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VANADIUM-RICH MINERALS OF THE PUMPELLYITE GROUP FROM THE HEMLO GOLD DEPOSIT, ONTARIO

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ABSTRACT

In green mica schist from the main ore zone of the Hemlo gold deposit, Ontario, a very fine-grained pumpellyite-group mineral, occurring sparsely in close association with vanadian titanite and barian tomichite, contains up to 25.7 wt.% V_2O_3; the end-member composition is $Ca_8(V,Mg,Fe)_4(V,Al)_8Si_{12}O_{56-n}(OH)_n$, and vanadium is the dominant cation in both X and Y positions. Vanadoan pumpellyite-(Mg) also occurs in green mica schist as prismatic grains in cross-cutting veins and along foliation planes. The vanadoan pumpellyite-(Mg) contains a substantial amount of V (ranging from 1.7 to 13.6 wt.% V_2O_3), and, in addition, is characterized by unusually high As, Mg, and F contents. Vanadium is incorporated into the pumpellyite-group minerals mainly by the direct substitution $Al^{3+} = V^{3+}$, with minor contributions from $2Al^{3+} = V^{4+} + (Mg,Fe)^{2+}$ or $3Al^{3+} = V^{5+} + 2(Mg,Fe)^{2+}$ (or both). In vanadoan pumpellyite-(Mg), As seems to substitute for Si in tetrahedral positions. This is the first observation of pumpellyite-group minerals in the Hemlo gold deposit, and is further support for a late, low- to very-low-grade calc–silicate alteration within the main ore zone. The vanadium-rich minerals of the pumpellyite group are considered to have formed at about 300–400°C and < 2 kbar in an aqueous fluid of moderate to high salinity.

Keywords: vanadium, pumpellyite group, green mica schist, calc–silicate alteration, gold deposit, Hemlo, Ontario.

SOMMAIRE

Nous avons découvert un minéral à grains très fins, du groupe de la pumpellyite, dans un schiste à mica vert de la zone minéralisée principale du gisement d'or de Hemlo, en Ontario; il est associé à une titanite et une tomichite vanadifères, et contient jusqu'à 25.7% (en poids) de V_2O_3. Le pôle vanadifère ayant le vanadium comme cation dominant dans les positions X et Y aurait la composition $Ca_8(V,Mg,Fe)_4(V,Al)_8Si_{12}O_{56-n}(OH)_n$. Nous trouvons aussi la pumpellyite-(Mg) vanadifère dans le même schiste, sous forme de grains prismatiques dans des veinules recoupant le plan de foliation ou parallèles à celui-ci. La pumpellyite-(Mg) vanadifère contient entre 1.7 et 13.6% de V_2O_3 et, de plus, des quantités anormalement élevées de As, Mg et F. La pumpellyite accepte le vanadium surtout selon la substitution directe $Al^{3+} = V^{3+}$, avec une contribution moins importante des couples $2Al^{3+} = V^{4+} + (Mg,Fe)^{2+}$ et $3Al^{3+} = V^{5+} + 2(Mg,Fe)^{2+}$. Dans la pumpellyite-(Mg) vanadifère, As semble remplacer le Si dans les positions tétraédriques. Cet article présente les premiers indices de la présence de minéraux du groupe de la pumpellyite à Hemlo, indication de plus d'un épisode tardif d'altération calco-silicatée de faible à très faible intensité qui a affecté la zone minéralisée principale. Les minéraux du groupe de la pumpellyite riches en vanadium se seraient formés à environ 300–400°C à une pression inférieure à 2 kbar dans un milieu hydrothermal à salinité moyenne à élevée.

(Traduit par la Rédaction)

Mots-clés: vanadium, groupe de la pumpellyite, schiste à mica vert, altération calco-silicatée, gisement d'or, Hemlo, Ontario.

INTRODUCTION

Pumpellyite-group minerals occur commonly in metamorphic rocks, particularly metabasites recrystallized in the subgreenschist facies (Deer *et al.* 1986, Liou *et al.* 1987). They are well known for their chemical complexity, which involves both a large diversity and wide range of cation substitutions (Deer *et al.* 1986). Passaglia & Gottardi (1973) presented a general formula $W_8X_4Y_8Z_{12}O_{56-n}(OH)_n$, where W = Ca, K, Na; X = Mg, Mn^{2+}, Fe^{2+}, Al, Cr; Y = Al, Fe^{3+}, Cr, Mn^{3+}, Ti; and Z = Si, and a scheme of classification and nomenclature based on the predominant cation in the Y position. Passaglia & Gottardi (1973) further distinguished pumpellyite-group minerals by a suffix, indicating the predominant cation in the X position. To date, the following end-member mineral species and their names have been reported: pumpellyite-(Mg), pumpellyite-(Mn), pumpellyite-(Fe^{3+}), pumpellyite-(Fe^{2+}), julgoldite-(Fe^{2+}), julgoldite-(Fe^{3+}), okhotskite-(Mn^{2+}), okhotskite-(Mg) and shuiskite-(Mg) (Palache & Vassar 1925, Moore 1971, Passaglia & Gottardi 1973, Ivanov *et al.* 1981, Togari & Akasaka 1987, Dasgupta *et al.* 1991, Nickel & Nichols 1991). In the present paper, we describe two unusual compositions of the pumpellyite group the main ore zone of the Hemlo gold deposit, Ontario, a new end-member with V as the dominant cation in both Y and X sites, and a vanadoan pumpellyite-(Mg) with significant sporadic enrichments in As and F.

