

A calcium-poor rhodonite from Xanthi (N. Greece)

ELIAS S. SAPOUNTZIS AND GEORGE CHRISTOFIDES

Laboratory of Systematic Mineralogy and Petrography, University of Thessaloniki, Thessaloniki, Greece

ABSTRACT. A Ca-poor rhodonite (CaO 1.31 wt. %), found in a quartz vein cutting manganese ore bodies, north of the Xanthi plutonic complex (northeastern Greece) was studied. Microprobe analyses with optical and physical properties are given. The cell dimensions, obtained by least squares calculation from direct θ value measurements on a Philips PW1100 single-crystal diffractometer are $a = 7.626$, $b = 11.844$, $c = 6.702$ Å, $\alpha = 92.44^\circ$, $\beta = 94.28^\circ$, $\gamma = 105.70^\circ$, $V = 579.89$ Å³, $Z = 10$, and space group $P\bar{1}$.

RHODONITE (Mn,Ca,Fe,Mg)SiO₃ is an important manganese mineral and occurs in Mn-bearing ore bodies as a result of metamorphic and commonly associated metasomatic activity. It also occurs as a rock-forming mineral of contact-metamorphosed calc-silicate rocks.

It is well known that rhodonite always contains in varying amounts Ca²⁺, Fe²⁺, and Mg²⁺ substituted for Mn²⁺. The changes of mineralogical properties, due to cationic substitution, in rhodonite and related minerals have been well studied by Sundius (1931) and Tilley (1937), and particularly with respect to Ca content by Momoi (1964) with sixteen new analyses and a review of published data.

The Ca content (1.31 wt. %) of the rhodonite from Xanthi area (northeastern Greece) is lower than the values so far cited for natural rhodonites. For this reason, and because this is the first description of rhodonite occurrence in Greece, we think that the study of this mineral is not without interest.

Chemical data. Rhodonite never occurs as pure MnSiO₃ but always contains a certain amount of divalent cations such as Ca²⁺, Fe²⁺, and Mg²⁺ in substitution for Mn²⁺. The maximum contents of these elements reported in the literature for natural rhodonites are about 20, 26, and 15 mol. % as CaSiO₃, FeSiO₃, and MgSiO₃ respectively.

Several electron probe analyses were performed on rhodonite crystals from Gorgona village, Xanthi, and the results, together with the number of ions calculated on the basis of eighteen oxygens,

are presented in Table I. The analyses were carried out partly in the Institute of Petrology, University of Vienna, Austria and partly in the Department of Geology, University of Reading, England. Total Fe and Mn were calculated as Fe²⁺ and Mn²⁺ respectively. However, ferric iron and trivalent manganese contents are usually low for rhodonites.

In his important mineralogical study of rhodonites from Japan, Momoi (1964), discussed the chemical characteristics of rhodonites with special reference to their Ca content because this element plays an important role in the rhodonite structure. He found that with increasing calcium content, iron and magnesium contents increase while manganese content decreases. The chemical data obtained

TABLE I. *Chemical analyses of rhodonites*

	1	2	3	4	5	6*
SiO ₂	46.91	46.36	46.44	46.12	46.62	46.49
TiO ₂	0.00	0.02	0.02	0.01	0.04	0.02
Al ₂ O ₃	0.00	0.02	0.00	0.00	0.03	0.01
FeO†	0.29	0.26	0.23	0.34	0.28	0.28
MnO	50.23	49.90	49.72	49.76	49.84	49.89
MgO	1.41	1.26	1.45	1.41	1.31	1.37
CaO	1.24	1.36	1.28	1.37	1.30	1.31
Na ₂ O	0.00	0.00	0.03	0.02	0.00	0.01
K ₂ O	0.04	0.03	0.04	0.03	0.03	0.03
Total	100.12	99.21	99.21	99.06	99.45	99.41
Numbers of ions on the basis of 18 oxygens						
Si	6.027	6.018	6.021	6.002	6.029	6.019
Ti	0.000	0.002	0.002	0.001	0.004	0.002
Al	0.000	0.003	0.000	0.000	0.005	0.002
Fe ²⁺	0.031	0.028	0.025	0.037	0.030	0.030
Mn	5.468	5.488	5.461	5.486	5.460	5.473
Mg	0.270	0.244	0.280	0.273	0.252	0.264
Ca	0.171	0.189	0.178	0.191	0.180	0.182
Na	0.000	0.000	0.008	0.005	0.000	0.003
K	0.007	0.005	0.007	0.005	0.005	0.005
Molecular ratio						
MnSiO ₃	92.05	92.25	91.87	91.63	92.20	92.00
CaSiO ₃	2.88	3.18	3.00	3.19	3.04	3.06
MgSiO ₃	4.55	4.10	4.71	4.56	4.25	4.44
FeSiO ₃	0.52	0.47	0.42	0.62	0.51	0.50

