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THE HIDAKA VIRIDINE: A SECOND LOOK

by

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(with 2 text-figures and 2 tables)

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Abstract

Viridine from the Chiroro River area, Hidaka Mountains, coexisting with Mn-phengite – spessartine-piedmontite – Mn-tourmaline – Ti-Mn haematite in a quartz schist has been reanalysed by EPMA.

Comparison with viridine compositions from other localities in the world indicates a range of $Al^{3+} \rightleftharpoons (Mn, Fe)^{3+}$ substitution ranging from 2.0:0.0 (andalusite) to 1.45:0.55 (the most Mn-rich andalusite yet reported).

Introduction

Viridine, a manganiferous andalusite, $(Al_{2-x}Mn, Fe_x^{3+}) SiO_5$, was first reported from the Chiroro River area, Hidaka Mountains, Hokkaido, by Suzuki et al. (1965) where it is associated with Mn-phengite – piedmontite-spessartine – Mn-tourmaline – Ti-Mn haematite in a manganiferous quartz mica schist which recrystallized under very high f_{O_2} conditions.

We have revisited this locality, mapped the manganiferous schists and associated epidote amphibolite outcrop in detail and have made a complete bulk chemical and mineralogical study of the rocks. The results of this study will be published elsewhere (Grapes and Hashimoto, submitted for publication) and this note is concerned with the composition of the viridine itself. Composition of the Hidaka Viridine and Comparisons.

Suzuki et al. (1965, 1968) gave optical properties, unit cell dimensions and a wet chemical analysis of the Hidaka viridine (Table 1). The purity of their separated sample, however, is somewhat in doubt as they mentioned that numerous inclusions of haematite and piedmontite are invariably present in the viridine (Fig.1). Their bulk analysis reflects this contamination in the high CaO, Fe_2O_3 , TiO_2 , H_2O (and Mn_2O_3) and low Al_2O_3 contents.

Reconnaissance EPMA analyses are also given by Suzuki et al., but these too, are in error because their bulk analysis was used as a standard for the conversion of counts to wt% oxides (all the totals are too low), (Suzuki et al. 1968) and a recalculation of wt% oxides to 100% (Suzuki et al. 1965) gives

Table 1 Analyses and formulae on the basis of 5(O) of the Hidaka Viridine, Chiroro River, Hidaka Mountains, Hokkaido.

	A	B *	
		Range	
SiO ₂	34.88	34.89	– 33.97
TiO ₂	0.30	0.03	– 0.16
Al ₂ O ₃	41.48	52.26	– 47.42
Fe ₂ O ₃	4.76	2.47	– 2.12
Mn ₂ O ₃	14.57	9.38	– 16.13
MgO	0.67	0.14	– 0.01
CaO	2.23	0.01	– 0.00
Na ₂ O	–	0.00	0.00
K ₂ O	–	0.00	0.00
H ₂ O ⁺	0.92	–	–
H ₂ O ⁻	0.65	–	–
Total	100.46	99.18	99.81
Si	1.032	0.992	0.983
Al	1.448	1.749	1.617
Fe ³⁺	0.107	0.053	0.045
Mn ³⁺	0.327	0.203	0.355
Mg	0.030	0.005	–
Ti	0.007	0.001	0.003
Ca	0.071	–	–
	1.990	2.011	2.020
mol. %			
Al ₂ SiO ₅	76.9	87.2	80.2
Fe ₂ SiO ₅	5.7	2.6	2.2
Mn ₂ SiO ₅	17.4	10.2	17.6

* Range of 19 EPMA analyses. Analyst: R. Grapes.

A. Bulk analysis given in Suzuki et al. (1965).

Analyst: K. Isono.

Methods of EPMA analyses given in Grapes and Hashimoto (submitted for publication).

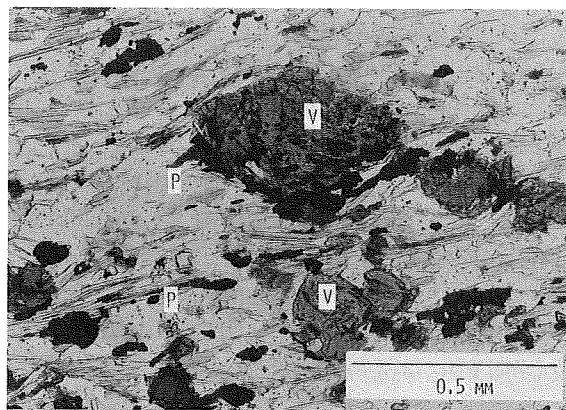


Fig. 1. Viridine – Muscovite – Quartz Schist
V: Viridine, P: Piedmontite

SiO₂ values that are too high (ranging from 37.7% to 38.9%) resulting in significant deviation from the theoretical structural formulae.