GEOLOGICAL SETTING AND THE HEMLO GOLD DEPOSIT

The Hemlo gold deposit, located approximately 35 km east of Marathon, Ontario, is situated within the late Archean (2800–2600 Ma; Corfu & Muir 1989) Hemlo – Heron Bay greenstone belt of the Wawa subprovince of the Superior Province (Muir 1982). The geology of the Hemlo – Heron Bay greenstone belt, and particularly of the Hemlo mining district, has been described in numerous studies (Muir 1982, Macdonald 1986, Corfu & Muir 1989, Harris 1989, Pan & Fleet 1990), and most agree that all supracrustal rocks have been subjected to a complicated history of deposition, magmatism, deformation, metamorphism and alteration.

The Hemlo gold deposit contains a total published reserve of approximately 80 Mt at 7.7 g/t Au (Harris 1989) and hosts the three biggest gold mines in current production in Canada, namely, the Williams, Golden Giant, and David Bell mines. The geological complexity of the Hemlo gold deposit, particularly the high intensity of deformation, pervasive alteration (mainly potassic) and association with host rocks of medium-grade metamorphism, have led to a lack of consensus among investigators regarding the style of mineralization. As a result, almost all known ore-forming processes have been proposed for its origin (Macdonald 1986).

OCCURRENCE AND PETROGRAPHY

Pumpellyite-group minerals occur in green mica schist from the main ore zone of the Golden Giant mine. Green mica schist is one of the important host rocks of the Hemlo gold deposit and is characterized by a well-developed schistosity defined by a combination of preferred orientation of vanadian muscovite and an alternation of quartzofeldspathic, micaceous and pyritiferous

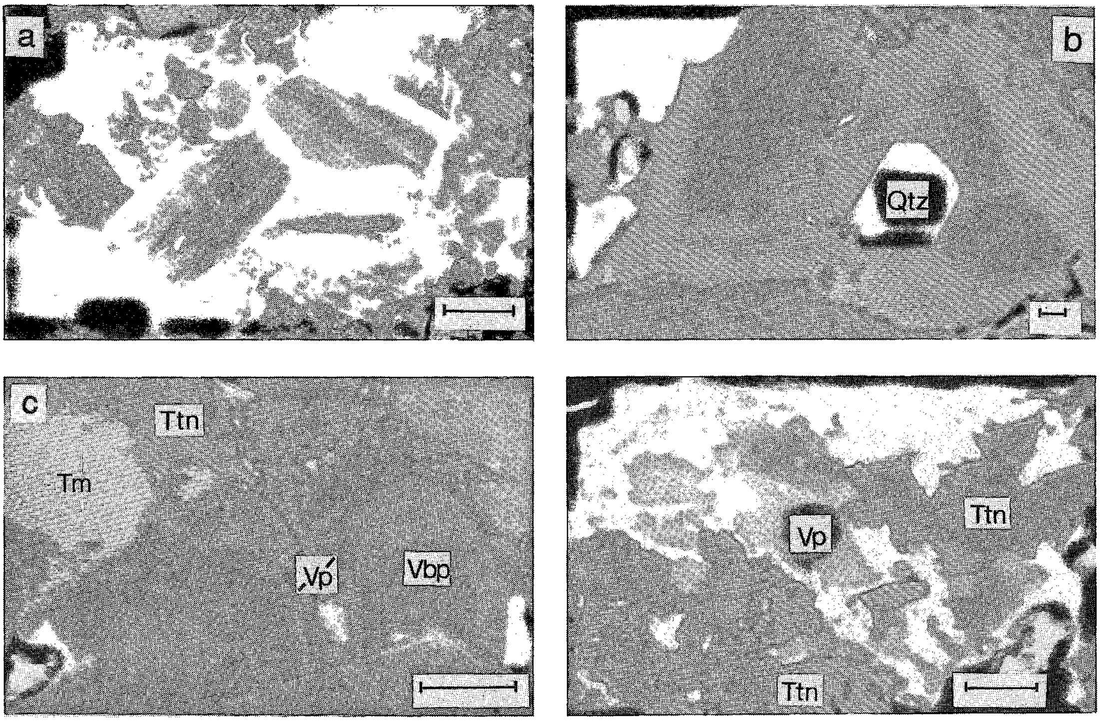

FIG. 1. Photomicrograph (a) and electron back-scattered images (b, c and d) of the pumpellyite-group minerals from the Hemlo gold deposit: a) prismatic vanadoan pumpellyite-(Mg) with polysynthetic twinning in cross-cutting vein, b) chemical zonation in vanadoan pumpellyite-(Mg) enclosing a quartz grain (Qtz), c) the V-rich pumpellyite-group mineral (Vp) and vanadoan pumpellyite-(Mg) (Vbp) associated with vanadian titanite (Ttn) and barian tomichite (Tm), and d) the V-rich pumpellyite-group mineral along grain fractures of vanadian titanite. Scale bar in a) is 50 μm, and in the rest, 10 μm.

layers. Pumpellyite-bearing green mica schist contains quartz, alkali feldspar, vanadian muscovite, barite, pyrite and molybdenite, with minor amounts of barian tomichite, vanadian titanite, epidote, allanite, antimonian vesuvianite and garnet; this assemblage is typical of green mica schist from the Hemlo gold deposit (*cf.* Harris 1989). Harris (1989) and Pan & Fleet (1991) recognized that some examples of green mica from the Hemlo gold deposit are chromium-bearing and do not have a detectable vanadium content. Pumpellyite has not been observed in green mica schist that shows an enrichment in Cr.

