



Article

Crystal chemistry and nomenclature of rhodonite-group minerals

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Abstract

This paper presents the nomenclature of the rhodonite group accepted by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA). An overview of the previous studies of triclinic (space group $P\bar{1}$) pyroxenoids belonging to the rhodonite structure type, with a focus on their crystal chemistry, is given. These minerals have the general structural formula $^{VI}M(5)^{VI}M(1)^{VI}M(2)^{VI}M(3)^{VI}M(4)[Si_5O_{15}]$. The following dominant cations at the M sites are known at present: $M(5) = Ca$ or Mn^{2+} , $M(1-3) = Mn^{2+}$; and $M(4) = Mn^{2+}$ or Fe^{2+} . In accordance with the nomenclature, the rhodonite group consists of three IMA-approved mineral species having the following the general chemical formulae: $^{M(5)}A^{M(1-3)}B_3^{M(4)}C[Si_5O_{15}]$, where $A = Ca$ or Mn^{2+} ; $B = Mn^{2+}$; and $C = Mn^{2+}$ or Fe^{2+} . The end-member formulae of approved rhodonite-group minerals are as follows: rhodonite $CaMn_3Mn[Si_5O_{15}]$; ferrorhodonite $CaMn_3Fe[Si_5O_{15}]$; and vittinkiite $MnMn_3Mn[Si_5O_{15}]$.

Keywords: rhodonite, ferrorhodonite, vittinkiite, rhodonite group, manganese silicate, inosilicate, pyroxenoid, mineral nomenclature

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Introduction

Rhodonite is a well-known and widespread mineral. It is an important, and quite often the major rock-forming, constituent of meta-sedimentary manganese ores; in addition, it occurs in some hydrothermal ores and in manganese-rich skarns. This pyroxenoid shows significant chemical variations, especially in the Ca:Mn ratio. This caused a paradoxical situation: until recently, this common mineral was not correctly defined as a mineral species. In different reference books and databases, its idealised formula is written in different ways. The following two formulae were mainly in use: $MnSiO_3$ ($Z = 10$) and $CaMn_4Si_5O_{15}$ ($Z = 2$). Sometimes both formulae occur in the same publication. For instance, in the 12th Edition of *Fleischer's Glossary of Mineral Species* (Back, 2018), the formula of rhodonite is given as $Mn^{2+}SiO_3$ (on page 216) and as $CaMn_4^{2+}Si_5O_{15}$ (on page 373, in the list of mineral groups). There are several reasons of such discrepancies: (1) wide chemical variations among samples with the rhodonite-type structure; (2) a confusion in the correct identification of Mn-rich pyroxenoids (rhodonite-, pyroxmangite- and bustamite-type minerals), especially in old publications; and (3) different approaches to writing the end-member formula, i.e. crystal chemical approach (taking into account the repeat unit of the inosilicate chain, Si_5O_{15}) vs. simple chemical approach, with aggregate M sites, maximum reduction of stoichiometric coefficients to integer values and formula calculation based on 3 O atoms per formula unit (apfu).

Thus, the definition of rhodonite as a mineral species and the elaboration of the nomenclature of rhodonite-type minerals, in

agreement with the current guidelines of mineral nomenclature, were necessary. The nomenclature of the rhodonite group reported here was accepted by the International Mineralogical Association Commission on New Minerals, Nomenclature and Classification (IMA–CNMNC) in March 2019 (IMA Proposal 18-I, Miyawaki *et al.* (2019)).

Rhodonite: a retrospective

The term 'rhodonite'

The term 'rhodonite' was first introduced by Germar (1819), on the basis of a proposal by Jasche, who described the same mineral two years earlier (Jasche, 1817). It originates from the Greek word $\rho\acute{o}\delta\omicron\nu$, rose (Germar, 1819), and it was initially given to a rock formed by pinkish-red Mn-rich silicates (today known as rhodonite and pyroxmangite), quartz, tephroite and manganese oxides. Later the name rhodonite was transferred to the major rock-forming mineral of these rocks, a Mn silicate having typically a pink or red colour. Such rocks and their minerals are common in nature, and during the 19th Century they were described independently with different names from different localities. Many synonyms of 'rhodonite' in both the mineralogical and petrological sense were used in the literature of that period: roter braunstein, rothbraunstein or rothbraunsteinerz, rothstein, kieselmangan, rothspat, manganese-spar, manganolite, marcelline, kapnikite, paisbergite or pajsbergite, hermannite and orlets (Chukhrov, 1981, and references therein).

Early chemical data and identification problems of Mn pyroxenoids

The first reliable quantitative chemical analyses of rhodonite as a mineral were published in the period from the end of the 19th to

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the beginning of 20th century. They were collected by Sundius (1931) who also firstly proposed the triangular diagram $\text{CaSiO}_3\text{--MnSiO}_3\text{--Fe(Mg)SiO}_3$ and marked separate fields of different 'pyroxenes': rhodonite (near the Mn corner, with the subfield 'iron rhodonites'), bustamite (around the $\text{Ca}_{0.5}\text{Mn}_{0.5}\text{SiO}_3$ point), wollastonite (near the Ca corner), hedenbergite [around the $\text{Ca}_{0.5}(\text{Fe,Mg})_{0.5}\text{SiO}_3$ point] and 'sobralite' [near the $\text{Mn}_{0.5}(\text{Fe,Mg})_{0.5}\text{SiO}_3$ point; now pyroxmangite–pyroxferroite series minerals].

It should also be noted that the rhodonite field in the diagram by Sundius (1931) includes only two points corresponding to formulae (recalculated based on 15 O apfu) with $\text{Ca} < 0.5$ apfu and more than ten points having $0.5 < \text{Ca} < 1.5$ apfu. In general, among chemical data on rhodonite published in the period which could be named 'pre-structural', the analyses corresponding to the formulae with Ca content close to 1 apfu (for 15 O apfu) prevail (Larsen and Shannon, 1922; Sundius, 1930, 1931; Henderson and Glass, 1936; Palache, 1944; Russel, 1946). Analyses of rhodonite with $\text{Ca} < 0.5$ apfu are reported in Sundius (1931), Ross and Kerr (1932) and Hietanen (1938).

