Bull. Natn. Sci. Mus., Tokyo, Ser. C, **20** (1), pp. 1–12, March 22, 1994

Vanadium-bearing Spessartine and Allanite in the Manganese-iron Ore from the Odaki Orebody of the Kyurazawa Mine, Ashio Town, Tochigi Prefecture, Japan

By

Akira KATO,[1] Masaaki SHIMIZU,[2] Yoshio OKADA,[3] Yoshiro KOMURO[4] and Kozo TAKEDA[4]

[1]Department of Geology, National Science Museum, 3–23–1 Hyakunin-cho, Shinjuku, Tokyo 169
[2]University Museum, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113
[3]2–19–7 Shimoshakujii, Nerima, Tokyo 177
[4]Komuro Hoshoku Company, 4–24–22 Hakusan, Bunkyo-ku, Tokyo 112

Abstract Vanadium-bearing spessartine and allanite occur as idiomorphic inclusions in coarse tephroite-fayalite grains forming manganese-iron ore together with minor rhodonite and manganpyrosmalite from the Odaki orebody of the Kyurazawa mine. They are compositionally zoned. The empirical formula of the core of the former is: $(Mn_{2.66}Ca_{0.38})_{\Sigma 3.04}(Al_{1.45}V_{0.56})_{\Sigma 2.01}Si_{2.97}O_{12}$ and that of the margin is: $(Mn_{2.23}Ca_{0.51}Fe^{2+}{}_{0.19}Mg_{0.04})_{\Sigma 3.00}(Al_{1.73}V_{0.17}Fe^{3+}{}_{0.12})_{\Sigma 2.02}Si_{2.98}O_{11.99}$. The outward decrease of V_2O_3 contents is clearer than that in allanite. The formula of the core of allanite is: $(Ca_{0.99}Ce_{0.50}La_{0.22}Nd_{0.03}Mn_{0.22}{}^{2+})_{\Sigma 1.96}(Al_{1.24}V_{0.73}Fe^{2+}{}_{0.45}Fe^{3+}{}_{0.36}Mn_{0.22}{}^{2+})_{\Sigma 3.00}Si_{3.00}O_{12}OH$ and that of the margin is: $(Ca_{0.90}Ce_{0.49}La_{0.19}Nd_{0.08}Mn^{2+}{}_{0.33})_{\Sigma 1.99}(Al_{1.12}V_{0.69}Fe^{2+}{}_{0.48}Fe^{3+}{}_{0.45}Mn^{2+}{}_{0.21}Mg_{0.05})_{\Sigma 3.00}Si_{3.00}O_{12}OH$, Tiny blebs of allanite also occur in spessartine grains. The sequence of formation is: allanite, spessartine, fayalite-tephoroite, rhodonite and manganpyrosmalite. The occurrences of vanadium or rare earths minerals are not uncommon in contact metamorphosed bedded manganese or manganese-iron ore deposits in Japan. The predominance of Fe^{2+}-bearing minerals at the Kyurazawa mine suggests the condition of formation to be relatively reducing. This is conformable with the existence of these V^{3+}-bearing minearls, but Fe^{3+} is bound to be involved in both of them after the interpretation of microprobe analyses. The coexistence of V^{3+} and Fe^{3+} reflective of two conflicting conditions in a single mineral is considered to be due to the presence of these ions not in their single forms but in combined forms with oxygen.

Introduction

The ore deposits the Kyurazawa mine are located about 4 km SSE of the Ashio station of Watarase Keikoku Railway, Co. Ltd. They consist of two orebodies named Odaki and Shinsanjin, and both of them were worked for manganese and iron till the end of 1960's. They are separate masses with about 400 meters distance from south to north situated along the local strike of sedimentary rocks and developed in moderately to weakly contact metamorphosed chert. They have very peculiar ores. The principal

ore mineral is manganpyrosmalite in both orebodies. The material from the former was firstly described as pyrosmaltie after the nomenclature at that time (WATANABE & KATO, 1957; WATANABE *et al.*, 1961), and that from the latter is richer in MnO than the former. The present study was initially due to the third, fourth and fifth authors finding a bright green translucent garnet embedded in coarse-grained olivine from the dump of the Odaki orebody and further works were undertaken by the first and second authors.

This is the results of chemical and X-ray powder studies identifying it to be a vanadian spessartine together with vanadian allanite as the microscopic associates. Also, the geneses of vanadium and rare earths minerals in bedded maganese ore deposits and the co-existence of V^{3+} with Fe^{3+} in single minerals reflective of conflicting conditions are considered.

