The Association of Henritermierite with Mg-Rich Vesuvianite in Mn Ores: Indicator Significance and an Example of Crystal Chemical Selectivity

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Abstract. Regularities of isomorphism at octahedrally coordinated sites of vesuvianite-group minerals have been investigated based on a representative data on samples from different geological occurrences. Most Mg-rich samples can be divided into two groups: wiluite and boron-free samples from associations with henritermierite. Geochemical and crystal-chemical factors determining the composition of associated Mn-rich vesuvianites and henritermierite are discussed.

Keywords: Vesuvianite group · Henritermierite · Kombat Mine · Wessels Mine

1 Introduction

Minerals of the garnet supergroup are characterized by wide variations in chemical composition. Their general formula is $[12]X_3[6]Y_2([4]Z\text{Ø}_4)_3$ where $X = \text{Mg, Ca, Mn}^{2+}$, Fe^{2+}, Y; $Y = \text{Mg, Al, V}^{3+}, \text{Cr}^{3+}, \text{Mn}^{3+}, \text{Fe}^{3+}, \text{Sc}^{3+}$, Si, Ti, Zr, Sn, Sb^{5+}, Te^{6+}, U^{6+}; $Z =$ Li, Zn, Al, Si, V^{5+}, As^{5+}, • (• is vacancy), Ø = O, OH, F; the numbers in square brackets indicate the coordination number. A garnet with the composition $\text{Ca}_3\text{Mn}^{3+}{}_2(\text{SiO}_4)_3$ is so far not known, despite the widespread occurrence of its constituent components. Most likely, this fact results from crystallochemical factors and is associated with the relatively large ionic radii of Ca and Mn^{3+}. However, the hydrogarnet henritermierite $\text{Ca}_3\text{Mn}^{3+}{}_2(\text{SiO}_4)_2[\bullet(\text{OH})_4]$ is known. This mineral is very rare and has so far only been found on the African continent, in the manganese deposits of the Kalahari Manganese Field, South Africa (the Wessels, Hotazel and N'Chwaning I and II Mines – Kuleshov 2012) and in the Zagora Province, Morocco (the Tachgagalt Mine – Gaudefroy et al. 1969). All finds of henritermierite belong to manganese ore assemblages that include Mn^{3+} oxides and Mg-containing minerals of the vesuvianite group. Unlike other representatives of the garnet supergroup, which – with the exception of holtstamite

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$Ca_3Al_2(SiO_4)_2[\bullet(OH)_4]$ – have cubic symmetry, henritermierite is tetragonal (Aubry et al., 1969).

The simplified crystal-chemical formula of vesuvianite-group minerals is $X_{18}(X'Y1)Y2_4Y3_8T_{0\text{–}5}(SiO_4)_{10}(Si_2O_7)_4O_{1\text{-}2}W_9$ where the X sites are predominantly occupied by Ca; the Y sites have octahedral coordination; $Y2$ is predominantly occupied by Al; $Y1$ and $Y3$ have a mixed occupancy which can involve Mg, Al, Fe^{2+}, Fe^{3+}, Mn^{2+}, Mn^{3+}, and Cu^{2+}; $T = $ B, Al, Fe, •; $W = $ OH, F, and minor O (Groat et al., 1992, 1994; Aksenov et al. 2016). Boron- and F-dominant members of the vesuvianite group (wiluite and fluorvesuvianite, respectively) are very rare in nature.

In this work, a new find of henritermierite is described, again from Africa. The mineral was discovered as a component of manganese ore from the Kombat deposit in Namibia, where it occurs associated with hausmannite, calcite, native copper, Mg-rich vesuvianite and late liebigite (Fig. 1 and 2).

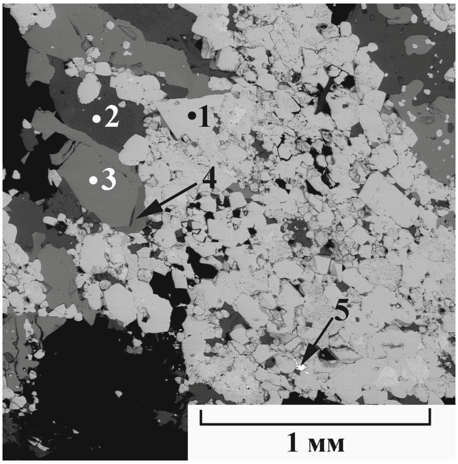

Fig. 1. Hausmannite (1), calcite (2), henritermierite (3), Mg-rich vesuvianite (4), and liebigite (5). BSE image.