*Mean analysis of 1 to 5.

† Total Fe as FeO.

from the Gorgona rhodonite are in accord with Momoi's CaSiO_3 - MnSiO_3 , CaSiO_3 - MgSiO_3 , and CaSiO_3 - FeSiO_3 diagrams (fig. 1). In the first diagram they occur either on the boundary separating rhodonites from pyroxmangites or just in the rhodonite field (low Ca, high Mn content). In the second diagram they fall between line Ca:Mg = 1:1 and line Ca:Mg = 1:2 (low Ca, relatively high Mg content). In the third diagram they occur very close to the intersection of the marginal line and the CaSiO_3 axis but in the field of rhodonites (low Ca, low Fe content).

The formula given by Liebau *et al.* (1959) for rhodonites is $(\text{Mn},\text{Mg})_{1-x}\text{Ca}_x\text{SiO}_3$ with $0 < x < 0.2$ while the mean composition of over fifty analysed rhodonites plotted by Momoi (1964) on a CaSiO_3 - MnSiO_3 - $(\text{Fe},\text{Mg})\text{SiO}_3$ diagram appears to be $\text{Mn}_{0.8}(\text{Fe},\text{Mg})_{0.1}\text{Ca}_{0.1}\text{SiO}_3$.

In analyses of natural rhodonites so far reported, one of the most manganese-rich (Deer *et al.*, 1978, Table 61) contains 2.25% CaO (0.05 atoms per formula unit), while, as far as we know, the most Ca-poor rhodonite has 1.53% CaO (Momoi, 1964).

The Ca content of the Gorgona rhodonite, as can be seen from Table I, ranges from 1.24 to 1.36 (mean value 1.31 wt. %). These values are lower than the above ones, and at least to our knowledge, are unique in the literature records.

Description, physical and optical properties. North of the city of Xanthi (N. Greece) there occur zones of contact metamorphism, formed between calcareous and intrusive rocks (Christofides, 1977). In one of these contact zones, very close to Gorgona village, a suite of manganese minerals was found which contains the Ca-poor rhodonite.

The samples collected consist mainly of rhodonite (about 40%), quartz, spessartine, and a black secondary oxidation product found with most Mn-rich assemblages. The rhodonite appears with characteristic rose-red to pink colour. Tabular, || to (001), crystals up to 0.8 cm in length were observed, usually cleavable to compact. Lustre is vitreous, hardness about 6, and specific gravity 3.68.

In thin section the mineral occurs as colourless to faint pink, stubby, subhedral to euhedral crystals ranging from 2 to 8 mm in length. Pleochroism is weak with α and γ yellowish pink to pale yellowish pink and β faint pink. It has two distinct cleavages parallel to (100) and (010) along which occur sometimes altered minerals, carbonates and oxides. Lamellar twinning with composition plane parallel to (010) is relatively common.

The optical data of the mineral were obtained on suitable thin sections using the U-stage. All crystals examined were biaxial positive with $2V_\gamma =$