There are two distinct modes of occurrence of pumpellyite-group minerals in the green mica schist. Firstly, prismatic pumpellyite occurs as either concordant or discordant aggregates in micaceous or pyritiferous layers, but only rarely in quartzofeldspathic layers. Concordant aggregates appear along foliation planes, and discordant aggregates occur in cross-cutting veins (Fig. 1a). Locally, the prismatic pumpellyite is rather abundant and constitutes up to 3 volume % of rock samples. In thin section, the prismatic pumpellyite is characterized by strong pleochroism, with α colorless to weakly red, β brown or deep brown with a violet tint, and γ pale brown. Locally, prismatic grains of pumpellyite display anomalous interference colors. Zoning is not uncommon and generally is characterized by a rim and a distinct core (Fig. 1b); oscillatory zoning also is locally developed. Polysynthetic twinning, with {100} as the twin plane, is common (Fig. 1a; *cf.* Coombs 1953).

A second pumpellyite-group mineral occurs as sparse, very fine grains (less than 15 μm in maximum dimension) and locally in close association with vanadian titanite and barian tomichite (Figs. 1c, d). This very fine-grained pumpellyite-group mineral is greenish brown, vitreous, transparent, and brittle. In thin section, it is strongly pleochroic (α colorless, β brown to deep brown, and γ pale brown), biaxial negative with strong dispersion ($r < v$) and an estimated $2V$ of 50 ±5°.

CHEMICAL COMPOSITION

Chemical compositions of the pumpellyite-group minerals were investigated with a JEOL JXA-8600 Superprobe electron microprobe fitted with automated wavelength-dispersion spectrometers at the University of Western Ontario (operating conditions: 15 kV, 10 nA, beam diameter 2-3 μm, 20-second counts, with minerals, synthetic glasses and metals as standards). Analytical results are summarized in Figures 2a, b and 3, and representative compositions are reported in Tables 1 and 2. The two texturally distinct pumpellyite-group minerals differ significantly in chemical composition. In particular, the prismatic pumpellyite in veins and along foliation planes is vanadium-bearing (Table 1), whereas the very fine-grained variety associated with vanadian titanite and barian

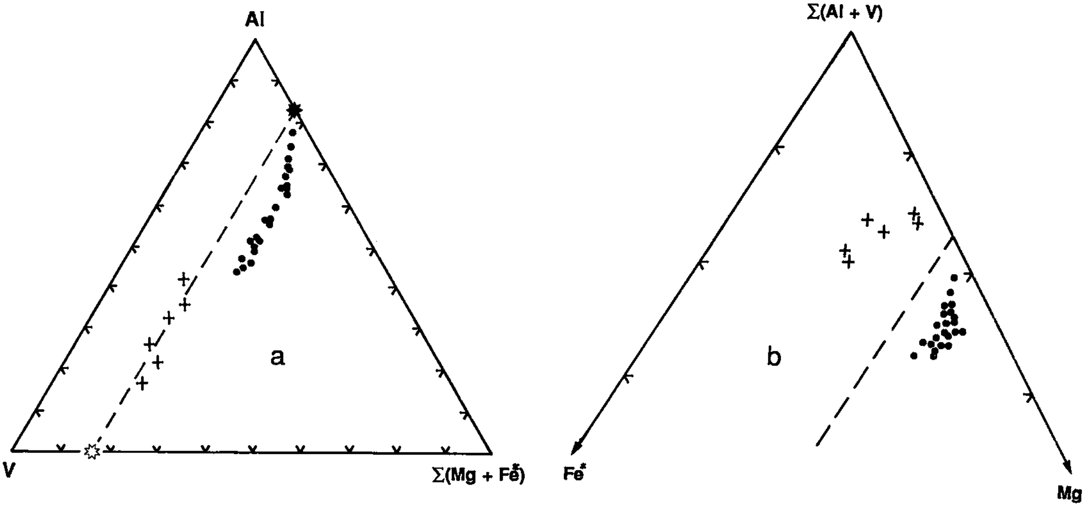

FIG. 2. Diagrams illustrating range in composition of pumpellyite-group minerals from the Hemlo gold deposit: a) Al-Σ(Mg + Fe*)-V and b) Σ(Al + V)-Mg-Fe*. Open star, $Ca_8(Mg_2Al_2)_4Al_8Si_{12}O_{42}(OH)_{14}$; solid star, $Ca_8(V_2Mg_2)_4V_8Si_{12}O_{56-n}(OH)_n$; crosses, the V-rich pumpellyite-group mineral; solid circles, vanadoan pumpellyite-(Mg).

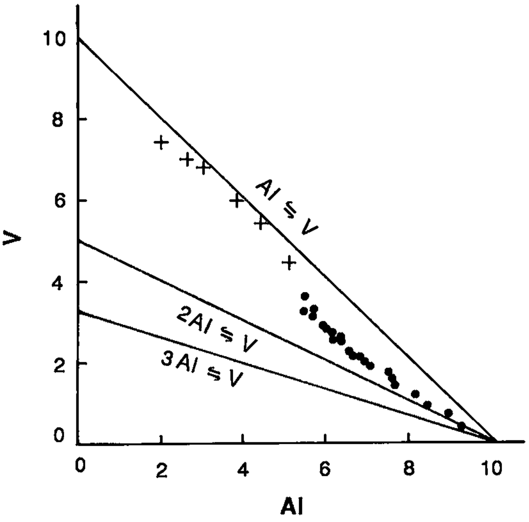

FIG. 3. Compositions of pumpellyite-group minerals from the Hemlo gold deposit on a plot of V *versus* Al. Note that the compositions of the V-rich pumpellyite-group mineral (crosses) plot close to the substitution of one Al for each atom of V, whereas those of the vanadoan pumpellyite-(Mg) (solid circles) deviate toward substitutions involving 2Al for each atom of V and 3Al for each atom of V, especially at low V contents.

tomichite is vanadium-rich and approaches the vanadium end-member composition (Table 2, Fig. 2a).

