Manganoan grossular-piemontite association in a low grade metamorphic manganese ore from the Dainichi mine, Hadano City, Kanagawa Prefecture, Japan

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Abstract

A ferrian manganoan grossular of the chemical composition $(\text{Ca}, \text{Mn}^{2+})_3(\text{Al}, \text{Fe}^{3+})_2(\text{SiO}_4)_3$ with $\text{Ca} : \text{Mn}^{2+} \approx 2 : 1$ and $\text{Al} : \text{Fe}^{3+} \approx 2 : 1$ was found in a lower grade metamorphic bedded manganese ore deposit of the Dainichi mine, Hadano City, Kanagawa Prefecture, in association with piemontite of the similar $\text{Ca} : \text{Mn}$ and $\text{Al} : \text{Fe}^{3+}$ ratios, where the metamorphic grade belongs to prehnite-pumpellyite facies. Grossular and piemontite occur as fine disseminations in a metabasite forming the wallrock of ore beds. The co-existence of Mn^{2+} with Mn^{3+} favoured the formation of two discrete but chemically related phases after their preferential lodging. Thus, in the grossular-spessartine continuous solid solution series the manganoan grossular with $\text{Ca} : \text{Mn}^{2+} \approx 2 : 1$ is to be partnered with a piemontite having $\text{Mn}^{3+} : (\text{Al} + \text{Fe}^{3+}) \approx 1 : 2$ as its oxidized derivative unless minor fluctuations of ratios and OH in the latter are considered. Apart from the occurrence in metabasite, manganoan grossular is found as a massive form involving hausmannite, caryopilite, chlorite, johannsenite, manganoan calcite, and an unknown mineral with the probable chemical formula $\text{CaMn}_3[\text{SiO}_4]_2 \cdot \text{H}_2\text{O}$. The metabasite and some ores are penetrated by the veinlets of piemontite with lower Mn_2O_3 contents. The massive manganoan grossular is superficially converted into rancieite through weathering.

Introduction

The stability relation of a piemontite of $\text{Ca}_2\text{Mn}^{3+}\text{Al}_2\text{Si}_3\text{O}_{12}\text{OH}$ composition to a manganoan grossular of $\text{Ca}_2\text{Mn}^{2+}\text{Al}_2[\text{SiO}_4]_3$ was created by Keskinen and Liou (1979), who realized the latter to be a high temperature product in their synthetic works at 2.0 kb of fluid pressure above 500°C using hematite-magnetite buffer. Also, they indicated that the available chemical analyses of natural piemontite include variable amounts of essential Fe_2O_3 , thus, a problem is left as to the application to the natural case how to treat the contribution due to this constituent vicarious to Al. The present find of the association of manganoan grossular with the compositionally related piemontite will be pertinent to the solution.

In Japan, piemontite is not an uncommon constituent of regionally metamorphosed rocks derived from manganese-bearing siliceous rocks where spessartine is also very common. As far as examined, all the spessartines of this occurrence are too highly manganese-rich to create a good correspondence to piemontite. However, a preliminary examination on some piemontite-bearing rocks and manganese ores from the regionally metamorphosed ore deposit of the Dainichi mine, Hadano City, Kanagawa Prefecture, informed the existence of garnet of expected composition in association with piemontite of corresponding garnet composition, where the metamorphic grade belongs to prehnite-pumpellyite facies (Seki *et al.*, 1969), or rather too low grade to expect the appearance of grossular, which is generally formed under higher temperature condition except for materials with higher contents of H substituting Si. Thus, the discovered association is to correspond to the natural analogue of that synthetically obtained by Keskinen and Liou (1979), where subordinate Fe^{3+} vicariously to Al participates. The present description emphasizes the existence of a mineralogically meaningful zone in the grossular-spessartine continuous solid solution series, or an emergence of a peculiar portion in series with a complete mineralogical continuity, where the contribution due to the oxidation-reduction relation is of prime importance in the described example.

