Fig. 3). Although the assemblage contains arsenic, siegenite of such a mode of occurrence would represent a lower concentration of arsenic than the case where sulphoarsenides or arsenides are the exclusive components of the assemblage.

Chemical Analyses of Spessartine and Rhodonite

Prior to the chemical analysis, the back-scattered electron scanning image was taken to know the compositional variation within the spessartine grains. The main part of grain is high in electron reflectivity and homogeneous in appearance, whereas

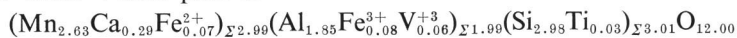
Table 1. Chemical analyses of spessartine and rhodonite.

	Spessartine					Rhodonite
	1.	2.	3.	4.	5.	6.
SiO ₂	35.51	35.80	36.30	35.87	36.74	46.67
TiO ₂	0.40	0.46	0.45	0.41	0.14	0.00
Al ₂ O ₃	20.41	19.06	19.12	19.60	20.25	0.00
Fe ₂ O ₃ *	1.22	1.77	1.29	1.13	1.38	0.00
V ₂ O ₃	0.21	0.59	0.87	0.76	0.28	0.00
MgO	0.00	0.00	0.00	0.00	0.00	1.57
FeO*	0.00	0.58	1.02	1.15	0.00	3.31
MnO	38.02	37.89	37.79	37.29	23.03	41.50
CaO	4.35	3.46	3.28	3.57	17.28	7.46
total	100.12	99.61	100.12	99.78	99.10	100.51
Number of atoms (total cation: 8 (spessartine); 2 (rhodonite))						
Si	2.91	2.96	2.98	2.95	2.94	0.99
Ti	0.02	0.03	0.03	0.03	0.01	0.00
Al	1.97	1.86	1.85	1.90	1.91	0.00
Fe ³⁺	0.08	0.11	0.08	0.07	0.08	0.00
V ³⁺	0.01	0.04	0.06	0.05	0.02	0.00
Mg	0.00	0.00	0.00	0.00	0.00	0.05
Fe ²⁺	0.00	0.04	0.07	0.08	0.00	0.06
Mn ²⁺	2.63	2.65	2.63	2.60	1.56	0.75
Ca	0.38	0.31	0.29	0.32	1.48	0.17

* Calculated.

Analyses were made on a line connecting core (point 1) and crust (point 5). No. 4 is for the highest V₂O₃ point on the line and very close to the margin of main part. No. 2 is for the midpoint between Nos. 1 and 4. No. 3 is for the highest V₂O₃ point in the grain. Its situation corresponds approximately to that of No. 4, but slightly inwards.

the crust has low electron reflectivity and less homogeneous, and the boundary is very sharp (Fig. 4). After the employment of the energy dispersive electron microprobe analysis instrument of Link Co. Ltd., one of the trapezohedral spessartine grains was analysed on four points in the main and one in the crustal parts, respectively, together with the associated rhodonite. V₂O₃ contents in the main part increase outward but become very low discontinuously in the crustal part (Table 1). The empirical formula of most V-rich part is



on the basis of total cation=8. The mole ratio Mn: Ca is nearly definite, 8: 1 to 9: 1 in the main part.

Discussion

In Japanese bedded manganese ore deposits the occurrence of vanadium is reported from the localities given in Table 2. Although the case of the Yamato mine is similar

Table 2. Vanadium carriers in Japanese bedded manganese ore deposits.

