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Rhodonite with a Low Calcium Content: Crystal Structure Determination and Crystal Chemical Calculations

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Summary. Rhodonite from St. Salvator, Carinthia, Austria, with low calcium content and the formula $(Mn_{4.60}Ca_{0.18}Fe_{0.12}Mg_{0.11})$ $(Si_{4.93}Al_{0.07})O_{15}$ is characterized by the cell constants $a = 7.638(2)$, $b = 11.862(4)$, $c = 6.701(2)$ Å, $\alpha = 92.40(3)$, $\beta = 94.23(3)$, $\gamma = 105.65(3)°$; space group $C_i^1 - P\bar{1}$, $Z = 2$. A refinement of the structure afforded an R value of 0.033 for 3651 observed X-ray data ($F_o > 4\sigma(F_o)$) and 237 variable parameters. The atomic arrangement exhibits a typical inosilicate structure in which $(SiO_3)_5$ chains are combined *via* MeO_x polyhedra with $x = 6$ or 7 to a framework. The mean $\langle Me\text{-}O\rangle$ distances, the sum of bond valences for the *Me* positions, and the volumina for the MeO_x *Voronoi* polyhedra are in accordance with the occupation of the individual atom positions determined by calculations from X-ray intensities. The coordination and deformation of the single MeO_x polyhedra are characteristic for the structure type and not the result of substitutions of these *Me* positions by atoms with different ionic radii.

Keywords. Rhodonite; Inosilicate; Crystal structure; Crystal chemistry; Bond valences.

Rhodonit mit geringem Kalziumgehalt: Kristallstrukturbestimmung und kristallchemische Berechnungen

Zusammenfassung. Rhodonit aus St. Salvator, Kärnten, Österreich, mit geringem Kalziumgehalt und der Formel $(Mn_{4.60}Ca_{0.18}Fe_{0.12}Mg_{0.11})$ $(Si_{4.93}Al_{0.07})O_{15}$ wird durch folgende Zellkonstanten charakterisiert: $a = 7.638(2)$, $b = 11.862(4)$, $c = 6.701(2)$ Å, $\alpha = 92.40(3)$, $\beta = 94.23(3)$, $\gamma = 105.65(3)°$; Raumgruppe C_i^1-$P\bar{1}$, $Z = 2$. Eine Verfeinerung der Struktur ergab einen R-Wert von 0.033 für 3651 beobachtete Röntgendaten ($F_o > 4\sigma(F_o)$) und 237 variable Parameter. Die Andordnung der Atome stellt eine typische Inosilikatstruktur dar, in der $(SiO_3)_5$-Ketten über MeO_x-Polyeder mit $x = 6$ oder 7 zu einem Gerüst verknüpft sind. Die mittleren $\langle Me\text{-}O\rangle$-Abstände, die Summe der Bindungsstärken für die *Me*-Positionen und die Volumina der MeO_x-*Voronoi*-Polyeder stehen in Übereinstimmung mit der Besetzung der individuellen Atompositionen, berechnet anhand von Röntgenintensitäten. Die Koordination und Deformation der einzelnen MeO_x-Polyeder sind ein Charakteristikum des Strukturtyps und nicht das Ergebnis von Substitutionen dieser *Me*-Positionen durch Atome mit unterschiedlichen Ionenradien.

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Introduction

Preliminary crystal structure determinations for the mineral rhodonite have been reported by [1–3]. The structural units described in these articles are more or less identic; the stacking of the (Si_5O_{15}) chains and MeO_x polyhedra differs in part. Nevertheless, these proposed atomic arrangements have been the basis for a redetermination and structure refinement [4]. The setting of the unit cell as well as the coordinates and the signation of the single atoms given in this paper, are followed throughout the present article. A compilation of lattice constants for rhodonites, natural or synthetic, from the literature is given in Table 1. With one exception (rhodonite from Xanthi, Northern Greece [11]), a structure determination exists in all cases.

