

Ardennite from Sanbagawa in Sanbagawa Metamorphic Terrane, Kanto Mountains, Japan

By

Satoshi MATSUBARA and Akira KATO

Department of Geology, National Science Museum, Tokyo 160, Japan

Abstract Ardennite from Sanbagawa, Gumma Prefecture, occurs as a subordinate constituent in piemontite schists from two separate quarries. All the analyses have $V > As$ in mole ratio and those with the highest and lowest V_2O_5 contents in one specimen are: SiO_2 30.04, 31.25; Al_2O_3 22.28, 22.42; Fe_2O_3 2.00, 1.54; MnO 26.33, 26.09; CaO 2.03, 2.88; MgO 2.94, 3.29; V_2O_5 7.30, 6.22; As_2O_5 2.08, 1.53; totals 95.00%, 95.22%, respectively, the second one being with the highest SiO_2 content to date. Those with the highest and lowest MnO contents in another specimen are: SiO_2 30.63, 29.92; Al_2O_3 21.65, 21.73; Fe_2O_3 3.07, 3.06; MnO 24.40, 22.38; CaO 3.81, 4.56; MgO 4.34, 4.23; V_2O_5 5.42, 6.26; As_2O_5 0.64, 1.70; totals 93.97%, 93.94%, respectively, the last one being with the lowest MnO and highest CaO contents to date. The calculation basis $Si + V + As = 6$ is the best one to derive the structural formula of ardennite, in which slight deficit and excess of octahedral cations are probable. The unit cell parameters of the former material are: $a = 5.832$, $b = 18.573$, $c = 8.707$ Å. A new type of vanadium and arsenic concentration is found in manganiferous metamorphic rocks formed under an oxidizing condition, where they are involved in a single mineral ardennite.

Introduction

There are two ardennite localities in Japan, Asemi-gawa area (ENAMI, 1986) and Kamogawa (MINAGAWA *et al.*, 1986), central Shikoku, occurring as a subordinate constituent in piemontite-schists with very similar mode of occurrence in each as well as the associated minerals including quartz, spessartine and braunite. The third occurrence in Japan is hereby reported. The mode of occurrence and the associated minerals are very similar to above two cases, proving the concentration of vanadium and arsenic in some piemontite schists.

One of the examined materials was firstly collected by Mr. Hideaki KUSAKA in a pebble of piemontite-schist from the river bed of the River of Sanba, Sanbagawa, Onishi-machi, Tano-gun, Gumma Prefecture, where the origin of the name Sanbagawa metamorphic terrane is located. Afterwards, the authors' visit led to the find of another ardennite in piemontite-schist from an active quarry near the original locality and to the decision of the source of pebble as an abandoned quarry. The studied materials are the pebble (NSM M-24847) and the fragments (NSM M-24950) both from the abandoned quarry. Both materials are vanadium-rich ones but the contents and $V/(V + As)$ are slightly fluctuating.

In order of compositional specification of the present ardennite, the chemical analyses are compared with those of known ardennites together with the search of calculation basis to obtain the structural formula, reaching the conclusion that $\text{Si} + \text{V} + \text{As} = 6$ is the best to substantiate the reciprocal relation between Si and (V+As) contents found by ENAMI (1986), although the basis bears slight deficit or excess of octahedral cations.

The chemical specification of the materials informed that they involve those with the highest SiO_2 , CaO and the lowest MnO contents known to date.

The occurrences of both vanadium and arsenic are known in manganiferous beds in cherty sedimentary piles or their metamorphic equivalents. The present case is their co-existence in a single mineral, requiring the creation of a new type of concentration of these elements in such a geologic unit.