However, the situation with early analyses of rhodonite is complicated by the possible confusion of this pyroxenoid with the visually indistinguishable and chemically close pyroxmangite (in that period any pink or red pyroxene-like Mn-dominant mineral was referred to as 'rhodonite'). The name pyroxmangite was introduced in 1913 for a Mn–Fe pyroxene-like mineral (Ford and Bradley, 1913). It is worth noting that the chemical composition of the original 'pyroxmangite' corresponds to the empirical formula $(\text{Fe}_{3.52}\text{Mn}_{2.59}\text{Al}_{0.40}\text{Ca}_{0.30})_{\Sigma 6.81}[\text{Si}_{7.00}\text{O}_{21}]$ (recalculated based on 21 O apfu) with Fe dominant over Mn, as pointed out by Henderson and Glass (1936), and, therefore, corresponding to a Mn-rich variety of pyroxferroite. Ford and Bradley (1913) noted that pyroxmangite was considered initially as a highly ferrous rhodonite based on the similarity of most physical properties and chemical composition. At that time, rhodonite and pyroxmangite were distinguished only by optical methods, based on differences in the cleavage angles and 2V values. The 2V value for rhodonite is typically in the range 63–87° whereas for pyroxmangite it is in the range 37–46° (Deer *et al.*, 1978). However, some specimens showed a wide variation in 2V values, filling the gap and ranging from 40 to 72° (Suzaki, 1963; Aikawa, 1984). Such intermediate values of 2V are explained by the lamellar structure of pyroxmangite–rhodonite micro-intergrowths in which lamellae are thinner than the wavelength of the light used for optical measurements (Aikawa, 1984). We report here this situation in detail to underline the great difficulties in the identification of Mn-rich pyroxenoids in the period when X-ray diffraction (XRD) methods were still not widely used. Thus, all data on the mineralogy of these inosilicates from this period must be carefully evaluated.

First XRD data and crystal structure studies

A new era in the mineralogy of Mn pyroxenoids began with the collection of XRD data. The first data on the unit-cell parameters of rhodonite were published by Gossner and Bruckl (1928): $a = 7.79$, $b = 12.48$, $c = 6.75$ Å, $\alpha = 85.10$, $\beta = 94.04$ and $\gamma = 111.29^\circ$, while unit-cell parameters of pyroxmangite were first obtained by Perutz (1937): $a = 6.69$, $b = 17.38$, $c = 7.55$ Å, $\alpha = 113.47$, $\beta = 85.25$ and $\gamma = 97.32^\circ$.

The first powder XRD data for rhodonite were reported by Mikheev and Dubinina (1948) for a specimen with the following

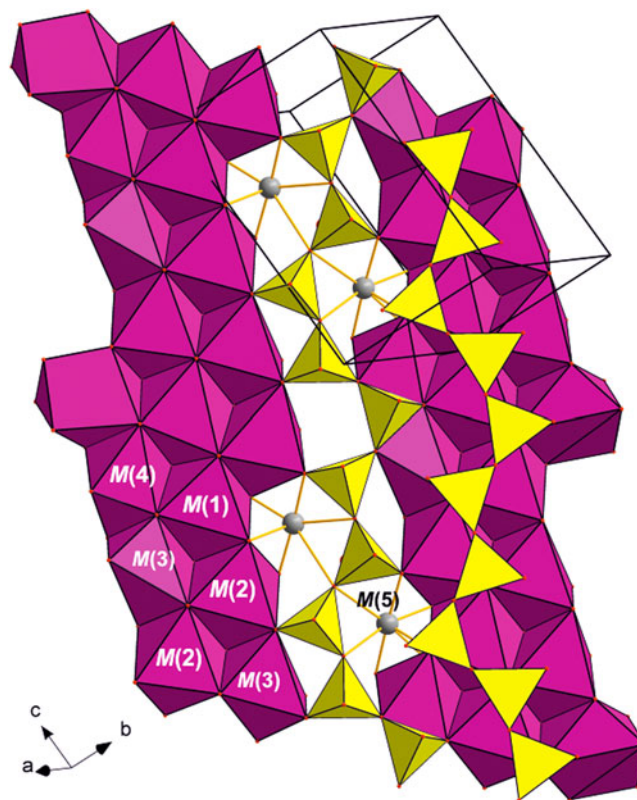


Fig. 1. General view of rhodonite-type crystal structure. SiO_4 tetrahedra are yellow.

chemical composition (wt.%): CaO 5.3, MnO 46.9, FeO 1.6, MgO 0.6, SiO_2 47.0, total 101.4, corresponding to the empirical formula $(\text{Mn}_{4.21}\text{Ca}_{0.59}\text{Fe}_{0.14}\text{Mg}_{0.09})_{\Sigma 5.03}[\text{Si}_{4.98}\text{O}_{15}]$. The specimen was collected from the Maloe Sedel'nikovskoe (alternate spelling: Malosedel'nikovskoe) deposit of rhodonite rock, used as an ornamental stone, at Middle Urals, Russia. Thus, a completely reliable identification of rhodonite in the modern sense became possible only at this period.

The crystal structure of rhodonite was firstly published by Mamedov (1958) for a specimen from Switzerland (the exact locality was not reported). The unit-cell parameters are: $a = 7.77$, $b = 12.20$, $c = 6.70$ Å, $\alpha = 85.15$, $\beta = 94.00$ and $\gamma = 111.29^\circ$; space group $P\bar{1}$. It should be noted that this author mentioned the paper by Liebau *et al.* (1956), who first suggested that rhodonite does not contain three-membered rings of SiO_4 tetrahedra, as assumed earlier, but contains chains of SiO_4 tetrahedra, like wollastonite. Mamedov (1958) found that the rhodonite structure contains chains of tetrahedra with a repeat unit of five tetrahedra, and ribbons of edge-sharing polyhedra $M(1)$, $M(2)$, $M(3)$, $M(4)$ and $M(5)$ (Fig. 1). Unfortunately, no chemical data are given in this paper. All M sites were refined as fully occupied by Mn.