Vanadium Minerals in Bedded Manganese Ore Deposits in Japan

Vanadium minerals in bedded manganese or manganese-iron ore deposits in siliceous sedimentary rocks or their metamorphic equivalents in Japan was firstly recognized in the Yamato mine, Kagoshima Prefecture by YOSHIMURA and MOMOI (1964), who described manganoan goldmanite and roscoelite in the lower grade ores together with an unknown bright green mineral later determined as a new vanadium mineral haradaite (WATANABE *et al.*, 1982). A comprehensive survey on vanadium in manganese minerals from a single ore deposit was made by MATSUBARA and KATO (1986 a) on the ores from the Fujii mine, Fukui Prefecture, where vanadium was detected in jacobsite, galaxite, spessartine, and titanite, all of them being quantitatively subordinate. Another independent vanadium mineral was found in a piedmontite-quartz schist from central Shikoku (ENAMI, 1984). It is a V^{5+}-dominant ardennite in which a part of V^{5+} is substituted by As^{5+} in the form of AsO_4^{3-} for VO_4^{3-}. The occurrence of this mineral was also confirmed in the other piedmonitite-quartz schists (MINAGAWA *et al.*, 1986; MATSUBARA and KATO, 1987). Apart from these examples in which nearly all the minerals are manganese-bearing, the occurrence of volborthite and roscoelite in siliceous sedimentary rocks comprising rhodochrosite masses was reported at Unuma, Gifu Prefecture (MATSUBARA *et al.*, 1990).

The area covering the western half of Tochigi Prefecture and the eastern half of Gumma Prefecture is occupied by chert dominant sedimentary rocks involving bedded manganese ore deposits of various scale up to 200 in total number (WATANABE *et al.*, 1970). They are also the source of vanadium minerals as represented by those from the Mogurazawa mine, Gumma Prefecture, where nagashimalite (MATSUBARA & KATO, 1982), suzukiite (MATSUBARA *et al.*, 1982), and barian roscoelite (MATSUBARA, 1985) are found. Also, an extensive survey on spessartines from the various part of the area indicated the occurrence of vanadian spessartine from Itaga, Tochigi Prefecture (MATSUBARA & KATO, 1986 b), which has V_2O_3 content up to 0.87 weight %.

Rare Earths Minerals in Bedded Manganese Ore Deposits in Japan

As compared with vanadium minerals, the occurrences of rare earths minerals in bedded maganese ore deposits are scarce. A preliminary examination on a piedmontite-like mineral at the Shiromaru mine, Tokyo, indicated high content of cerium group rare earths (MATSUBARA & KATO, unpublished). Also, a few grains in a manganese silicate ore at the Fujii mine, Fukui Prefecture were identified as rhabdophane from the optic properties and chemical composition (MATSUBARA & KATO, unpublished).

Allanite in a manganese silicate ore was reported by SHINGU *et al.* (1989) at a small manganese ore deposit in Mito-cho, Shimane Prefecture. Besides this, one of the authors (A.K.) has observed minor allanite in a rhodonite-bearing quartz-feldspathic vein cutting a lower grade manganese silicate ore from the Nippyô mine, Tochigi Prefecture, located about 4 km east of the Kyurazawa mine, where the grade of contact morphism reaches up to pyroxene hornfels facies due to the very close situation to the intruding granitic body.

Occurrence

The Odaki orebody of the Kyurazawa mine is briefly described by WATANABE and KATO (1957). The wallrocks are principally occupied by recrystallized chert and subordinately by mudstone in which incipient formation of such metamorphic minerals as biotite and garnet are microscopically observed.

According to the observation of one of the authors (A.K.) while the mine was under operation, the Odaki orebody had a massive form with the marginal part principally composed of rhodonite and the core part rich in olivine which forms coarse-grained aggregates with ferroan manganpyrosmalite (WATANABE & KATO, 1957; WATANABE *et al.*, 1961). Besides them, dannemorite, ordinary spessartine and rhodochrosite were present, and sphalerite, galena, pyrrhotite, pyrite and minor nickeline were found in manganese silicate ores of lower grade.

The material comprising vanadian spessartine is the coarse-grained aggregates composed of olivine and minor manganpyrosmalite. The former is dark brown in colour and semi-translucent. The grains have a clear parting, which informs the size exceeding 5 cm across. The closer observation reveals the presence of less brownish and more pinkish cleavable grains of interstitial manganpyrosmalite reaching a millimeter across, translucent bright green grains of vanadian spessartine of a millimeter order size, and microscopical black prisms of allanite of submillimeter size. Both of the vanadian minerals are exclusively found in such a coarse-grained aggregate of olivine with manganpyrosmalite. The compositions of olivine are found to cover both of fayalite and tephroite compositions due to fluctuating Fe : Mn ratio near unity even in a single grain, and neither visibly nor microscopically distinguishable.

