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SYNTHESIS OF VANADIUM SILICATES: HARADAITE, GOLDMANITE AND ROSCOELITE

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ABSTRACT

Haradaite, a new strontium vanadyl silicate $SrVOSi_2O_6$, goldmanite, calcium vanadic garnet, $Ca_3V_2Si_3O_{12}$ and roscoelite, vanadium mica, $KV_2AlSi_3O_{10}(OH)_2$ have been hydrothermally synthesized from chemically prepared starting materials at moderate P. T. conditions, ranging over 200°C-800°C and 15,000-45,000 psi for 20-96 hour.

Equilibrium conditions of these minerals as expressed in the VO_2-V_3O_5-V_2O_3 system and valency states of vanadium have been determined.

Introduction

Lately two new vanadium bearing silicates, haradaite and goldmanite, have been discovered. Among these, haradaite was discovered by Watanabe and Kato in 1960 at the Nodatamagawa manganese mine, Iwate, Japan, and its chemical composition has been determined by the present author as $SrVOSi_2O_6$. A full account of their study of this mineral will be published shortly (Watanabe *et al.*). Though the structure of the crystal has not been elucidated yet, it can definitely be stated from our preliminary survey that it is classified into neither the neso- nor the phyllo-silicates.

Goldmanite, $Ca_3V_2Si_3O_{12}$, was first reported by Moench and Meyrowitz from the Laguna mine, New Mexico, U. S. A. In their complete description of this mineral, they have concluded that it is the vanadium analogue of grossular and andradite (Moench & Meyrowitz, 1964). A manganese bearing variety of this species with the composition, $(Ca, Mn)_3V_2Si_3O_{12}$, has also been found from the Yamato mine, Kagoshima, Japan (Momoi, 1964).

Roscoelite, another material for the present investigation, is a vanadium mineral first described by Blake (1876). Rare as it is in nature, a number of studies have since been carried out on this mineral, and it has been recognized as a kind of mica with the composition, $KV_2AlSi_3O_{10}(OH)_2$ (Wells & Brannock, 1964; Heinrich & Levinson, 1955; Weeks *et al.*, 1959; Foster, 1959).

Besides these descriptions of individual species, a report has been given of paragenetic occurrence of these three minerals (Yoshimura & Momoi, 1964).

On the other hand, as is widely recognized, the problem of interest on these vanadium bearing silicates is on the valency states of the vanadium ions. If the valency states of the element in these silicates are determined, it is expected that these will enable us to study the equilibrium relationships between these minerals with reference to the stability region of vanadium oxides. However, the amounts of specimens from those localities available for the research are scanty, and synthetic work has to be involved in the investigation. In order to establish the equilibrium relations as expressed in the VO_2-V_3O_5-V_2O_3 system, therefore, the author began the present study with hydrothermal syntheses of these vanadium bearing minerals and then proceeded to the valency determination of the vanadium ions in the synthetic products.

Hydrothermal syntheses

As the starting materials for syntheses, so-called co-precipitated gel mixtures containing vanadium in the form of V^{4+} were prepared from the following C. P. grade chemicals: strontium carbonate, barium chloride, calcium carbonate, sodium silicate, potassium silicate, ammonium vanadate, *l*-ascorbic acid, alminum chloride, ammonium hydroxide and ammonium carbonate. Each of these mixtures was then brought into hydrothermal reaction with the aid of Tem-press equipment operated at temperatures ranging from 200°C to 800°C and under pressure between 13,000 and 50,000 psi. Gold tubings, 2-5 mm in diameter and electrically welded to secure complete sealing, were used as the liner. No water was added in the linear, because these starting materials contained sufficient amounts of water for the maintenance of H_2O vapor pressure during the run. Residual liquid, if found in the system after a run, was slightly alkaline according to the test with hydrion paper, but the products in most cases came out as completely dry crystalline aggregates. Precise control over the atmosphere in the running system was impossible owing to the small capacity of the gold tubing as well as the minute quantity of the specimen. The atmosphere, intended to be inert, was always weakly reducing because the starting precipitates, after drying below 100°C, carried small amounts of organic matter such as methyl alcohol, ascorbic acid and NH_4Cl which consumed oxygen during the course of the experiment at high temperature. The conditions for and the products of the syntheses are given in Table 1, 2 and 3 for haradaite, goldmanite and roscoelite respectively.