Knowledge of Fe^{2+}/Fe^{3+} is essential in the procedure of Passaglia & Gottardi (1973) for cation assignment and nomenclature, but this ratio cannot be determined by electron-microprobe analysis. The limited material available for either of the present pumpellyite-group minerals prevents a determination of this ratio by other analytical techniques, and estimation based on charge-balance calculations is not possible either, owing to uncertainty regarding the valence states of other cations, such as V and As, and substitutions involving F^- or OH^- for O^{2-}. In this study, the total iron content was calculated as Fe^{2+}. This is probably justified by the low Fe^{3+} content of coexisting epidote [$Fe^{3+}/(Al + Fe^{3+}) < 0.2$; Pan & Fleet, unpubl. data], because Fe^{3+} is expected to strongly partition into epidote, as demonstrated experimentally by Schiffman & Liou (1983). Moreover, the total iron content is generally low in both pumpellyite-group minerals from the study area (Tables 1, 2, Fig. 2b), and therefore would not have a significant effect on the present discussion.

TABLE 1. COMPOSITIONS OF VANADOAN PUMPELLYITE-(Mg) FROM THE HEMLO GOLD DEPOSIT

Analysis	1	2	3	4	5#	6	7
SiO_2 (wt. %)	32.45	35.49	34.46	36.35	35.83	36.39	37.15
TiO_2	0.00	0.16	0.11	0.08	0.00	0.00	0.00
Al_2O_3	13.52	15.33	15.22	15.94	17.49	20.37	24.82
Cr_2O_3	nd	nd	nd	0.14	nd	nd	0.03
V_2O_3	13.62	11.14	11.12	10.61	8.87	5.03	1.67
As_2O_5	4.77	0.29	2.70	nd	0.80	0.40	nd
Sb_2O_5	0.00	0.10	0.06	nd	0.05	0.00	nd
FeO*	1.73	2.93	1.64	2.70	3.16	2.61	0.87
MgO	5.13	3.79	4.89	4.35	4.01	4.57	4.45
MnO	0.16	0.11	0.08	0.07	0.09	0.10	0.06
CaO	21.97	22.87	22.70	22.34	22.93	23.56	23.26
BaO	nd	nd	nd	0.06	nd	nd	0.00
Na_2O	0.01	0.01	0.03	0.03	0.04	0.03	0.02
F	0.73	0.44	0.74	0.70	0.61	0.97	0.00
O=F	0.31	0.19	0.31	0.29	0.26	0.41	0.00
Total	93.78	92.47	93.44	93.08	93.62	93.62	92.33
	chemical formulae calculated on the basis of 49 atoms of oxygen						
Si	11.04	12.00	11.56	12.13	11.89	11.91	11.94
As	0.85	0.05	0.47	----	0.14	0.07	----
^{IV}Al	0.11	0.00	0.00	0.00	0.00	0.02	0.06
Z	12.00	12.05	12.03	12.13	12.03	12.00	12.00
^{VI}Al	5.30	6.11	6.02	6.27	6.84	7.83	9.33
Ti	0.00	0.04	0.03	0.02	0.00	0.00	0.00
Cr	----	----	----	0.04	----	----	0.01
V	3.71	3.02	2.99	2.84	2.36	1.32	0.43
Sb	0.00	0.01	0.01	----	0.01	0.00	----
Fe	0.49	0.83	0.46	0.75	0.88	0.72	0.21
Mg	2.60	1.91	2.45	2.17	1.99	2.23	2.13
Mn	0.05	0.03	0.02	0.02	0.03	0.03	0.02
Σ(X + Y)	12.15	11.95	11.98	12.11	12.10	12.13	12.06
Ca	8.00	8.24	8.16	7.99	8.15	8.24	8.02
Ba	----	----	----	0.01	----	----	----
Na	0.01	0.01	0.02	0.03	0.02	0.02	0.01
W	8.01	8.25	8.18	8.03	8.17	8.26	8.03
F	0.79	0.47	0.78	0.74	0.64	1.00	----

is grain 5 studied by X-ray diffraction (see Table 3); wt. % is weight percent; FeO* is total iron content; nd is not determined; W, X, Y, and Z are as defined by Passaglia & Gottardi (1973).

The composition of prismatic pumpellyite in cross-cutting veins and along foliation planes is quite variable, ranging from 32.5 to 37.2 wt.% SiO_2, 13.5 to 24.8 wt.% Al_2O_3, 1.7 to 13.6 wt.% V_2O_3, 3.8 to 5.1 wt.% MgO, 0.9 to 3.2 wt.% FeO*, and 22.0 to 23.6 wt.% CaO (Table 1). These compositional variations exist not only from grain to grain but also as pronounced zonation within individual grains (Fig. 1b). Such zoned grains show an increase in V, accompanied by (Mg + Fe*), and a decrease in Al, from core to margin. With rare exceptions, color in plane-polarized light directly reflects the V content, *i.e.*, the deeper the color, the higher the V content. Minor amounts of As typically are present in the prismatic pumpellyite. In a few cases, exceptionally high As contents (up to 4.8 wt.% As_2O_5) have been obtained in grains of relatively high V contents (Table 1). In addition, appreciable amounts of fluorine (up to 1.0 wt.% F) are not uncommon (Table 1). Titanium, Cr, Mn, Sb and Na are locally present in minor amounts;