Under the microscope, large grains of fayalite-tephroite involve idiomorphs of

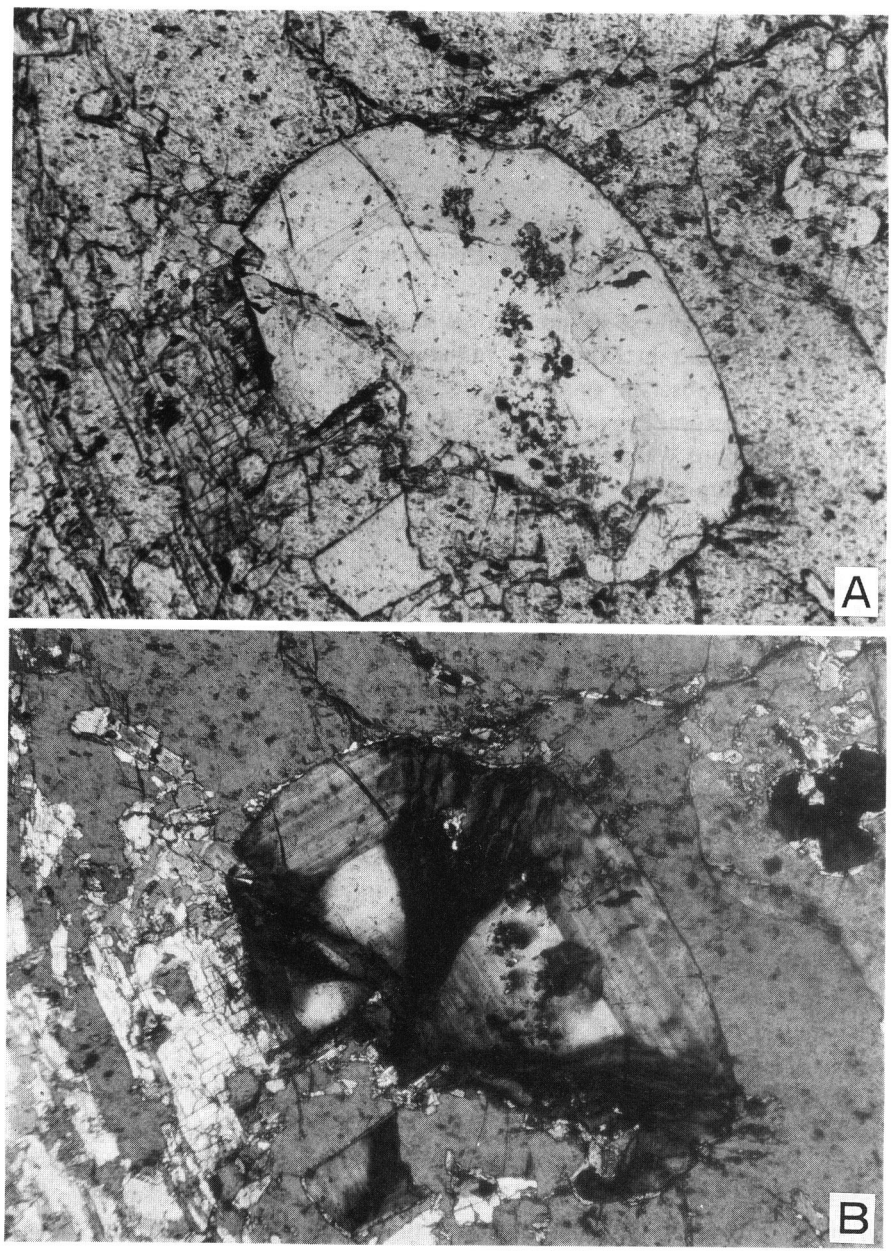

Fig. 1. Vanadian spessartine grains in ferroan tephroite or manganoan tephroite in association with rhodonite. Field view 1.8×1.25 mm. A. One polar. B. Crossed polars. Note the textural difference of the and outer and inner parts of the grain.