The synthetic products of the runs from No. 1 to No. 4 in Table 1 were all derived from the starting materials with vanadium in excess and were fine-grained crystals greenish black in color. Those of No. 5-No. 7 were blue. The rest of the runs, beginning from No. 8 and arranged according to the order of increasing temperatures, were all carried out with strontium in excess and their products were light blue in color, except those at the two extremes of the temperature range, pale greenish gray for Nos. 9 and 10 and bluish white for Nos. 14 and 15. After the runs made above 700°C, unidentified blue acicular crystals of a high refractive index (1.86) were found in appreciable amounts under the microscope. These were probably a multioxide of Sr and V. Corresponding to the appearence of this phase, four additional lines of medium intensities were recorded

Table 1. Syntheses of haradaite.

No.	Mixture	*T*(C)	*P*(psi)	Time (hr)	Atmosphere	Products as identified in X-ray diffraction pattern
1	Sr-H-*a*[1]	540	33,000	48	weakly reducing	Haradaite, quartz, V_2O_3
2	Sr-H-*b*[2]	680	23,000	48	alcohol	Haradaite, quartz, V_2O_3
3	Sr-H-*a*	700	25,000	48	ascorbic acid	Haradaite, V_2O_3
4	Sr-H-*a*, *b*	700	37,000	48	weakly reducing	Haradaite, quartz, V_2O_3
5	Sr-H-*a*, *c*[4]	450	36,000	48	weakly reducing	Haradaite
6	Sr-H-*a*, *c*[4]	600	35,000	72	weakly reducing	Haradaite
7	Sr-V-Si[5] 3:2:3	550	45,000	20	alcohol	Haradaite, $SrSiO_3$, V_2O_3
8	Sr-H-*c*[3]	200	20,000	24	weakly reducing	Amorphous
9	Sr-H-*c*	300	20,000	24	weakly reducing	Haradaite
10	Sr-H-*c*	400	20,000	24	weakly reducing	Haradaite
11	Sr-H-*c*	550	40,000	24	weakly reducing	Haradaite
12	Sr-H-*c*	600	40,000	48	weakly reducing	Haradaite, $SrSiO_3$
13	Sr-H-*c*	730	25,000	72	weakly reducing	Haradaite, $SrSiO_3$
14	Sr-H-*c*	750	22,000	72	weakly reducing	$SrSiO_3$, haradaite
15	Sr-H-*c*	780	13,000	96	ascorbic acid	$SrSiO_3$, haradaite

1), 2): Almost identical with each other, with VO_2 and SiO_2 in excess, precipitated by NH_4OH.

3): With SrO and SiO_2 in excess, precipitated by NaOH.

4): Sr-H-*a* and Sr-H-*c* mixed so as to simulate approximately the right composition of haradaite.

5): Originally intended to synthesize the Sr-analogue of goldmanite.

Table 2. Syntheses of goldmanite.

No.	Mixture	T(C)	P(Psi)	Time (hr)	Atmosphere	Products as identified in X-ray diffraction pattern
1	G-*a*1)	400	20,000	24	weakly reducing	$Ca_2SiO_4 \cdot H_2O$, VO_2
2	G-*a*	500	33,000	45	weakly reducing	Goldmanite, quartz, V_2O_3
3	G-*a*	580	18,000	48	alcohol	Goldmanite, cristobalite, V_2O_3
4	G-*b*2)	600	35,000	72	weakly reducing	Goldmanite, V_2O_3, V_3O_5
5	G-*b*	700	37,000	48	weakly reducing	Goldmanite, V_2O_3, quartz
6	G-*c*3)	760	15,000	24	ascorbic acid	Goldmanite
7	G-*d*4)	450	36,000	48	ascorbic acid	Goldmanite, wollastonite
8	G-*d*	450	36,000	48	weakly reducing	$Ca_2SiO_4 \cdot H_2O$, quartz
9	G-*d*	600	36,000	72	ascorbic acid	Goldmanite, wollastonite
10	G-*d*	600	40,000	48	weakly reducing	Goldmanite, wollastonite
11	G-*d*	680	23,000	48	weakly reducing	Wollastonite, goldmanite
12	V-Si mix 1 : 1	700	35,000	48	weakly reducing	V_3O_5, quartz