localities	materials
Tanohata mine Iwate Pref.	suzukiite (MATSUBARA <i>et al.</i> , 1982) aegirine (V ₂ O ₃ 8.18%) (NAKAI <i>et al.</i> , 1976)
Noda-Tamagawa mine, Iwate Pref.	haradaite (WATANABE <i>et al.</i> , 1982) hornfels (V 250–4000 ppm) (WATANABE & HAMACHI, 1961)
Gozaisho mine, Fukushima Pref.	manganberzeliite (V ₂ O ₅ 0.81%) (MATSUBARA, 1975)
Mogurazawa mine, Gumma Pref.	suzukiite (MATSUBARA <i>et al.</i> , 1982) nagashimalite (MATSUBARA <i>et al.</i> , 1980) barian roscoelite (MATSUBARA, 1985)
Hamayokokawa mine, Nagano Pref.	suzukiite (HIROWATARI & YOSHIE, 1978)*
Taguchi mine, Aichi Pref.	mica schist (V 800–1000 ppm) (WATANABE & HAMACHI, 1961)
Kurisu mine, Aichi Pref.	slate (V 400 ppm) (WATANABE & HAMACHI, 1961)
Matsuo mine Kochi Pref.	haradaite (HIROWATARI <i>et al.</i> , 1972)
Shidō mine, Ehime Pref.	slate (V 150–800 ppm) (WATANABE & HAMACHI, 1961)
Ippō mine, Ehime Pref.	slate (V 600 ppm) (WATANABE & HAMACHI, 1961)
Yamato mine, Kagoshima Pref.	manganian goldmanite (MOMOI, 1964) manganian roscoelite (MOMOI, 1964) haradaite (WATANABE <i>et al.</i> , 1982)

* reported as an unnamed mineral.

the present one, the occurrence of goldmanite in the ore deposits is far prevalent, needing a different interpretation. That vanadium is camouflaged by octahedrally coordinated aluminum means the similar geochemical behaviours of these elements at the site of spessartine formation. Among the tabulated examples, vanadium carriers in hornfels are considered to be micas formed as metamorphic minerals. Where the grade of metamorphism is very low, this role may be partaken by such an argillaceous material possibly in slate from the Kurisu mine (WATANABE & HAMACHI, 1961). In these examples, cations camouflaging vanadium are to have an ability of octahedral coordination. One of the most significant difference from the present case is the availability of manganese around the sites of formation. If sufficient manganese is available in association with a material containing any cation capable of camouflaging vanadium and aluminum is the most probable candidate, a vanadium-bearing spessartine will be formed prior to the formation of micas at the incipient stage of metamorphism.

While, vanadium-bearing aegirine from the Tanohata mine, Iwate Prefecture (NAKAI *et al.*, 1976) occurs in veinlets cutting a slaty wallrock in association with suzukiite according to the author's observation, which also informs the absence of any minerals containing aluminum as their essential constituents except for potash feldspar in the assemblage. This let the authors examine mineral associations of aegirine or aegirine-augite from bedded manganese ore deposits in Japan, and seven materials from the different sources were observed. Although two modes of occurrence were realized therein, *i.e.*, materials in veinlets and in hematite-quartz rocks or their coarser-

grained derivatives, no co-existence with spessartine is found. All the clinopyroxenes in association with spessartine are not sodic but calcic. Although the source of soda needs consideration as to the origin, syngenetic concentration or epigenetic supply, an apparent incompatibility of two minerals informs discrete geochemical behaviours of materials loaded with Al_2O_3 against those with Fe_2O_3 . The present discussion yields a conclusion that the former could be a primary carrier of vanadium and the latter is another carrier with a different geochemical implication in bedded manganese ore deposits in Japan.

Very recently, a similar spessartine is found by the authors from a manganese silicate ore suffering contact metamorphism from the Fujii mine, Fukui Prefecture, where spessartine grains are found in association with rhodonite, bustamite, manganite, diopside, quartz and interstitial manganite calcite. Spessartine contains about 5 wt. % of CaO and 1.4 wt. % of V_2O_5 , and, furthermore, the grains are rimmed with a high calcic spessartine without any detectable amount of V_2O_5 . The detailed description will be made separately near future. These observations are quite similar to the described case and inform the commoner occurrence of such vanadium-bearing spessartine in similar mode of occurrence. Also, the prevalence of mechanism of formation and of assemblage of cations is expected with a higher possibility in bedded manganese ore deposits suffering contact metamorphism due to granitic intrusion.

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