Occurrence

The localities are geographically included in Ohnara, Sanbagawa, Onishi-machi, Tano-gun, Gumma Prefecture. Around them the Sanbagawa metamorphic rocks are well exposed along the River of Sanba, and quarried at several places especially near Ohnara. Ardennite is found in two of them at the both sides of the River of Sanba (Fig. 1), where green schist is exposed with a few intercalating layer of piemontite-

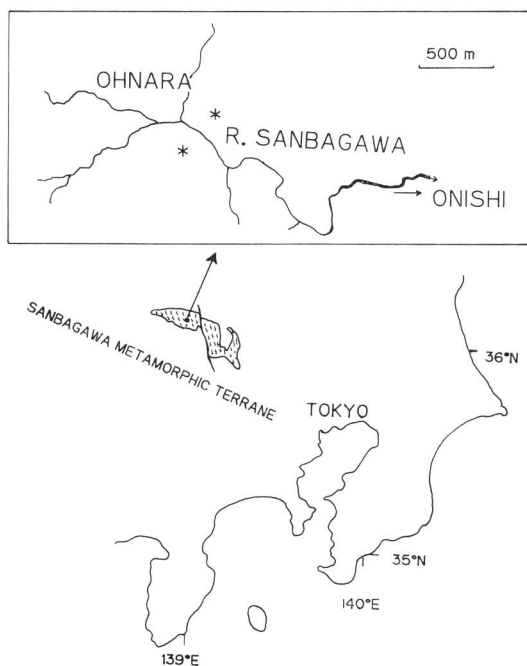


Fig. 1. The index map of ardennite localities (* mark) in the Sanbagawa Metamorphic Terrane.

schist in which ardennite is exclusively found.

The quarry in the south side of the river is an abandoned one and ardennite was found in the dump with two modes of occurrence. One of them is coarse-grained blade or fiber with a very similar appearance to the pebble material (NSM M-24847), and the shorter distance to the site of collection of pebble by KUSAKA enabled the authors to consider the quarry as the source of pebble. The other one is very fine-grained prism or blade embodied within quartz layers in finer-grained piemontite-schist (NSM M-24950). The mineral association of ardennite-bearing rocks involves quartz, piemontite, muscovite, chlorite, hematite and spessartine with or without albite and dravite. Braunite and sulphides are lacking. Minerals in direct contact with ardennite include quartz, piemontite, chlorite, hematite and spessartine, but muscovite is excluded. Ardennite in No. 24847 forms yellowish brown blades or fibers less than 3 mm long elongated along one direction and a perfect cleavage is developed in coarse-grained blades or fibers, which occur in quartz veinlets up to 8 mm wide, traversing the schistosity. Under the microscope, ardennite is associated with quartz, piemontite, and hematite in general, and forms bundles (Figs. 2a and 2b), which are exclusively found in certain layers. Ardennite in No. 24950 is with an orange colour and the blades are arranged concordantly to the schistosity with piemontite, hematite and quartz (Figs. 3a and 3b).