TABLE 2. COMPOSITIONS OF THE V-RICH PUMPELLYITE-GROUP MINERAL FROM THE HEMLO GOLD DEPOSIT

Analysis	1	2	3	4	5	6	7
SiO_2 (wt. %)	33.23	33.32	34.52	34.52	34.62	34.58	34.72
TiO_2	1.13	0.73	0.63	0.11	0.00	0.18	0.21
Al_2O_3	4.55	5.23	6.09	7.12	10.72	10.48	12.48
Cr_2O_3	0.56	0.47	0.40	0.43	0.90	nd	0.78
V_2O_3	25.67	25.53	24.57	24.05	21.30	19.67	18.89
As_2O_5	nd	nd	nd	nd	nd	0.20	nd
Sb_2O_5	nd	nd	nd	nd	nd	0.39	nd
FeO*	3.34	2.82	3.59	2.29	0.89	2.70	0.87
MgO	2.10	2.11	2.35	2.17	2.94	2.47	2.99
MnO	0.50	0.44	0.43	0.62	0.04	0.37	0.11
CaO	20.56	20.65	20.39	20.12	21.48	21.53	21.11
BaO	0.09	0.04	nd	0.06	0.00	nd	0.00
Na_2O	0.14	0.19	0.07	0.10	0.05	0.11	0.00
K_2O	0.09	0.22	0.06	0.20	0.00	nd	0.04
F	0.00	0.00	0.00	0.00	0.00	0.12	0.12
O=F	0.00	0.00	0.00	0.00	0.00	0.05	0.05
Total	91.96	91.75	93.10	91.79	92.94	92.75	92.27
	chemical formulae calculated on the basis of 49 atoms of oxygen						
Si	11.94	11.89	12.11	12.19	11.86	11.96	11.86
As	—	—	—	—	—	0.04	—
^{IV}Al	0.06	0.11	0.00	0.00	0.14	0.00	0.14
Z	12.00	12.00	12.11	12.19	12.00	12.00	12.00
^{VI}Al	1.87	2.25	2.52	2.96	4.18	4.27	4.95
Ti	0.30	0.20	0.17	0.03	0.00	0.05	0.05
Cr	0.16	0.13	0.11	0.12	0.25	—	0.21
V	7.39	7.31	6.91	6.81	5.85	5.45	5.17
Fe	1.00	0.84	1.08	0.68	0.25	0.78	0.25
Mg	1.13	1.13	1.23	1.14	1.50	1.27	1.52
Mn	0.15	0.13	0.13	0.19	0.02	0.11	0.03
$\Sigma(X + Y)$	12.00	11.99	12.15	11.93	12.05	11.98	12.18
Ca	7.93	7.83	7.67	7.62	7.88	7.98	7.73
Ba	0.01	0.01	0.00	0.01	0.00	—	0.00
Na	0.10	0.13	0.01	0.07	0.03	0.07	0.03
K	0.04	0.10	0.00	0.09	0.00	—	0.00
W	8.08	8.06	7.68	7.79	7.91	8.05	7.76
F	0.00	0.00	0.00	0.00	0.00	0.13	0.13

wt.% is weight percent; FeO* is total iron content; nd is not determined; W, X, Y and Z are as defined by Passaglia & Gottardi (1973).

Ba, K and Cl are generally below detection limits (Table 1).

The composition of the very fine-grained pumpellyite-group mineral in close association with titanite and barian tomichite from the Hemlo gold deposit ranges from 33.2 to 34.9 wt.% SiO_2, 4.6 to 10.0 wt.% Al_2O_3, 18.9 to 25.7 wt.% V_2O_3, 2.1 to 3.2 wt.% MgO, 0.9 to 3.3 wt.% FeO*, and 20.1 to 21.5 wt.% CaO (Table 2). In addition, minor amounts of Ti, Cr and Na are common, but As and F are typically low in abundance (Table 2). In contrast to the prismatic pumpellyite, individual grains of this V-rich pumpellyite-group mineral are generally homogeneous in composition (Fig. 1d). In a few cases, however, it occurs only as a thin margin to a core of considerably lower V content (Fig. 1c), which is similar to that of the prismatic pumpellyite.

UNIT-CELL DIMENSIONS

TABLE 3. UNIT–CELL PARAMETERS OF VANADOAN PUMPELLYITE–(Mg) FROM THE HEMLO GOLD DEPOSIT, AND COMPARISON WITH PUMPELLYITE–GROUP MINERALS

Mineral	Y site	a(Å)	b(Å)	c(Å)	β(°)	references
pumpellyite-(Mg)	Al	8.82(3)	5.92(3)	19.11(4)	97.71(2)	1
pumpellyite-(Mg)	Al	8.82(4)	5.91(1)	19.15(2)	97.69(5)	2
pumpellyite-(Mg)	Al	8.83(1)	5.95(1)	19.15(3)	97.70(6)	3
pumpellyite-(Mg)	Al	8.83	5.90	19.17	97.12	4
pumpellyite-(Mg)	Al	8.812	5.895	19.116	97.41	5
Julgoldite-(Fe^{2+})	Fe^{3+}	8.922	6.081	19.432	97.60	6
shuiskite-(Mg)	Cr	8.897	5.843	19.14	98	7
ohktoskite-(Mn^{2+})	Mn^{3+}	8.887	6.000	19.53	97.08	8

1 to 3 are vanadoan pumpellyite-(Mg) from this study (2.3, 4.6 and 8.9 wt. % V_2O_3, respectively); 4, Galli & Alberti (1969); 5, Yoshiasa & Matsumoto (1985); 6, Allmann & Donnay (1973); 7, Ivanov et al. (1981); 8, Togari & Akasaka (1987).