Almost at the same time, the crystal structure of rhodonite was independently solved by Liebau *et al.* (1959) for a sample with the ideal formula $\text{CaMn}_4[\text{Si}_5\text{O}_{15}]$ (the locality was not reported) and turned out to be consistent with the structural model by Mamedov (1958). However, the data on the cation distribution between the five M sites demonstrated that Ca dominates at $M(5)$ and Mn is dominant at all other [$M(1)$ to $M(4)$] cation sites. The paper by Liebau *et al.* (1959) also contains a table of comparative data on chemically different samples with the rhodonite-type unit cell. The specimens corresponding to the

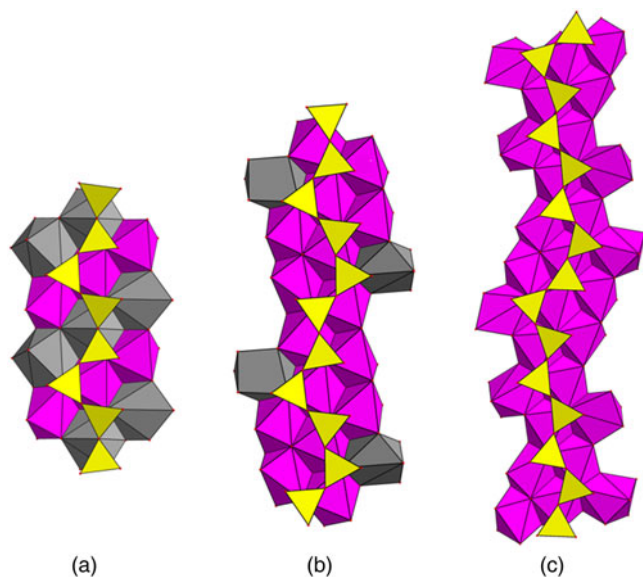


Fig. 2. Fragments of crystal structures of manganese pyroxenoids: (a) bustamite $\text{Ca}_3\text{Mn}_3[\text{Si}_3\text{O}_9]_2$ (Peacor and Buerger, 1962); (b) rhodonite $\text{CaMn}_4[\text{Si}_5\text{O}_{15}]$ (Peacor and Niizeki, 1963); and (c) pyroxmangite $\text{Mn}_7[\text{Si}_7\text{O}_{21}]$ (Ohashi and Finger, 1975). The colour of polyhedra indicates the predominant M cation: pink for Mn and grey for Ca.

ideal formulae $\text{CaMn}_4[\text{Si}_5\text{O}_{15}]$ and $\text{MnMn}_4[\text{Si}_5\text{O}_{15}]$ were joined by Liebau *et al.* (1959) under the same name: ‘rhodonite’.

Currently, H-free manganese pyroxenoids with inosilicate chains $[\text{SiO}_3]_\infty$ include three structure types which differ from each other in the conformation of the silicate chain, the number of SiO_4 tetrahedra in the repeat unit of the chain (Si_3O_9 in bustamite, Si_5O_{15} in rhodonite and Si_7O_{21} in pyroxmangite) and in the number and arrangement of non-equivalent M sites (Fig. 2).

The rhodonite group

In line with the IMA–CNMNC guidelines (Mills *et al.*, 2009), members of the rhodonite group are structurally characterised by chains of Si-centred tetrahedra with the repeat unit Si_5O_{15}

and ribbons formed by edge-sharing polyhedra $M(1)$, $M(2)$, $M(3)$, $M(4)$ and $M(5)$ (Fig. 1).

Chemical variability in the rhodonite group

Chemical data for those samples having the rhodonite-type structure that were investigated both chemically and structurally, including the low-Ca species vittinkiite, ideally $\text{MnMn}_3\text{Mn}[\text{Si}_5\text{O}_{15}]$ (IMA2017–082a; Shchipalkina *et al.*, 2019b) are given in Table 1.

The approximate compositional fields of minerals belonging to the rhodonite, bustamite and pyroxmangite structure types, plotted based on literature data and our new analyses, and end-member compositions of IMA-approved mineral species, are shown in the Ca–Mn–(Fe + Mg + Zn) triangular diagram (Fig. 3). The field corresponding to rhodonite-group minerals overlaps with the fields of bustamite-group and pyroxmangite-group members in its Ca-richest and Ca-poorest parts, respectively.

As shown in Fig. 3, the end-member pyroxmangite $\text{Mn}_7[\text{Si}_7\text{O}_{21}]$ may be considered as dimorphous with vittinkiite, $\text{Mn}_5[\text{Si}_5\text{O}_{15}]$ (the Ca-free rhodonite-type compound is also known among synthetic Mn inosilicates, see Narita *et al.*, 1977; Table 2).

Crystal chemistry of the rhodonite group

Currently, crystal structure studies are available for eleven samples having the rhodonite-type structure. Data on the cation distribution between M polyhedra in these samples [including those from the first publication by Mamedov (1958) who, unfortunately, did not report any chemical data] are given in Table 2. The numbering of the M sites in structures of rhodonite-type minerals is ‘traditional’, in agreement with the designations used in first publications.

The $M(1)$ -, $M(2)$ - and $M(3)$ -centred polyhedra are weakly distorted octahedra, with mean cation–oxygen distances in the range 2.21–2.23 Å. They are predominantly occupied by Mn^{2+} in all the samples studied.

Table 1. Quantitative chemical data of structurally investigated samples of rhodonite-group minerals.