Substitutions of manganese atoms not only by magnesium but also by calcium and iron are very common in the atomic arrangement of rhodonite. One analysis of a rhodonite variety, fowlerite, is remarkable for its pronounced content of zinc [12]. For the synthetic compounds $Mn_5Si_5O_{15}$ [6] and $(Mn_{3.10}Mg_{1.90})Si_5O_{15}$ [9] well done structure determinations exist, and chemical analyses of natural rhodonites show a variability of this mineral more or less within these limiting compositions.

The distribution of magnesium over the nontetrahedral cation positions in the structure of a magnesian rhodonite [8] shows that the positions *Me*(1) to *Me*(3) have nearly equal magnesium occupancies of not more than 0.1 and that the ordering of magnesium in *Me*(4) is near the maximum to be expected for naturally occuring rhodonite. Further investigations by single crystal X-ray data [5] demonstrate that the positions *Me*(1) to *Me*(3) are preferentially occupied by manganese and magnesium, iron prefers *Me*(4), and calcium is ordered in position *Me*(5). The more or less inexact conclusion is that *Me*(4) is preferred by magnesium and *Me*(5) by calcium atoms. In Table 2, site occupancy values for the non-tetrahedral cation positions from literature, refined by X-ray work are compiled. Not mentioned in this table are Refs. [7] and [4], in which only qualitative assumptions about occupancy factors are given.

On the basis of an interpretation of *Mössbauer* spectra, it has been concluded that iron occupies the positions *Me*(1) to *Me*(4) with a slight preference for site *Me*(4) [17]. The interconnection of the single MeO_x polyhedra in the rhodonite type structure together with the notation of the single atoms (polyhedra) is given in Fig. 1.

The description of a calcium-poor rhodonite from Xanthi (Greece) with the formula $(Mn_{4.56}Mg_{0.22}Ca_{0.15}Fe_{0.03})Si_{5.02}O_{15}$ [11] draws attention to a semiquantitative rhodonite analysis [13]. Chemical analyses of this special rhodonite from St. Salvator (Carinthia) were recalculated to the formula $(Mn_{4.60}Ca_{0.18}Fe_{0.12}Mg_{0.11})(Si_{4.93}Al_{0.07})O_{15}$ [4]. These analyses confirm the assumption that the rhodonite crystals from this occurrence represent a species with the lowest substitution of manganese atoms by iron or alkaline earth atoms ever found in nature. Preliminary articles about analyses, chemical composition, and mineralogical environment have been published [14–16].

The crystals of the title compound were chosen for a structure refinement and calculations of geometric features for the following reasons:

Table 1. Lattice constants (Å, °) and volumina (Å^3) of unit cells determined by X-ray work as well as chemical composition of natural (*nat*) and synthetic (*syn*) rhodonites; unit cell setting according to *Peacor* and *Niizeki* [4] in some cases transformed by the authors; e.s.d.s in parentheses

	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**
a	7.6816(2)	7.618(1)	7.616(3)	7.6816(2)	7.633(3)	7.511(3)	7.545(2)	7.626(1)	7.638(2)
b	11.8180(4)	11.812(1)	11.851(5)	11.8180(4)	11.796(3)	11.741(3)	11.782(3)	11.844(2)	11.862(4)
c	6.7073(4)	6.685(1)	6.707(2)	6.7073(4)	6.695(3)	6.641(3)	6.663(2)	6.702(1)	6.701(2)
α	92.355(6)	92.43(1)	92.55(10)	92.355(6)	92.43(4)	92.90(2)	92.69(2)	92.44(1)	92.40(3)
β	93.948(5)	94.23(1)	94.35(10)	93.948(5)	93.99(4)	94.26(2)	94.32(3)	94.28(2)	94.23(3)
γ	105.665(4)	105.67(1)	105.67(10)	105.665(4)	105.77(4)	105.68(2)	105.71(1)	105.70(1)	105.65(3)
V	583.71	576.43	579.75	583.8	577.54	560.79	567.16	579.89	581.82