Also, the mineralogical examination of probable garnet bearers in the ores informed the existence of hausmannite, which is generally found apart from garnet in ordinary manganese ores from contact or regionally metamorphosed manganese ore deposits in Japan. However, the examined ore involves garnet and johannsenite. Both of them have never been found in direct association with hausmannite in manganese ores from bedded manganese ore deposits in Mesozoic to Tertiary sedimentary rocks and their metamorphic equivalents in Japan. The present garnet is in direct contact with hausmannite while chlorite intervenes between hausmannite and johannsenite. Also, an unknown mineral of $\text{CaMn}_3[\text{SiO}_4]_2 \cdot \text{H}_2\text{O}$ composition is found in direct contact with hausmannite. And the superficial oxidation product of manganoan grossular was also subjected to identification, which informed it to be rancieite.

Occurrence

The manganese ore deposit of the Dainichi mine is located in the southwestern flank of Mt. Togatake of altitude of about 1100 meters, along the valley of Sedonosawa, Hadano City (Lat. $35^\circ 06' 21'' \text{N}$, long. $139^\circ 09' 42'' \text{E}$). Geologically it is involved within the zone of prehnite-pumpellyite facies after Seki *et al.* (1969), who employed the term pumpellyite-prehnite green rock zone. The above name refers to that in the textbook of Miyashiro (1994).

The ore deposit consists of at least two ore beds of a few meters thick each developed conformably in the wallrock principally composed of metabasite apparently of tuff and tuff breccia origin belonging to Tanzawa Group of early to middle Miocene. In the same group, another regionally metamorphosed bedded manganese ore deposit of the Takamatsu mine, where three manganese-bearing minerals of pumpellyite series were found (Hirata *et al.*, 1992), is

located about 10 km southwest of the Dainichi mine. The beds are traceable more than 30 meters on exposure. According to the personal communication of Kijima, more than 20 minor orebodies are distributed nearby the locality and that of the maximum dimension reaches 15 meters thick and 20 meters in the longest extension. The ore minerals therefrom known to date include hausmannite (Yoshimura, 1969), tephroite, braunite, and rhodonite (Kijima, personal communication).

Two pieces involving manganese minerals were subjected to the chemical analyses and microscopic observation and one thickly coated by dark brown manganese dioxide were examined. One of the analysed material is a dense fine-grained brown gray piece of metabasite origin thinly coated by black manganese dioxide and minutely veined by calcite and by piemontite. Another one is a more dense piece also coated thinly by manganese dioxide under which the fresh part is found to be composed of massive gray brown fine-grained grossular finely disseminated by dark spots of hausmannite with a white interstitial calcite. Under the microscope, the former is found to retain the original texture of basaltic rock and unaltered

FIG. 1. Backscattered electron image of the dense fine-grained brown grey piece of metabasite. Chlorite (ch) (darkest, left upper) is invaded by a wedge-like shaped high Mn³⁺ piemontite (p) (1–2a) at the right side of grain. At the lower side of the chlorite, garnet (g) with a distorted H-shaped outline is in direct contact with elongated piemontite grains (p') (1–2b). A large area occupying the right side of figure is a part of piemontite veinlet (p'') with the chemical composition 1–2c. Analysed diopside (d) grain is in the uppermost left, or just above the chlorite grain. The parenthesized numbers correspond to those in Table 1.

diopside, though finely disseminated by piemontite and light brown turbid garnet both without any definite outline. Some of piemontite grains have slender outline elongated along one direction (Fig. 1). Besides them manganoan chlorite and minor titanite are involved. Piemontite of different chemical compositions (Table 1, columns 1–2b and 1–2c) forms nearly monomineralic veinlets of visible dimension. While, the principal constituent of the massive gray brown piece is also manganoan grossular solid solution of variable compositions, always with $\text{Ca} > \text{Mn}^{2+}$ and $\text{Al} > \text{Fe}^{3+}$. In Fig. 2, the grain contact relations of hausmannite, caryopilite, chlorite, johannsenite, an unnamed mineral of $\text{CaMn}_3[\text{SiO}_4]_2 \cdot \text{H}_2\text{O}$ composition, and hausmannite are demonstrated. All of them have no linear grain boundaries against the neighbouring minerals. Except for johannsenite, they are in direct contact with hausmannite. In this material piemontite is extremely small in quantity and grain size. The material coated by a thick manganese dioxide consists principally of the massive aggregate of caryopilite and manganoan grossular, both having similar appearance. The coating consists of dark chocolate brown film with locally developed scaly portions, which are subjected to the X-ray powder

