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Manganese-rich minerals of the pumpellyite group from the Precambrian Sausar Group, India

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ABSTRACT

Mn-rich minerals of the pumpellyite group are developed in Mn oxide ores of the Precambrian Sausar Group, India. The ores were intruded by late pegmatite dikes and calcite veins. A hydrothermal origin for these phases through Ca-Mg-Fe-Al metasomatism is evident from their mode of occurrence and textures. The phases studied show widespread substitution between Mn^{3+} and Al in the *Y*-site and between Mn^{2+} and Mg in the *X*-site. An Mg equivalent of okhotskite, reported for the first time, is present. This study establishes that okhotskite represents the Mn^{3+} end-member of the pumpellyite group of minerals and that solid solution between pumpellyite (Al dominant) and okhotskite is nearly complete.

INTRODUCTION

Minerals with the pumpellyite structure having the general formula $(Ca,K,Na)_8(Mn^{2+},Al^{3+}Mg,Fe^{2+})_4(Fe^{3+},Al^{3+},Ti^{4+},Mn^{3+})_8Si_{12}O_{56-n}(OH)_n$ are named on the basis of relative concentration of trivalent cations in their octahedral sites. The phase is called pumpellyite if Al is dominant; if Fe^{3+} is dominant it is designated as julgoldite (Moore, 1971; Passaglia and Gottardi, 1973). Further subdivisions in the group by adding suffixes according to the dominant octahedral divalent cations have been suggested [viz. pumpellyite-(Mn^{2+}), Kato et al., 1981; pumpellyite-(Mg), Passaglia and Gottardi, 1973; Lucchetti, 1983]. Recently, a Mn^{3+}-dominant member of the pumpellyite group has been reported (Togari and Akasaka, 1987) and named okhotskite.

Data are presented here for Mn-rich phases that vary compositionally between pumpellyite and okhotskite from the Precambrian Sausar Group, India. This is the first report of such minerals from any Indian Mn deposit as well as from any Precambrian rock. The wide compositional range of these phases from Indian deposits provides additional data on the solid solution relationships in the pumpellyite group of minerals.

OCCURRENCE

The Mn-rich pumpellyite group of minerals (henceforth referred to as pumpellyite in a group sense) occur in metamorphosed manganese oxide ores that have been intruded by pegmatite dikes and calcite veins subsequent to amphibolite facies regional metamorphism at Gowari Wadhona, Madhya Pradesh, India. The ores occur at the contact of the pelitic Mansar Formation and dolomites of the Bichhua Formation of the Sausar Group. In addition to pumpellyite, diverse Ca-Mg-Mn-Al-Na silicates such as tirodite, Mn-rich pyroxene, and piemontite have developed at the contact of pegmatite dikes and the ores (Roy and Purkait, 1968). Samples of pumpellyite-bearing rocks described in this work were collected from a small outcrop of Mn ores at the contact of pegmatite dikes and calcite veins. Mineral assemblages that contain pumpellyite are as follows:

braunite + potassium feldspar + calcite + pumpellyite ± bixbyite (1)
braunite + phlogopite + pumpellyite + calcite ± diopside ± bixbyite. (2)

Thè Mn-Mg-Ca-Al silicates occur either within or close to the pegmatite dikes and calcite veins. In Assemblage 1, pumpellyite occurs as narrow rims around braunite at the contact with calcite and/or potassium feldspar. Pumpellyite intercleaved with phlogopite occurs between braunite and calcite (Fig. 1) in Assemblage 2. It also occurs as veins in braunite (Fig. 1).

ANALYTICAL TECHNIQUES

A powder X-ray diffraction pattern (Cu*K*α radiation) was obtained using a Philips X-ray diffractomter and a Si internal standard. Because of low modal abundance and the mode of occurrence, it was not possible to separate pumpellyite grains for single crystal analysis.

Chemical analyses of pumpellyite samples and the associated phases were carried out using a JEOL JXA-733 electron probe microanalyzer (EPMA) operated at 15 kV accelerating voltage. The following standards were used: wollastonite (Ca,Si), magnetite (Fe), rutile (Ti), MnO (Mn), periclase (Mg) and corundum (Al).