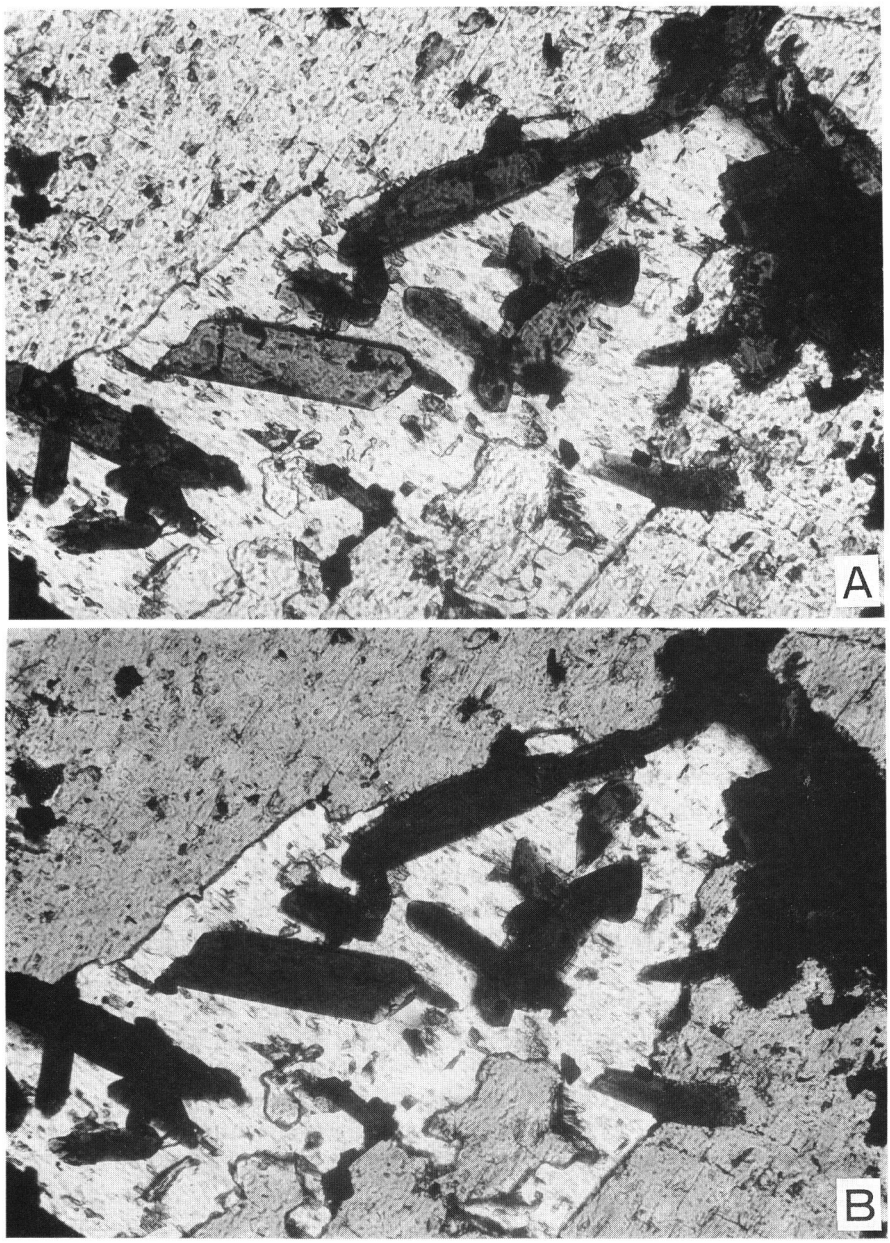

Fig. 2. Vanadian allanite idiomorphs in ferroan tephroite or manganoan tephroite. Field view 1.8×1.25 mm. A. One polar above. B. Crossed polars. Note the pleochroism.

spessartine and allanite. The former occurs as single round grains with partially developed forms probably composed of {110} and its modifications. They have faintly yellow margin with zoning texture between crossed polars and less yellowish core with a cross-marked extinction figure as seen in chalcedonic quartz. In the boundary between the core and margin tiny aggregates of non-idiomorphic allanite are also observed (Fig. 1). The allanite idiomorphs are composed of forms belonging to [010] characteristic to the minerals of clinozoisite series and flattened to {001} (Fig. 2). It is strongly pleochroic with axial colours changing from brownish yellow to deep olive green. The maximum length reaches 70 μm. The colour difference between the core and margin could not be realized microscopically. The aggregates of fayalite-tephroite involve smaller grains of manganpyrosmalite and rhodonite along their boundaries. The sequence of formation from early to late would be reconstructed under the microscope as: allanite, spessartine, fayalite-tephroite, rhodonite, and manganpyrosomalite, which is further followed by rhodochrosite as one of the latest primary minerals.

Chemical Analyses

The chemical analyses of vanadian spessartine (core and margin), vanadian allanite (core and margin;, managanoan fayalite, ferroan tephrotie, ferroan manganpyrosmalite, and ferroan rhodonite were made by using Link Systems energy dispersive X-ray spectrometer (Table 1).

The core of spessartine is compositionally characterized by the higher V_2O_3 content and the absence of Fe despite the direct association with olivine, whereas the margin bears Fe. The calculation of the empirical formulae on the basis of total cations=8 and total cationic valency=24 requires the allotment of Fe into Fe^{2+} and Fe^{3+} in the analysis of the margin. V^{3+} and Fe^{3+} are considered to reflect reducing and oxidizing conditions, respectively. Their co-existence in the same site of a single mineral will be considered later. The Mn : Ca ratios in the spessartine analyses range from 7 : 1 (core) to 4.43 : 1 (margin), these encompassing that of rhodonite, 5.66 : 1. It is uncertain whether the slight deficit of tetrahedral cations in spessartine analyses is due to $H_4 \leftrightarrow Si$ substitution or not. The reason why the valency of vanadium was taken as trivalent

Table 1. Chemical analyses of vanadian spessartine.
(1.: core 2.: margin)

Weight percentages: (*: allotment after the bases given below)

	SiO_2	Al_2O_3	Fe_2O_3*	V_2O_3	FeO*	MnO	MgO	CaO	Total
1.	35.35	14.66		8.36		37.38		4.23	99.98
2.	36.16	17.84	3.07	2.58	1.74	32.47	0.32	5.79	99.72