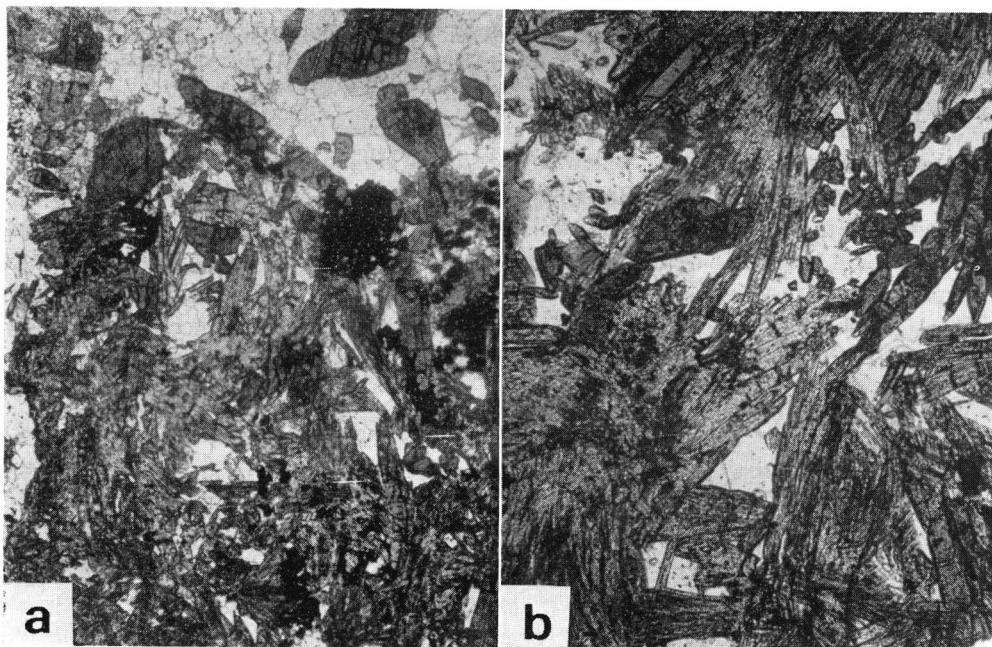


Fig. 2. The photomicrographs of No. 24847 ardennite (grey) associated with piemontite (dark grey), quartz (white) and hematite (opaque). a; One polar. Field view, approx. 1.4×1.9 mm. b; One polar. Field view, approx. 0.6×0.8 mm.

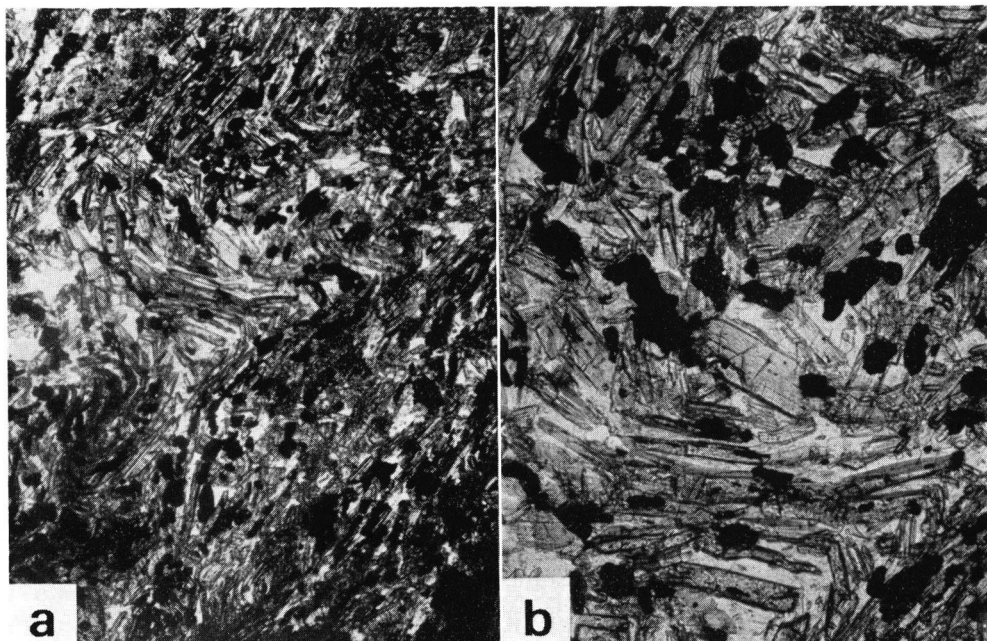


Fig. 3. The photomicrographs of No. 24950 ardennite (grey) associated with piemontite (dark grey), quartz (white) and hematite (opaque). a; One polar. Field view, approx. 1.4×1.9 mm. b; One polar. Field view, approx. 0.6×0.8 mm.

The other occurrence is in a quarry in the north side of the river, where ardennite occurs in thicker quartz-rich layers with spessartine (Fig. 4) and in hematite-rich lenses in piemontite-schist (Fig. 5). Braunitz and rutile are not found with ardennite.

Ardennite in No. 24847 was subjected to the optical study. It is biaxial and positive with moderate optic axial angle, $r > v$ strong, and strongly pleochoric with axial colours: X=brownish yellow, Y=reddish brown yellow and Z=light yellow. The sign of elongation is positive and negative. The refractive indices measured by the immersion method are: $\alpha = 1.798(5)$ and $\gamma = 1.822(5)$.

X-ray Powder Diffraction Pattern

A hand-picked material including minor quartz (No. 24847) was subjected to X-ray powder diffraction study. The obtained pattern (Table 1) comprises some intensity additions due to quartz, but the close analogy to that of Asemi-gawa material (ENAMI, 1986) is realized. The indexing yields the unit cell parameters: $a = 5.832$, $b = 18.573$, $c = 8.707$ Å after his axial setting. Some indices are dropped after the reference to the structural factors of DONNAY & ALLMANN (1968).