1), 2) : With VO_2 and SiO_2 in excess, precipitated by NH_4OH.

3) : With the right composition of goldmanite, precipitated by NH_4OH and $(NH_4)_2CO_3$.

4) : With CaO and SiO_2 in excess, precipitated by NaOH.

Table 3. Syntheses of roscoelite.

No.	Mixture	T(C)	P(psi)	Time (hr)	Products as identified in X-ray diffraction pattern
1	K_2SiO_3, V-Al silicate	300	18,000	48	Roscoelite
2	,,	400	20,000	25	Roscoelite
3	,,	450	36,000	48	Roscoelite
4	,,	500	38,000	48	Roscoelite
5	,,	500	33,000	48	Roscoelite
6	,,	500	24,000	24	Roscoelite
7	,,	600	35,000	72	Roscoelite

in the X-ray diffraction patterns of the products.

The syntheses of goldmanite were carried out, as listed in Table 2, in a sequence similar to that for haradaite in Table 1. The products from starting materials bearing vanadium in excess were grayish black in color. That of run No. 6 made with a material of the correct composition for goldmanite showed yellowish green color typical of the material. The runs from No. 7 to No. 11 with calcium in excess gave products of greenish gray color. The starting materials used for No. 12 was vanadium hydrous silicates and the products was reddish black.

The results of the syntheses of roscoelite are much simpler than haradaite and goldmanite and the results are listed in Table 3. The products were all pale yellowish green in color.

X-ray studies

X-ray powder diffraction patterns were obtained with an X-ray diffractometer from synthetic haradaite, goldmanite, and roscoelite and were compared respectively with those of the corresponding natural crystals.

The diffraction pattern of synthetic haradaite as listed in Table 4 was indexed according to the orthorhombic cell constants, $a_0=7.00$Å,

Table 4. X-ray powder diffraction data of haradaite
(Cu $K\alpha$, λ=1.54050 Å, Ni-filtered)

Synthetic haradaite No. 6				Natural haradaite from the Yamato mine (Watanabe *et al.*)	
I	$d_{obs.}$ (Å)	$d_{calc.}$	*hkl*	*d*(Å)	*I*
30	7.30	7.31	020	7.33	60
20	4.08	4.07	111	4.07	5
40	3.65	3.66	040	3.66	100
20	3.59	3.59	031	3.60	5
15	3.24	3.24	140	3.24	30
100	3.20	3.20	131	3.20	50
90	2.88	2.87	211	2.871	10
40	2.65	2.65	002	2.653	10
30	2.55	2.56	051	2.563	20
20	2.51	2.51	231	2.513	1
5	2.44	2.44	060	2.437	5
15	2.41	2.41	151	2.406	5
30	2.30	2.30	160	2.303	20
40	2.12	2.12	311, 202	2.120	5
35	2.05	2.05	142	2.054	10
25	2.04	2.03	222	2.039	1
30	1.971	1.971	340	1.971	2
10	1.943	1.945	071	1.947	10
10	1.876	1.874	171	1.875	10
5	1.829	1.829	080	1.829	5
25	1.757	1.757	013	1.771	2
10	1.740	1.739	162	1.742	5
5	1.707	1.706 1.703	322 113	1.705	1
15	1.620	1.622	280	1.621	2
15	1.572	1.576 1.570	431 213	1.573	2
10	1.517	1.518	191	1.518	5
10	1.463	1.463	0, 10, 0	1.463	10
15	1.423	1.424	460, 362	1.423	10
10	1.282	1.282	124	1.282	10

