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Crystal chemistry of natural Mn^{3+}-bearing calderite-andradite garnets from Otjosondu, SWA/Namibia

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Dedicated to Theo Hahn on the occasion of his 60th birthday

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Abstract. Five calderite-andradite garnets from Otjosondu, Namibia, were studied chemically and by optical absorption and Mössbauer spectroscopy. The combined results of chemical analyses and Mössbauer and optical absorption spectroscopy make small amounts of octahedral Mn^{3+} likely, corresponding to up to 4.8 mol% of the blythite endmember, $Mn_3^{2+}Mn_2^{3+}Si_3O_{12}$.

Introduction

Natural garnets frequently contain divalent manganese in the eightfold coordinated X-position: Spessartines and spessartine-almandine solid solutions are widespread in metamorphic rocks, and not uncommon in granites and granite pegmatites. Garnets with considerable amounts of the calderite molecule $Mn_3^{2+}Fe_2^{3+}(SiO_4)_3$ are much rarer. They have been described from several occurrences of $Mn^{2+}-Fe^{3+}$-rich metasediments, metamorphosed under P-T conditions of the blueschist, amphibolite and granulite facies (Lattard and Schreyer, 1983; Dasgupta et al., 1987; Reinecke, 1987).

The presence of trivalent manganese in the sixfold coordinated Y-position of natural garnets, however, either as $Mn_3^{2+}Mn_2^{3+}(SiO_4)_3$, blythite end member (Fermor, 1926) or $Ca_3Mn_2^{3+}(SiO_4)_3$ end member has been doubted for crystal chemical reasons (Strens, 1965; Rickwood, 1968). In fact, the only garnet analysis indicating a high amount of blythite (34 mol%) was performed on impure material (Fermor 1909, 1926, 1938) and remains questionable. On the other hand, conventional (de Villiers, 1951; Katz, 1978) and microprobe analyses (Dunn, 1979; Lattard, this work) of calderite-rich garnets from Otjosondu (SWA/Namibia) consistently yielded a sum of $Al + Fe_{tot}^{3+} < 2$, and, simultaneously, a sum of $Ca + Mg + Mn_{tot}^{2+} > 3$. This fact is best explained by a small amount of Mn^{3+} in the Y position. Sastri (1963) arrived at the same conclusion in interpreting the conventional analysis of a Mn-rich andradite from Kodur, Andhra Pradesh, India. Microprobe analysis presented in some recent works also display the same features indicating Mn^{3+} in garnets of Mn-rich rocks from Andra Pradesh, India (Sivaprakash, 1980), from the Sausar Group, India (Dasgupta et al., 1987) and from the Vestpolltind Fe–Mn deposit, Lofoten, Norway (Krogh, personal communication 1983). It should also be noted that a tetragonal Mn^{3+}-bearing hydrogarnet, henritermierite, $Ca_3(Mn_{1.5}^{3+}Al_{0.5})(SiO_4)_2(OH)_4$, has been described by Gaudefroy et al. (1969), while its crystal structure has been determined by Aubry et al. (1969).

A definite proof of the presence of trivalent manganese in the Y position of the garnet structure was provided by the successful synthesis of the end members $Ca_3^{2+}Mn_2^{3+}(SiO_4)_3$ (Nishizawa and Koizumi, 1975) and blythite, $Mn_3^{2+}Mn_2^{3+}(SiO_4)_3$ (Fursenko, 1982). A Mn^{3+}-rich garnet $(Ca_{2.07}Mn_{0.90}^{2+})(Al_{1.21}Mn_{0.78}^{3+})(SiO_4)_3$ was synthesized by Frentrup and Langer (1981), blythite-bearing calderites $Mn_3^{2+}(Fe_{2-x}^{3+}Mn_x^{3+})(SiO_4)_3$ by Lattard and Schreyer (1983). Optical spectroscopy of these two types of synthetic garnets revealed the two spin-allowed dd bands typical of Mn^{3+} at 20400 and 17000 cm^{-1} (Frentrup and Langer, 1981) and at 21000 and 19200 cm^{-1} (Langer and Lattard, 1984) respectively. A structure determination of the Mn^{3+}-rich ternary garnet of Frentrup and Langer (1981) showed that the incorporation of Mn^{3+} did not lead to a Jahn-Teller distortion of the YO_6 octahedron (Arni et al., 1985). This is in contrast to the prediction of Strens (1965).

