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Three Mn^{2+}-bearing pumpellyite series minerals from the Takamatsu mine, Yamakita-machi, Kanagawa Prefecture, Japan

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神奈川県足柄上郡山北町高松鉱山産含Mn^{2+}パンペリー石系鉱物

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神奈川県足柄上郡山北町高松鉱山からブラウン鉱を含む鉱石中に三種のMn^{2+}を含むパンペリー石系鉱物，オホーツク石，マンガンパンペリー石およびジュルゴルド石のMn^{2+}置換体の存在を確認した。これらは沸石相に属する変成相の産物で，単一薄片中にもかかわらず組成的不均質のままブラウン鉱・チタン鉄鉱・方解石と共存しており，三種の中ではオホーツク石が量的に最も多い。Al に富む含 Mn^{2+} パンペリー石は組成的に $Mn^{3+}OOH$ による $Mn^{2+}(OH)_2$ の置換で関連づけられる紅簾石の低温条件下での対応物と判断される。

Abstract Okhotskite, pumpellyite-(Mn^{2+}) and Mn^{2+} analogue of julgoldite are found in a massive manganese ore from the iron-manganese ore deposit of the Takamatsu mine as the products of zeolite facies metamorphism. They co-exist in grain-by-grain relation despite their mutual chemical discrepancy even in a single thin section, though the first one is most dominant in quantity. The associated minerals include calcian braunite, calcite, manganoan ilmenite and johannsenite. Of Mn^{2+}-bearing pumpellyite series minerals Al_2O_3-richer members will be low temperature equivalents of piemontite, which is stable at higher temperatures under rather an oxidizing condition through such a near isochemical substitution as of $Mn^{3+}OOH$ for $Mn^{2+}(OH)_2$ unless low in Al_2O_3 content.

INTRODUCTION

The recent studies on pumpellyite series minerals initiated by Gottardi and

Passaglia (1973) have served to the creation of some new species such as pumpellyite-(Mn^{2+}) (Kato et al., 1981), shuiskite (Ivanov et al., 1981), and okhotskite (Togari and Akasaka, 1987). Besides them the Mn^{2+} analogue of julgoldite has been found (Minagawa and Momoi, 1990), though it has not acquired the species status.

The present find disclosed the co-existence of three phases among them, that is, okhotskite, pumpellyite-(Mn^{2+})and the Mn^{2+} analogue of julgoldite in a specimen from the iron-managanese ore deposit of the Takamatsu mine as the products of very weak metamorphism of zeolite facies after the survey of Seki et al. (1969). Among three members of pumpellyite series, the last named one has not had species status yet. Therefore, it is referred to as Mn^{2+} analogue of julgoldite. The tentative name "Fe^{3+} analogue of okhotskite" used by Minagawa and Momoi (1990) was not employed in favour of the proposal of Gottardi and Passaglia (1973), who allowed the creation of a new name according to the predominance of cations in the smaller octahedral site (Gottardi, 1965) rather than the larger octahedral site.

The ideal formula of pumpellyite-(Mn^{2+}) is very close to that of piemontite to which a near isochemical conversion is probable after the partial dehydration and oxidation of Mn^{2+}. While pumpellyite-(Al), that has a potence to involve additive Al (precisely (Al, Fe^{3+})) up to the half of Y-site (Gottardi and Passaglia, 1973), the rest being occupied by (Mg, Fe), has no corresponding counterpart as above due to the higher Al_2O_3 content.

OCCURRENCE

The ore deposit of the Takamatsu mine is located near Takamatsu, Yamakita-machi, Ashigara-kami-gun, Kanagawa Prefecture, or about 2km NNE of Higashi Yamakita station of Gotenba Line of East Japan Railway Company and said to have been worked for a short while during the world war II (Fig. 1). At present only a small dump is left in front of a collapsed portal, where the examined material was collected.

The ore deposit is involved within sedimentary rocks belonging to Tanzawa Group, which suffer very weak metamorphism of zeolite facies. Nearby the deposit, they include sandstone, pyroclastic rocks, and andesitic lava flow as the principal constitutents. The sandstone comprises small limestone lens, in which manganese oxide ores are disseminated, although the ores of this kind are seldom found in the dump at present.