Empirical formulae: (bases: total cations=8, total cationic valence=24)

1. $(Mn_{2.66}Ca_{0.38})_{\Sigma 3.04}(Al_{1.45}V_{0.56})_{\Sigma 2.01}Si_{2.97}O_{12.00}$
2. $(Mn_{2.26}Ca_{0.51}Fe^{2+}_{0.19}Mg_{0.04})_{\Sigma 3.00}(Al_{1.73}V_{0.17}Fe^{3+}_{0.12})_{\Sigma 2.02}Si_{2.98}O_{11.99}$

Table 2. Chemical analyses of vanadian allanite. (1.: core 2.: margin)

Weight percentages: (*: allotment after the bases given below. **: calculated)

	SiO_2	Al_2O_3	Fe_2O_3*	V_2O_3	FeO*	MnO	MgO	CaO	Ce_2O_3	La_2O_3	Nd_2O_3	H_2O**	Total
1.	31.59	11.10	5.04	9.58	5.67	5.43	0.31	9.77	14.30	6.27	0.87	1.58	101.20
2.	30.69	9.75	6.12	8.83	5.87	6.48		8.56	13.67	5.33	2.17	1.53	99.31

Empirical formulae: (bases: total cations=12, total cationic valence except H=25)

1. $(Ca_{0.99}Ce_{0.50}La_{0.22}Nd_{0.03}Mn_{0.22})_{\Sigma 1.96}(Al_{1.24}V_{0.73}Fe^{2+}_{0.45}Fe^{3+}_{0.36}Mn_{0.22})_{\Sigma 3.00}Si_{3.00}O_{12}OH$
2. $(Ca_{0.90}Ce_{0.48}La_{0.19}Nd_{0.08}Mn_{0.33})_{\Sigma 1.99}(Al_{1.12}V_{0.69}Fe^{2+}_{0.48}Fe^{3+}_{0.45}Mn_{0.21}Mg_{0.05})_{\Sigma 3.00}Si_{3.00}O_{12}OH$

Table 3. Chemical analyses of fayalite (1.), tephroite (2.), manganpyrosmalite (3.) and rhodonite (4.).

Weight percentages: (*: calculated)

	SiO_2	FeO	MnO	MgO	CaO	Cl	H_2O*	$-O=Cl_2$	Total
1.	30.26	35.00	32.18	2.50					99.94
2.	30.43	33.84	34.79	1.92					100.98
3.	35.15	20.37	30.90	2.34		5.08	7.46	1.14	100.16
4.	46.67	9.15	37.50	1.26	5.46				100.04

Empirical formulae: (bases: 1. & 2.; O=4. 3.; total cationic charge=40. 4.; O=3)

1. $(Fe_{0.97}Mn_{0.90}Mg_{0.12})_{\Sigma 1.99}Si_{1.00}O_4$
2. $(Mn_{0.97}Fe_{0.93}Mg_{0.09})_{\Sigma 1.99}Si_{1.00}O_4$
3. $(Mn_{4.47}Fe_{2.91}Mg_{0.60})_{\Sigma 7.98}Si_{6.01}O_{15}((OH)_{8.55}Cl_{1.47})_{\Sigma 10.02}$
4. $(Mn_{0.68}Fe_{0.16}Ca_{0.12}Mg_{0.04})_{\Sigma 1.00}Si_{1.00}O_3$

is simply due to the available information on garnets, in which no material containing V^{4+} or V^{5+} has been known.

The analysed grains of allanite have the same tendency as to the variation of V_2O_3 contents, which are high in the core and lowered outwards (Table 2). The empirical formulae were calculated on the basis of total cations=2 and total cationic valence except H=25, although they required the existence of rather higher Fe_2O_3 contents in both of them. They are thus speciefied as vanadian allanite-(Ce). Mn is allotted to larger and smaller cationic sites to fit to the general formula of clinozoistie series, in which such vanadium-dominant species as mukhinite is known as the V^{3+} analogue of clinozoisite. If the formula of this mineral, $Ca_2Al_2V[OH|O|SiO_4|Si_2O_7]$, is taken into consideration, the present material could be handled as a cerian variety of mukhinite, But the present analyses are nearer to allanite than to mukhinite and the optical properties are also suggestive of the present material to be a simple variety of allanite.

The chemical analyses of olivines necessitated two names due to the slight fluctuation in Fe : Mn ratios around unity.