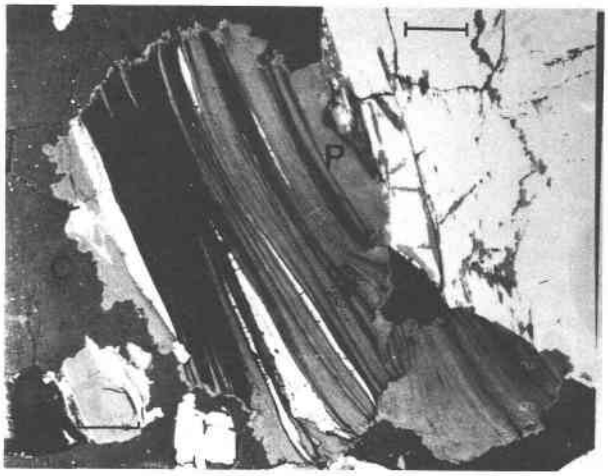

Fig. 1. Backscattered electron image of pumpellyite (P) intercleaved with phlogopite (black) between braunite (white) and calcite (C) in Assemblage 2. Note veins of pumpellyite in braunite. Length of the bar is 0.01 cm.

RESULTS

The pumpellyite samples studied show the following pleochroic scheme: X = light yellow, Y = light pink, Z = rose pink, absorption $X > Y < Z$. The mineral has parallel extinction with respect to the length of the prismatic crystals. Unit-cell valves, calculated from the powder X-ray diffraction pattern on the basis of monoclinic symmetry are $a = 8.98 \pm 0.08$ Å, $b = 6.00 \pm 0.06$ Å, $c = 19.19 \pm 0.06$ Å, $\beta = 98.1 \pm 0.03°$.

Chemical compositions of pumpellyite and the structural formulae, calculated after the method of Passaglia and Gottardi (1973) are given in Table 1. Presence of braunite in both assemblages indicates that the ambient f_{O_2} was above the hematite-magnetite buffer (Lattard and Schreyer, 1983) where Mn exists in both di- and trivalent states but Fe_{tot} in pumpellyite can be considered as Fe^{3+}. Following the scheme of Passaglia and Gottardi (1973), Al, Ti, and Fe^{3+} were placed in the Y-site and Mn^{3+} was added until this site was fully occupied. The remaining Mn was placed in the X-site as Mn^{2+} with Mg (Kato et al., 1981).

The most striking compositional characteristic is the wide difference in cation occupancy in the X and Y sites of the pumpellyite samples studied. The X^{3+}_{Mn} [= $Mn^{3+}/(Mn^{3+} + Al + Fe^{3+})$] vs. X^{2+}_{Mn} [= $Mn^{2+}/(Mn^{2+} + Mg)$] plots of pumpellyites (Fig. 2) depicts the compositional variations in the two sites. Figure 2 shows that the phases studied are either pumpellyite or okhotskite, and they might be further designated as pumpellyite-(Mn^{2+}), okhotskite-(Mn^{2+}), and okhotskite-(Mg) following Passaglia and Gottardi (1973). However, okhotskite-(Mg) and okhotskite-(Mn^{2+}) have not been approved by the IMA Commission on New Minerals and New Mineral Names. Pumpellyite-(Mn^{2+}) and okhotskite-(Mn^{2+}) associated with phlogopite in Assemblage 2 are always more magnesian relative to those associated with potassium feldspar in Assemblage 1 (Fig. 2).

Of the associated phases in the assemblages, braunite may contain up to 7.43 wt% CaO (when recalculated on the basis of 12 O atoms according to the structural formula ($R^{2+}R^{3+}_6SiO_{12}$), neltnerite content is 69 mol%) and up to 3.64 wt% MgO (Table 2). Such high calcic and high