Owing to the compositional complexity including vacant site (DONNAY & ALLMANN, 1968), the variation of unit cell parameters cannot be strictly connected

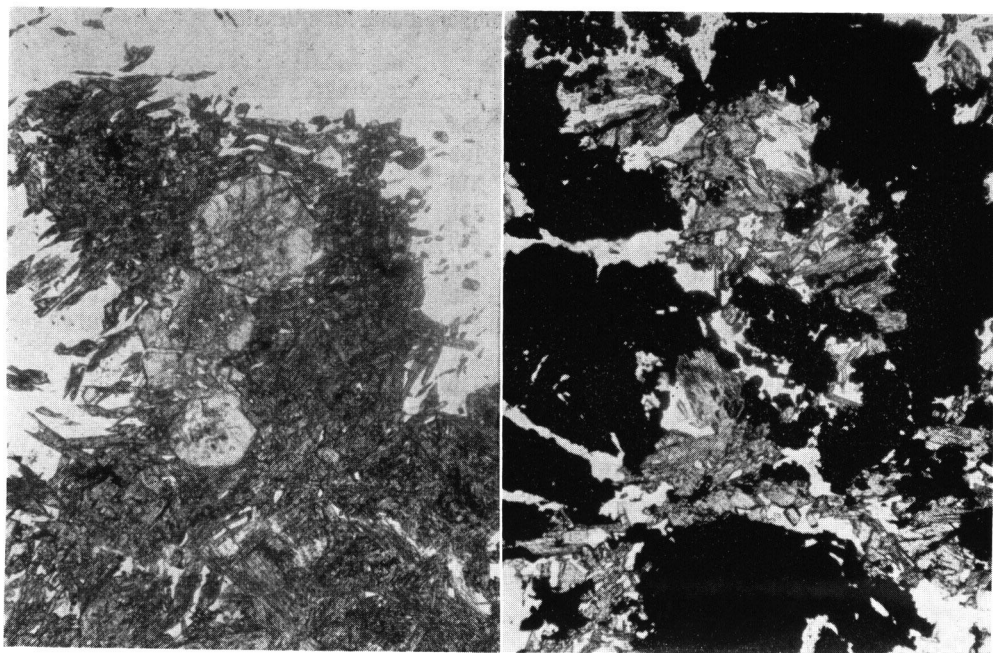


Fig. 4. (left) The photomicrograph of close association of ardennite (grey) and spessartine (euhedral grains). One polar. Field view, approx. 1.4×1.9 mm.

Fig. 5. (right) The photomicrograph of ardennite (grey) in hematite (opaque)-rich layer in piemontite-schist. One polar. Field view, approx. 1.4×1.9 mm.

with those of chemical compositions. The pattern is apparently similar to that of sursassite, which corresponds dimensionally to monoclinic equivalent of ardennite alike to the relation between zoisite and clinozoisite.

Chemical Compositions

Ardennites in two specimens Nos. 24847 and 24950 were analysed by using Link Systems energy-dispersive X-ray spectrometer (Table 2), specifying them to be vanadium-rich materials. They are compositionally similar in each except for lower MnO and higher CaO contents in the latter, both exceeding the limits known to date. Alike to the material from Asemi-gawa (ENAMI, 1986), the examined materials have higher SiO₂ contents, and one of the analyses of No. 24847 has the highest SiO₂ contents, 31.25%, known to date. The valency states of cations is estimated after the reference to the structural formula of DONNAY and ALLMANN (1978), in which all the cations are in the highest valency states, except for manganese, it being in the divalent state, despite the co-existence with piemontite.