Manganpyrosmalite at the Odaki orebody described by WATANABE and KATO (1957) and WATANABE *et al.*, (1961) also occurs with olivine, which is less abundant in their analysed material (Table 3). It is slightly low in FeO than the present one, which gives a good total after the addition of calculated H_2O content. Using the same basis

as the calculation of the present material (total cationic charge=40), the empirical formula of the material of WATANABE, *et al.* (1961) is here reproduced as follows: $(Mn_{4.08}Fe^{2+}_{3.52}Mg_{0.43})_{\Sigma 8.03}(Si_{5.84}Fe^{3+}_{0.14}Al_{0.02}Ti_{0.01})_{\Sigma 6.01}O_{15.00}((OH)_{7.61}Cl_{1.67}O_{0.36})_{\Sigma 9.64}$. Their wet chemical analysis was for marginal parts of coarse-grained zoned crystals forming a large aggregate, and the core parts of grains involve very minute discrete grains of olivine without any trace of vanadian spessartine. The association is slightly different from the present case.

The associated rhodonite occasionally found in fayalite-tephroite as an irregular form has higher FeO content, which is not seen in any ordinary contact metamorphosed bedded manganese ore deposits in Japan, though the Fe : Mn ratio is far lower than those of fayalite, tephroite and manganpyrosmaltie.

X-ray Powder Study

The X-ray powder patern of a grain of vanadian spessartine was obtained by the diffractometer method (Table 4). The pattern includes slightly broad peak probably

Table 4. X-ray powder pattern of spessartine.

1.		2.			
d(Å)	I	$d_{obs.}$	$d_{cal.}$	I	hkl
4.76	6	4.787	4.772	5	211
3.10	8	3.123	3.124	5	321
2.91	25	2.927	2.923	45	400
2.60	100	2.617	2.614	100	420
2.48	10	2.497	2.492	5	332
2.37	16	2.386	2.386	20	422
2.28	10	2.292	2.293	10	431,510
2.13	16	2.134	2.134	15	521
2.06	6	2.063	2.067	2	440
1.886	20	1.896	1.896	20	611
1.836	2				620
1.797	2				541
1.710	2				631
1.681	20	1.687	1.687	10	444
1.650	6				543
1.614	30	1.621	1.621	20	640
1.586	6				721,633
1.557	40	1.561	1.562	25	642
1.482	2				732,651
1.456	16	1.460	1.461	7	800
	a=11.63 Å		a=11.69 Å		

1. Spessartine. JCPDS Card No. 10-354.
2. Spessartine. Odaki orebody, Kyurazawa mine. The present study. Cu/Ni radiation. Diffractometer method.

due to the slightly fluctuating chemical composition. The observed and calculated d-values using a cubic cell with $a=11.69$ Å are rather well coincident.

Consideration on the Genesis of Mineral Association Including Vanadian Spessartine

Although the previous studies on "pyrosmalite" (WATANABE & KATO, 1957) and on manganpyrosmalite from the neighbouring Shinsanjin orebody of the same mine (WATANABE *et al.*, 1961) did not deal with the genesis of these peculiar ore minerals, the unusually coarse-grained nature of the ores, especially along with olivines and manganopyrosmalite, was interpreted to be due to recrystallization and subsequent crystallization of iron and manganese-bearing materials, and under a favourable condition where such volatile materials as H_2O and Cl must have been incorporated to invite the formation of the unusually coarse-grained ores dominated by olivines.

If so, any source of them must be considered. As stated above, less ferroan manganpyrosmalite also occurs abundantly at the Shinsanjin orebody located about 400 meters north of Odaki, where the associated manganese silicates are devoid of olivines and not rich in FeO, the content being rhodonite, tirodite, spessartine, and later rhodochrosite (WATANABE *et al.*, 1961). The independet iron minerals thereat are pyrite, pyrrhotite, chalcopyrite and ferroan sphalerite. Since both the orebodies have similar dimension and siliceous wallrocks, it is unlikely that any preferential incorporation of Fe took place onto the Odaki orebody. Thus, the difference of manganpyrosmalite compositions between the two orebodies is ascribed to that of the original rocks, that is, among those of the Odaki orebody were high iron materials, whereas at the Shinsanjin orebody such high iron phases are lacking. As to the expected assemblage of their original minerals, the most probable one seems to be the combination of rhodochrosite and hematite. The latter had been prevalent before the incorporation of volatile materials at Odaki, whereas hematite had been absent at Shinsanjin. Hematite in bedded manganese ore deposits is very common as a principal constituent in siliceous wallrocks of so-called "red chert". As to the exclusive appearance of olivines at Odaki, incorporated materials were less siliceous qualitatively, or the quantitative dominance of rhodochrosite thereat.

Despite the frequent appearance of vanadium minerals in contact or regionally metamorphosed bedded manganese ore deposits in Japan, the pre-metamorphic mutual relationship between manganese and vanadium minerals has been recognized, since MATSUBARA *et al.*, (1990) found the occurrence of volborthite and roscoelite in siliceous sediments with rhodochrosite nodule in the underlying layer at Unuma, where the grade of metamorhism is very low and the original relation of the layer including the rhodochrosite nodule to that including vanadium minerals has been preserved. They are not in direct contact but separated with intervening siliceous sediments of thicker than 10 meters, and the vanadium minerals are exclusively found in a layer including copius bituminous materials. The layer is overlain by hematite- or goethite-bearing chert

indirectly with the intervening light grey green chert, which is probably inclusive of Fe^{2+}-bearing chlorite produced under the influence of bituminous material.