Three grains of the prismatic pumpellyite with 2.3, 4.6 and 8.9 wt.% V_2O_3, respectively, were removed from thin sections for X-ray-diffraction study using a Gandolfi camera (Cr*Kα* radiation). The calculated unit-cell parameters do not show any systematic variation, despite the large differences in the V content (Table 3). The grain with 8.9 wt.% V_2O_3 (and also containing 0.8 wt.% As_2O_5; Table 1) yielded unit-cell parameters of *a* 8.83(1), *b* 5.95(1), *c* 19.15(3) Å, *β* 97.70(6)°, which are almost identical to those of pumpellyite-(Mg) (Galli & Alberti 1969, Yoshiasa & Matsumoto 1985; Table 3). A similar X-ray-diffraction study on a titanite fragment containing the very fine-grained V-rich pumpellyite-group mineral yielded only the lines of titanite.

DISCUSSION

Enrichments in V, As, Mg and F

All grains of the pumpellyite-group minerals in green mica schist from the main ore zone of the Hemlo gold deposit are characterized by high vanadium contents (Tables 1, 2, Fig. 2a). In particular, the extremely fine-grained aggregates in association with vanadian titanite and barian tomichite have as much as 25.7 wt.% V_2O_3 and represent a possible new mineral with end-member composition $Ca_8(V,Mg,Fe)_4(V,Al)_8Si_{12}O_{56-n}(OH)_n$, and vanadium as the dominant cation in both *Y* and *X* sites (Table 2, Fig. 2a). However, the limited amount of material available and its very fine grain-size prohibit a more complete characterization; therefore, this phase is reported here as an unnamed possible new mineral. The prismatic variety in veins and along foliation planes also contains a significant amount of V (1.3 to 13.6 wt.% V_2O_3) and thus is a vanadoan pumpellyite-(Mg), because Mg and Al are known to preferentially partition into *X* and *Y* sites, respectively (Yoshiasa & Matsumoto 1985), and V is assumed (below) to be mainly in the trivalent state.

The high concentration of V in pumpellyite-group minerals from the Hemlo gold deposit is readily explained by an adequate local source of this element, because the Hemlo gold deposit is well known for a high V enrichment, and a large number of V-bearing minerals (including vanadian muscovite, barian tomichite, vanadian garnet, vanadian epidote-group minerals, vanadian titanite, vanadian rutile, karelianite, cafarsite, and hemloite) have been documented in the main ore zone (Harris 1989). Also, octahedrally coordinated vanadium cations (V^{3+}, V^{4+} and V^{5+}) all are similar in ionic radius to $^{VI}Al^{3+}$ (0.64, 0.58, 0.54 *versus* 0.535 Å, respectively; *cf.* Shannon 1976) and, therefore, can readily substitute for the latter in octahedral positions (discussed below).

Yoshiasa & Matsumoto (1985) recognized that Mg atoms do not occupy more than half of the available X sites [M(2)] in pumpellyite. This is apparently the case in the V-rich pumpellyite-group mineral from the study area (Table 2, Fig. 2b). However, many of our analyses of vanadoan pumpellyite-(Mg) reveal more than 2 Mg atoms per formula unit, the highest value being 2.6 and equivalent to 65% occupancy of X sites (Table 1, Fig. 2b). Therefore, vanadoan pumpellyite-(Mg) from the study area is also unusually Mg-enriched and cannot be considered to be an intermediate composition between pumpellyite-(Mg) and the V-rich pumpellyite-group mineral (Figs. 2a, b). It has been noted above that vanadoan pumpellyite-(Mg) and the V-rich pumpellyite-group mineral from the study area also differ in other constituents, such as As and F.

Substantial amounts of As and F have not been reported previously in pumpellyite-group minerals (*cf.* Deer *et al.* 1986). In fact, neither of these two elements is routinely sought in most studies of the pumpellyite-group minerals. The high As and F contents (up to 4.8 wt.% As_2O_5 and 1.0 wt.% F, respectively) in vanadoan pumpellyite-(Mg) of the study area may be unusual. Arsenic is characteristically high in abundance in the main ore zone of the Hemlo gold deposit, and is present mainly in arsenopyrite, barian tomichite and native arsenic (Harris 1989). Similarly, substantial halogen contents have been obtained in several vein minerals, such as phlogopite, titanite, garnet, apatite, synchysite, and antimonian vesuvianite, from the main ore zone (Pan *et al.* 1991).