The examined ore is composed of minor braunite and apparently heterogeneous mass of pumpellyite series minerals with the various shades of grayish salmon pink to chocolate brown colour. It is sharply traversed by thin calcite veinlets without regularity. Under the magnifier braunite grains forming black smears therein are very minute and equigranular, whereas pumpellyites form elongate

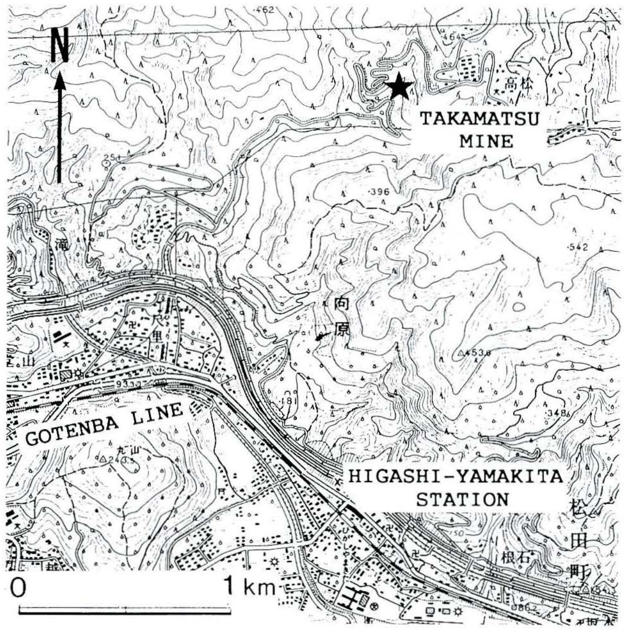

Fig. 1. Index map of the locality. The approximate location is: N 35°22.3′, E 139°7.4′.

blades or tablets aggregated radially to constitute minute spherules of submillimeter order, which are conglutinated each other. Such a texture is observed in the lighter coloured parts only. The ore is devoid of any discernible arrangement of mineral aggregates except for the smears of braunite, running parallel to each in a few pieces.

Under the microscope the portion occupied by the minerals of pumpellyite series consists of dense aggregate of spherules as stated above (Fig. 2a). In the other parts calcite cements masses of various dimensions, the larger one consisting of blocks and matrices (Fig. 2b). In the former smaller blades form radial aggregates as just stated. The back scattering electron images inform that the blocks themselves are highly heterogeneous (Fig. 2c, 2b). According to the chemical analyses one of them consists of pumpellyite-(Mn^{2+}) and julgoldite, whereas the matrix is occupied by okhotskite and julgoldite. The most dominant phase is okhotskite after the X-ray powder diffraction study as stated later. Besides them a few grains of manganiferous ilmenite are involved within the matrix, in which johannsenite forms a tiny patch of submillimeter order composed of fan-shaped grains.

CHEMICAL ANALYSES

The chemical analyses was made by employing Link Systems Energy Dispersive X-ray Spectrometer. Since the valency states of Fe and Mn cannot be determi-