In this work the calderite-rich garnets from Otjosondu have been analyzed and investigated by optical absorption and Mössbauer spectroscopy in order to verify the assumed Mn^{3+} content in these natural garnets.

Provenance and description of investigated garnets

The metamorphic manganese deposit of Otjosondu is situated about 165 km NE of Windhoek (at 21°15′S, 17°54′E) in the intracontinental branch of the Damara Orogen. The Fe–Mn-rich metasediments form three to four distinct stratigraphic horizons, intercalated within a succession of quartzites (Roper, 1956, 1959) which constitutes a stratigraphic equivalent to the Chuos formation (Martin, 1965 and personal communication 1979). Metamorphism reached *P-T* conditions of the high-grade amphibolite facies. The manganese ores at Otjosondu exhibit a striking textural, modal and chemical variability with all transitions between virtually pure oxidic ore and almost pure silicate rock (de Villiers, 1951; Roper 1959; Katz, 1978). The predominant ore minerals are braunite and hematite, whereas jacobsite, hausmannite and bixbyite are subordinate. Alteration products are pyrolusite and psilomelane. Predominant non-opaque phases, present in highly variable proportions, are Mn-rich garnets, Mn-rich clinopyroxenes, rhodonite, ternary (Ba, K, Na) feldspars of variable composition (Viswanathan and Kielhorn, 1983), quartz and baryte. Aegirine and magnesioriebeckite are restricted to Mn-poor, Fe^{3+}-rich layers. The phase relationships between oxides and silicates in the Otjosondu deposit will be discussed in a forthcoming article (Katz-Lehnert et al., in prep.).

The andradite-calderite garnets from Otjosondu show a reddish-brown colour in hand-specimen and a moderate yellow (5Y7/6), sometimes pale greenish-yellow (1OY8/2) colour in thin section. The investigated samples are described in the order of increasing calderite content in the garnets.

Sample Ot 23 is a massive, coarse grained garnet-pyroxene fels with inhomogenous distribution of the main constituents. The mineral assemblage is garnet – Mn-pyroxene – hyalophane – rhodonite (widely altered to MnO_2 and quartz) – baryte – braunite – hematite.

Sample Ot 212 is an indistinctly banded, medium grained manganese ore consisting of the assemblage Fe–Mn-oxides (not specified) – Mn-pyroxene – garnet – hyalophane.

Sample Ot 199. The massive, medium to coarse grained rock is formed by the assemblage, quartz – hyalophane – Mn-pyroxene – garnet – Fe–Mn-oxides (not specified).

Sample Ot 15. Owing to an alternation of silicate- and oxide-rich layers, the medium to coarse grained rocks exhibits a distinct banding. The mineral assemblage of the silicate-rich part is hyalophane – Mn-pyroxene – garnet – baryte – braunite – hematite.

Sample Ot 16. The indistinctly banded manganese ore is characterized by extremely variable, fine to medium grain size and irregular distribution of the constituents. The assemblage is braunite – garnet – Mn-pyroxene – hyalophane – baryte – hematite.

Mineral chemistry

Experimental methods

For **conventional analyses** of the calderite-andradite garnets, concentrates were prepared using the Frantz Isodynamic Magnetic Separator, and additional density separation by Clerici solution. The purity of the separates is estimated at 98% for garnets Ot 15 and Ot 16, and at 99% for garnets Ot 23, Ot 199 and Ot 212.

Si, Al, Fe^{tot}, Ca and Ti were analyzed by XRF using $Li_2B_4O_7$ fusion disks with La_2O_3 as heavy absorber (1:1:9). To minimize matrix effects, the measurements were performed in two steps: After having determined the approximate composition of the garnets against international standards, the ultimate composition was measured against standards which were specifically prepared to match the composition of the garnets as close as possible. Careful background measurements were performed on unknowns and standards. After decomposition of the garnet concentrates in $HF-HClO_4$, Mn and Mg were determined by AAS.

Electron microprobe analyses have been performed using two similar automated microprobes (Cameca Company). Garnets of samples Ot 23 and Ot 199 were analyzed using as standards MgO, Al_2O_3, synthetic rutile, synthetic pyroxmangite and a synthetic glass of the composition of end member andradite and were corrected with a ZAF program (CORREX, Cameca). In case of samples Ot 15 and Ot 16, the standards were MgO, Al_2O_3, metallic Fe, metallic Mn, wollastonite and synthetic rutile and the raw data were corrected using the PAP program (Cameca).