	Rhodonite	Mg-rich rhodonite	Ferro-rhodonite	Vittinkiite	Zn-rich rhodonite	Mg- and Fe-rich rhodonite
Wt. %						
CaO	8.98	4.58	7.09	0.93	6.70	4.40
MgO	1.97	4.72	0.24	0.52	1.51	2.13
MnO	39.42	42.62	32.32	51.82	35.15	41.88
FeO	1.77	0.37	14.46	1.26	3.01	3.77
ZnO			0.36	0.11	7.22	
Al_2O_3		0.06			0.08	0.49
SiO_2	47.42	47.66	46.48	46.48	46.26	46.84
Total	99.56	100.01	100.95	101.12	99.93	99.51
Formula coefficients calculated on the basis of 15 O apfu						
Ca	1.00	0.51	0.80	0.11	0.76	0.50
Mg	0.31	0.73	0.04	0.08	0.24	0.34
Mn	3.52	3.77	2.92	4.71	3.20	3.78
Fe^{2+}	0.16	0.03	1.29	0.11	0.27	0.34
Zn	0.00	0.00	0.03	0.01	0.57	0.00
Al	0.00	0.00	0.00	0.00	0.01	0.04
Si	5.00	4.98	4.96	4.99	4.97	4.99
Ref.	[1]	[2]	[3]	[4]	[5]	[6]

[1] Peacor and Niizeki (1963); [2] Peacor *et al.* (1978); [3] Shchipalkina *et al.* (2017); [4] Shchipalkina *et al.* (2019b); [5] Nelson and Griffen (2005); [6] Leverett *et al.* (2008).

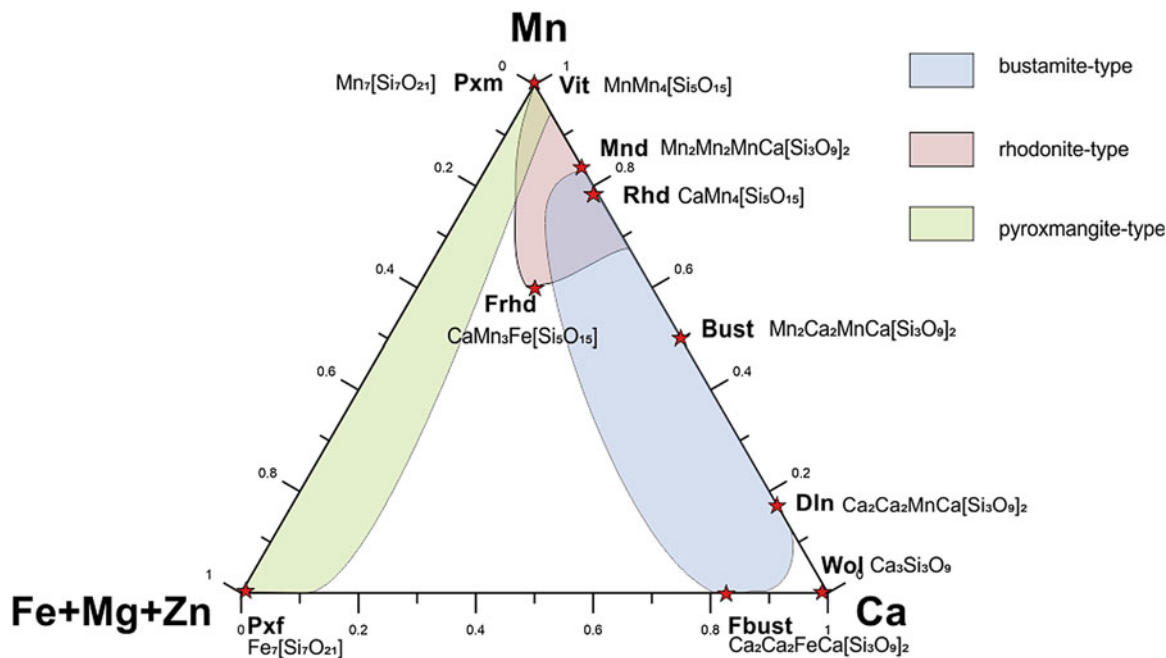


Fig. 3. Compositional fields of pyroxenoids in the Ca–Mn–(Fe + Mg + Zn) space, with end-member compositions of minerals marked with red stars: Wol – wollastonite, Bust – bustamite, Mnd – mendigite, Fbust – ferrobustamite, Dln – dalnegorskite (Shchipalkina et al., 2019a), Rhd – rhodonite, Frhd – ferrorhodonite, Vit – vittinkiite, Pxm – pyroxmangite and Pxf – pyroxferroite.

The $M(4)$ -centred polyhedron is a strongly distorted octahedron with the shortest and the longest cation–oxygen distances in the ranges 1.95–1.99 and 2.77–2.91 Å, respectively. The $M(4)$ site is typically Mn^{2+} -dominant and can host Fe, Mg and Zn (Peacor and Niizeki, 1963; Ohashi and Finger, 1975; Peacor et al., 1978; Nelson and Griffen, 2005); in the Fe-richest sample, $M(4)$ is Fe^{2+} -dominant, and for that reason this mineral has been approved by the IMA–CNMNC as a distinct mineral species, ferrorhodonite (Shchipalkina et al., 2017).

The $M(5)$ site has seven-fold coordination and the mean cation–oxygen distance in the range 2.40–2.42 Å. This site preferentially hosts Ca; another constituent at $M(5)$ can be Mn^{2+} . Six out of the eleven samples in Table 2 have Ca > Mn at $M(5)$. Nelson and Griffen (2005) hypothesised the distribution of admixed Ca between several M sites (Table 2). However, they gave no evidence to support this assumption.

Nomenclature of the rhodonite group

The definition of minerals belonging to the rhodonite group is based on the cation distribution over the M sites (Fig. 4).

In agreement with the currently available crystal chemical data, three mineral species belonging to the rhodonite group can be defined (Table 3).

Rhodonite was reported in the official IMA–CNMNC List of Mineral Names (Pasero, 2019) with the formula $Mn^{2+}SiO_3$, which is not compatible with its crystal structure. Thus, the historical name rhodonite required an up-to-date redefinition, and this is a keystone of this nomenclature. As shown in Table 2, the name rhodonite was used in the literature for samples with two end-member formulae, i.e. $Mn_5[Si_5O_{15}]$ and $CaMn_4[Si_5O_{15}]$. Now, the name **rhodonite** is applied to samples with the ideal formula $CaMn_3Mn[Si_5O_{15}] = CaMn_4[Si_5O_{15}]$, for the following reasons: (1) the first reliable chemical analyses of

Table 2. Arrangement of M cations in chemically and structurally studied samples of rhodonite-type minerals and an isostructural synthetic compound.