Table 5. X-ray diffraction data of goldmanite
(Cu $K\alpha$, λ=1.54050Å Ni-filtered)

Synthetic goldmanite No. 2				Laguna goldmanite (Moench & Myerowitz, 1964)		Mn-goldmanite (Momoi, 1964)	
$d_{\mathrm{obs.}}$ (Å)	$d_{\mathrm{calc.}}$ (Å)	I	hkl	d(Å)	I	d(Å)	I
4.27	4.26	30	220	4.225	12	—	—
3.02	3.02	65	400	3.005	65	2.995	55
2.70	2.69	100	420	2.668	100	2.678	100
2.57	2.57	5	332	2.565	9	2.553	6
2.47	2.46	70	422	2.453	38	2.445	72
2.371	2.367	8	510	2.357	16	2.349	21
2.206	2.204	5	521	2.194	16	2.186	23
1.955	1.958	10	611	1.951	22	1.942	34
1.911	1.908	2	620	1.901	8	1.894	9
1.745	1.742	2	444	1.735	8	1.729	13
1.676	1.674	10	640	1.667	18	1.660	40
1.615	1.613	40	642	1.607	49	1.600	75
1.510	1.509	2	800	1.502	10	1.497	15
1.353	1.349	5	840	1.345	9	1.339	17
1.319	1.317	2	842	1.312	10	1.306	19
1.289	1.287	2	664	1.282	4	1.276	13

b_0=14.63Å, c_0=5.31Å, which had been derived by K. Kamiya, formerly of this laboratory, from his preliminary study on the natural single crystal. (The structure has been found as based upon an A-centered lattice). In Table 4, the powder data for natural haradaite are also given, and an excellent agreement will be seen between these two patterns as far as the spacings are concerned. These two sets of data also agree with each other in general in their relative intensities of lines. However, as easily recognized from the fact that the intensities of (020) and (040) are very much stronger in the powder data of natural haradaite than in those of the synthetic product, the former set obviously suffer disturbances due to preferred orientation of crystal fragments. Therefore, the powder data derived here with the synthetic material should be adopted as standard. The lattice

Table 6. X-ray powder diffraction data of roscoelite
(Cu $K\alpha$, λ=1.54050Å Ni-filtered. Indexed as the 1M-type mica)

Synthetic roscoelite, No. 1				Roscoelite from California, USNM 84451 (Heinrich & Levinson, 1955)		Roscoelite from Colorado (Wells & Brannock, 1946)	
$d_{\text{obs.}}$ (Å)	I	hkl	$d_{\text{calc.}}$	d(Å)	I	d(Å)	I
10.2	70	001	10.1	10.0	*ms*	10.0	*vs*
5.05	3	002 $10\bar{1}$	5.03 5.00	—		5.01	*vw*
4.51	95	020 110	4.55 4.48	4.55	*vs*	4.54	*vs*
4.39	10	012 $11\bar{1}$	4.41 4.39	4.39	*mw*	4.39	*vw*
4.13	2	021	4.15	4.15	*vw*	4.13	*vw*
3.67	50	$11\bar{2}$	3.66	3.66	*s*	3.66	*m*
3.36	70	022 $12\bar{1}$ 003	3.39 3.37 3.36	3.34	*vs*	3.35	*s*
3.11	50	121, 112, $10\bar{3}$	3.11	3.11	*s*	3.11	*m*
2.93	2	$11\bar{3}$	2.93	2.89	*w*	2.90	*mw*
2.70	3	023	2.70	2.69	*m*	2.70	*w*
2.58	100	103 200	2.59 2.58	2.60	*ms*	2.60	*s*
2.41	30	$21\bar{2}$	2.42	2.42 2.35	*m* *vw*	2.42	*m*
2.27	3	040 $22\bar{1}$, $20\bar{3}$	2.28 2.27	2.28	*w*	2.28	*w*
2.22	1	041	2.22	2.22	*vw*	2.21	*vw*
2.16	20	$12\bar{4}$	2.16	2.16 2.03	*vw* *vw*	2.16	*vw*
2.01	5	005, $10\bar{5}$ 141	2.01	2.00	*w*	2.00	*m*
1.72	2	311, 300 $24\bar{1}$	1.72	1.73	*vw*	1.72	*vw*
1.67	10	$14\bar{4}$	1.67	1.66	*m*	1.67	*mw*
1.517	20	$33\bar{1}$ 060, 312	1.518 1.517	1.52	*w*	1.52	*w*
				1.44	*vw*	1.44 1.38	*vw* *vw*
1.353	2	136	1.353	1.35	*w*	1.35	*w*
1.317	3	$26\bar{1}$	1.313	1.31	*mw*	1.31	*w*