Mössbauer spectra were taken from samples Ot 15, Ot 16, Ot 23, Ot 199 and Ot 212 with a multichannel analyzer (1024 channels) operated in conjunction with an electromechanical drive system with symmetric triangular velocity shape. The two simultaneously obtained spectra (512 channels each) were folded and evaluated assuming Lorentzian line shape. During the measurements, source (25 mCi^{57}Co/Pd) and absorber were kept at room temperature. The iron density of the absorber was 5 mg Fe/cm^2.

The optical absorption spectra [log $I_o/I = f(\nu)$] were recorded from polished thin sections (25–190 μm thick) between 4000 and 40000 cm^{-1} in a single-beam step scanning procedure with steps of 1 nm between 40000 and 12500 cm^{-1} and steps of 5 nm between 4000 and 12500 cm^{-1}. The microscope spectrometer used (Zeiss UMSP 80) is similar to the one described recently by Frentrup and Langer (1981) and Cemič et al. (1986). The measured areas had a diameter of 20 µm. The spectral band-widths were 1 nm at energies higher than 12500 cm^{-1} and 10 nm at energies lower than 12500 cm^{-1}. Spectra were taken from garnets Ot 15, Ot 16, Ot 23, and Ot 199. The crystals were polished from both sides and fixed by an adhesive (koeropox 439) to UV-transparent glass plates. Reference spectra (I_o) were taken from the glass and the glue. UV-transparent ultrafluor (10 ×) were used as objective and condensor.

Analytical results

Chemical analyses of the five garnet concentrates are listed in Table 1. For the garnets Ot 15, Ot 16, Ot 23 and Ot 199, additional microprobe analyses are given, which agree well with the respective conventional analyses, within the limits of analytical error (estimated at 1 – 2% relative for most oxides, 10% for Al_2O_3 and 50% for MgO).

Judging from the microprobe analyses, the compositional variation of the garnets within each sample is rather limited. In general, the calculated standard deviation of the average values of both garnets is not higher than the estimated analytical uncertainty. In garnet Ot 23, a spot listed separately in Table 1 (No. 11) deviates from the other eleven spots in showing a significantly lower MnO content and a higher CaO concentration.

Calculation of the mineral formulas – based on 24 oxygens and assuming total iron as Fe^{3+}, total manganese as Mn^{2+} – led to total cation contents between 15.975 and 16.073 which is close to ideality. The calculated Si contents range from 5.969 to 6.074, conforming to an analytical error of about 1%. The fact that most of the conventional analyses yielded Si contents somewhat higher than the theoretical value may be due to impurities of quartz and feldspar in the garnet concentrates.

A conspicuous feature of all calculated formulas is a distinct deficiency in the sixfold coordinated Y-position which is matched by an excess in the eightfold coordinated X-position. Except for samples Ot 15 and Ot 16, the sums of all cations in the structural formulas are higher than the theoretical one i.e. 16. Both observations suggest the presence of some trivalent manganese in the Y sites of most Otjosondu garnets. In case of sample Ot 15 the cation deficiency could point to a larger amount of divalent cations than that calculated, i.e. to a small proportion of Fe^{2+}.

Therefore, in order to estimate the contents of divalent and trivalent manganese and iron the garnet formulas were recalculated under the following assumptions:

1. In contrast to the conventional procedure, a deficit in the fourfold coordinated Z position is *not* filled by Al or Fe^{3+} since it is assumed that the corresponding deviations are merely due to analytical error.
2. The sum of valencies of the eightfold X and sixfold coordinated Y cations is 24.
3. Ti^{4+} occupies only octahedral Y-positions and is assigned to the end member titan-andradite $Ca_3Ti_{1.5}(SiO_4)_3$. This is consistent with a slight deficiency in the Y-sites. The sum of the X and Y cations is thus fixed to $10 - Ti/3$.
4. Mn^{3+} and Fe^{2+} are considered to be incompatible.

The re-calculated structural formulas are listed in Table 1.

The recasting of the re-calculated formulas into end-member molecules has been performed according to the scheme proposed by Rickwood (1968),

Table 1. Chemical analysis of calderite-andradite garnets from Otjosondu.