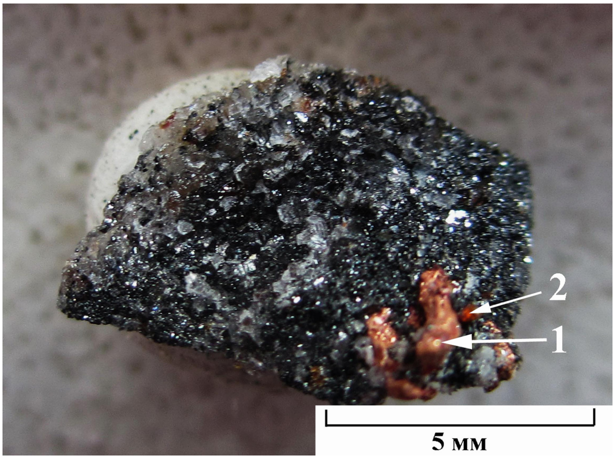

Fig. 2. Native copper (1) and henritermierite (2) in hausmannite ore.

2 Methods and Approaches

The study of the chemical composition (Table 1) was carried out by X-ray spectral microanalysis using a scanning electron microscope Tescan Vega-II XMU (EDS mode, 20 kV, 400 pA) with the INCA Energy 450 system for X-ray spectroscopy and calculation of the sample composition. The diameter of the electron beam was 157–180 nm for chemical composition analysis and 60 nm for imaging. The excitation area was max 5 μm in diameter. The signal accumulation time was 100 s. Images were enlarged to × 45. The distance from the sample to the detector was up to 25 mm. The standards used were as follows: MgF_2 for F, MgO for Mg, Al_2O_3 for Al, SiO_2 for Si, wollastonite for Ca, SrF_2 for Sr, *REE* monophosphates for *REE* (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Yb); pure Ti, V, Cr, Mn, Fe, Cu, Y for the corresponding elements.

Data on the chemical composition of henritermierite from different localities are given in Table 1. The compositions of the associated mineral of the vesuvianite-milanriederite solid-solution series correspond to the crystal chemical formulae $(Ca_{17.61}Mn_{0.43}La_{0.38}Ce_{0.19}Pr_{0.19}Nd_{0.10}Y_{0.10})_{\Sigma 19.00}$ $^{Y1}Fe^{3+}$ $^{Y2}Al_4$ $^{Y3}(Al_{4.19}Mg_{3.43}Fe^{3+}_{0.24}Mn^{3+}_{0.14})_{\Sigma 8.00}$ $Si_{18.00}[O_{68.53}(OH)_{0.47}]_{\Sigma 69.00}(OH)_9$ (Sample 1) and $(Ca_{18.36}Sr_{0.28}Y_{0.19}Sm_{0.04}Gd_{0.04}Nd_{0.03}Eu_{0.02}Dy_{0.02}Pr_{0.01}Yb_{0.01})_{\Sigma 19.00}$ $^{Y1}(Fe^{3+}_{0.59}Cu^{2+}_{0.41})_{1.00}$ $^{Y2}Al_4$ $^{Y3}(Mg_{2.90}Al_{2.71}Mn^{3+}_{1.41}Fe^{3+}_{0.59}Sc^{3+}_{0.18}Ti_{0.11}Cr_{0.10})_{\Sigma 8.00}$ $^{T}Al_{1.00}$ $Si_{18.00}$ $O_{69.00}$ $[(OH)_{6.84}O_{2.16}]_{9.00}$ (Sample 2). For comparison: in milanriederite, the $Y3$ site is Mg-dominant and the content of $Y3$ cations is $[Mg_{4.48}Al_{2.00}(Fe,Mn)_{1.52}]_{\Sigma 8.00}$ (Chukanov et al. 2019). The presence of copper in Sample 2 is noteworthy (by analogy with cyprine from the Kalahari manganese deposits, we assume that the ion Cu^{2+} occurs at the $Y1$ site).