constants derived from these powder data are: $a_0=7.02\text{Å}$, $b_0=14.63\text{Å}$, $c_0=5.30\text{Å}$.

The powder data of synthetic goldmanite are given in Table 5, together with those of the Laguna goldmanite and the manganese bearing variety from the Yamato mine. Since the crystal possesses cubic symmetry, indices have straightforwardly been assigned to each of the diffraction lines, and the lattice constant deduced from these data is $a_0=12.06\text{Å}$ in good agreement with the value, $a_0=12.09\text{Å}$, reported by Mill (1964).

Finally, the X-ray data of roscoelite are listed in Table 6 and are shown to be successfully indexed if a 1 M mica structure is assumed for this crystal. The cell constants derived from the data of synthetic roscoelite are: $a_0=5.26\text{Å}$, $b_0=9.09\text{Å}$, $c_0=10.25\text{Å}$ $\beta=101.0°$.

Optical properties

Haradaite, goldmanite and roscoelite crystals in the synthetic products were studied microscopically with the results as summarized in Table 7, together with the optical data of the natural minerals.

Well developed crystals of synthetic haradaite show a flaky appearance elongated along the optical *X*-axis as seen in Fig. 1. The largest crystal obtained in the course of the present work measures $85\,\mu\times 17\mu\times 6\,\mu$.

Goldmanite invariably grows into isometric crystals up to $3\,\mu$ in diameter as shown in Fig. 3. Roscoelite crystallizes out as green aggregates of flakes as illustrated in Fig. 4. Some of the flakes were large enough to make $2V$-mearsurements possible on them.

Though the general appearance of the crystals is such as described above, the detailed crystal habits were observed to show considerable variations according to the environmental effects, pH and Eh, chemical compositions, and the procedures of preparations for the starting materials.

The optimum conditions for crystallization of these synthetic

Table 7. Optical properties of haradaite, goldmanite and roscoelite, synthetic and natural.

	Haradaite		Goldmanite		Roscoelite	
	synthetic	natural (Watanabe *et al.*)	synthetic	natural (Moench & Meyrowitz, 1964)	synthetic	natural (Wells & Brannock, 1946)
N_x	1.71	1.713	1.82	1.821	1.595	1.59
N_y	—	1.721			—	—
N_z	1.73	1.734	—	—	1.600	1.64
N_z-N_x	.02	.021	weakly anisotropic		.005	.05
$2V$	n. d.	(+) 90	—	—	(−) 9	n. d.
Color	light blue	bluish green	light green	dark green	green	green
Pleochroism X	pale blue	pale green			olive green	olive green
Y	—	light yellow				olive green
Z	light yellow	blue green			green	green brown