Sample	Ot 23	Ot 23	Ot 23	Ot 23	Ot 212
Method	conv.	EMP $\bar{x} \pm \sigma$(12 tu)	EMP No. 11	EMP No. 3	conv.
wt %					
SiO_2	34.7	34.0 ±0.2	34.6	33.9	34.2
TiO_2	0.52	0.50±0.04	0.49	0.42	0.41
Al_2O_3	1.44	1.25±0.04	1.16	1.22	1.29
Fe_2O_3(tot)	26.0	26.55±0.5	27.9	26.3	26.7
MnO(tot)	15.9	15.8 ±1.1	12.4	16.05	17.6
MgO	0.08	0.04±0.02	0.02	0.06	0.08
CaO	20.4	20.35±0.3	22.9	20.32	18.7
Sum	99.04	98.49±0.5	99.47	98.27	98.98
Formula based on 24 O, $Fe^{tot} = Fe^{3+}$, $Mn^{tot} = Mn^{2+}$					
Si	6.056	5.992	5.994	5.995	6.013
Ti	0.068	0.066	0.064	0.056	0.054
Al	0.297	0.260	0.237	0.254	0.267
Fe^{3+}	3.415	3.521	3.637	3.499	3.533
Y	3.779	3.847	3.938	3.809	3.854
Mn	2.350	2.359	1.819	2.404	2.621
Mg	0.021	0.011	0.005	0.016	0.021
Ca	3.815	3.843	4.250	3.850	3.523
X	6.186	6.213	6.074	6.270	6.165
Sum	16.021	16.051	16.006	16.073	16.032
Formula based on: $(cat^{IV} + cat^{VIII}) = 10 - Ti/3$; valencies $(cat^{VI} + cat^{VIII}) = 24$, $Fe^{tot} =$					
Si	6.063	5.944	5.973	5.936	5.991
Ti	0.068	0.066	0.064	0.055	0.054
Al	0.297	0.258	0.236	0.252	0.266
Fe^{3+}	3.419	3.493	3.625	3.466	3.520
Mn^{3+}	0.193	0.162	0.055	0.209	0.142
Y	3.977	3.978	3.979	3.982	3.982
Mn^{2+}	2.168	2.177	1.759	2.171	2.469
Mg	0.021	0.010	0.005	0.016	0.021
Ca	3.819	3.812	4.236	3.812	3.510
X	6.000	5.999	6.000	5.999	6.000
End members (mol%)					
Andradite	61.4	61.3	68.5	61.7	56.7
Ti-andradite	2.3	2.2	2.1	1.8	1.8
Calderite	24.1	26.0	22.1	24.9	31.3
Blythite	4.8	4.1	1.4	5.2	3.6
Spessartite	7.1	6.2	5.8	6.0	6.3
Pyrope	0.3	0.2	0.1	0.3	0.4

Ot 199	Ot 199	Ot 15	Ot 15	Ot 16	Ot 16
conv.	EMP $\bar{x}\pm\sigma$(4 tu)	conv.	EMT $\bar{x}$(9 tu)	conv.	EMP $\bar{x}\pm\sigma$(3 tu)
34.2	33.6 ±0.15	34.9	34.1 ±0.2	34.6	33.74±0.03
0.73	0.65±0.06	0.20	0.13±0.03	0.16	0.11±0.03
1.61	1.46±0.09	2.44	2.29±0.04	2.33	2.39±0.31
26.0	25.9 ±0.3	25.7	26.3 ±0.2	25.3	25.4 ±0.55
18.9	19.2 ±0.2	19.6	19.0 ±0.3	21.0	20.8 ±1.0
0.04	0.06±0.02	0.23	0.23±0.03	0.14	0.15±0.02
17.8	17.5 ±0.3	16.5	16.9 ±0.2	15.5	15.4 ±0.9
99.28	98.37±0.6	99.57	98.95	99.03	97.99

5.999	5.969	6.067	5.987	6.074	6.000
0.096	0.087	0.026	0.017	0.021	0.015
0.333	0.306	0.500	0.474	0.482	0.501
3.432	3.462	3.362	3.476	3.342	3.401
3.858	3.855	3.888	3.967	3.845	3.917
2.808	2.889	2.886	2.827	3.122	3.139
0.010	0.016	0.060	0.060	0.037	0.040
3.345	3.331	3.073	3.179	2.915	2.938
6.163	6.236	6.019	6.066	6.074	6.117
16.023	16.060	15.975	16.021	15.993	16.034