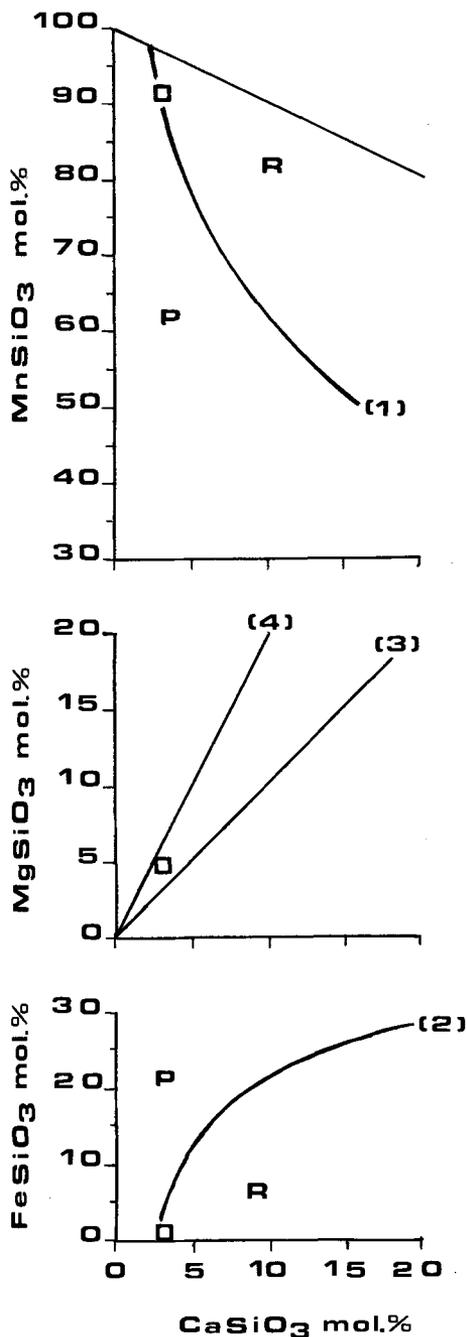


FIG. 1. Variation of MnSiO_3 , MgSiO_3 and FeSiO_3 relative to CaSiO_3 for rhodonites (after Momoi, 1964). \square = area of plotted analyses. (1) and (2) show the compositional boundary between rhodonite (R) and pyroxmangite (P). (3) and (4) show Ca:Mg = 1:1 and 1:2 respectively.

63–66° and $r < v$. The extinction $\beta:y$ ranges between 19 and 22° while $\gamma:z$ is $\approx 27^\circ$.

The refractive indices α and β were determined by the immersion method and the Becke line and were found to be 1.734 ± 0.002 and 1.740 ± 0.002 respectively. The accuracy of the refractive indices of the standard immersion oils was checked with a refractometer.

A comparison between these optical properties and those of the rhodonites referred to in the literature shows that the $2V_\gamma$ values of the Gorgona rhodonite are among the lowest, while the values of the refractive indices are among the highest. Correlating this with the low Ca content of this mineral we can see that the optical properties determined here confirm the relationships pre-

viously noted (Hey, 1929; Momoi, 1964), namely that with decreasing Ca (and Mg) contents, the refractive indices increase while the $2V_\gamma$ values decrease.

X-ray data. The basic features of the crystal structure of rhodonite $(\text{Mn,Fe,Ca,Mg})\text{SiO}_3$ were determined by Liebau *et al.* (1959) and a more detailed version was given by Peacor and Niizeki (1963). Recently, Ohashi and Finger (1975) studied the crystal structures of rhodonite and pyroxmangite and discussed the cation distributions. The structure of rhodonite contains chains of SiO_4 tetrahedra with a repeat unit of five tetrahedra. Layers of chains alternate between planes of close-packed oxygen ions with layers of co-ordinated cations. There are five equally populated cation positions on rhodonite, four M_1, M_2, M_3, M_4 have sixfold co-ordination and the fifth, M_5 has an irregular sevenfold co-ordination. From the work of Peacor and Niizeki (1963) it is presumed that Ca prefers the M_5 site while the other metallic cations are distributed among the other sites. In low-Ca rhodonite Mn^{2+} will occupy M_5 sites also. Mössbauer study (Dickson, 1975) indicates that in an iron-rich rhodonite Fe atoms prefer the M_4 to the other sites. The M_4 site is very distorted and possibly can accommodate Ca as well.

Because of its triclinic symmetry, the unit cell for rhodonite is not uniquely defined and several different unit-cell settings have been used. In this study, however, the $P\bar{1}$ reduced unit cell is used.