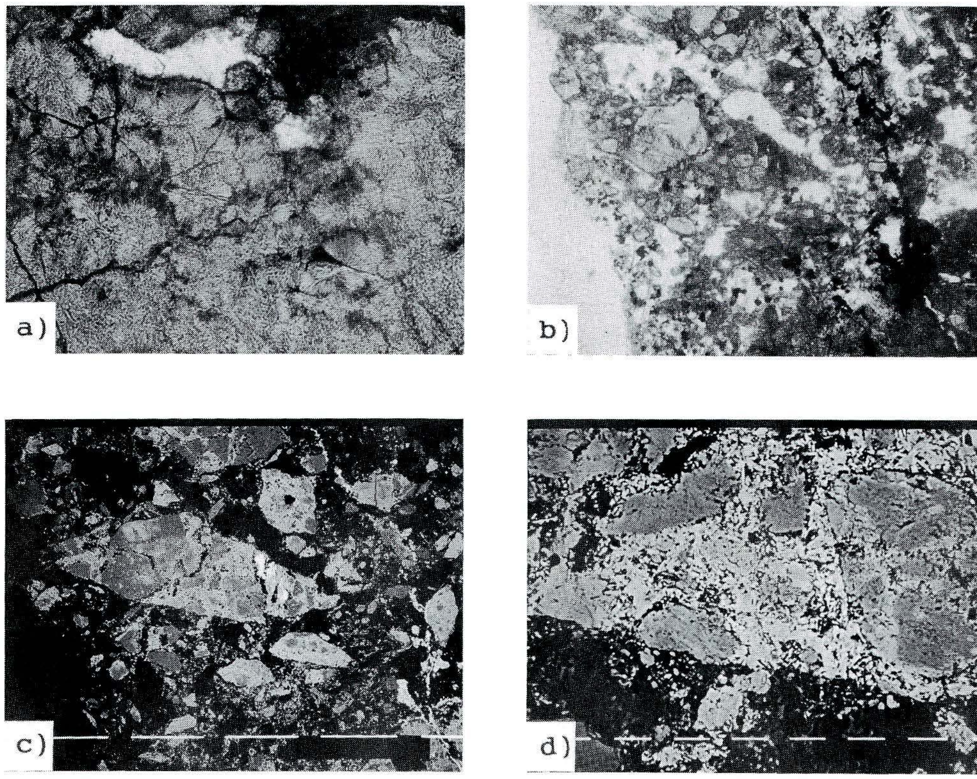

Fig. 2. a) Photomicrograph of dense aggregate of Mn^{2+}-bearing pumpellyite series minerals. White grains are calcite. One polar. Field view: ca. 0.55mm. b) Photomcrograph of calcite-cemented masses composed of Mn^{2+}-bearing pumpellyite series minerals. One polar. Field view: ca. 0.55mm. c) Back scattered electron images of the same portion as b), demonstrating the heterogeneity of masses involving blocks and matrices. Bright spots are maganoan ilmenite. Field view: ca. 0.5mm. d) Ditto. The constituents of block in the right and the adjacent matrix were analysed. Field view: ca. 0.1mm.

ned, the empirical formulae were derived in the following way. The total cation is taken as 8. Unless Si does not reach 3, a part of Al is taken to replace Si. The rest of Al, Fe, V and Ti are grouped together, where Fe is taken as Fe^{3+}. If the total does not reach 2, a part of Mn was added to this figure as Mn^{3+}. The rest of Mn is taken as Mn^{2+}. Mg is added to Mn^{2+}, which is also used to fill the site for Ca to give total number 2. Eight representative analyses after the addition of required H_2O content and the recalculation to 100% are thus obtained as given in Table 1 together with their molecular ratios. The most dominant cation in the larger octahedral site (position X after Gottardi and Passaglia (1973)) is occupied by Mn^{2+} and minor Mg in all of them, but thoses in the smaller octahedral site are not definite but Al-, Fe^{3+}- and Mn^{3+}-dominant phases are present. These correspond respectively to pumpellyite-(Mn^{2+}), okhotskite and Mn^{2+} analogue of julgoldite.

X-RAY POWDER STUDY

X-ray powder study was made on the material with the lightest, or grayish salmon pink colour to know which is the most dominant phase among three. As given in Table 2, the obtained pattern corresponds to that of okhotskite (Togari and Akasaka, 1987) among the known patterns of pumpellyite series minerals. Owing to the reason that the tabulated pattern is for the material including three mutually related phases probably with very similar unit cell dimensions, the calculation to derive the unit cell parameters was not carried out. Repeated examinations on materials provided similar pattern despite the apparent discrepancy, informing the predominance of okhotskite in the ore.

CONSIDERATION OF THE MINERAL ASSOCIATION

The textural relation indicates that the association of three compositionally dif-

Table 1. Chemical analyses of Mn^{2+}-bearing pumpellyite series minerals. (They are tentatively arranged in the order of decreasing Al_2O_3 content.)

Weight percentages

	1	2	3	4	5	6	7	8
SiO_2	34.61	34.16	33.52	33.67	32.80	32.59	33.66	33.25
TiO_2	-	0.48	1.43	0.50	-	-	-	-
Al_2O_3	11.44	10.82	8.67	6.54	4.04	3.39	2.69	0.78
Fe_2O_3*	5.22	7.34	10.94	13.37	9.49	6.65	7.50	17.54
Mn_2O_3**	7.59	6.05	4.45	6.23	14.51	17.40	17.44	9.46
V_2O_3	-	-	-	-	-	1.10	0.71	-
MnO**	11.60	11.41	11.73	10.14	9.22	9.06	9.79	11.34
MgO	1.62	1.24	1.81	2.05	2.10	2.28	1.93	1.18
CaO	20.99	21.59	20.85	20.74	21.05	20.83	20.66	19.98
H_2O***	6.93	6.91	6.60	6.76	6.79	6.70	6.72	6.46
total	100.00	100.00	100.00	100.00	100.01	100.00	99.99	100.00

*total Fe. **calculated (see text). ***calculated (see text).