Actual species name	Original name*	Octahedrally coordinated sites M					Reference
		$M(1)$	$M(2)$	$M(3)$	$M(4)$	$M(5)$	
Rhodonite	Rhodonite	Mn	Mn	Mn	Mn	Ca	Liebau et al. (1959)
Rhodonite	Rhodonite	Mn	Mn	Mn	Mn, Mg, Fe	Ca, Mn	Peacor and Niizeki (1963)
Rhodonite	Rhodonite Mg-rich	Mn _{0.89} Mg _{0.11}	Mn _{0.86} Mg _{0.14}	Mn _{0.86} Mg _{0.14}	Mn _{0.53} Mg _{0.47}	Ca _{0.60} Mn _{0.40}	Peacor et al. (1978)
Rhodonite	Rhodonite Zn-rich	Mn, Fe, Ca	Mn, Ca, Fe	Mn, Ca, Fe	Mn, Zn, Fe, Mg	Ca, Mn, Fe	Nelson and Griffen (2005)
Rhodonite	Rhodonite Ca,Mg,Fe	Mn, Mg, Fe	Mn, Mg, Fe	Mn, Mg, Fe	Mn, Mg, Fe	Ca, Mn, Fe	Leverett et al. (2008)
Ferrorhodonite	Ferrorhodonite	Mn _{0.84} Fe _{0.16}	Mn _{0.84} Fe _{0.16}	Mn _{0.84} Fe _{0.16}	Fe _{0.81} Mn _{0.12} Mg _{0.04} Zn _{0.03}	Ca _{0.81} Mn _{0.19}	Shchipalkina et al. (2017)***
Vittinkiite	Rhodonite	Mn, Mg	Mn, Mg	Mn, Mg	Mn, Fe, Mg	Mn, Ca	Ohashi and Finger (1975)
Vittinkiite	Rhodonite	Mn, Fe	Mn, Fe	Mn, Ca	Mn, Mg, Fe, Zn	Mn, Ca	Nelson and Griffen (2005)
Vittinkiite	Rhodonite	Mn	Mn	Mn	Mn, Mg, Fe	Mn, Ca	Pertlik and Zahiri (1999)
Vittinkiite	Vittinkiite	Mn	Mn	Mn	**Mn _{0.83} Fe _{0.11} Mg _{0.06}	Mn _{0.92} Ca _{0.08}	Shchipalkina et al. (2019b)***
Synthetic analogue of end-member vittinkiite	Rhodonite	Mn	Mn	Mn	Mn	Mn	Narita et al. (1977)

Note: Species-defining cations are given in bold. *Original name given by authors of the cited paper. **For the $M(4)$ site, the Mn:Mg ratio was refined because Mn and Fe (with the atomic numbers 25 and 26, respectively) could not be distinguished by means of XRD; Fe content was added based on the electron-microprobe data. ***Holotype specimen.

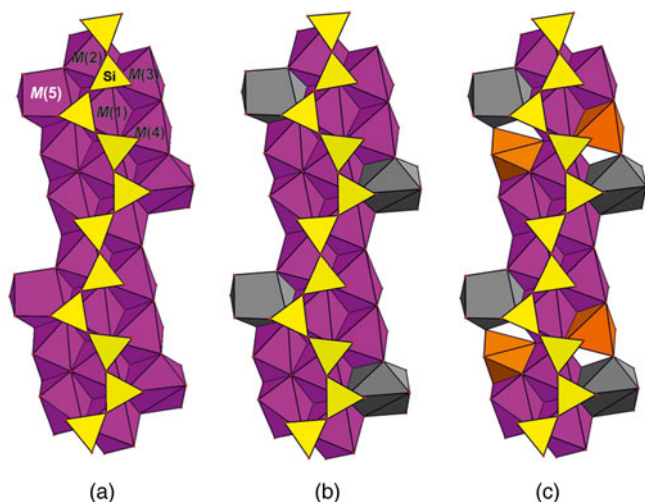


Fig. 4. Cation ribbons and chains $[\text{Si}_5\text{O}_{15}]^\infty$ in the crystal structures of: (a) vittinkiite; (b) rhodonite; and (c) ferrorhodonite. The colour of polyhedra indicates the predominant cation: pink for Mn, grey for Ca and orange for Fe. For site labels and references see Table 2.

rhodonite belong mainly to samples with $0.5 < \text{Ca} < 1.5$ apfu (Sundius, 1931); (2) the first published powder XRD data (Mikheev and Dubinina, 1948) were obtained on a sample with the empirical formula $(\text{Mn}_{4.21}\text{Ca}_{0.59}\text{Fe}_{0.14}\text{Mg}_{0.09})_{\Sigma 5.03}[\text{Si}_{4.98}\text{O}_{15}]$, i.e. with $\text{Ca} > 0.5$ apfu; (3) the first description of the crystal structure of a rhodonite-group mineral with reported chemical data was for a sample with the ideal formula $\text{CaMn}_4[\text{Si}_5\text{O}_{15}]$, thus being Ca-dominant at the $M(5)$ site (Liebau *et al.*, 1959); and (4) the rhodonite-group mineral corresponding chemically to the formula $\text{CaMn}_4[\text{Si}_5\text{O}_{15}]$ (i.e. with $0.5 < \text{Ca} < 1.5$ apfu) is much more widespread in nature than the mineral with $\text{Ca} < 0.5$ apfu.