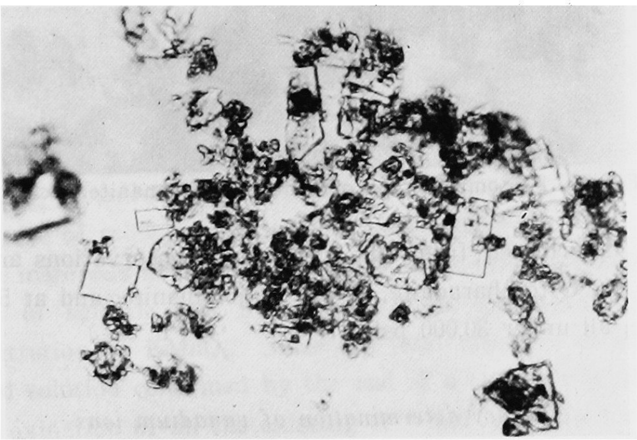

Fig. 1. Photomicrograph of synthetic haradaite. (×250)

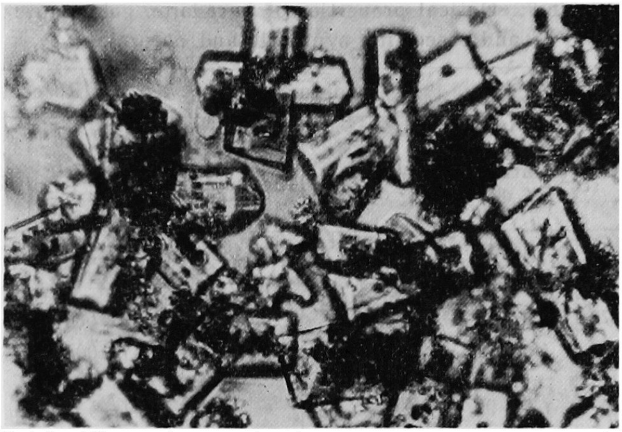

Fig. 2. Photomicrograph of synthetic haradaite. (×250)

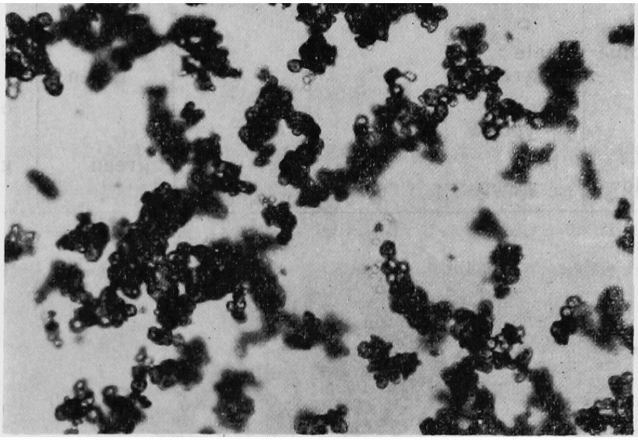

Fig. 3. Photomicrograph of synthetic goldmanite. (×250)

minerals, determined from the microscopic observations are as follows: at 550°C for haradaite, at 700°C goldmanite, and at 500°C for roscoelite, all under 30,000 psi.

Valency determination of vanadium ions

A synthesis carried out in a large gold liner (5 mm in diameter and 30 mm in length) yields 250 mg of the product after each run.

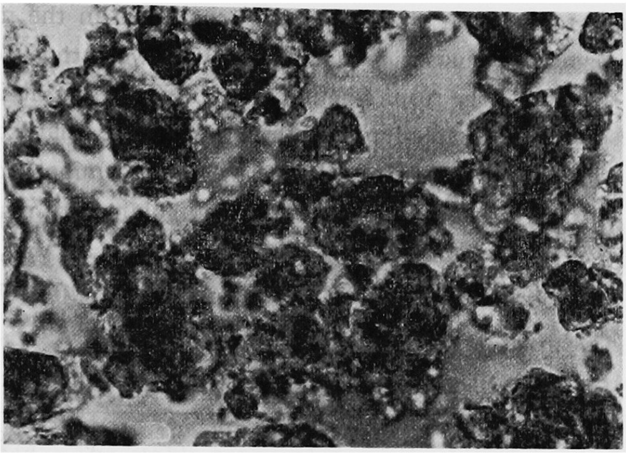

Fig. 4. Photomicrograph of synthetic roscoelite. (×250)

The conventional wet semi-micro chemical analysis has, therefore, been applied to the valency determination of vanadium ions in these minerals.