After the reference to the available chemical analyses of ardennite (SEMET &

Table 1. The X-ray powder diffraction data for ardenmites

hkl	1			2		hkl	1			2	
	I	d(obs.)	d(calc.)	I	d		I	d(obs.)	d(calc.)	I	d
111	10	4.72	4.69	10	4.68	252	10	2.031	2.029	20	2.025
002	5	4.37	4.35			163	3	1.991	1.990		
121		*		15	4.28	310				5	1.931
022	18	3.96	3.94			271				5	1.910
131	5	3.81	3.82	10	3.82	243	12	1.881	1.881		
032	25	3.57	3.56	5	3.58	144				5	1.863
112				5	3.42	330				5	1.853
042	38	3.18	3.18	10	3.18	280				15	1.814
132	1	3.037	3.039	5	3.038	272	2	1.791	1.789	5	1.787
151	15	2.945	2.948	100	2.944	1101				10	1.730
200	100	2.910	2.916			332				10	1.705
061			2.916			351	2	1.686	1.690	5	1.685
013	1	2.882	2.868			244	5	1.636	1.633	5	1.631
052	15	2.831	2.825	5	2.825	361	9	1.617	1.618	10	1.615
142	30	2.781	2.789	5	2.791	174			1.617		
211	4	2.735	2.735			323	1	1.589	1.591	5	1.588
161	75	2.606	2.608	75	2.606	084			1.588		
231	20	2.524	2.525			254	17	1.580	1.579		
062			2.522	10	2.518	055			1.577	10	1.572
043				10	2.452	2100				5	1.564
222	1	2.346	2.344			371	40	1.541	1.543	30	1.545
171	5	2.324	2.327	25	2.321	155				10	1.520
080			2.322			225	7	1.473	1.474	5	1.472
143	2	2.266	2.267	15	2.263	400	17	1.458	1.458	10	1.457
251				5	2.209	0122			1.458		
004	10	2.170	2.176			274			1.458		
260	25	2.122	2.122	15	2.117	390	8	1.415	1.415	5	1.412
261	13	2.059	2.062			1122			1.415		
082				15	2.045	440	2	1.389	1.391	5	1.381

* masked by (100) of quartz.

1. Ohnara, Sanbagawa, Onishi, Gumma Prefecture, Japan. $a=5.832$, $b=18.573$, $c=8.707$ Å. Cu/Ni radiation. Diffractometer method.
2. Asemi-gawa, Motoyama, Kochi Prefecture, Japan. $a=5.828$, $b=18.540$, $c=8.692$ Å. (ENAMI, 1986).

MOREAU, 1965; NAYAK, 1967; DONNAY & ALLMANN, 1968; ENAMI, 1986), the elimination of calculation basis for the best structural formula is made, and, as the result, the basis $\text{Si}+\text{V}+\text{As}=6$ is chosen, as far as neither V nor As has lower valency than 5.

The basis of total $\text{O}=25$ used by ENAMI (1986) is fundamentally valid unless ferrous iron is contained. However, all of his analyses have excess of tetrahedral cations. In relation to this interpretation, it is worth mentioning that all of his analyses have the relation $\text{Si}+\text{As}\sim 6$ and the total of cation number close to 16. This may suggest the possibility of lodging of vanadium in the octahedral site, where valency state of

Table 2. The representative chemical analyses of ardennite (*: total iron)

	1.	2.	3.	4.
SiO ₂	30.04	31.25	30.63	29.92
Al ₂ O ₃	22.28	22.42	21.65	21.73
Fe ₂ O ₃ *	2.00	1.54	3.07	3.06
MnO	26.33	26.09	24.40	22.38
CaO	2.03	2.88	3.81	4.56
Mg	2.94	3.29	4.34	4.23
V ₂ O ₅	7.30	6.22	5.42	6.26
As ₅ O ₅	2.08	1.53	0.64	1.70
totals	95.00	95.22	93.97	93.94

Empirical formulae (basis: Si+V+As=6) (calculated H₂O contents added):