That such a bituminous material could be a source of some metallic elements including Mn is confirmed at Nabae Coast, Kochi Prefecture (MATSUBARA *et al.*, 1993). The prevalence of thin black shale layer is frequently reported in close association with bedded manganese ore deposits in Japan (WATANABE *et al.*, 1970), and that some of them contain vanadium (WATANABE & HAMACHI, 1961). These evidences lead to the conclusion that vanadium in spessartine was originally contained in such a black shale probably derived from a bituminous material before metamorphism. The material had diagenetically disappeared, though it invited the survival of vanadium nearby, by the involvement in clay minerals or mica being most likely. The present vanadian spessartine is the product of contact metamorphism, but in case of the Odaki orebody the growth was favoured through the incorporation of volatile materials forming such manganese-iron silicate as manganpyrosmalite, which excludes vanadium together with olivines, and it would enable the preferential incorporation of vanadium to spessartine and to allanite. In case of the former, all the constitutents were available from nearby sediments. Therefore, if the original situation of vanadium-bearing bituminous material and rhodochrosite bed is recovered, they must be so closely located that material transfer could be so readily probable. This is evidenced by closer situations of black shales to manganese ore beds in many bedded manganese ore deposits (WATANABE *et al.*, 1970). Also, both of vanadium-bearing spessatine from Itaga and the Fujii mine are contained in highly recrystallized manganese silicate ores without any trace of the original bedded texture, where material transfer accompanied by thermal metamorphism due to granitic intrusion was very likely. As to the constitution of vanadium-bearing spessartine, the manganese came from a manganiferous bed, or rhodochrosite bed with or without hematite, while the silicon, aluminum, and vanadium were from a bituminous layer unless the two were remotely located.

The formation of vanadian allanite is to be considered from the mechanism of concentration of rare earths dominated by cerium group. However, the available information on allanite of such a mode of occurrence is too few to have any implicative discussions on the genesis.

Interpretation on the Co-existence of V^{3+} with Fe^{3+} in Spessartine

The co-existence of V^{3+} and Fe^{3+} in garnet was reported in the original description on goldmanite (MOENCH & MEYROWITZ, 1964), although no attention was paid. Prior to this description, the same pair was reported in karelianite (V_2O_3) (LONG *et al.*, 1963) and in montroseite (V, Fe)OOH) after the structural analysis, which created this formula (EVANS & BLOCK, 1953). The former co-exists with graphite, nolanite, and (Mn, Fe)V_2O_4 later named vuorelainenite (ZAKRZEWSKI *et al.*, 1982), implying the reducing condition of formation. In case of montroseite at Unuma, Gifu Prefecture, the condition of formation is obviously reducing due to the close association with bitumi-

nous materials (MATSUBARA *et al*,. 1990). From these evidences, it is concluded that Fe^{3+} can survive even under a reducing condition if partnered with V^{3+}, or else, there are any reasons to allow the existence of Fe^{3+} even under a reducing condition.

From the standpoint of solution chemistry, the co-existence of these two cations or the survival of Fe^{3+} under a reducing condition is unlikely. In case of Odaki, the generation of Fe^{3+} in co-existence with V^{3+} in both spessartine and allanite was not controlled by the rule of solution chemistry where Fe^{3+} and V^{3+} do not co-exist in their uncombined states but by a peculiar state including the existence of any other form of Fe^{3+} that is capable of protecting reduction. For example, we know that V^{3+} can form VO^{1+} called vanadyl. Likewise, it Fe^{3+} forms such an atomic group as FeO^{1+}, the energy level to derive FeO^{0} or Fe^{2+} from it is to be different from the case of crude Fe^{3+}. There are other probable forms of ions along with them, respectively. At least, such atomic groups as VO_2^{1-} and FeO_2^{1-} are likely where parental cation is single. Anyway, the existence of O around the cation in question may impede the reduction.

The existence of the cationic pair seems probable. The close co-existence in minerals formed under various geologic conditions suggests the presence of complex cationic or anionc radicals composed of V^{3+}, Fe^{3+}, and O with or without H.

Acknowledgements

The authors thank Dr. Satoshi MATSUBARA, Department of Geology, National Science Museum, for his chemical analyses of studied minerals. The idea of incompatible cation pair in minerals was firstly noted by the late Dr. Jun ITO to whom the authors' sincere gratitude is subjected. A part of this study was financially supported by the Grand-in-Aid for Scientific Research for A. K. (No. 0340311) by Ministry of Education, Science and Culture, Japan.

References

ENAMI, M., 1984. Ardennite in a quartz schist form the Asemi-gawa area in the Sanbagawa metamorphic terrane, central Shikoku, Japan. *Miner. Jour.*, **13**: 151–160.