Ferrorhodonite was described recently in a specimen from Broken Hill, Yancowinna Co., New South Wales, Australia Shchipalkina *et al.* (2017). It is characterised by an unusually high Fe content (the average FeO content is 14.5 wt.%, Table 1). It was named as the analogue of rhodonite with Fe^{2+} prevailing at the $M(4)$ site. Ferrorhodonite was approved by the IMA–CNMNC (IMA2016–016) as a new mineral species with the ideal formula $\text{CaMn}_3\text{Fe}[\text{Si}_5\text{O}_{15}]$ (Shchipalkina *et al.*, 2017).

Vittinkiite is the rhodonite-group mineral with the ideal formula $\text{MnMn}_3\text{Mn}[\text{Si}_5\text{O}_{15}] = \text{Mn}_5[\text{Si}_5\text{O}_{15}]$. The formal border between rhodonite $\text{CaMn}_4[\text{Si}_5\text{O}_{15}]$ and vittinkiite $\text{Mn}_5[\text{Si}_5\text{O}_{15}]$ lies at the composition $\text{Ca}_{0.5}\text{Mn}_{4.5}[\text{Si}_5\text{O}_{15}]$. Thus the chemical criterion for the definition of vittinkiite is $\text{Ca} < 0.5$ apfu. Taking into account mean cation–oxygen distances, the occurrence of Ca at the $M(1-4)$ sites seems unlikely. The name ‘vittinkiite’ was given for the type locality, the Vittinki (an old Swedish name for Vittinge) iron mines, Isokyrö, Western and Inner Finland Region, Finland. This is the first locality from which a low-Ca rhodonite-type mineral was reported reliably (with 1.3 wt.% CaO: Sundius, 1931). Rhodonite-type minerals with low Ca content (< 0.5 Ca apfu) are much rarer than rhodonite s.s. corresponding to the idealised formula $\text{CaMn}_4[\text{Si}_5\text{O}_{15}]$. It is worth noting that presumed ‘rhodonite’ from Vittinge was first described by Nordenskiöld (1863). Shchipalkina *et al.* (2019b) studied in detail the mineral from Vittinki using an old specimen from the Fersman Mineralogical Museum of the Russian Academy of Sciences and confirmed that it is Ca-poor, with all M sites being Mn-dominant (Table 2).

Data on two structurally studied specific chemical varieties of rhodonite are also given in Tables 1 and 2. One is a Mg-rich rhodonite – an unusually Mg-rich and low-Fe variety of rhodonite. It occurs in a metamorphosed sedimentary evaporite sequence at the Balmat Mine No. 4, New York, USA. The mineral is associated with the pyroxene donpeacorite, ideally $\text{MnMgSi}_2\text{O}_6$ (Peacor *et al.*, 1978). The second variety is a Zn-rich rhodonite that has a significant Zn content (up to 10 wt.% ZnO: Roberts *et al.*, 1992). The only known occurrence for this variety is the famous Franklin zinc deposit, Sussex Co., New Jersey, USA. It was initially named ‘fowlerite’ (Shepard, 1832) but was later identified as a Zn-rich variety of rhodonite (Camac, 1852).

Available structural data indicate that the $M(4)$ site tends to concentrate cations smaller than Mn^{2+} (namely, Fe^{2+} , Mg^{2+} and Zn^{2+}). If rhodonite-type minerals with the predominance of Zn or Mg at one of the M sites [$M(4)?$] are found in the future, they should be considered as distinct mineral species. By analogy with ferrorhodonite, minerals with cations other than Mn dominant at the $M(4)$ site should be named by adding to the root-name ‘rhodonite’ an appropriate prefix (e.g. ‘zincorhodonite’ or ‘magnesorhodonite’). The historical name ‘fowlerite’ should not be applied to the hypothetical Zn-dominant mineral species because it was earlier applied to a Zn-rich variety of rhodonite.

Table 3. Mineral species belonging to the rhodonite group.

Mineral	Rhodonite	Vittinkiite	Ferrorhodonite
End-member formula	${}^{\text{A}}\text{Ca}^{\text{B}}\text{Mn}_3^{\text{C}}\text{Mn}[\text{Si}_5\text{O}_{15}]$	${}^{\text{A}}\text{Mn}^{\text{B}}\text{Mn}_3^{\text{C}}\text{Mn}[\text{Si}_5\text{O}_{15}]$	${}^{\text{A}}\text{Ca}^{\text{B}}\text{Mn}_3^{\text{C}}\text{Fe}[\text{Si}_5\text{O}_{15}]$
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
a (Å)	6.67–6.70	6.70–6.71	6.677
b (Å)	7.62–7.68	7.62–7.64	7.675
c (Å)	11.78–11.84	11.84–11.86	11.803
α (°)	105.4–105.6	105.6–105.7	105.50
β (°)	92.4–92.5	92.4	92.28
γ (°)	93.9–94.0	94.2–94.3	93.92
V (Å ³)	577–580	579–580	580.4
Z	2	2	2
References	Liebau (1959); Peacor and Niizeki (1963); Peacor <i>et al.</i> (1978); Nelson and Griffen (2005); Leverett <i>et al.</i> (2008)	Ohashi and Finger (1975); Pertlik and Zahiri (1999); Nelson and Griffen (2005); Shchipalkina <i>et al.</i> (2019b)*	Shchipalkina <i>et al.</i> (2017)*

* Holotype specimen

Related minerals

Minerals structurally close to rhodonite-group members are babingtonite, $\text{HCa}_2(\text{Fe},\text{Mn})\text{FeSi}_5\text{O}_{15}$, manganbabingtonite, $\text{HCa}_2(\text{Mn},\text{Fe})\text{FeSi}_5\text{O}_{15}$, marsturite, $\text{HNaCaMn}_3\text{Si}_5\text{O}_{14}(\text{OH})$, lithio-marsturite, $\text{HLiCa}_2\text{Mn}_2\text{Si}_5\text{O}_{15}$, nambulite, $\text{HLiMn}_4\text{Si}_5\text{O}_{15}$, and natronambulite, $\text{H}(\text{Na},\text{Li})(\text{Mn},\text{Ca})_4\text{Si}_5\text{O}_{15}$ (Pasero, 2019). These inosilicates have chains of tetrahedra $\text{Si}_5\text{O}_{14}(\text{OH})$ with the same topology as that of rhodonite-group minerals but differ from them: (1) in motifs formed by metal cations (Nagashima et al., 2014a,b and references therein); and (2) by the presence of hydrogen (the crystal chemical role of hydrogen in these minerals is discussed by Chukanov and Chervonnyi, 2016). This is a reason for considering all these H-bearing inosilicates outside the rhodonite group.