Number of atoms

	1	2	3	4	5	6	7	8
Si	2.99	2.97	2.97	2.98	2.94	2.93	2.95	3.05
Ti	-	0.03	0.10	0.03	-	-	-	-
Al	1.17	1.11	0.91	0.68	0.43	0.36	0.29	0.08
Fe^{3+}	0.34	0.48	0.73	0.89	0.64	0.45	0.51	1.21
Mn^{3+}	0.50	0.40	0.30	0.42	0.99	1.19	1.20	0.66
V^{3+}	-	-	-	-	-	0.08	0.05	-
Mn^{2+}	0.85	0.84	0.78	0.76	0.70	0.69	0.84	0.88
Mg	0.21	0.16	0.24	0.27	0.28	0.31	0.26	0.16
Ca	1.94	2.01	1.98	1.97	2.02	2.01	1.99	1.96
H	4.01	4.01	3.90	3.99	4.06	4.02	4.05	3.95

Nos. 1～4 in block; 5～8 in matrix.
1～3 : Pumpellyite-(Mn^{2+}). 4,8 : Mn^{2+} analogue of julgoldite.
5～7 : Okhotskite.

ferent phases are not homogenized under the metamorphic condition of zeolite facies and rather higher oxidizing condition where the association of Mn^{2+}, Fe^{3+}, and Mn^{3+} in a single mineral is likely. Also, the compositional variation seen in the components of aggregate are so dispersed that it covers far extensive area than the compositional variation in pumpellyite-(Mn^{2+}) in a gabbroic breccia in ophiolite from Eastern Liguria, Italy (Lucchetti, 1983), where the metamorphic grade belongs to prehnite-pumpellyite metagraywacke facies, or slightly higher than the present case. Also, the distribution pattern of chemical compositions of pumpellyite-(Mn^{2+}) in this locality does not always indicate any compositional gap within the mineral therefrom. While, the present material involves three members of pumpellyite series with discrete compositions coexisting in grain-by-grain relation. But it is not certain whether the coexistence of such compositionally different phases implies the presence of compositional gap among them or not.

No member of pumpellyite series minerals survive in the higher grades than prehnite-pumpellyite metagraywacke facies but piemontite appears instead unless the metamorhic condition is so reducing. Piemontite is less hydrous than pumpellyite. Also, the of compositional variation of piemontite is less extensive than manganiferous members of pumpellyite series. This relation may be comparable with that seen between the ordinary members of pumpellyite series excluding those rather rich in Mg and epidote.

Table 2. X-ray powder pattern of okhotskite.

1		2		1		2	
d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I
4.76	60	4.79	80	2.197	40		
4.43	30	4.45	30	2.164	25	2.155	20
3.96	15			2.096	30	2.099	20
3.87	70	3.87	70	1.915	20	1.913	20
3.84	15			1.906	10		
3.43	25	3.45	10	1.873	20	1.873	15b
3.093	20	3.081	5	1.815	45		
3.025	15			1.724	10	1.721	20
2.961	100	2.945	100			1.688	5b
2.879	25			1.669	25	1.667	10
2.720	70	2.730	55	1.636	30	1.625	20
2.665	45	2.663	35	1.627	20		
2.553	45	2.543	35	1.588	15	1.588	15
2.491	10	2.491	10	1.561	20	1.560	15
		2.454	30	1.514	15	1.513	2
2.384	45			1.512	15		
2.376	30	2.374	30	1.492	25	1.499	5b
		2.287	15			1.491	10b
2.214	30	2.206	40				
2.197	40						

1. Okhotskite. Kokuriki mine, Hokkaido. Cu/Ni radiation. Diffractometer method. After Togari and Akasaka(1987).
2. Okhotskite. Takamatsu mine, Kanagawa Prefecture. Cu/Ni radiation. Diffractometer method. The present study.

Including manganiferous pumpellyites of this time, all the members of pumpellyite series are low but inclusive of MgO. This tendency is comparable with the cases of clinozoisite, epidote and piemontite, all of them excluding Mg. Though less common than pumpellyite-(Al), pumpellyite-(Mg) is known as a metamorphic mineral (Seki, 1958). The behaviours of pumpellyite-(Mg) in the processes of progressive metamorhism will differ from that of pumpellyite-(Mn^{2+}) due to the absence of compositional counterpart thereof, namely the former will yield an assemblage of epidote or clinozoisite plus any magnesian mineral whereas the latter will be converted into piemontite directly without any change of components but discharge of minor water.

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