For these reasons, and the fact that this locality has the importance of being the only known occurrence of viridine in Japan and S.E. Asia, the mineral has been reanalysed by EPMA by one of us (R.H.G.).

The range of viridine compositions from 19 points taken from 8 grains in two sections are listed in Table 1. As expected the Fe₂O₃ values are almost half that of the bulk analysis and CaO was barely detectable. The calculated "Mn³⁺SiO₅" component ranges from 10.2 to as much as 17.6 mol.%, the highest values comparable to those recently reported by Abraham and Schreyer (1976; Table 2).

With respect to minor elements in the viridine analyses, TiO₂ ranged from 0.00 – 0.15% (the highest value being half that of the bulk analysis), MgO varied from 0.14 – 0.89%, CaO from 0.01 – 0.11% and small amounts of alkalis (less than 0.05%) were detected. These values generally fall within the range of andalusite compositions given by Deer et al. (1962, Table 23). The most abundant of the minor elements, MgO, is probably connected with the five-coordination of each Al ion in the andalusite structure as Mg entering such a structure would be more easily accommodated in a coordination higher than four (Roy, 1954).

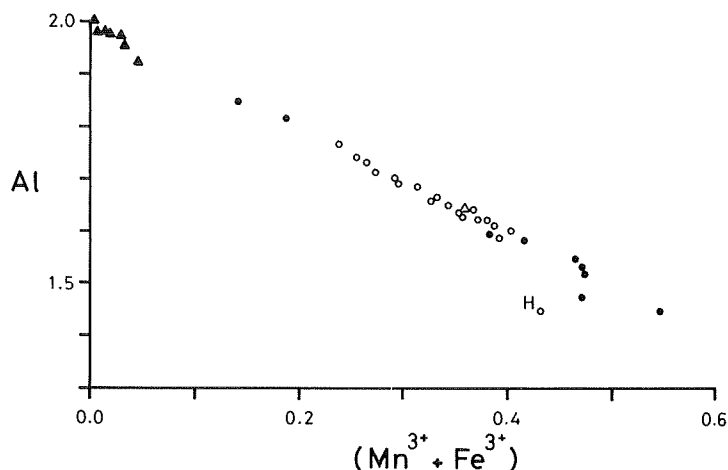


Fig. 2. Plot of Al³⁺ \rightleftharpoons (Mn³⁺, Fe³⁺) Substitution in Viridines. Filled triangles – natural andalusites from Deer et. al. (1962) Filled circles – natural viridines analyses from Table 2; Open circles – Hidaka viridines; Open triangle – synthetic viridine of Abs-Wurnbach and Langer (1975). The open circle marked by H is the bulk analyses given by Suzuki et. al (1965), which has a notable Al deficiency.

Table 2 Analyses and formulae on the basis of 5(O) of Viridines from various localities in the world.