FIG. 2. Backscattered electron image of massive gray brown fine-grained aggregate of grossular. Hausmannite (h) (whitest, middle; 2–6) is accompanied by a low Mn^{2+} grossular (g) (2–1a) at the upper and high Mn^{2+} grossular (g') (2–1b) at the left side. Caryopilite (c) (2–2) is just at the right side of hausmannite and the unknown mineral (x) (2–5) is at the right of caryopilite and the down side of hausmannite grain. Johannsenite (j) (2–4) corresponds to the less dark and larger area with minute fractures in the right of figure, and is surrounded by chlorite (ch) (2–3). The parenthesized numbers correspond to those in Table 2.

diffraction study. Although the obtained pattern is contaminated by the associated grossular, three diffractions with $d = 7.60\text{\AA}$ (s), $3.78\text{\AA}$ (w), and $1.422\text{\AA}$ (w) correspond to those of rancieite from Oriente Province, Cuba (Richmond *et al.*, 1969).

Chemical analyses

Chemical analyses were made by using Links Systems energy dispersive X-ray spectro-chemical analysis. The analysed materials are termed metabasite and massive ore, respectively. In the former, the chemical analyses of garnet, piemontite and diopside are given (Table 1), while in the latter those of garnet, caryopilite, chlorite, hausmannite and johannsenite are demonstrated (Table 2).

TABLE 1. Chemical analyses of grossular (1-1), piemontite (1-2a, 1-2b, 1-2c), and diopside (1-3) in metabasite.

Weight percentages: (*calculated)

	1-1	1-2a	1-2b	1-2c	1-3
SiO ₂	36.56	35.51	37.26	36.76	52.02
Al ₂ O ₃	13.50	12.68	20.76	21.00	2.27
Fe ₂ O ₃	10.95	10.88	11.28	4.56	
Mn ₂ O ₃	1.63	16.83	6.21	12.08	
FeO					6.78
MnO	13.69				1.05
MgO	0.62		0.34		16.53
CaO	24.36	23.12	22.21	22.69	19.77
H ₂ O*		1.56	1.88	1.92	
Total	99.79	100.58	99.94	99.01	98.42

Empirical formulae: (bases of calculation are given below)

- (1-1: total cation = 8 with the partial conversion of Mn into Mn³⁺)
 (1-2a, 2b, 2c: total cation = 8 with the conversion of total Mn into Mn³⁺ and addition of calculated H₂O)
 (1-3: total oxygen = 6)
- 1-1. (Ca_{2.10}Mn²⁺_{0.83}Mg_{0.07})_{Σ3.00} (Al_{1.23}Fe³⁺_{0.66}Mn³⁺_{0.10})_{Σ1.99}
 (Si_{2.95}Fe³⁺_{0.05})_{Σ3.00}O_{11.96}
- 1-2a. Ca_{2.06}(Mn³⁺_{1.06}Al_{1.24}Fe³⁺_{0.68})_{Σ2.98}Si_{2.95}O_{12.00}(OH)_{0.86}
- 1-2b. (Ca_{1.92}Mg_{0.04})_{Σ1.96}(Al_{1.97}Fe³⁺_{0.68}Mn³⁺_{0.38})_{Σ3.03}Si_{3.00}O_{12.00}(OH)_{1.01}
- 1-2c. Ca_{1.98}(Al_{2.01}Mn³⁺_{0.75}Fe³⁺_{0.28})_{Σ3.04}Si_{2.99}O_{12.00}(OH)_{1.04}
- 1-3. (Ca_{0.79}Mn²⁺_{0.03}Fe²⁺_{0.18})_{Σ1.00}(Mg_{0.92}Fe²⁺_{0.03}Al_{0.05})_{Σ1.00}
 (Si_{1.95}Al_{0.05})_{Σ2.00}O_{6.00}