Fe^{3+}; Mn^{2+}/Mn^{3+} calculated

5.965	5.898	6.119	5.964	6.119	5.978
0.096	0.086	0.026	0.017	0.021	0.014
0.331	0.302	0.504	0.472	0.486	0.499
3.412	3.421	3.391	3.462	3.367	3.389
0.129	0.163	0.070	0.043	0.119	0.093
3.968	3.972	3.991	3.994	3.993	3.995
2.663	2.692	2.841	2.773	3.026	3.034
0.010	0.016	0.060	0.060	0.037	0.039
3.326	3.291	3.099	3.167	2.937	2.927
5.999	5.999	6.000	6.000	6.000	6.000

52.2	52.0	50.8	52.2	48.3	48.3
3.2	2.9	0.9	0.6	0.7	0.5
33.1	33.5	34.0	34.3	35.9	36.4
3.2	4.1	1.7	1.1	3.0	2.3
8.1	7.3	11.6	10.8	11.5	11.8
0.2	0.3	1.0	1.0	0.6	0.5

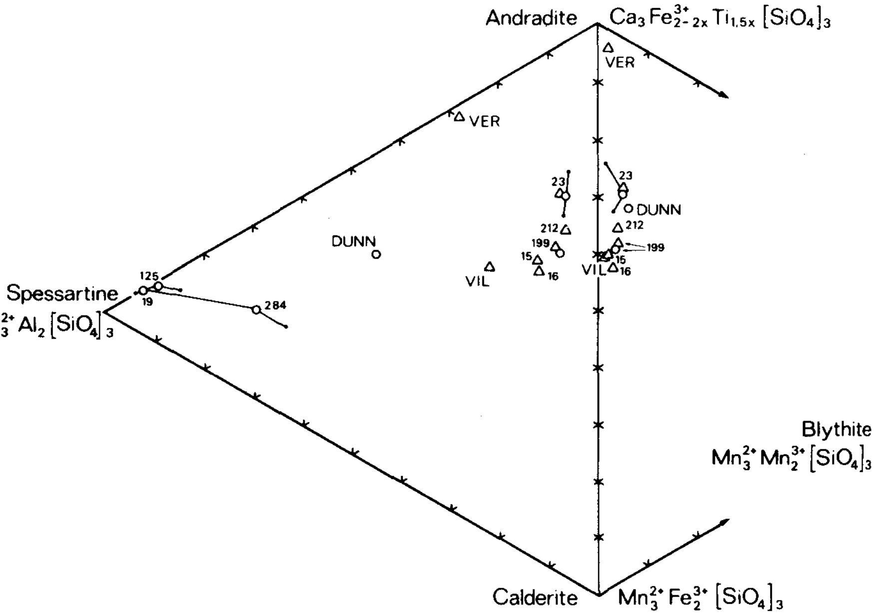

Fig. 1. Chemical composition of the garnets, studied as plotted in the triangular diagrams (andradite + Ti-andradite) – calderite – spessartine and (andradite + Ti-andradite) – calderite – blythite. Triangles = conventional analysis, circles = averages of microprobe analyses, numbers refer to the analyses in Table 1 or are mentioned in the text. VER = results of Vermaas (1952), VIL = results of de Villiers (1951), Dunn = results of Dunn (1979).

except for Ti, which has been allocated to the Ti-andradite end-member molecule. The calculation sequence used here was thus: Ti-andradite, andradite, pyrope, spessartine, calderite and blythite. The alternative end member calculations used by Vermaas (1952) and Dunn (1979) would yield grossular instead of spessartine and lead to higher calderite/andradite ratios, but the bythite contents would remain virtually the same as those given in Table 1.

According to the values given in Table 1, the Fe – Mn-rich garnets from Otjosondu consist predominantly of the end members andradite (48 – 69 mol %) and calderite (22 – 36 mol %), with minor spessartine (6 – 12 mol %) and subordinate Ti-andradite (0.5 – 3.2 mol %) and pyrope ($\leq$ 1.0 mol %) contents. The blythite contents range between 1.1 and 5.2 mol %. These analytical results are plotted in the triangular diagrams (andradite + Ti-andradite) – calderite – spessartine and (andradite + Ti-andradite) – calderite – blythite (Fig. 1).

For comparison, the three chemical analyses published earlier (de Villiers, 1951; Vermaas 1952; Dunn, 1979) have been re-calculated according to the proposed scheme and added to the diagram in Figure 1. Although markedly richer in the spessartine end member, de Villiers (1951) garnet resembles our garnets in composition, whereas the sample of Vermaas (1952) is virtually an andradite spessartine garnet. The microprobe analyses carried out by Dunn (1979) on de Villiers sample deviates strikingly from the initial conventional analysis in having a much higher spessartine and a much lower calderite content (see Fig. 1).