TABLE 1. Chemical composition of Mn-rich pumpellyites determined by EPMA

Sample number Assemblage	1 (1)	2 (1)	3 (1)	4 (1)	5 (1)	6 (1)	7 (1)	8 (2)	9 (2)
SiO_2	33.86	34.14	31.90	33.09	33.39	34.76	32.81	34.10	34.25
Al_2O_3	8.40	9.64	1.60	2.15	3.59	12.04	3.08	9.23	8.72
TiO_2	0.06	0.01	0.01	0.19	0.02	*—	0.17	0.01	—
Fe_2O_3	5.38	0.40	—	4.48	0.05	0.08	3.93	0.06	0.19
Mn_2O_3	9.84	12.35	25.93	20.96	24.17	11.82	20.43	13.77	16.32
MnO	12.19	12.36	11.95	11.92	11.76	12.95	11.81	10.73	7.59
MgO	0.45	0.36	0.38	0.26	0.57	0.19	0.28	1.31	3.31
CaO	10.02	20.17	19.77	21.08	21.30	22.05	21.11	20.28	20.91
Na_2O	0.04	0.05	0.04	0.01	0.01	—	—	0.04	0.02
(H_2O)	7.08	7.17	6.60	6.61	6.72	6.96	6.60	7.19	7.20
Total	97.32	96.55	98.18	100.75	101.58	100.86	100.22	96.72	98.51
Si	12.27	12.36	11.95	12.00	11.92	11.98	11.92	12.30	12.04
$^{[4]}Al$	—	—	0.10	—	0.08	0.02	0.08	—	—
$^{[6]}Al$	3.80	4.11	0.71	0.92	1.43	4.87	1.24	3.92	3.61
Ti^{4+}	0.01	—	—	0.05	—	—	0.05	—	—
Fe^{3+}	1.47	0.11	—	1.24	0.01	0.02	1.08	0.02	0.05
Mn^{3+}	2.71	3.78	7.39	5.78	6.55	3.11	5.64	4.06	4.34
Mn^{2+}	3.73	3.42	3.79	3.66	3.57	3.76	3.65	2.99	2.26
Mg	0.24	0.20	0.21	0.14	0.30	0.09	0.15	0.71	1.74
Ca	7.77	7.82	7.93	8.19	8.15	8.14	8.22	7.83	7.88
Na	0.03	0.04	0.03	—	—	—	—	0.03	0.01
O	40.97	40.32	40.28	40.00	39.97	39.90	40.16	40.28	40.01
OH	15.03	15.68	15.72	16.00	16.03	16.10	15.84	15.72	15.99

Note: Total Fe as Fe_2O_3. Total Mn recalculated to Mn_2O_3 and MnO following Passaglia and Gottardi (1973).
* Dashed portions indicate below detection limit.

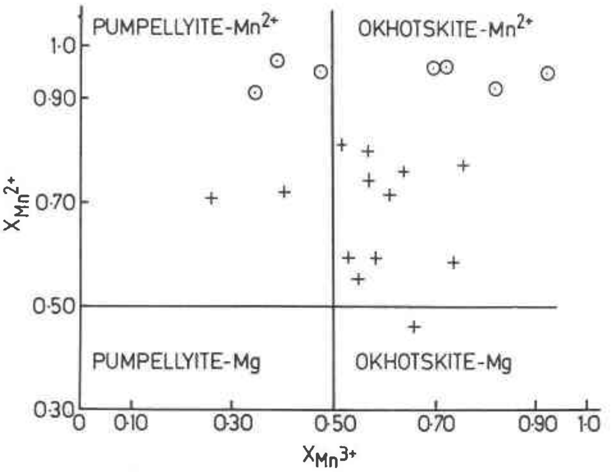

Fig. 2. Compositional plots of the pumpellyites studied in $X^{3+}_{\mathrm{Mn}}[= \mathrm{Mn^{3+}/(Mn^{3+} + Fe^{3+} + Al)}] - X^{2+}_{\mathrm{Mn}}[= \mathrm{Mn^{2+}/(Mn^{2+} + Mg)}]$ space showing the fields of pumpellyite-(Mg), pumpellyite-(Mn^{2+}), magnesian okhotskite, designated okhotskite-(Mg), and manganoan okhotskite, designated okhotskite-(Mn^{2+}) [following Passaglia and Gottardi (1973) and Kato et al. (1981); note that okhotskite-(Mg) and okhotskite-(Mn^{2+}), although following from nomenclature approved by the IMA Commission, have themselves not been approved]. Pumpellyite from type 1 assemblage = circle, pumpellyite from type 2 assemblage = plus sign.