A: $(Mn_{4.01}Ca_{0.81}Mg_{0.16}Fe_{0.15})(Si_{4.98}Al_{0.02})O_{15.12}$, *nat* [4]; **B**: $(Mn_{4.05}Fe_{0.35}Mg_{0.30}Ca_{0.25})Si_5O_{15}$, *nat* [5]; **C**: $Mn_5Si_5O_{15}$, *syn* [6]; **D**: $Mn_4CaSi_5O_{15}$, *nat* [7]; **E**: $(Mn_{3.73}Mg_{0.73}Ca_{0.51}Fe_{0.03})Si_5O_{15}$, *nat* [8]; **F**: $(Mn_{3.10}Mg_{1.90})Si_5O_{15}$, *syn* [9]; **G**: $(Mn_{3.425}Mg_{1.575})Si_5O_{15}$, *syn* [10]; **H**: $(Mn_{4.56}Mg_{0.22}Ca_{0.15}Fe_{0.03})Si_{5.02}O_{15}$, *nat* [11]; **I**: $(Mn_{4.60}Ca_{0.18}Fe_{0.12}Mg_{0.11})(Si_{4.93}Al_{0.07})O_{15}$, *nat*; this work

Table 2. Refined site occupancies for the nontetrahedral cation positions in rhodonite type structures with different chemical compositions; e.s.d.s in parentheses

	$(Mn_{4.05}Fe_{0.35}Mg_{0.30}Ca_{0.25})Si_5O_{15}$ [5]		$(Mn_{3.73}Mg_{0.73}Ca_{0.51}Fe_{0.03})Si_5O_{15}$ [8]		$(Mn_{3.425}Mg_{1.575})Si_5O_{15}$[10]		this work	
	Mn (%)	Mg (%)	Mn (%)	Mg (%)	Mn (%)	Mg (%)	Mn (%)	^{2}
Me(1)	93	7	89(1)	11(1)	69.6	30.4	95.4(8)	4.6(8)
Me(2)	93	7	86(1)	14(1)	74.6	25.4	99.4(8)	0.6(8)
Me(3)	91	9	86(1)	14(1)	63.4	36.6	94.9(8)	5.1(8)
Me(4)	78	22	53(1)	47(1)	48.1	51.9	82.8(8)	17.2(8)
Me(5)	83	17	40(1)	60(1)^1	86.8	13.2	78.6(8)	21.4(8)

^{1} Calculated for Ca atoms; ^{2} occupation factors calculated for a mean scattering function (Ca+Mg)/2(%)

Fig. 1. Interconnection of the MeO_x polyhedra in rhodonite to chains *via* common O atom edges in a projection parallel to [001]; the polyhedra favoured for substitutions by alkaline earth atoms *Me*(4) and *Me*(5) are branched to the main chain formed by the interconnection of *Me*(1) to *Me*(3)

A: A consequence of the chemical composition of the investigated rhodonite with the formula $(Mn_{4.60}Ca_{0.18}Fe_{0.12}Mg_{0.11})\ (Si_{4.93}Al_{0.07})O_{15}$ must be that none of the five crystallographic different *Me* positions is occupied by more than ~50 atom-% by cations like magnesium, calcium, or iron. The differences between the scattering functions of the atoms manganese and magnesium or calcium are big enough to give representation of the substitution of special atomic positions by these elements in the title compound.

B: On the basis of crystal chemical calculations, *e.g.*, bond valences, mean ⟨*Me*-O⟩ distances and volumina of the *Voronoi* polyhedra for rhodonite type structures determined up to now, the authors tried to find out whether the deformation of the nontetrahedral MeO_x polyhedra is forced by a substitution (Mn by Mg, Ca, Fe) or is a peculiarity of the structure type rhodonite.