It should be noted that the metamorphic manganese ores at Otjosondu also contain another type of garnet which is yellow to yellow-green in hand-specimen and faint yellowish to colourless in thin section. According to unpublished microprobe analyses (M.O.) these garnets are predominantly spessartines, but display a marked compositional variability even within individual crystals. Some analyses reveal small blythite and calderite contents (Fig. 1, numbers 19, 125 and 284).

Spectroscopical results

The Mössbauer spectrum of the garnet Ot 199 in Figure 2 exhibits a quadrupole doublet with an isomer shift IS = 0.39 mm/s (relative to alpha-iron) and a quadrupole splitting QS = 0.50 mm/s, which are typical of octahedral Fe^{3+} in garnets (Amthauer et al., 1976). The small half-width HW = 0.29 mm/s shows that the sample is rather homogeneous. The isomer shifts and quadrupole splittings of the other garnets of this study (Ot 15, Ot 16, Ot 23, Ot 199, Ot 212) were the same within the experimental error (± 0.01 mm/s). If there would be any Fe^{3+} at the tetrahedral sites or Fe^{2+} at the dodecahedral or octahedral sites, its amount would be below 5% of the total iron. Consequently, total iron can be attributed to the end members andradite and calderite, in agreement with the calculation procedure described above.

In thin sections the garnets of samples Ot 15, Ot 16, Ot 23 and Ot 199 exhibit yellow colours. They were investigated by optical absorption spectroscopy. The main feature of the optical absorption spectrum of garnet Ot 199 (crystal thickness: 30 μm) in Figure 3 is an increase of the absorbance (I_0/I) towards the UV starting from about 16000 cm^{-1}, which is assigned to electron transitions between the oxygen anions and the cations. The corresponding absorption bands are known to be very intense in the case of O^{2-} to Fe^{3+} and of O^{2-} to Mn^{3+} charge transfer in garnets (Amthauer, 1976; Langer and Lattard, 1984) and are mainly responsible for the yellow colours of the studied garnets. There are only small absorption bands in the visible spectral region superimposed on the UV-absorption edge, which are due to electron transitions between the *d* orbitals. In agreement with the energies of the corresponding levels in other garnets, the 22700 cm^{-1} band is assigned to the $^4A_{1g}{}^4E_g$ level of Fe^{3+} in octahedral

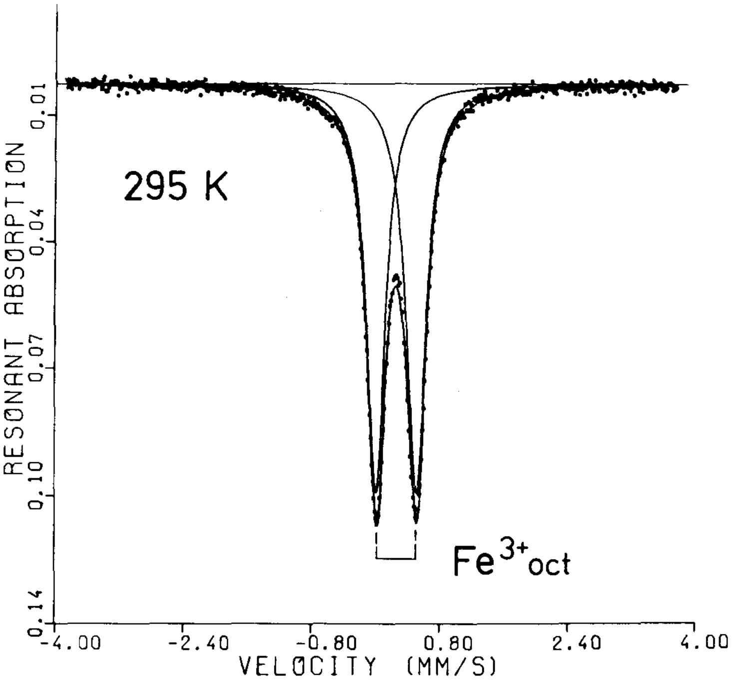

Fig. 2. Mössbauer spectrum of garnet Ot 199 taken at room temperature of source (^{57}Co/Pd) and absorber. The solid line represents a least-squares fit of one quadrupole doublet to the experimental data. The doublet is assigned to Fe^{3+} at the octahedral sites.