Table 2. Chemical composition of phlogopite and braunite determined by EPMA

Mineral	Phlogopite			Braunite		
Sample number	15	18	20	7	16	18
SiO_2	37.92	36.32	41.58	11.58	10.13	10.62
TiO_2	*—	0.03	0.01	0.01	0.01	0.05
Al_2O_3	16.40	14.41	11.73	0.01	0.55	0.03
Fe_2O_3	0.82	2.20	1.39	2.07	3.30	5.64
Mn_2O_3	—	—	—	74.38	76.53	72.32
MnO	2.34	6.34	7.94	4.25	3.47	4.09
MgO	27.70	26.18	21.55	0.02	3.64	0.09
CaO	0.03	0.05	0.04	7.43	1.65	6.59
Na_2O	0.09	0.02	0.08	—	—	—
K_2O	6.90	3.80	9.63	—	0.01	—
BaO	0.09	—	—	—	0.04	0.12
H_2O	4.19	4.02	4.11	—	—	—
Total	96.48	93.37	98.06	99.75	99.33	99.55
Si	2.716	2.708	3.037	1.139	0.992	1.053
Ti	—	0.002	0.001	0.001	0.001	0.004
Al	1.384	1.266	1.010	0.001	0.063	0.004
Fe^{3+}	0.044	0.123	0.076	0.153	0.243	0.421
Mn^{3+}	—	—	—	5.567	5.706	5.459
Mn^{2+}	0.142	0.400	0.491	0.354	0.288	0.343
Mg	2.957	2.909	2.346	0.003	0.531	0.013
Ca	0.002	0.004	0.003	0.783	0.173	0.700
Na	0.012	0.003	0.011	—	—	—
K	0.630	0.361	0.897	—	0.001	—
Ba	0.003	—	—	—	0.002	0.005

Note: Total Fe as Fe_2O_3.
* Dashed portions indicate below detection level.

magnesian braunite in the Indian deposits are recorded only when these are intruded by pegmatite dikes and calcite veins. Phlogopite contains up to 7.94 wt% MnO (Table 2).

The compositional plots of the coexisting phases in Assemblages 1 and 2 on the SiO_2-$KAlO_2$-(Mn,Mg)O plane projected from braunite (number 18 in Table 2) and calcite show that the composition of pumpellyite varies with the nature of the coexisting phases (Fig. 3). Pumpellyite coexisting with phlogopite and diopside in Assemblage 2

Table 1—*Continued*

10	11	12	13	14	15	16	17	18	19	20
(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)	(2)
34.40	33.24	35.02	31.90	32.97	34.19	33.95	34.38	34.03	34.27	33.65
8.83	5.41	10.50	1.60	4.27	8.05	4.78	6.78	7.25	6.10	6.14
0.03	0.02	—	0.01	0.01	0.03	0.07	0.05	0.07	0.05	0.03
0.40	2.87	1.85	—	0.19	0.71	0.23	2.31	1.58	0.61	0.90
16.14	17.03	11.61	25.93	21.12	17.75	22.09	16.92	16.58	19.61	18.32
7.97	10.52	9.90	11.95	10.12	7.61	7.49	10.44	9.36	6.34	9.69
3.12	1.32	2.05	0.04	1.57	3.07	2.93	1.49	1.82	3.89	1.64
20.81	19.95	20.94	19.77	20.69	22.06	21.73	21.61	21.68	21.47	21.19
0.04	—	0.04	0.04	—	0.01	0.02	—	0.02	—	—
7.20	6.93	7.27	6.60	6.86	6.91	6.79	6.84	6.78	6.83	6.67
98.94	97.29	99.18	97.84	97.80	100.39	100.08	100.82	99.17	99.17	98.23
12.04	12.18	12.19	11.95	12.08	11.86	11.99	12.05	12.04	12.04	12.09
—	—	—	0.05	—	0.14	0.01	—	—	—	—
3.64	2.34	4.31	0.71	1.85	3.15	1.98	2.80	3.02	2.52	2.60
0.01	0.01	—	—	—	0.01	0.02	0.01	0.02	0.01	—
0.10	0.79	0.49	—	0.05	0.18	0.06	0.61	0.42	0.16	0.24
4.25	4.86	3.21	7.39	6.10	4.56	5.94	4.58	4.54	5.30	5.15
2.36	2.81	2.79	3.79	2.94	2.26	2.24	3.04	2.74	1.82	2.81
1.63	1.06	1.06	0.21	0.86	1.59	1.54	0.78	0.96	2.04	0.88
7.81	7.83	7.81	7.93	8.13	8.20	8.22	8.11	8.22	8.08	8.16
0.03	—	0.03	0.03	—	0.01	0.01	—	0.01	—	—
39.99	40.11	40.12	40.28	40.20	39.67	40.00	40.10	40.05	40.04	40.10
16.01	15.89	15.88	15.72	15.80	16.33	16.00	15.90	15.95	15.96	15.90