Results and Discussion

From the compilation of lattice constants and volumina of the unit cells for rhodonites from different occurences, no clear correlation between these values and the chemical composition is deducible. This fact is the expression of substitutions in different proportions and in a wide range for the manganese atoms by atoms like magnesium, calcium, and iron.

The variations in the occupancies of the different nontetrahedral cation positions confirmed for the title compound that it is poor in earth alkaline atoms and that a great preference by the atoms magnesium and calcium for the positions *Me*(4) and *Me*(5) exists. The structure refinement shows that only a model with more or less the same density of electrons for positions *Me*(4) and *Me*(5), significantly lower than for the positions *Me*(1) to *Me*(3), fits well with the

Table 3. Bond valences for rhodonite (V_{ij}) according to *Brese* and *O'Keeffe* [20] calculated for the five *Me* positions; structure data from literature with references in brackets; **A** to **I**: cf. Table 1; the parameter R_{ij} in equation $V_i = \exp(R_i\text{-}d_i)/0.37)$ is 1.790 for all *Me* positions (value for Mn–O); in ⟨⟩ the mean values for each *Me*-O$_x$ polyhedron is given; the coordination number for *Me*(1) to *Me*(4) is six, for *Me*(5) it is seven

	A [4]		**B** [5]		**C** [6]		**D** [7]		**E** [8]		**F** [9]		**G** [10]		**I**	
	V_i		V_i		V_i		V_i		V_i		V_i		V_i		V_i	
Me(1)	1.93	⟨2.22⟩	1.95	⟨2.21⟩	1.92	⟨2.22⟩	1.92	⟨2.22⟩	1.92	⟨2.22⟩	2.10	⟨2.19⟩	2.02	⟨2.20⟩	1.90	⟨2.22⟩
Me(2)	1.96	⟨2.22⟩	1.88	⟨2.23⟩	1.82	⟨2.24⟩	1.96	⟨2.21⟩	1.92	⟨2.22⟩	2.01	⟨2.21⟩	1.93	⟨2.22⟩	1.83	⟨2.24⟩
Me(3)	1.83	⟨2.23⟩	1.95	⟨2.22⟩	1.91	⟨2.22⟩	1.92	⟨2.23⟩	1.96	⟨2.22⟩	2.14	⟨2.18⟩	2.07	⟨2.20⟩	1.91	⟨2.22⟩
Me(4)	2.08	⟨2.27⟩	2.14	⟨2.25⟩	1.99	⟨2.27⟩	2.08	⟨2.27⟩	2.25	⟨2.23⟩	2.40	⟨2.19⟩	2.34	⟨2.21⟩	2.05	⟨2.26⟩
Me(5)	1.39	⟨2.42⟩	1.68	⟨2.40⟩	1.80	⟨2.40⟩	1.39	⟨2.42⟩	1.50	⟨2.41⟩	1.79	⟨2.36⟩	1.84	⟨2.37⟩	1.69	⟨2.40⟩