Table 1. Chemical composition of henritermierite

	Kombat Mine (this work)	Wessels Mine (this work)	Tachgagalt Mine (Gaudefroy et al. 1969)
	Content (wt.%)		
CaO	31.45 (30.51–31.88)	36.07	35.45
MgO	5.32 (5.00–5.68)	0.13	bdl
Mn2O3	28.41 (27.22–29.73)	31.00	24.90
Fe2O3	0.20 (0–0.56)	0.90	0.95
Al2O3	0.14 (0–0.30)	1.19	5.95
SiO2	30.74 (30.27–31.21)	25.76	24.65
TiO2	0.02 (0–0.08)	bdl	bdl
V2O5	0.09 (0–0.31)	bdl	bdl
H_2O	No data	No data	7.93
F	1.01 (0.23–2.34)	bdl	bdl
– O = F2	0.43 (0.10–0.99)	–	–
Сумма	96.95	95.05	99.83
	Formula coefficients calculated for five $(X + Y)$ cations		
Ca	2.54 (2.50–2.56)	3.00	2.94
Mg	0.61 (0.57–0.64)	0.02	0
Mn3+	1.81 (1.75–1.92)	1.83	1.47
Fe^{3+}	0.01 (0.00–0.03)	0.05	0.06
Al	0.01 (0.00–0.03)	0.11	0.54
Si	2.32 (2.30–2.35)	2.00	1.91
Ti	0.00 (0.00–0.01)	0	0
V	0.00 (0.00–0.02)	0	0
F	0.25 (0.06–0.55)	0	0

Note: bdl means "below detection limit"

The main specific feature of vesuvianite-group minerals associated with henritermierite is a high content of Mg (2.90–4.24 atoms per formula unit, *apfu*). Such contents of Mg are typical for wiluite $Ca_{19}Mg(Al, Mg, Fe, Ti, Mn)_{12}(B, Al, \square)_5(Si_2O_7)_4(SiO_4)_{10}(O, OH)_9O_{2-3}$ (Panikorovskii et al. 2017), but are very unusual for boron-depleted members of the vesuvianite group. Figure 3 illustrates this regularity. When constructing this triangular diagram, we used data on the chemical composition of minerals of the vesuvianite group from Chukanov et al. (2018), studied in detail using methods of electron probe analysis, analytical chemistry, Mössbauer and infrared spectroscopy, and X-ray structural analysis. The samples studied in that work come from different types of metasomatic and metamorphic assemblages. As can be seen from Fig. 3, the highest magnesium contents are characteristic of samples with high boron contents (above 0.75

atoms per formula unit), and among low-boron samples – minerals from the association with henritermierite.

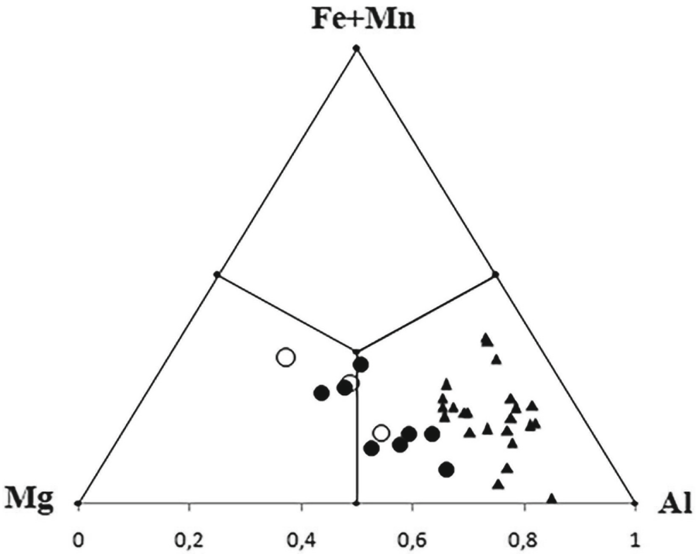

Fig. 3. Relative contents of Mg, Al, and Fe+Mn at the mixed-occupancy *Y*1 and *Y*3 sites of vesuvianite-group minerals. Boron-free samples from the associations with henritermierite, boron-rich samples (with B $>$ 0.75 *apfu*) and other samples correspond to open circles, black circles, and triangles, respectively.

For only one pair of cations (namely, Mg and Al) there is a correlation with a relatively high absolute value of the correlation coefficient equal to -0.65 (Fig. 4). Hence, it can be concluded that heterovalent isomorphism between Mg and Al prevails in minerals of the vesuvianite group, in which charge compensation is carried out by substitution of OH/F for O and/or with the participation of several cations with valences of 3 and 4 (Fe^{3+}, Mn^{3+}, Ti^{4+}). The absence of a significant correlation between Mg and Mn (the correlation coefficient is -0.11) indicates that this type of isomorphism is generally not typical for minerals of the vesuvianite group.