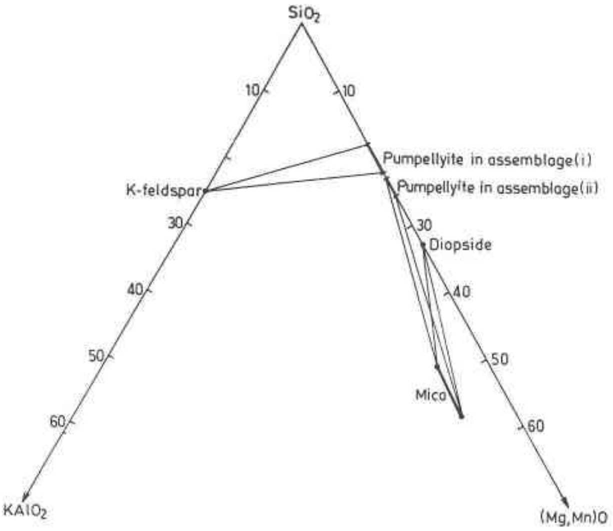

Fig. 3. Compositional plots of pumpellyites in Assemblages 1 and 2, diposide, mica, and potassium feldspar on SiO_2-$KAlO_2$-(Mg,Mn)O plane projected from braunite and calcite.

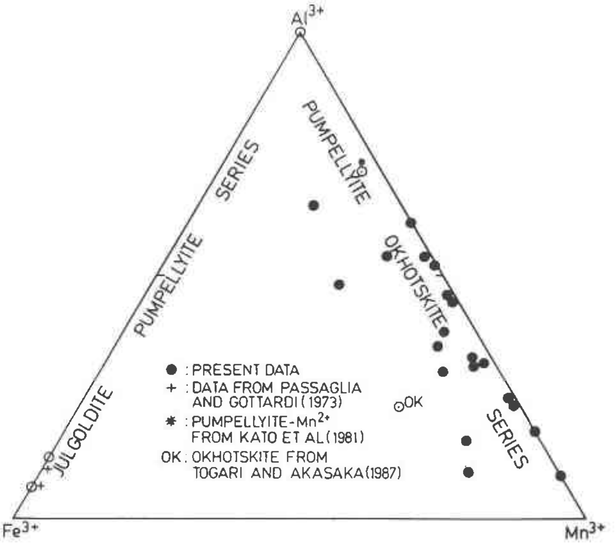

Fig. 4. Composition of Mn-rich pumpellyites and okhotskites in Al^{3+}-Fe^{3+}-Mn^{3+} space.

shows sympathetic variations in (Mg,Mn)O content with that in phlogopite.

DISCUSSION

Condition of formation

Roy and Purkait (1968) described a number of Ca-Al-Mg-Mn-Na silicates that are developed at the contact of late pegmatite dikes and calcite veins in the manganese oxide ore deposit at Gowari Wadhona. The Mn-rich phases of the pumpellyite group described herein are new additions to this list of silicates. Development of this phase in Precambrian rocks is especially intriguing. The restriction of pumpellyite studied here to late pegmatite dikes and calcite veins and textural features such as replacement of braunite by pumpellyite indicate a hydrothermal origin for pumpellyite where Ca, Al, Mg, and Fe are metasomatically introduced in preexisting manganese oxide ores. The process is thus distinct from the metamorphic origin of pumpellyite elsewhere in the world (Kawachi, 1975; Coombs et al., 1976; Kato et al., 1981; Trzcienski and Birkett, 1982; Lucchetti, 1983; Togari and Akasaka, 1987).

Compositional plots of the pumpellyite in Al^{3+}-Fe^{3+}-Mn^{3+} space (Fig. 4) reveal a wide range of substitution between Al^{3+} and Mn^{3+} in the presence of aluminous phases such as potassium feldspar and phlogopite. Within the limits of a single thin section, however, the composition of the phases does not show any appreciable variation. The widely varying Al content in pumpellyite from closely spaced samples suggests differential partitioning of cations in the pumpellyite minerals in response to coexisting phases such as potassium feldspar and phlogopite rather than to temperature (cf. Schiffman and Liou, 1980, 1983). Although the Mg content of pumpellyite is considerably higher in Assemblage 2 (Fig. 2) where high-Mg braunite and phlogopite are the associates, the presence of phlogopite does not assure a constantly high Mg content; Mg can be quite variable (Table 1, numbers 8–20; Fig. 2). However, there is a positive correlation between the Mg contents of coexisting pumpellyite and phlogopite in Assemblage 2 (Fig. 5). These features indicate that the compositional variations in the pumpellyite samples studied are related to local bulk composition.