TABLE 2. Chemical analyses of grossular (2-1a, 2-1b), caryopilite (2-2), chlorite (2-3), johannsenite (2-4), unnamed mineral (2-5), and hausmannite (2-6) in a massive aggregate of grossular.

Weight percentages:

	2-1a	2-1b	2-2	2-3	2-4	2-5	2-6
SiO ₂	36.49	36.65	36.49	24.26	48.91	29.46	
TiO ₂	0.53						
Al ₂ O ₃	17.36	17.58	0.38	18.00	0.41	0.34	
Fe ₂ O ₃	4.68	3.84		0.99			2.67
Mn ₂ O ₃	3.50	3.31					65.32
V ₂ O ₃		0.35					
FeO					0.49	4.36	
MnO	8.25	13.70	51.57	32.00	23.29	46.03	30.53
MgO	0.42	0.38	0.32	9.32	3.16	0.98	
CaO	28.39	23.99	0.27		23.61	14.18	
Total	99.62	99.80	89.03	84.86	99.88	95.35	98.52

Empirical formulae: (bases of calculation are given below)(2-1a, 1b: total cation = 8 with the partial conversion of Mn into Mn³⁺)

(2-2: total oxygen = 13)

(2-3: total oxygen = 14)

(2-4: total oxygen = 6)

(2-5: total oxygen = 8)

(2-6: total oxygen = 4 with the partial conversion of Mn into Mn³⁺)

2-1a. (Ca_{2.40}Mn²⁺_{0.55}Mg_{0.05})_{Σ3.00} (Al_{1.48}Fe³⁺_{0.28}Mn³⁺_{0.21}Ti_{0.03})_{Σ2.00}
(Si_{2.87}Al_{0.13})_{Σ3.00}O_{11.95}

2-1b. (Ca_{2.04}Mn²⁺_{0.92}Mg_{0.04})_{Σ3.00} (Al_{1.55}Fe³⁺_{0.23}Mn³⁺_{0.20}V³⁺_{0.02})_{Σ2.00}
(Si_{2.91}Al_{0.09})_{Σ3.00}O_{11.96}

2-2. (Mn²⁺_{4.81}Mg_{0.05}Al_{0.05}Ca_{0.03})_{Σ4.94}Si_{4.02}O_{13.01}

2-3. (Mn²⁺_{3.10}Mg_{1.59}Al_{1.19}Fe³⁺_{0.09})_{Σ5.97}(Si_{2.77}Al_{1.23})_{Σ4.00}O_{14.00}

2-4. Ca_{1.02}(Mn²⁺_{0.80}Mg_{0.19}Fe²⁺_{0.02})_{Σ1.01}(Si_{1.97}Al_{0.02})_{Σ1.99}O_{6.00}

2-5. Ca_{1.03}(Mn²⁺_{2.62}Fe²⁺_{0.25}Mg_{0.10}Al_{0.01})_{Σ2.98}(Si_{1.98}Al_{0.02})_{Σ2.00}O_{8.00}