Mechanisms of substitution

Vanadium may be present in silicates as V^{3+}, V^{4+} and V^{5+} (Evans 1969). All compositions of the V-rich pumpellyite-group mineral from Hemlo plot close to the line for a simple substitution of $Al^{3+} = V^{3+}$ (Fig. 3). At low V contents, the vanadoan pumpellyite-(Mg), however, shows a significant deviation toward substitutions involving 2Al for each V and 3Al for each V (Fig. 3). Additional elements, such as Cr, Ti and Fe^{3+}, in the vanadoan pumpellyite-(Mg) may have contributed to this deviation, but cannot be entirely responsible owing to their low concentrations. Figure 4a illustrates that vanadium in vanadoan pumpellyite-(Mg) has a positive correlation with (Mg + Fe*), indicating coupled substitutions of V and (Mg,Fe) for Al, which may be written as: $2Al^{3+} = V^{4+} + (Mg,Fe)^{2+}$ and $3Al^{3+} = V^{5+} + 2(Mg,Fe)^{2+}$. The presence of V^{4+} is supported by the characteristic weak red absorption color of vanadoan pumpellyite-(Mg) (*cf.* Staples *et al.* 1973). It is noteworthy that the V contents (cations p.f.u.) of vanadoan pumpellyite-(Mg) generally plot above values for these coupled substitutions (Figs. 3, 4a), and that (Mg + Fe*) does not significantly exceed 3 atoms p.f.u. (Fig. 4a). These compositional features indicate that the simple substitution $Al^{3+} = V^{3+}$ also operates in vanadoan pumpellyite-(Mg) and predominates where concentrations of V are high.

In respect to As contents, there are clearly two populations of vanadoan pumpellyite-(Mg): As-bearing and As-poor (Figs. 4c, d). Vanadoan pumpellyite-(Mg) with a substantial amount of As is invariably Si-deficient (Table 1), and there is a negative correlation between As and Si (Fig. 4b). These observations indicate that As in vanadoan pumpellyite-(Mg) probably substitutes for Si. Arsenic also tends to correlate negatively with Al (Fig. 4c), and is elevated only where the (Mg + Fe*) content is high (Fig. 4d). It is possible, therefore, that As is incorporated into vanadoan pumpellyite-(Mg) by a coupled substitution of $Si^{4+} + Al^{3+} = As^{5+} + (Mg,Fe)^{2+}$, assuming As to be present as As^{5+} (*cf.* Donnay & Allmann 1968).

The substitutions involving V and As are most likely responsible for the unusually high Mg content of vanadoan pumpellyite-(Mg) from the study area. Fluorine can be incorporated into vanadoan pumpellyite-(Mg) by either a simple substitution for $(OH)^-$ or a coupled substitution for O^{2-}. We favor the latter scheme, which is probably related to the unusually high Mg contents, *e.g.*, $Al^{3+} + O^{2-} = (Mg,Fe)^{2+} + F^-$, similar to that in epidote-group minerals (*cf.* Peacor & Dunn 1988). The former substitution is probably less important, because published data on pumpellyite-group minerals do not indicate a high F content despite its high stoichiometric $(OH)^-$ content (*cf.* Yoshiasa & Matsumoto 1985).

Substitution of As for Si

The substitution of As for tetrahedrally coordinated Si has been postulated in several rare