1. (Mn_{3.64}Ca_{0.36})^{-4.00}(Mg_{0.73}Al_{0.38}Fe_{0.25}Mn_{0.08})^{±1.54}Al_{4.00}
(V_{0.80}As_{0.18}Si_{0.01})^{-0.99}Si_{5.00}O_{21.45}(OH)_{6.55}(H₂O 5.88, total 100.88%)
 2. (Mn_{3.49}Ca_{0.51})^{-4.00}(Mg_{0.81}Al_{0.38}Fe_{0.19}Mn_{0.18})^{-1.56}Al_{4.00}
(V_{0.88}Si_{0.19}As_{0.13})^{±1.00}Si_{5.00}O_{21.50}(OH)_{6.50}(H₂O 5.87, total 101.09%)
 3. (Mn_{3.26}Ca_{0.71})^{-4.00}(Mg_{1.12}Al_{0.43}Fe_{0.40}Mn_{0.30})^{-2.25}Al_{4.00}
(V_{0.82}Si_{0.32}As_{0.06})^{-1.00}Si_{5.00}O_{21.90}(OH)_{6.01}(H₂O 5.19, total 99.16%)
 4. (Mn_{3.16}Ca_{0.84})^{-4.00}(Mg_{1.08}Al_{0.40}Fe_{0.40}Mn_{0.09})^{-2.07}Al_{4.00}
(V_{0.71}As_{0.15}Si_{0.14})^{-1.00}Si_{5.00}O_{21.60}(OH)_{6.40}(H₂O 5.59, total 99.53%)
1. Ardennite (NSM M-24847). Ohnara, Sanbagawa, Onishi-machi, Tano-gun, Gumma Prefecture, Japan.
 2. Ardennite (NSM M-24847). Ditto. The most high SiO₂ analysis.
 3. Ardennite (NSM M-24950). Ditto.
 4. Ardennite (NSM-24950). Ditto. The most low MnO and high CaO analysis.

vanadium may be lowered to the trivalent state.

The other calculation basis (O+OH)=56 employed by DONNAY & ALLMANN (1968) is also fundamentally reliable, if water content is exactly measured. However, as seen in some structural formulae calculated by them, some old analyses give cationic excess, probably coming from the lower water contents than the real value. (In their Table 8, Al content is misprinted. It should be 1.60 for 0.60, therefore, the total of octahedral cations becomes 12.12. A minor excess may be used to fill the tetrahedral site.) Besides these bases, another one such as total cation=16 is applicable unless any deficit is in the octahedral site. And, the ideal formula of ardennite should be conformable with all of them, namely, (Mn, Ca)₄MgAlAl₄(V, As)₄(SiO₄)₂Si₃O₁₀(OH)₆ where Mn>Ca, V>As or As>V. Any deficit of total cationic valency may be compensated by excess lodging Si in place of (V, As) or substitution of OH for O in Si₃O₁₀.

According to the crystal structure of ardennite (DONNAY & ALLMANN, 1968), calcium partially substituting manganese is preferentially incorporated into a site with longer M-O distances with sevenfold coordination. In the calcium rich analysis of No. 24950, the ratio Mn:Ca in that site is 58:42. The reciprocal relation between manganese and calcium is not linear on account of an overflow of manganese to enter the octahedral site as seen some recent analyses (Table 3). Among the octahedral

Table 3. Updated chemical analyses of ardennites and their empirical formulae.
(basis: 1.-3. and 5. Si+V+As=6; 4. Si+As+P=6)

	1.	2.	3.	4.	5.
SiO ₂	28.20	27.85	28.14	27.77	31.2
TiO ₂	—	—	0.00	0.05	—
Al ₂ O ₃	23.80	23.55	23.22	20.70	21.7
Fe ₂ O ₃	1.22	0.86	1.50	3.28	1.79**
MnO	26.75	25.70	25.33	28.53	24.2
CaO	1.17	1.17	1.50	1.13	3.05
MgO	2.30	2.30	3.83	5.26	4.11
CuO	0.57	0.26	0.46	—	0.23
V ₂ O ₅	1.86	0.89	0.82	0.01	1.34
As ₂ O ₅	11.25	13.25	9.85	7.71	6.12
P ₂ O ₅	—	—	—	0.53	—
F	—	—	0.14	—	n.d.
H ₂ O ⁺	5.10	5.10	5.04	5.24	n.d.
H ₂ O ⁻	0.02	0.02	0.00	0.00	n.d.
total	101.26	100.95	100.06*	100.21	93.81
less O=F			0.06		
			100.00		