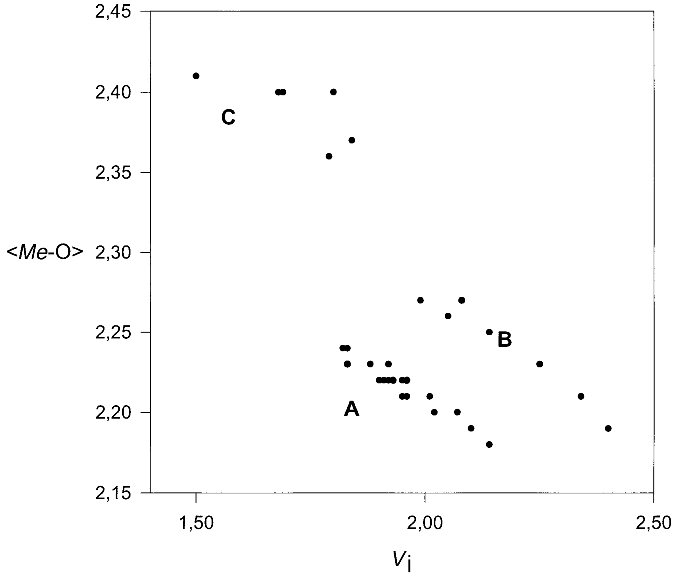

Fig. 2. Bond valences and mean $\langle Me\text{-O}\rangle$ distances calculated from eight structure analyses for rhodonite; the V_i values for the *Me* atoms (centre of the coordination polyhedron) are plotted against the mean $\langle Me\text{-O}\rangle$ values; the areas for the polyhedra are: $A = Me(1)$ to $Me(3)$, $B = Me(4)$, $C = Me(5)$

measured X-ray intensities. These atom positions are remarkable because they are irregularly coordinated by oxygen atoms with pronounced differences in the single *Me*-O distances and the shape of the coordination polyhedra. The polyhedra under discussion are branched to the main edge sharing MeO_6 octahedra chain as shown in Fig. 1. They have doubtless the greatest mobility within the whole structure, allowing substitution of the manganese atoms by atoms with different ionic radii, *e.g.*, magnesium and calcium, in a wide range.

In Table 3, the bond valences for the *Me* positions and the mean $\langle Me\text{-O}\rangle$ distances for rhodonite structures are listed. The two calculated values for each atom position are plotted against each other in Fig. 2. There is no doubt that the

Table 4. Summary of data for X-ray measurements and structure refinement on rhodonite

Measured reflections ($\pm h$, $\pm k$, $\pm l$)	8146
Range of data	$4° < 2\Theta < 75°$
Internal R (F_0^2)	0.104
Unique data set	6159
Data with $F_o > 4\sigma F_o$	3651
Number of variables	237
R (based on $F_o > 4\sigma F_o$)	0.033
Absorption correction	Ψ-scan data
Transmission factors (%)	0.06–0.11
Final difference *Fourier* map (e/Å^3)	$+0.68$ to -1.00