From a suitable specimen a well-developed transparent single crystal was selected. After centering the specimen on a computer-controlled Philips PW1100 four circle single-crystal diffractometer using Mo- $K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) and a graphite monochromator, the cell constants were determined using the peak hunting routine of the instrument. To obtain greater accuracy the θ angles of 120 strong reflections with large θ values were directly measured on the diffractometer and subsequently used in the least-squares program CSD 104 (Venetopoulos, 1977) for further treatment. The final values obtained are given in Table II

TABLE II. Cell dimensions ($P\bar{1}$ cell) of rhodonites

	Present study	(1)	(2)	(3)
$a \text{ \AA}$	7.626(1)	7.545(2)	7.682	7.614
$b \text{ \AA}$	11.844(2)	11.782(3)	11.818	11.848
$c \text{ \AA}$	6.702(1)	6.663(2)	6.707	6.699
α°	92.44(1)	92.69	92.355	92.39
β°	94.28(2)	94.32(3)	93.948	94.24
γ°	105.70(1)	105.71(2)	105.665	105.41

(1) Murakami and Takeuchi (1979), (2) Peacor and Niizeki (1963), (3) J.C.P.D.S File No. 25-1369.

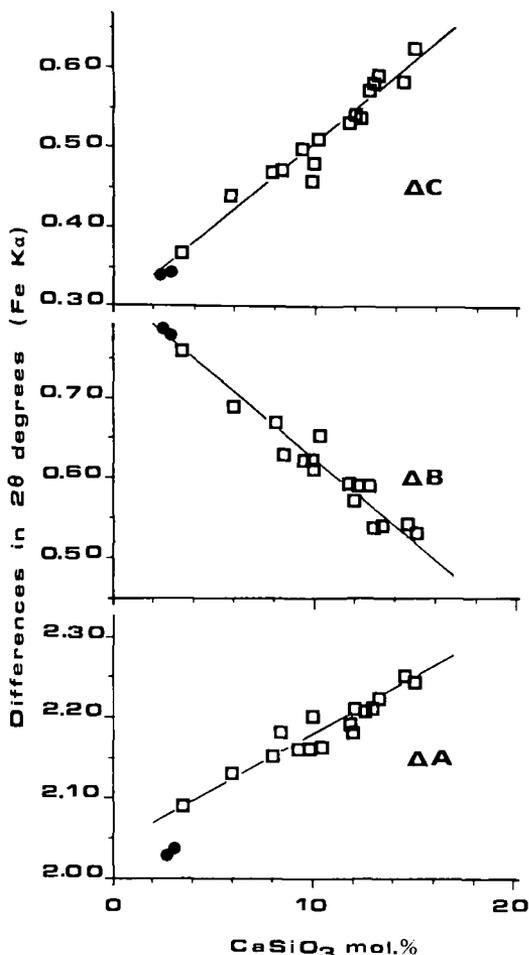


FIG. 2. Relation between Ca content and the angle differences ΔA , ΔB , and ΔC in rhodonites (after Momoi, 1964). \square = Momoi's samples, \bullet = present study (samples 1 and 4).

together with those of Peacor and Niizeki (1963), Murakami and Takeuchi (1979), for comparison. The unit cell dimensions of the studied rhodonite fall within the range of cell constants for natural and synthetic specimens reported in the literature.

The relationship between the powder patterns and chemical compositions of rhodonites was investigated by Momoi (1964). To compare the powder patterns he selected six distinct reflections at $d = 3.56, 3.34, 3.14, 3.09, 2.97,$ and 2.93 \AA and measured the differences between diffraction angles ($2\theta, \text{Fe-K}\alpha$) for successive pairs ($\Delta A, \Delta B,$ and ΔC). The differences show a linear correlation with Ca content in rhodonite, i.e. with increasing Ca content ΔA and ΔC increase and simultaneously ΔB decreases.

Measurements of the differences in diffraction angles of two samples of the studied rhodonite from XRD traces, gave values for $\Delta A = 2.03$ and 2.04° , for $\Delta B = 0.76$ and 0.79° and for $\Delta C = 0.36$ and 0.39° respectively. It is shown in fig. 2 that the present Ca-poor rhodonite conforms to the linear relation found by Momoi.

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