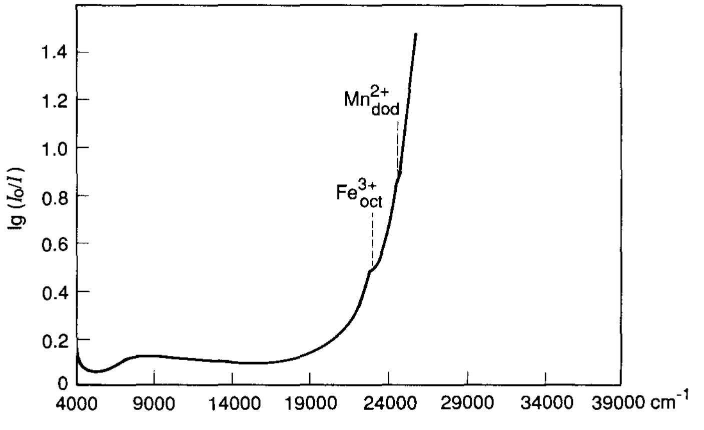

Fig. 3. Optical absorption spectrum of garnet Ot 199. Absorption bands of Fe^{3+} are observed at 22700 cm^{-1} and of Mn^{2+} at 24500 cm^{-1} (crystal thickness = 30 μm).

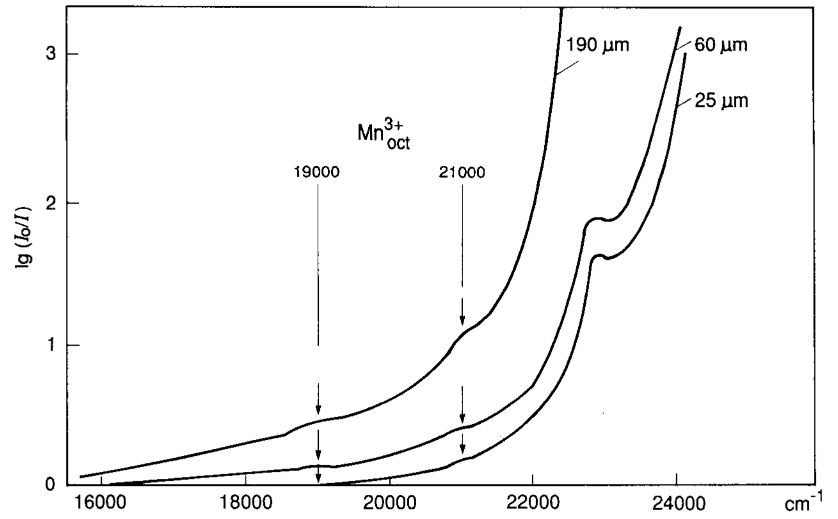

Fig. 4. Detail of the optical absorption spectrum of garnet Ot 16. With increasing crystal thickness (25 μm, 60 μm, 190 μm) two absorption bands are observed at 19000 cm^{-1} and 21000 cm^{-1}, which are assigned to Mn^{3+} at the octahedral sites of the garnet structure.

sites and the 24500 cm^{-1} band to the $^4A_1{}^4E$ level of Mn^{2+} in the dodecahedral sites (Moore and White, 1972; Amthauer, 1976).

Absorption bands of Mn^{3+}, which are expected between 17000 cm^{-1} and 21000 cm^{-1} (Frentrup and Langer, 1981; Langer and Lattard, 1984) could not be observed in crystals with a thickness smaller than 50 µm. However, with increasing crystal thickness two weak but distinct absorption bands appear and increase in intensity at 19000 cm^{-1} ($\pm$ 200 cm^{-1}) and at 21000 cm^{-1} ($\pm$ 200 cm^{-1}). This is shown in detail for sample Ot 16 in Figure 4. Microscope analyses of the same crystal yielded a Mn^{3+} content of 0.093 pfu or 2.3% blythite, respectively (cf. Table 1). Therefore, in agreement with the results of Frentrup and Langer (1981) and Langer and Lattard (1984) both absorption bands are assigned to spin-allowed dd transitions of Mn^{3+}. Most probably, they correspond to the transitions ^5E to $^5A_1$ (19000 cm^{-1}) and ^5E to ^5E (21000 cm^{-1}) (Frentrup and Langer, 1981). However, it should be emphasized, that, due to the small amount of Mn^{3+}, we are just working at the lower limit of detectibility of Mn^{3+} by optical absorption spectroscopy.