Stoe four circle diffractometer AED2, graphite monochromatized Mo-radiation

Table 5. Structural parameters of rhodonite with e.s.d.s in parentheses; the anisotropic displacement factor is defined by $\exp(-2\pi^2 \sum_i \sum_j U_{ij}\, h_i h_j\, a_i^* a_j^*)$ ($\mathrm{\AA}^2 \times 10^4$); all atoms at position 2i in space group $\mathrm{C}_{\mathrm{i}}^1 - \mathrm{P}\bar{1}$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Me(1)	0.88022(5)	0.85202(3)	0.97098(5)	165(2)	185(2)	162(2)	−1(1)	21(1)	42(1)
Me(2)	0.68377(5)	0.55436(3)	0.87211(5)	179(2)	173(2)	184(2)	1(1)	18(1)	41(1)
Me(3)	0.48965(5)	0.26948(3)	0.81294(6)	170(2)	175(2)	172(2)	−8(1)	15(1)	39(1)
Me(4)	0.29693(6)	0.97311(3)	0.79390(6)	229(2)	168(2)	221(2)	21(1)	65(1)	61(1)
Me(5)	0.03934(5)	0.70205(4)	0.64997(6)	175(2)	246(2)	223(2)	5(1)	4(1)	31(1)
Si(1)	0.2200(1)	0.1248(1)	0.4953(1)	161(3)	158(3)	150(3)	0(2)	15(2)	38(2)
Si(2)	0.2612(1)	0.4680(1)	0.6370(1)	165(3)	151(3)	157(3)	1(2)	10(2)	35(2)
Si(3)	0.4543(1)	0.7355(1)	0.7040(1)	160(3)	152(3)	163(3)	7(2)	14(2)	35(2)
Si(4)	0.7437(1)	0.0887(1)	0.7546(1)	170(3)	156(3)	162(3)	−4(2)	6(2)	49(2)
Si(5)	0.9229(1)	0.3454(1)	0.8473(1)	145(3)	153(3)	162(3)	5(2)	17(2)	35(2)
O(1)	0.9564(2)	0.6790(2)	0.9583(3)	187(7)	191(7)	189(8)	9(6)	2(6)	52(6)
O(2)	0.5967(2)	0.7312(2)	0.8924(3)	175(7)	210(7)	179(7)	12(6)	19(6)	51(6)
O(3)	0.7475(2)	0.3886(2)	0.8915(3)	147(7)	192(7)	226(8)	−8(6)	15(6)	48(6)
O(4)	0.4004(2)	0.4357(2)	0.8048(3)	182(7)	188(7)	192(8)	14(6)	12(6)	51(6)
O(5)	0.5469(2)	0.0958(2)	0.8093(3)	189(7)	202(8)	236(8)	2(6)	24(6)	59(6)
O(6)	0.2000(2)	0.1316(2)	0.7330(3)	179(7)	207(7)	166(7)	−1(6)	23(6)	53(6)
O(7)	0.3113(2)	0.8095(2)	0.7416(3)	222(8)	220(8)	223(8)	4(6)	20(6)	85(6)
O(8)	0.9346(2)	0.8546(1)	0.6612(3)	199(7)	190(7)	175(7)	12(6)	8(6)	65(6)
O(9)	0.2565(2)	−0.0048(1)	0.4462(3)	213(7)	165(7)	177(8)	−18(6)	−2(6)	58(6)
O(10)	0.7638(3)	0.5960(2)	0.5818(3)	320(9)	214(8)	170(8)	−14(6)	2(7)	85(7)
O(11)	0.8432(2)	0.0399(2)	0.9426(3)	183(7)	198(7)	181(8)	3(6)	10(6)	51(6)
O(12)	0.5767(2)	0.7808(1)	0.5169(3)	174(7)	188(7)	182(7)	20(6)	24(6)	17(6)
O(13)	0.3175(2)	0.6095(2)	0.6185(3)	230(8)	157(7)	237(9)	14(6)	−20(6)	19(6)
O(14)	0.0525(2)	0.4381(2)	0.7105(3)	172(7)	256(8)	272(9)	85(7)	37(7)	45(6)
O(15)	0.8597(2)	0.2222(1)	0.7018(3)	225(8)	154(7)	201(8)	−13(6)	18(6)	34(6)

points for the polyhedra *Me*(1) to *Me*(3), *Me*(4) and *Me*(5) are located at three quite different areas A, B, and C strongly isolated from each other. This splitting of the polyhedra is common for rhodonite structures without any remarkable trend for different chemical compositions or occupations of the *Me* positions by different elements. The authors' interpretation of this feature is that there is no influence of composition on the above mentioned parameters and the deformation of the polyhedra *Me*(4) and *Me*(5). This deformation is typical for the structure type, may be an effect of stacking for the single polyhedra, and not forced by variations in the chemical composition.

Worth mentioning are also the volumina of the *Voronoi* polyhedra for the *Me* positions with equal radii for all atoms. These values are generally within the range of 11.0 to 11.5 $Å^3$ for the positions *Me*(1) to *Me*(4), but significantly greater for *Me*(5) (12.3 $Å^3$).

Experimental

The chemical compositions of the investigated crystals were determined by electron microprobe analyses. A detailed description of the analytical procedure is given in Ref. [15].

Crystals of rhodonite from St. Salvator, Carinthia, Austria, suitable for X-ray work, were checked by classical film methods. The start parameters for structure refinement were taken from Ref. [4]. Informations about the collection of X-ray data and structure calculations are compiled in Table 4, the atomic parameters in Table 5. Structure refinements were performed with the program system SHELX-76[18] using neutral scattering functions [19]. F_o-F_c lists are deposited at the *Institut für Mineralogie und Kristallographie*, University of Vienna, Austria.

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