EVANS, H. T. JR. & S. BLOCK, 1953. The crystal structure of montroseite, a vanadium member of the diaspore group. *Amer. Miner* , **38**: 1242–1250.

LONG, J. V. P., Y. VUORELAINEN & O. KOUVO, 1963. Karelianite, a new vanadium mineral. *Amer. Miner.*, **48**: 33–41.

MATSUBARA, S., 1985. The mineralogical implication of barium and strontium silicates. *Bull. Natn. Sci. Mus. Tokyo*, Ser. C, **11**: 37–95.

——— & A. KATO, 1982. Nagashimalite, $Ba_4(V^{3+}, Ti)_4[(O, OH)_2|Cl|Si_8B_2O_{27}]$, a new mineral from the Mogurazawa mine, Gumma Prefecture, Japan. *Miner. Jour.*, **10**: 122–130.

——— & ———, 1986 a. Mineral chemistry of contact metamorphosed manganese ores from the Fujii mine, Fukui Prefecture, Japan. *Mem. Natn. Sci. Mus. Tokyo.* (19), 7–18.

——— & ———, 1986 b. A vanadium-bearing spessartine from Itaga, Kanuma City, Tochigi Prefecture, Japan. *Bull. Natn. Sci. Mus. Tokyo.* Ser. C, **12**: 1–6.

——— & ———, 1987. Ardennite from Sanbagawa in Sanbagawa Metamorphic terrane, Kanto

Mountains, Japan. *Ibid.*, **13**: 1–11.

———, ——— & S. YUI, 1982. Suzukiite, $Ba_2V^{4+}{}_2[O_4|Si_4O_{12}]$, a new mineral from the Mogurazawa mine, Gumma Prefecture, Japan. *Miner. Jour.*, **11**: 15–20.

———, Y. SAITO & A. KATO, 1990. Vanadium minerals in siliceous sedimentary rocks from Unuma, Gifu Prefecture, Japan, with special reference to volborthite and roscoelite. *Jour. Petrol. Miner. Econ. Geol.*, **85**: 522–530.

———, ——— & ———, 1993. Cobalt and nickel minerals from Nabae Coast, Muroto City, Kochi Prefecture, Japan. *Bull. Natn. Sci. Mus. Tokyo.* Ser. C, **19**: 127–137.

MINAGAWA, T., H. MOMOI & S. NOTO, 1986. Ardennite in a quartz vein in piedmontite schist. *Abstr. Annual Meeting Miner. Soc. Japan, Nagoya.* 50. (In Japanese.)

MOENCH, R. H. & R. MEYROWITZ, 1964. Goldmanite, a vanadium garnet from Laguna, New Mexico. *Amer. Miner.*, **49**: 644–655.

SHINGU, A., M. AKASAKA & Y. YAMAGUCHI, 1989. Preliminary report on Mn ores discovered from the Sangun metamorphic rocks in the northeastern part of Mito-cho, Shimane Prefecture, Japan. *Stud. San'in Region*, (5), 67–74. (In Japanese with English abstract.)

WATANABE, T. & T. HAMACHI, 1961. Mode of occurrence and genetical consideration on uranium ores accompanied by bedded manganese ore deposits, pp. 205–213. *In* Commission on Researches of Uranium and Thorium Minerals (ed.), Uranium and its Resources and Minerals. Tokyo, Asakura Shoten. (In Japanese.)

——— & A. KATO, 1957. A new occurrence of pyrosmalite in the Kyurazawa mine, Tochigi Prefecture, Japan. *Miner. Jour.*, **2**: 180–186.

———, ——— & J. ITO, 1961. Manganpyrosmalite from the Kyurazawa mine, Tochigi Prefecture. *Ibid.*, **3**: 130–138.

———, ———, ———, T. YOSHIMURA, H. MOMOI & K. FUKUDA, 1982. Haradaite, $Sr_2V_2[O_2|Si_4O_{12}]$, from the Noda-Tamagawa mine, Iwate Prefecture and the Yamato mine, Kagoshima Prefecture, Japan. *Proc. Japan Acad.*, Ser. B, **58**: 21–24.

———, S. YUI & A. KATO, 1970. Bedded manganese deposits in Japan: A review, pp. 119–142. *In* T. TATSUMI (ed.), Volcanism and Ore Genesis. Tokyo, Univ. of Tokyo Press.

YOSHIMURA, T., & T. MOMOI, 1964. Vanadian silicate minerals from the Yamato mine, Kagoshima Prefecture. *Sci. Rept. Fac. Sci. Kyushu Univ.* Geol. Ser. **7**: 85–90.

ZAKRZEWSKI, M. A., F. A. J. BURKE & W. J. LUSTERNHOUWER, 1982. Vuorelainenite, a new spinel, and associated minerals from the Sätra (Discoverstorp), central Sweden. *Can. Miner.*, **20**: 281–290.