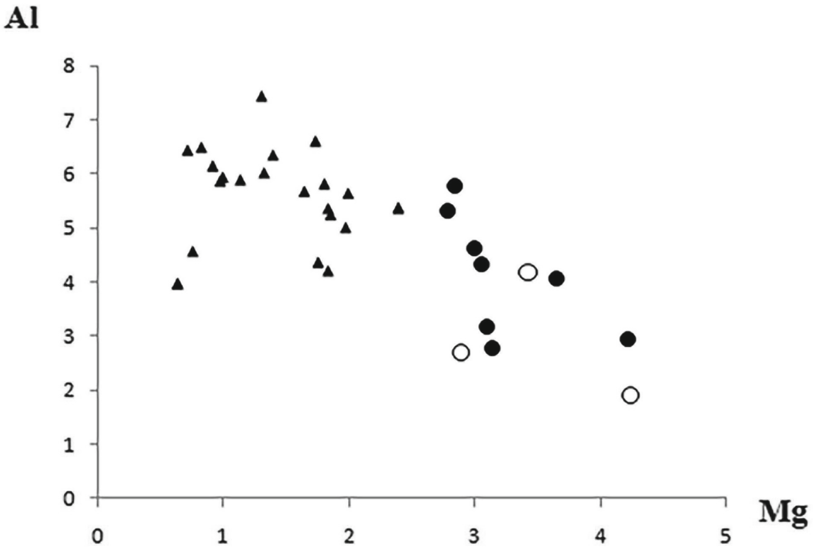

Fig. 4. Correlation between the contents of Mg and Al at the *Y*1 and *Y*3 sites of vesuvianite-group minerals (*apfu*). Boron-free samples from the associations with henritermierite, boron-rich samples (with $B > 0.75$ *apfu*) and other samples correspond to open circles, black circles, and triangles, respectively.

The most low-Mg point deviating from the correlation in Fig. 4 corresponds to a sample with the highest Ti content (2.21 Ti *apfu*). Thus, heterovalent isomorphism between Mg and Ti may play a significant role in vesuvianite-group minerals.

3 Conclusions

The obtained results allow us to draw a number of conclusions. The presence of the rare garnet henritermierite and its association with high-magnesium minerals of the vesuvianite group is seemingly a characteristic feature of specific assemblages in manganese ores, formed at relatively low oxygen fugacity and containing manganese in relatively low-valency states (Mn^{3+}, Mn^{2+}). Despite a number of analogies between the crystalline structures of garnet and vesuvianite, in ores of this type, the Mn^{3+} and Mg^{2+} cations exhibit a pronounced affinity for henritermierite and minerals of the vesuvianite group, respectively.

Relatively low contents of Mg (below 2 *apfu*) in manganvesuvianite from its type locality in the Kalahari manganese fields (Armbruster et al. 2002) may be due to a low activity of Mg in specific mineral assemblages formed by hydrothermal alteration of primary manganese ores and containing accessory henritermierite.

Henritermierite is the only member of the garnet supergroup containing Mn^{3+} as a species-defining component. In other silicate garnet-supergroup minerals corresponding site is occupied by smaller tri- or tetravalent cations. The large radius of the Mn^{3+} cation results in a large unit-cell volume of henritermierite (about 1828 Å^3), which promotes the substitution of the SiO_4 group with the $(OH)_4$ tetrahedron.

On the other hand, there are only two vesuvianite-group minerals in which Mg plays a species-defining role: milanriederite, ideally $(Ca_{13}La_6)Fe^{3+}Al_4Mg_8Si_{18}O_{69}(OH)_9$, and manaevite-(Ce) $(Ca_{11}Ce_8)_{19}MgAl_4Mg_8(SiO_4)_8(H_4O_4)_2](Si_2O_7)_4[(OH)_8O_2]_{10}$. Both minerals are extremely rare. The association of the most Mn^{3+}-rich garnet with Mg-rich vesuvianite-group minerals (including milanriederite) is remarkable not least since it is a clear-cut example of crystal-chemical selectivity. Obviously, this selectivity can be realized only under specific conditions because generally the occurrence of significant amounts of Mn^{3+} in the vesuvianite-type structure is possible, as is known from manganvesuvianite, as an example of a vesuvianite-group mineral with Mn^{3+} as a species-defining component. A significant factor promoting the substitution of Al for Mg is the heterovalent isomorphism ${}^{Y3}Al + {}^{X}Ca \leftrightarrow {}^{Y3}Mg + {}^{X}REE$: most Mg-rich samples of vesuvianite-group minerals contain significant amounts of rare-earth elements. The fugacities of oxygen and hydrogen may be additional geochemical factors influencing homo- and heterovalent isomorphism involving the pairs $SiO_4/(OH)_4$, O/OH, Fe^{2+}/Fe^{3+}, and Mn^{2+}/Mn^{3+} in associated minerals belonging to the vesuvianite group and garnet supergroup.

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