Total amounts of vanadium were first determined by EDTA titration with Cu-Pan indicator in a solution of acetic acid (pH 3). It was obvious that the none of the minerals under consideration contained V^{5+} ions; this had been confirmed by the author's chemical analysis of natural haradaite for one thing. However, during the course of the chemical treatments, some of the V^{4+} ions in the samples were liable to oxidation into V^{5+}. Therefore, before proceeding to the total vanadium determination, ascorbic acids was applied for the purpose of reducing these V^{5+}'s back to V^{4+}'s.

The materials in different weights were then decomposed in a mixture of sulfuric and hydrofluoric acids and were brought into redox titration by $KMnO_4$. Since the total amounts of the $KMnO_4$ standard solution consumed by the end of a titration is that needed for the oxidation of all the existing V^{3+} and V^{4+} into V^{5+}, the difference between the above and that calculated by assuming the whole content of vanadium in the sample to consist solely of V^{4+}, exactly corresponds to half the quantity of V^{3+} contained in the mineral.

The respective quantities of VO_2 and V_2O_3 were thus determined for each specimen, the results being given in Table 8. It is obvious from these that the vanadium ions in haradaite are characterized by V^{4+} and those in goldmanite by V^{3+}. Although minor amounts of V^{3+} and V^{4+} were detected in haradaite and goldmanite respectively, these have in all probability come from oxides such as V_2O_3 and VO_2 carried in small quantities in the present synthetic products.

Table 8. Valency determination of vanadium ions in synthetic haradaite, goldmanite and roscoelite.

	Haradaite		Goldmanite			Roscoelite	
	Synthetic No. 4	Natural (Watanabe *et al.*)	Synthetic No. 5	Natural		Synthetic No. 4	Natural (Weeks & Brannock, 1946)
				(Moench & Moyrowitz, 1964)	(Momoi, 1964)		
VO_2	33.0	26.16	3.0	n. d.	nil	12.4	1.69
V_2O_3	4.0	—	27.0	18.3	24.9	16.6	17.57
$H_2O(+)$	1.4*	1.2*	—	—	—	5.9	3.94
SiO_2						44.5	40.40
Al_2O_3						19.5	18.31
Na_2O						0.1	—
K_2O						9.2	11.26

* Possibly haradaite is slightly hydrous.

On the other hand, roscoelite may contain both V^{4+} and V^{3+}. In order to give an estimation of the vanadium content in the octahedral layers in this mica structure, a full chemical analysis was carried out on this minerals as seen in Table 8. The structural formula derived by this analysis will be expressed as $(K_{0.8}V^{3+}_{0.6}V^{4+}_{0.8}Al_{0.3})(Al_{1.1}Si_{2.9})O_{10}(OH)_2$, which showed a higher content of V^{4+} in the synthetic roscoelite than its natural counterpart (Heinrich & Levinson, 1955; Weeks *et al.*, 1959).

Equilibrium relations

The X-ray pattern characteristic of haradaite begins to appear at a temperature as low as 300°C, and there was observed no trace of a phase intermediate between crystalline haradaite phase and amorphous one. At higher temperatures, while a mixture with vanadium in excess produces V_2O_3 above 500°C, one bearing strontium in excess gives strontium metasilicate from 400°C. Above 700°C where the diffraction lines from strontium metasilicate increase their intensities, a fairly clear pattern of haradaite is still maintained, though observed under the microscope that its crystallinity seems to have deteriorated. The stable range of synthetic haradaite deduced from the present observations in reducing atmosphere is between 250°C and 750°C and between 15,000 and 40,000 psi.