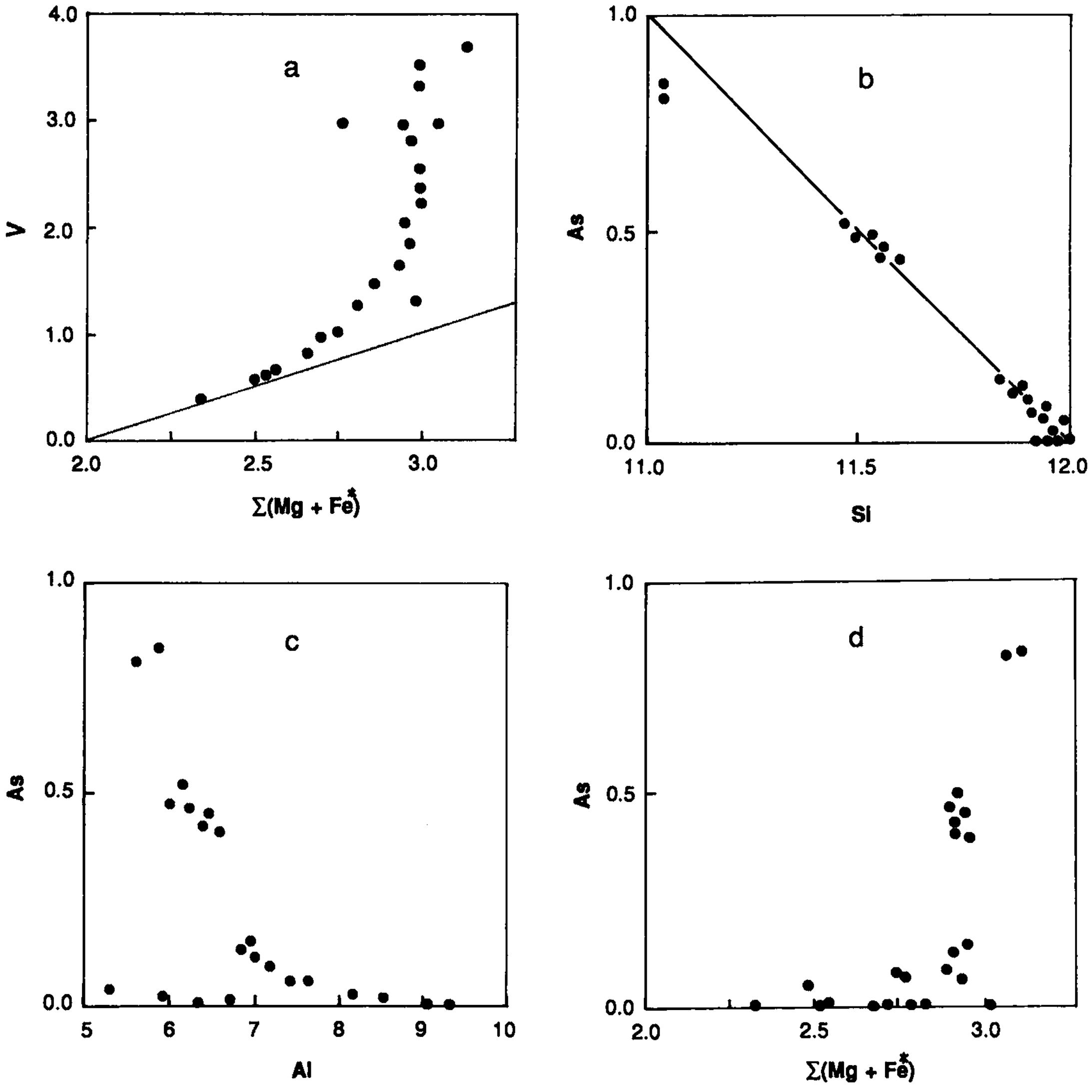

FIG. 4. Diagrams indicating possible mechanisms of substitution in vanadoan pumpellyite-(Mg) from the Hemlo gold deposit: a) V *versus* Σ(Mg + Fe*), b) As *versus* Si, c) As *versus* Al, and d) As *versus* Σ(Mg + Fe*).

manganoan arsenosilicates, such as ardennite, holdenite, parwellite, tiragalloite, and kolicite, but was found to be unlikely in all cases on the basis of crystal-structure determinations (Donnay & Allmann 1968, Allmann & Donnay 1971, Moore & Araki 1977a, b, Gramaccioli *et al.* 1980, Peacor 1980). These authors recognized that As in these minerals is accommodated in a separate tetrahedral position. For example, Allmann & Donnay (1971) reported that ardennite is structurally related to epidote, in which chains of AlO_6 and $AlO_4(OH)_2$ octahedra are bridged by SiO_4 and Si_2O_7 groups. However, ardennite differs slightly in structural topology, and contains Si_3O_{10} groups and isolated SiO_4 and $(As,V)O_4$ tetrahedra (Donnay & Allmann 1968, Allmann & Donnay 1971).

The substitution of As for Si in tetrahedral positions might be expected on crystal-chemical grounds: the ionic radii of tetrahedrally coordinated As^{5+} and Si^{4+} are 0.335 and 0.26 A, respectively (Shannon 1976). It is noteworthy that more than 20% of the tetrahedrally coordinated As^{5+} in manganostibite, Mn_7SbAsO_{12}, is replaced by Si (Moore 1970, Dunn 1987). Pumpellyite-group minerals also are structurally related to epidote and contain $Si_2O_6(OH,O)$ groups and isolated SiO_4 tetrahedra (Galli & Alberti 1969, Allmann & Donnay 1973, Yoshiasa & Matsumoto 1985). The calculated chemical formula for vanadoan pumpellyite-(Mg) clearly indicates a substitution of Si by As, most likely involving the isolated SiO_4 tetrahedron (*cf.* Allmann & Donnay 1971).

In ardennite, V is also accommodated in an independent tetrahedral site, and the complete solid-solution involves As (Donnay & Allmann 1968). A minor substitution of V for As occurs similarly in tiragalloite (Gramaccioli *et al.* 1980). However, there is no evidence for either a significant substitution of As by V or incorporation of a significant amount of V in tetrahedrally coordinated positions in the pumpellyite-group minerals from the study area. A weak positive correlation between V and As (not presented here) in vanadoan pumpellyite-(Mg) is readily attributable to the negative correlation between V and Al (Fig. 3).

Paragenetic significance

This is the first observation of pumpellyite-group minerals in the main ore zone of the Hemlo gold deposit. Pumpellyite-(Mg) is one of the characteristic minerals of a late, low- to very-low-grade, calc–silicate alteration in mafic metavolcanic rocks in the vicinity of the Hemlo gold deposit (Pan & Fleet 1990). Walford *et al.* (1986) also reported a late, pervasive calc–silicate alteration in the hanging-wall metasedimentary rocks of the Williams mine. Harris (1989) noted that calc–silicates are rare in the main ore zone, except for some parts of the David Bell mine. However, Fleet & Pan (1990) and Pan *et al.* (1991) reported a large number of calc–silicate minerals, including epidote, titanite, tremolite, prehnite, allanite, garnet, antimonian vesuvianite, and armenite in the main ore zone of the Golden Giant mine. With rare exceptions, these calc–silicate minerals occur either in cross-cutting veins or along foliation planes. In addition, tremolite (with calcite, phlogopite, dolomite, clinopyroxene, tourmaline, talc and titanite) occurs in the diffuse westward extension of the orebody, and is abundant in the North zone of the Golden Sceptre Resources Limited property and the C zone of the Williams mine (Fleet & Pan 1990, Pan *et al.* 1991). These observations have led to our suggestion that the late calc–silicate alteration event also occurred in the Hemlo gold deposit (Fleet & Pan 1990, Pan *et al.* 1991). The present report of pumpellyite-group minerals in the main ore zone is, therefore, further support for this late calc–silicate alteration in the Hemlo gold deposit.

Preliminary results of mineral equilibria and a fluid-inclusion study indicate that the late calc–silicate alteration event in the Hemlo gold deposit occurred at about 300–400°C and less than 2 kbar in an aqueous fluid of moderate to high salinity. The V-rich minerals of the pumpellyite group are considered to have formed under similar conditions, largely through reaction of constituents already present or locally remobilized. We believe that the initial enrichment in V in the host rocks of the deposit occurred in an earlier metasomatic event.

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