Summary

This report aims at defining the rhodonite group and its constituent mineral species belonging to it.

(1) The rhodonite group contains mineral species having a rhodonite-type structure based on tetrahedral chains with the repeat unit Si_5O_{15} and ribbons formed by edge-sharing polyhedra $M(1)$, $M(2)$, $M(3)$, $M(4)$ and $M(5)$. Their structural formula is $^{VII}M(5)^{VI}M(1)^{VI}M(2)^{VI}M(3)^{VI}M(4)[\text{Si}_5\text{O}_{15}]$; the chemical formula is $^{M(5)}A^{M(1-3)}B_3^{M(4)}C[\text{Si}_5\text{O}_{15}]$. The following dominant (species-defining) constituents are currently known: $A = \text{Ca}$ or Mn^{2+} , $B = \text{Mn}^{2+}$ and $C = \text{Mn}^{2+}$ or Fe^{2+} .

(2) The nomenclature of the members of the rhodonite group is based on occupancy of the M sites.

(3) Rhodonite is redefined as the mineral species having the end-member formula $\text{CaMn}_3\text{Mn}[\text{Si}_5\text{O}_{15}] = \text{CaMn}_4[\text{Si}_5\text{O}_{15}]$.

(4) The root-name 'rhodonite' is applied to rhodonite-group minerals with $M(5) = \text{Ca}$. A prefix is added in accord with the cation which is dominant at $M(4)$ [if $M(4) \neq \text{Mn}$], as in ferrorhodonite $\text{CaMn}_3\text{Fe}[\text{Si}_5\text{O}_{15}]$. Such names could be constructed for potentially new species, e.g. 'magnesorhodonite', $\text{CaMn}_3\text{Mg}[\text{Si}_5\text{O}_{15}]$ or 'zincorhodonite', $\text{CaMn}_3\text{Zn}[\text{Si}_5\text{O}_{15}]$ for the hypothetical members of the group with Mg or Zn as a dominant constituents at the $M(4)$ site.

(5) The root-name 'vittinkiite' is used for rhodonite-group minerals with $M(5) = \text{Mn}^{2+}$. The IMA-approved species vittinkiite (IMA2017-082a) has the ideal formula $\text{MnMn}_3\text{Mn}[\text{Si}_5\text{O}_{15}] = \text{Mn}_5[\text{Si}_5\text{O}_{15}]$. A prefix could be added in agreement with the dominance at $M(4)$ [if $M(4) \neq \text{Mn}$].

(6) Hydrogen-bearing minerals with the babingtonite- and the nambulite/marsturite-type structures are not included in the rhodonite group.

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References

- Aikawa N. (1984) Lamellar structure of rhodonite and pyroxmangite intergrowth. *American Mineralogist*, **69**, 270–276.
- Back M.E. (2018) *Fleischer's Glossary of Mineral Species*. 12th Edition. The Mineralogical Record Inc., Tucson.
- Camac M.D. (1852) Analysis of fowlerite. *American Journal of Science*, **14**, 418–419.
- Chukanov N.V. and Chervonnyi A.D. (2016) *Infrared Spectroscopy of Minerals and Related Compounds*. Springer Verlag, Cham, Switzerland.
- Chukhrov F.V. (editor) (1981) *Minerals. Volume 3. Part 2*. Nedra Publishing, Moscow [in Russian].