1. Salm-Château, Ardennes, Belgium. SEMET & MOREAU (1965). (Mn_{3.78}Ca_{0.21})_{Σ4.00}(Al_{0.77}Mg_{0.58}Fe_{0.16}Cu_{0.07}Mn_{0.08})_{Σ1.64}Al_{4.00}As_{1.00}(Si_{4.79}V_{0.21})_{Σ5.00}O_{21.85}(OH)_{5.78}.
2. Ditto. SEMET & MOREAU (1965). (Mn_{3.68}Ca_{0.21}Mg_{0.10})_{Σ4.00}(Al_{0.71}Mg_{0.58}Fe_{0.11}Cu_{0.03})_{Σ1.33}Al_{4.00}As_{1.00}(Si_{4.72}As_{0.18}V_{0.10})_{Σ5.00}O_{21.50}(OH)_{5.77}.
3. Ditto. DONNAY & ALLMANN (1968). * includes Cr₂O₃ 0.12, SnO₂ 0.03, CoO 0.01, ZnO 0.04, Na₂O 0.01. (Mn_{3.72}Ca_{0.28})_{Σ4.00}(Mg_{1.01}Al_{0.85}Fe_{0.20}Mn_{0.09}Cu_{0.06}Cr_{0.02})_{Σ2.13}Al_{4.00}(As_{0.90}V_{0.10})_{Σ1.00}(Si_{4.90}As_{0.01})_{Σ5.00}O_{22.28}(OH)_{5.86}.
4. Kajlidongri, India. NAYAK (1967). (Mn_{3.77}Ca_{0.23})_{Σ4.00}(Mg_{1.46}Mn_{0.77}Al_{0.54}Fe_{0.46}Ti_{0.01})_{Σ3.24}Al_{4.00}(As_{0.75}Si_{0.17}P_{0.08})_{Σ1.00}Si_{5.00}O_{22.91}(OH)_{8.50}.
5. Asemi-gawa area, Shikoku, Japan. ENAMI (1986). ** total Fe. (Mn_{3.44}Ca_{0.56})_{Σ4.00}(Mg_{1.04}Al_{0.33}Fe_{0.23}Mn_{0.05}Cu_{0.3}Ti_{0.01})_{Σ1.70}Al_{4.00}(As_{0.34}Si_{0.31}V_{0.15})_{Σ1.00}Si_{5.00}O_{20.69}(OH)_{7.31}. (H₂O (calc.) 6.45, total 100.26%).

sites, two thirds of them are occupied by aluminum and the rest by aluminum and divalent ion which is dominantly occupied by magnesium and overflowed manganese. The excess of octahedral cations will be placed in the vacant site in the fundamental block termed by MOORE *et al.* (1985). The cations constituting tetrahedral sites are Si⁴⁺, As⁵⁺ and V⁵⁺ among which As⁵⁺ and V⁵⁺ grouped together in a larger tetrahedron, although this accepts a fraction of overflowed Si⁴⁺ from the smaller tetrahedra. But even in the most silicon-rich material, it cannot be the most dominant cation in that site. The material from Kajlidongri, India (NAYAK, 1967) may comprise tetrahedral Al despite its low Al₂O₃ content (Table 3) due to the low SiO₂ content and the dominant lodging of magnesium.

After the reference to these considerations, the analyses of material in No. 24847 are characterized by the deficit in the octahedral site, and one of them has an over-

flowed silicon up to about 1/5 in the site for (V, As). The same tendency is seen in one of the analyses of No. 24950 ardennite, in which about 1/3 of that site is occupied by silicon. The most manganese-poor and calcium-rich analysis of this material has very low content of overflowed manganese. The low totals of all the analyses are neatly sufficed by calculated H₂O contents.