Goldmanite begins to crystallize at 450°C in a strongly reducing atmosphere caused by the decomposition of organic materials at elevated temperatures. On the other hand, in weakly reducing atmosphere, its crystallization is rather slow, but at any rate at temperature above 700°C, VO_2 is reduced completely to V_2O_3 by the decrease of the oxygen pressure in the present experimental conditions. Thus the crystallization of goldmanite will eventually be accelerated. From mixture with Ca in excess, wollastonite always appears at temperatures above 450°C, and calcium hydrous silicate (Heller & Taylor, 1956) and VO_2 below 400°C. In the X-ray powder pattern of goldmanite produced by run No. 4 (600°C, 35,000 psi), the presence of V_3O_5 was detected. Also after run No. 12 (700°C, 35,000 psi) with hydrous vanadyl silicate as the starting material, the products turned out to be V_3O_5 and SiO_2. V_3O_5 is a distinct phase first synthesized by Andersen (1954) by heating a mixture of metallic vanadium and V_2O_3 at 900°C in vacuum. Under the hydrothermal conditions brought about in this work, however, it was formed at a temperature as low as 600°C. Andersen (1954) produced several non-stoichiometric oxides having the compositions intermediate between VO_2 and V_2O_3, but none of these was observed in the experiments. VO_2 was detected in the products of No. 1 (400°C, 20,000 psi) of goldmanite, confirming the first report of the synthesis by Laudise and Nielsen (1961).

Roscoelite was synthesized from 300° to 700°C and under the pressure of 10,000-40,000 psi. The products consist mostly of pure green micaceous flakes of a microscopic size. No other phase was observed by X-ray means, though very tiny spots of opaque vanadium oxides were detected under the microscope only along the fringes of a few flakes.

From the results described above, it is to be concluded that vanadium in haradaite is tetravalent and the mineral is a metasilicate of the structure formula, $SrVO(SiO_3)_2$, possibly with a very small quantity of H_2O. Vanadium in goldmanite is trivalent as described by Momoi (1964) and the ion is co-ordinated by six oxygen atoms octahedrally in the crystal structure. Roscoelite contains both V^{3+} and V^{4+} ions, the ratio of which should depend upon the oxygen partial pressure during the formation of the crystals.

The results will also throw light on the paragenetic relationship among these three vanadium minerals when their equilibrium relations are expressed in the VO_2-V_3O_5-V_2O_3 system as shown in Fig. 5. Evidently, the boundary between VO_2 and V_2O_3 in the system can not be represented by a single line, but by a broad intermediate band in which V_3O_5 is stable. This band presents the conditions under which the paragenesis of haradaite, goldmanite and roscoelite is realized, and it is so indicated in the figure as to satisfy our experimental results as nearly as possible. Below this band (approximately below 400°C) goldmanite does not appear, and above it (above 800°C) haradaite bocomes unstable because of the decomposition of VO_2 in this range. The ratio of the V^{4+} and V^{3+} contents in roscoelite may suggest an oxygen environment in which these minerals crystallized paragenetically in the Yamato mine.

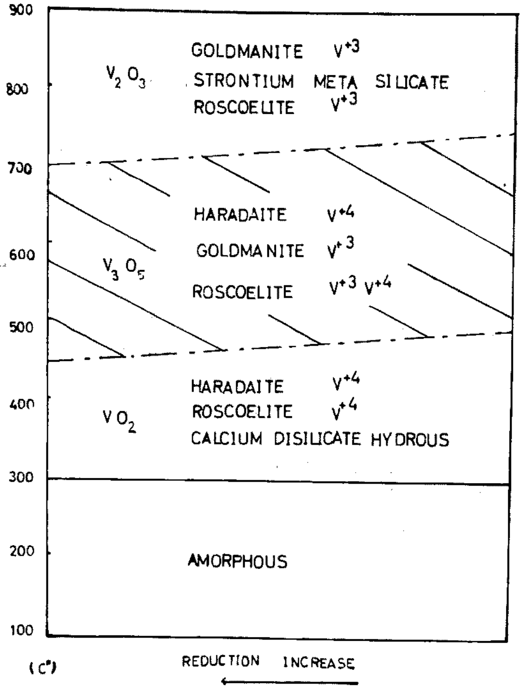

Fig. 5. Diagram representing paragenetic relationship of haradaite, goldmanite and roscoelite in the Yamato mine.

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