Experimental data on Mn-free pumpellyite (Schiffman and Liou, 1980, 1983; Schreyer et al., 1986) are clearly inadequate to explain the stability relations of the Mn-rich pumpellyite studied here. However, Schiffman and

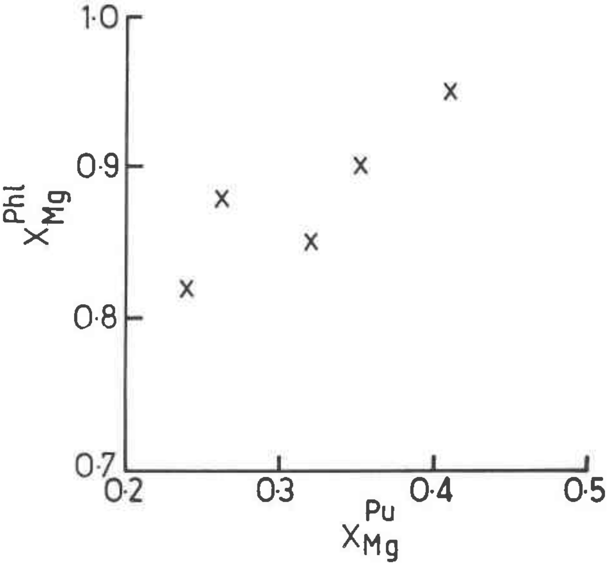

Fig. 5. Plot of X_{Mg}^{Pu} [= Mg/(Mg + Mn^{2+})] vs. X_{Mg}^{Phl} [= Mg/(Mg + Mn^{2+})]. Data from Tables 1 and 2 and unpublished source.

Liou (1980) noted that the compositional variabilities in the pumpellyite group of minerals are complex functions of temperature, pressure, f_{O_2} and local chemical environment of crystallization. The primary factors that influenced the composition of the present pumpellyite formed under similar *P-T* conditions were high Mn content in the rock, the high, but variable, contents of Ca, Al, Mg, and Fe in the metasomatic fluids, and a high enough f_{O_2} for Mn to exist in both di- and trivalent states.

Solid solution in Mn-rich pumpellyites and nomenclature of the pumpellyite group

Figure 4 illustrates the variation in Al, Fe^{3+}, and Mn^{3+} in the pumpellyite group of minerals studied by us, okhotskite (Togari and Akasaka, 1987), pumpellyite-(Mn^{2+}) (Kato et al., 1981), and some of the pumpellyite samples and julgoldites described by Passaglia and Gottardi (1973). Some of the phases reported here are rich in Mn^{3+}, even richer than the okhotskite of Togari and Akasaka (1987), and approach the Mn^{3+} end-member composition. Therefore, the compositional field of okhotskite is shown to be extended farther to the Mn^{3+} end-member of the pumpellyite group of minerals. Solid solution between pumpellyite and okhotskite is nearly complete (Fig. 4). Such a relationship has already been recognized between pumpellyite and julgoldite (Passaglia and Gottardi, 1973).

As already discussed by Passaglia and Gottardi (1973), the nomenclature of the pumpellyite group of minerals is difficult owing to intersite exchange of Al and Fe^{3+} (also Mn^{3+}) as well as variable cation occupancy in the *X* and *Y* sites. We looked for any possible correlation between the atomic ratios of the major components in the *X* and *Y* sites from the available data on the Mn-rich pumpellyite group of minerals. The Mn^{2+}/Mg vs. Mn^{3+}/Al plot did not show any correlation between *X*- and *Y*-site occupancies. Such independent variations in the two site occupancies justify the classification of pumpellyite solid solution phases based on the occupancy of *Y*-site which characteristically accommodates mainly, if not solely, trivalent cations.

Both the pumpellyite-(Mn^{2+}) and okhotskite-(Mn^{2+}) varieties studied here (Fig. 2) have widely varying Mg content in the *X*-site, evidently dictated by the nature of the associated phases. Naming a mineral of the pumpellyite group with only the dominant *X*-site cation as suffix (Passaglia and Gottardi, 1973) or prefix (Moore, 1971) thus loses its relevance. Naming with suffix or prefix will be meaningful only where the *X*-site is almost completely filled by only one cation, a situation which may be rare in nature. If the alternative suggestion of Passaglia and Gottardi (1973) is followed, the pumpellyite group of minerals described here might be designated as magnesian pumpellyite-(Mn^{2+}), magnesian okhotskite-(Mn^{2+}), and manganoan okhotskite-(Mg) (Fig. 2).

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