- Deer W.A., Howie R.A. and Zussman J. (1978) *Rock-Forming Minerals. V. 24*, John Wiley and Sons Inc., NY.
- Ford W.E. and Bradley W.M. (1913) Pyroxmangite, a new member of the pyroxene group and its alteration product, skemmatite. *American Journal of Science*, **186**, 169–174.
- Germar H. (1819) Ueber die kohlenstoff- und kieselsauren Manganerze des Unterharzes. *Journal für Chemie und Physik*, **26**, 108–120.
- Gossner B. and Bruckl K. (1928) Über strukturelle Beziehungen von Rhodonit zu anderen Silikaten. *Centralblatt für Mineralogie, Geologie und Paläontologie*, **1928**, 316–322.
- Henderson E.P. and Glass J.J. (1936) Pyroxmangite, a new locality: identity of sobralite and pyroxmangite. *American Mineralogist*, **21**, 273–294.
- Hietanen A. (1938) On the petrology of Finnish quartzites. *Bulletin de la Commission Géologique de Finlande*, **122**, 1–119.
- Jasche C.F. (1817) Das Rothmanganerz in der Gegend von Elbingerode am Harz. *Kleine Mineralogische Schriften*, **1**, 1–19.
- Larsen E.S. and Shannon E.V. (1922) Notes on some new rhodonite specimens from Franklin Furnace, New Jersey. *American Mineralogist*, **9**, 149–152.
- Leverett P., Williams P.A. and Hibbs D.E. (2008) Ca-Mg-Fe-rich rhodonite from the Morro da Mina mine, Conselheiro Lafaiete, Minas Gerais, Brasil. *The Mineralogical Record*, **44**, 149–184.
- Liebau F., Hilmer W. and Thilo E. (1956) Ein neuer Kettentyp in der Kristallstruktur des Rhodonits $[(\text{Mn},\text{Ca})\text{SiO}_3]_x$. *Naturwissenschaften*, **43**, 177–178.
- Liebau F., Hilmer W. and Lindemann G. (1959) Über die Kristallstruktur des Rhodonits $(\text{Mn},\text{Ca})\text{SiO}_3$. *Acta Crystallographica*, **12**, 182–187.
- Mamedov H.S. (1958) The crystal structure of rhodonite. *Doklady Akademii Nauk AzSSR*, **14**, 445–450 [in Russian].
- Mikheev V.I. and Dubinina V.N. (1948) Materials to X-ray handbook of minerals. *Zapiski Vsesouznogo Mineralogicheskogo Obshchestva*, **77**, 125–135 [in Russian].
- Mills S.J., Hatert F., Nickel E.H. and Ferraris G. (2009) The standardisation of mineral group hierarchies: application to recent nomenclature proposals. *European Journal of Mineralogy*, **21**, 1073–1080.
- Miyawaki R., Hatert F., Pasero M. and Mills S.J. (2019) NEWSLETTER 49. New minerals and nomenclature modifications approved in 2019. IMA Commission on New Minerals, Nomenclature and Classification (CNMNC). *Mineralogical Magazine*, **83**, 479–483, p. 483.
- Nagashima M., Armbruster T., Kolitsch U. and Pettke T. (2014a) The relation between Li – Na substitution and hydrogen bonding in five-periodic single-chain silicates nambulite and marsturite: a single-crystal X-ray study. *American Mineralogist*, **99**, 1462–1470.
- Nagashima M., Mitani K. and Akasaka M. (2014b) Structural variation of babingtonite depending on cation distribution at the octahedral sites. *Mineralogy and Petrology*, **108**, 287–301.
- Narita H., Koto K. and Morimoto N. (1977) The crystal structures of MnSiO_3 polymorphs (rhodonite- and pyroxmangite-type). *Mineralogical Journal of Sapporo*, **8**, 329–342.
- Nelson W.R. and Griffen D.T. (2005) Crystal chemistry of Zn-rich rhodonite ("fowlerite"). *American Mineralogist*, **90**, 969–983.
- Nordenskiöld A.E. (1863) *Beskrifning öfver de i Finland funna mineralier. Helsingfors*, P. Th. Stolpes förlag (2nd edition). [in Swedish].
- Ohashi Y. and Finger L.W. (1975) Pyroxenoids: a comparison of refined structures of rhodonite and pyroxmangite. *Carnegie Institution of Washington Year Book*, **74**, 564–569.
- Palache C., Berman H. and Frondel C. (1944) *Dana's System of Mineralogy, 7th edition*. John Wiley, NY.
- Pasero M. (2019) The New IMA List of Minerals. <http://cnmnc.main.jp/>
- Peacor D.R. and Buerger M.J. (1962) Determination and refinement of the crystal structure of bustamite, $\text{CaMnSi}_2\text{O}_6$. *Zeitschrift für Kristallographie*, **117**, 331–343.
- Peacor D.R., Essene E.J., Brown P.E. and Winter G.A. (1978) The crystal chemistry and petrogenesis of a magnesian rhodonite. *American Mineralogist*, **63**, 1137–1142.
- Peacor D.R. and Niizeki N. (1963) The redetermination and refinement of the crystal structure of rhodonite. $(\text{Mn},\text{Ca})\text{SiO}_3$. *Zeitschrift für Kristallographie*, **119**, 98–116.

- Pertlik F. and Zehri R. (1999) Rhodonite with a low calcium content: crystal structure determination and crystal chemical calculations. *Monatshefte für Chemie*, **130**, 257–265.
- Perutz M. (1937) 'Iron-rhodonite' (from slag) and pyroxmangite and their relation to rhodonite. *Mineralogical Magazine*, **24**, 573–576.
- Roberts W.L., Campbell T.J. and Rapp G.R. (1992) *Encyclopedia of Minerals*. 2nd Edition, Van Nostrand Reinhold, New York.
- Ross C.S. and Kerr P.F. (1932) The manganese minerals of a vein near Bald Knob, North Carolina. *American Mineralogist*, **17**, 1–18.
- Russel A. (1946) On rhodonite and tephroite from Treburland manganese mine, Alernum, Cornwall and rhodonite from other localities in Cornwall and Devonshire. *Mineralogical Magazine*, **27**, 221–235.
- Shchipalkina N.V., Chukanov N.V., Pekov I.V., Aksenov S.M., McCammon C., Belakovskiy D.I., Britvin S.N., Koshlyakova N.N., Schafer C., Scholz R. and Rastsvetaeva R.K. (2017) Ferrorhodonite $\text{CaMn}_3\text{Fe}[\text{Si}_5\text{O}_{15}]$, a new mineral species from Broken Hill, New South Wales, Australia. *Physics and Chemistry of Minerals*, **44**, 323–334.
- Shchipalkina N.V., Pekov I.V., Ksenofontov D.A., Chukanov N.V., Belakovskiy D.I., and Koshlyakova N.N. (2019a) Dalnegorskite, $\text{Ca}_5\text{Mn}(\text{Si}_3\text{O}_9)_2$, a new pyroxenoid of the bustamite structure type, a rock-forming mineral of calcic skarns of the Dalnegorskoe boron deposit (Primorskiy Krai, Russia). *Zapiski Rossiiskogo Mineralogicheskogo Obshchestva*, **148**, 61–75 [in Russian].
- Shchipalkina N.V., Pekov I.V., Chukanov N.V., Zubkova N.V., Belakovskiy D.I., Britvin S.N. and Koshlyakova N.N. (2019b) Vittinkiite, IMA 2017-082a. CNMNC Newsletter No. 51. *Mineralogical Magazine*, **83**, doi: 10.1180/mgm.2019.58.
- Shepard C.U. (1832) Sketch of the mineralogy and geology of the counties of Orange, N.Y., and Sussex, N.J. *American Journal of Science*, **21**, 321–334.
- Sundius N. (1930) Iron-rhodonite from Tuna Hästberg. *Geologiska Föreningen i Stockholm Förhandlingar*, **52**, 403–406.
- Sundius N. (1931) On the triclinic manganiferous pyroxenes. *American Mineralogist*, **16**, 411–429, 488–518.
- Suzaki Y. (1963) Pyroxmangite, rhodonite and bustamite series minerals. *Geoscience Magazine*, **14**, 72–87 [in Japanese with English abstract]