2-6. Mn²⁺_{1.00}(Mn³⁺_{1.92}Fe³⁺_{0.08})_{Σ2.00}O_{4.00}

The garnet analyses in metabasite are less fluctuated and one of them is tabulated in Column 1-1. Although summation is very satisfactory, the calculation on the basis of total cation = 8 yields a slightly low total oxygen atoms if all Fe is trivalent and a part of Mn is dealt with as trivalent to satisfy the general formula of garnet. Together with the slightly lower SiO₂ content, these may be ascribed to minor H₂O involved in the form of Si $\leftrightarrow$ H₄ substitution, though low even if present. The ratios Ca : Mn²⁺ and Al : Fe³⁺ are close to 2 : 1. The chemical

composition of piemontite in direct contact with garnet (Column 1–2a) has the similar Ca : Mn²⁺ and Al : Fe³⁺ ratios to garnet. Piemontite occupying an extensive portion in the figure is a part of visible minute veinlets. The chemical analyses given in Columns 1–2b and 1–2c have lower Mn₂O₃ contents than 1–2a and fluctuating Fe₂O₃ contents, or chemically misfitting to the partnered garnet. All the piemontite analyses are satisfactory, since the additions of calculated H₂O contents provide good summations in all of them. Diopside is probably the remnant of the primary constituent, containing moderate FeO and minor MnO (Column 1–3).

Garnet in the massive aggregate has rather wide compositional variation range due to the substitution of Mn²⁺ for Ca (Columns 2–1a and 2–1b). The lower Si content than the previous case may be also due to the substitution of H for Si. Caryopilite analysis (Column 2–2) is tentatively calculated into the anhydrous general formula with M₅Si₄O₁₃, where M is dominantly occupied by Mn²⁺. Chlorite analysis indicates it to be specified as pennantite, though more magnesian than the original material (Smith *et al.*, 1946). This is an intervening material between johannsenite and hausmannite. Johannsenite is in direct contact with chlorite, grossular and the unknown mineral stated next. The chemical composition (Column 2–4) is close to that found from Choujagoya (Kato, 1986), located about 10km northwest of the Dainichi mine, where the weakly metamorphosed members of Tanzawa Group are exposed. In direct contact with hausmannite, caryopilite, grossular, and johannsenite, a few colourless grains of less than 50 µm across are found. Three chemical analyses are essentially same and the cationic ratio of Ca : (Mn + Fe + Mg) : Si is very close to 1 : 3 : 2. One of them is given in Column 2–5, with a lower summation. If the rest is ascribed to H₂O, it requests 4.45 wt.%, leading to a new total very close to 100%. Therefore, it is highly likely that the ideal formula of this mineral is Ca(Mn,Fe,Mg)₃Si₂O₈•H₂O, where Mn>Fe, Mg, or simply CaMn₃Si₂O₈•H₂O. The presentation employing such a silicate radical as Si₂O₇ is probable, giving an alternative formula of CaMn₃Si₂O₇(OH)₂. The chemical analysis of hausmannite (Column 2–6) indicates that the other constituents than Mn is Fe, which is very probably in the ferric state. The calculation of the empirical formula after the allotment of Mn into di- and trivalent states gives near 100% total.

Summary

The co-existence of a manganoan grossular with piemontite of related composition is found in the products of regional metamorphism of prehnite-pumpellyite facies, where Mn²⁺ and Mn³⁺ were equally available and preferentially allotted to them, respectively. The discrepancy between two is simply ascribed to the valency state of Mn and OH in the latter.

This yields a genetical connection between a grossular of special composition and piemontite beyond the remote situation in the structural classification of silicate minerals. Also, this connection informs the existence of a special point on the grossular-spessartine (plus andradite molecule if exactly described) continuous solid solution series apart from the

compositional and crystallographic continuity, where a genetical relation is to emerge under the oxidizing condition. Said precisely, this is not a point but a zone extended onto spessartine side, since there is Ca-poor piemontite in which a part of Ca is substituted by Mn^{2+} such as the material appeared in JCPDS Card No. 29-288. This may lead to an important evidence, since this provides a range in the state of oxidation at which a fraction of Mn^{2+} is allowed to survive. The compositional diversity of examined piemontite suggests the prevalence of non-equilibrium condition. So, the present description is a kind of allusion that the observed combination is a potential candidate of near isochemical oxidation-reduction pair created despite the structural difference of silicate framework.

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