Geochemistry of Vanadium and Arsenic in Manganiferous Beds

As to the occurrence of vanadium in metamorphosed bedded manganese ore deposits developed in siliceous metamorphic rocks of various grades in Japan, the tri- and tetravalent states are known except for ardennite. Namely, tri-valent vanadium is essential in roscoelite (MOMOI and YOSHIMURA, 1964; MATSUBARA, 1985) and nagashimalite (MATSUBARA & KATO, 1980), goldmanite (MOMOI, 1964), and subordinate in aegirine (NAKAI *et al.*, 1976), in spessartine (MATSUBARA & KATO 1986a; 1986 b), and in galaxite and jacobsite (MATSUBARA & KATO, 1986 b). While, the tetravalent vanadium forms its independent minerals such as haradaite (WATANABE *et al.*, 1982) and suzukiite (MATSUBARA *et al.*, 1982). The occurrence of pentavalent vanadium is not essential but subordinate in manganberzeliite (MATSUBARA, 1975), in which the substitution of vanadium for arsenic takes place in a lesser degree.

While, arsenic in metamorphosed bedded manganese ore deposits is in most cases sulphide of wide sense, that is, niccolite, gersdorffite, and cobaltite. Such As³⁺-bearing mineral as schallerite is not found in Japan. Arsenic in the pentavalent state is known in manganberzeliite as stated already, except for the appearance in the product of supergene alteration, such as annabergite from the Hagidaira mine, Gumma Prefecture (TAKANO *et al.*, 1960) and pharmacosiderite from the Takara mine, Aichi Prefecture (MATSUBARA & NOMURA, 1972). Obviously, the present case is different from all of the above-stated ones on account of substitutional co-existence of these elements in a single mineral, which was formed under an oxidizing condition, though divalent manganese ion was fully available thereat.

It is worth mentioning that the occurrence is similar to that in Kajlidongri, India (NAYAK, 1967), where ardennite occurs in manganiferous quartz schist (gondite) and in pegmatitic veins traversing it. Also, the associated minerals include quartz, spessartine, rutile and manganese oxide ore in gondite, and quartz and hematite in veins. However, there is a significant difference in the associated minerals between two, that is, the occurrence of piemontite in all the Japanese occurrences. Provided that the physical conditions are alike, the difference is ascribed to that of the chemical condition of the original rock. The most probable factor is the higher CaO contents in the cases of Japanese ardennites, whereas at Kajlidongri calcium is concentrated within ardennite and any other calcium-bearing minerals are not recorded. The interpretation is that higher concentration of calcium in the original rock does not impede the formation of ardennite. And, it is highly probable that the manganese oxide ore

Table 4. Chemical analyses of piemontite. (Total Fe is given as Fe_2O_3 . Total Mn is allotted to MnO and Mn_2O_3 to fill the deficit of Ca. H_2O is calculated.)

	1.	2.		1.	2.
SiO_2	36.62	36.97	MnO	4.02	1.30
Al_2O_3	19.53	19.16	CaO	19.54	21.71
Fe_2O_3	8.44	6.74	H_2O	1.84	1.94
Mn_2O_3	9.27	11.38	total	99.26	99.20

Empirical formulae (basis: total cation=8):

1. $(\text{Ca}_{1.72}\text{Mn}_{0.28})_{2.00}(\text{Al}_{1.89}\text{Mn}_{0.58}\text{Fe}_{0.52})_{2.00}\text{Si}_{3.01}\text{O}_{12.00}(\text{OH})_{1.01}$
2. $(\text{Ca}_{1.91}\text{Mn}_{0.09})_{2.00}(\text{Al}_{1.85}\text{Mn}_{0.71}\text{Fe}_{0.42})_{2.00}\text{Si}_{3.03}\text{O}_{12.00}(\text{OH})_{1.06}$

1. Piemontite (NSM M-24950). Ohnara, Sanbagawa, Onishi-machi, Tano-gun, Gumma Prefecture, Japan, in association with ardennite.
2. Piemontite (NSM M-24951). Ditto, without ardennite.

in gondite form Kajlidongri is braunite. If so, the excess of calcium produces low calcium piemontite possibly involving Mn^{2+} (Table 4) after the consumption of braunite provided that SiO_2 and Al_2O_3 are fully available. In Table 4 the chemical analyses of piemontite without associated ardennite in the material (NSM M-24951) is also demonstrated to indicate the compositional similarity.

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We express our sincere gratitude to Mr. Hideaki KUSAKA for his donation of the studied material and for his help to the field works including the recognition of the source of ardennite in the locality.

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