	A	B	Ci	Cii	D	E	F	G	
SiO ₂	36.72	35.30	32.35	34.09	39.5	31.52	35.41	33.84	33.47
TiO ₂	—	1.04	0.35	—	0.07	0.40	—	—	—
Al ₂ O ₃	56.99	55.52	45.72	45.60	51.8	41.41	46.95	44.07	40.98
Fe ₂ O ₃	—	4.16	6.60	10.01	3.3	12.03	0.85#	4.49#	6.08#
FeO	—	—	0.93	—	—	2.16	—	—	—
Mn ₂ O ₃	6.91	4.77	12.14*	11.46*	3.63	8.71*	16.75	16.45	17.96
MgO	—	—	0.21	—	0.33	0.42	—	—	—
CaO	tr.	—	1.61	—	0.40	2.48	—	—	—
Na ₂ O	—	—	—	—	0.18	0.23	—	—	—
K ₂ O	—	—	—	—	0.33	0.22	—	—	—
H ₂ O ⁺	—	—	—	—	0.31	—	—	—	—
H ₂ O ⁻	—	—	1.31	—	0.37	1.23	—	—	—
Total	100.62	100.79	101.22	101.16	100.32**	100.81	99.96**	98.85	98.49
Si	1.008	0.978	0.950	0.984	1.098	0.950	1.018	0.998	1.003
Al	1.845	1.813	1.583	1.552	1.699	1.472	1.591	1.533	1.448
Fe ³⁺	—	0.087	0.146	0.217	0.068	0.273	0.018	0.100	0.137
Fe ²⁺	—	—	0.023	—	—	0.054	—	—	—
Mn ³⁺	0.144	0.101	0.272	0.252	0.077	0.200	0.367	0.369	0.410
Ti	—	0.022	0.008	—	0.001	0.009	—	—	—
Mg	—	—	0.009	—	0.013	0.019	—	—	—
Ca	—	—	0.051	—	0.012	0.080	—	—	—
Na	—	—	—	—	0.010	0.013	—	—	—
K	—	—	—	—	0.012	0.008	—	—	—
	1.989	2.023	2.092	2.021	1.892	2.128	1.977	2.002	1.995
mol. %									
Al ₂ SiO ₅	92.8	90.6	79.1	76.8	92.1	75.7	80.5	76.2	72.6
Fe ₂ SiO ₅	—	4.3	7.3	10.7	3.7	14.0	0.9	5.1	6.9
Mn ₂ SiO ₅	7.2	5.1	13.6	12.5	4.2	10.3	18.5	18.7	20.5

* Mn originally given as MnO.

All Fe as Fe₂O₃.

** Includes 0.10% F.

** Includes 0.03% Cr₂O₃. 0.0007 Cr³⁺ atoms.

- A. Bäckstrom (1896). Viridine from Vestanå, Sweden.
Quartz-*viridine*-*muscovite*-*garnet*-*zircon* schist.
- B. Klemm (1911). Viridine from Darmstadt, Germany. From metasomatic 'granite' veins crosscutting hornfels.
- Ci, ii. Serdyuchenko (1949). Viridine from Timptonsk, S. Yakutia, U.S.S.R.
Quartz-*viridine*-*feldspar*-*biotite*-*sillimanite*-*garnet*-*rutile*-*apatite*-*chlorite*-*graphite*-*magnetite*-*haematite* quartzite.
An analysis of viridine from the same locality by Shabynin (1948) gave 9.60% Fe₂O₃ and 9.89% MnO (11.00% Mn₂O₃).
- D. Ödman (1950). Viridine from Ultevis, Sweden.
Quartz-*viridine*-*white mica*-*feldspar*-*pidmontite*-*epidote*-*tourmaline*-*apatite*-*zircon*-*scheelite*-*haematite* quartzite.
- E. Kulish (1961). Viridine (anal.5) from the Aldan Shield, Siberia.
Quartz-*viridine*-*feldspar*-*biotite*-*sillimanite*-*cordierite*-*rutile*-*apatite*-*chlorite*-*Fe oxide* quartzite.
- F. Kramm (1973). Viridine from the Venn-Stavelot Massif, Ardennes.
Quartz-*viridine*-*white mica*-*garnet*-*chlorite*-*carbonate*-*haematite* low grade semi-schist. EPMA analysis.
- G. Abraham and Schreyer (1975). Viridine from Darmstadt, Germany.
Quartz-*viridine* - Mn-phlogopite - Mn-phengite-spessartine-braunite-haematite hornfels.
Range of EPMA analyses of three grains.

Viridine analyses from other localities in the world are listed in Table 2 and show a large variation in the $\text{Mn}_2^{3+}\text{SiO}_5$ component, from 5.05% to 20.5 mol.%. It is apparent from the high contents of TiO_2 , CaO and H_2O (and probably also Fe_2O_3) contents that many of these analyses were made on impure separates, which is shown by significant deviations from the calculated formulae. As with the Hidaka viridine, haematite and/or piedmontite are the likely main contaminants judging from the coexisting mineral assemblages in the viridine-bearing rocks (key of Table 2).

The range of $\text{Al}^{3+} \rightleftharpoons (\text{Mn}, \text{Fe})^{3+}$ substitution in the viridine analyses is shown in Fig.2 and a continuous variation from pure andalusite with no Mn_2O_3 to manganiferous andalusite with 17.96% Mn_2O_3 is apparent.

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