Discussion

In summary, no divalent iron has been detected in the samples Ot 15, Ot 16, Ot 23, Ot 199, and Ot 212, as shown by Mössbauer spectroscopy. In addition, no spin allowed absorption bands of Fe^{2+} could be detected in the NIR region. Thus all the iron is ferric and belongs to the calderite $Mn_3^{2+}Fe_2^{3+}Si_3O_{12}$ or andradite $Ca_3Fe_2^{3+}Si_3O_{12}$ molecules, respectively.

The occurrence of Mn^{3+} bands in the optical absorption spectra proves the existence of Mn^{3+} in the garnets of this study.

As all the other garnets in Table 1 have similar chemical composition and occur in similar paragenesis, it is reasonable to extend the spectroscopic results to all these garnets. These results are in good agreement with the Fe^{3+} and Mn^{3+} contents calculated from both the conventional and microprobe analysis.

Except for some spessartine-rich garnets (samples Ot 19, 125 and 284; see Fig. 1), the garnets occurring in the metamorphic manganese ores of Otjosondu represent essentially solid solutions between the end members andradite (50–70 mol%) and calderite (20–35 mol%). These unusual garnet composition reflect the unusual bulk compositions of the Otjosondu silicate rocks, which are characterized by high manganese but low aluminium and magnesium contents.

The garnet compositions are also controlled by the P-T and fO_2 during metamorphism. Experimental work in the system Ca–Mn–Fe–Si–O–H (Lattard, unpublished results) has shown that a complete solid solution series exists between the garnet end members calderite and andradite. Whereas the stability of calderite is restricted to very high pressures and low temperatures (Lattard and Schreyer, 1983), andradite is stable over a large range of P-T conditions up to high temperature even at normal pressure (Huckenholz and Yoder, 1971). The stability limits of the solid solutions are shifting gradually with composition between these two extremes. The composition of a calderite-andradite garnet coexisting with hematite and a Mn-pyroxenoid/pyroxene is an indicator of the minimum equilibrium pressure (Lattard and Schreyer, 1983). Preliminary experimental results show that calderite$_{30}$-andradite$_{70}$ garnets, i.e. with compositions close to those of Otjosondu, are stable at 850° C at least down to 5 kbar ($P_{H2O} = P_{tot}$). Still lower minimum pressures can be expected at temperatures around 650° C which prevailed during peak metamorphism in the Otjosondu complex.

End members calderite and andradite, as well as their solid solutions, are stable only under high oxygen fugacities, corresponding at least to those of the magnetite-hematite buffer (Huckenholz and Yoder, 1971; Lattard and Schreyer, 1983; Lattard, personal communication). Moreover, the calderite-andradite garnets of Otjosondu frequently coexist with hematite and braunite and occasionally with bixbyite or hausmanite. Even considering that braunite and bixbyite may contain appreciable amounts of iron, which shift their stability fields towards lower fO_2 values, both minerals still indicate very high fO_2 conditions, in any case significantly higher than those of the magnetite-hematite buffer (Abs-Wurmbach et al., 1983). High xygen fugacities and high Mn potentials were favourable conditions for he growth of blythite-bearing garnet solid solutions in Otjosondu. It may hus be assumed that the blythite concentrations in the order of 2 – 5 mol% epresent maximum values under the pressure and temperature conditions of metamorphism in Otjosondu.

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Note added in proof

Dr. Thomas Reinecke (Ruhruniversität Bochum) kindly analyzed the garnet concentrate of sample Ot 23 for Mn_2O_3 using a modification of the oxidimetric vanadate method (Peters, 1968) and assuming that the intracrystalline redox equilibrium $Mn^{3+} + Fe^{2+} = Mn^{2+} + Fe^{3+}$ is completely shifted to the right. The accuracy of this method has been shown to be better than ± 4% relative (Reinecke et al., 1985). For garnet Ot 23, four different analyses yielded 1.94, 2.01, 2.16 and 2.18, on average 2.1 ± 0.1 wt.-% Mn_2O_3, corresponding to 0.277 Mn^{3+} p.f.u. and 7.1 mole-% of the blythite molecule, as compared to the estimated 0.192 Mn^{3+} and 4.8 mole-% blythite (Table 1).

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