

## Heat capacities and thermodynamic properties of braunite ( $\text{Mn}_7\text{SiO}_{12}$ ) and rhodonite ( $\text{MnSiO}_3$ )

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### ABSTRACT

The heat capacities,  $C_p^\circ$ , of synthetic rhodonite ( $\text{MnSiO}_3$ ) and braunite ( $\text{Mn}_7\text{SiO}_{12}$ ) have been measured by adiabatic calorimetry from 6 to  $\sim 350$  K. The heat capacity of braunite was also measured to  $\sim 900$  K by differential scanning calorimetry. Braunite exhibits a  $\lambda$ -peak (paramagnetic to antiferromagnetic transition) in  $C_p^\circ$  in the temperature region 93.4–94.2 K. Rhodonite did not show the expected peak in  $C_p^\circ$  characteristic of the cooperative ordering of the  $\text{Mn}^{2+}$  spins at temperatures above 6 K.

At 298.15 K the standard molar entropy of rhodonite is  $100.5 \pm 1.0$  and that of braunite is  $416.4 \pm 0.8$  J/(mol·K). For rhodonite,  $\Delta_f H^\circ(\text{MnSiO}_3, 298.15 \text{ K})$  is  $-1321.6 \pm 2.0$  kJ/mol. For braunite, the value for  $\Delta_f H^\circ(\text{Mn}_7\text{SiO}_{12}, 298.15 \text{ K})$ ,  $-4260 \pm 3.0$  kJ/mol, was obtained by considering both calorimetric and phase-equilibrium data. Our heat capacity and entropy values were combined with existing thermodynamic data for  $\text{MnCO}_3$ ,  $\text{CO}_2$ ,  $\text{SiO}_2$ ,  $\text{MnO}$ , and  $\text{Mn}_3\text{O}_4$  in a “third-law” analysis of several phase equilibrium studies and yielded  $\Delta_f G^\circ(\text{MnSiO}_3, 298.15 \text{ K}) = -1244.7 \pm 2.0$  kJ/mol and  $\Delta_f G^\circ(\text{Mn}_7\text{SiO}_{12}, 298.15 \text{ K}) = -3944.7 \pm 3.8$  kJ/mol from the elements.

A revised petrogenetic grid for the system Mn-Si-O-C at 2000 bars is presented and is consistent with both thermochemical values and occurrence of natural assemblages.

### INTRODUCTION

In a general way, the occurrence of  $\text{Mn}^{4+}$ -bearing minerals reflects the influence of the Earth's atmosphere, and the occurrence of  $\text{Mn}^{2+}$ -bearing minerals reflects deep crustal processes or the influence of organic C. Most Mn that occurs naturally reflects, both volumetrically and by number of species, one or the other of these two oxidation states. Of the Mn-rich minerals in which the Mn is generally divalent, rhodonite and its polymorph, pyroxmangite (for which rhodonite can be easily mistaken), are the most abundant silicates and are exceeded in abundance only by rhodochrosite,  $\text{MnCO}_3$ . Natural  $\text{Mn}^{3+}$ -minerals are uncommon. Of the naturally occurring manganese oxides, carbonates, and silicates, only five silicates (namsilitite, piemontite, kanonaite, macfallite, and okhotskite), members of the braunite group (braunite, braunite-II, neltnerite, and abschwurmbachite), bixbyite, and hausmannite contain  $\text{Mn}^{3+}$  as an essential constituent. Thus, there are relatively few Mn-rich minerals that contain  $\text{Mn}^{3+}$ , which might reflect environments where atmospheric and crustal processes interact. Braunite is the most common of these 11 phases.

Accurate thermochemical data for rhodonite and braunite are desirable for a number of reasons. First, because braunite is one of the few minerals that reflects conditions of the interface between the crust and the atmosphere or hydrosphere, knowledge of braunite equilibria can help improve the deduction of regional metamorphic conditions, particularly those at relatively high

$f_{\text{O}_2}$ . Second, braunite occurs in zones that have been subjected to intense postdepositional soft-sediment and tectonic deformation, resulting in broken or dismembered rock units that are no longer in horizontal or vertical stratigraphic continuity, and the occurrence of this distinctive mineral may prove to be a valuable indicator of paleoconditions and, thus, paleoenvironments with intermediate oxidation states, such as the ocean floors. Finally, knowledge of braunite phase equilibria may improve the extractive metallurgy of Mn. Similar arguments can be made for studying rhodonite, although rhodonite is not as significant as braunite for deducing inherited high  $f_{\text{O}_2}$  values.

### OCCURRENCE

Braunite is both an ore-forming mineral and a precursor of supergene (quadrivalent) oxide ores in stratabound Mn deposits worldwide. Examples of economically important deposits include the extensive, unmetamorphosed Mamatwan-type ores of the Hotazel Formation, Kalahari Basin, South Africa (Nel et al., 1986; Miyano and Beukes, 1987) and the metamorphosed Sausar Group, India (Roy et al., 1986). Small braunite-bearing lenses, enclosed by rhythmically interbedded chert and shale, are common in tectonically active (and biologically productive) zones thought to be related to midocean-ridge hydrothermal activity (Bonatti et al., 1976; Crerar et al., 1982) and to diagenesis within continental margin sediments (Hein et al., 1987). Huebner et al. (1992) suggest

that some such deposits might have been precipitated at the seafloor where relatively reducing, subseafloor fluids mixed with fresh seawater.

The ultimately sedimentary origin of most braunite is best revealed by its occurrence in Mn-rich lithologies that have been altered by little more than diagenetic processes (Nel et al., 1986). Huebner and Flohr (1990) suggest that some braunite layers were formed as a gel-like precipitate. Ostwald and Bolton (1990) describe braunite concretions of diagenetic origin within shales in Western Australia.

Knowledge of the mineral assemblages in which braunite occurs will prove useful in constructing the Mn-Si-C-O petrogenetic grid, particularly in positioning equilibria with large uncertainties in the  $\Delta_r G$ . Braunite assemblages are found in rocks of all metamorphic grades. Roy (1965), Dasgupta and Manickavasagam (1981), and Dasgupta et al. (1990) summarized mineral assemblages or associations. The critical assemblages involving braunite range from pyrolusite + braunite + quartz at greenschist grade; pyrolusite + braunite + quartz and braunite + bixbyite + quartz at biotite grade; braunite + rhodonite + quartz at garnet and staurolite-kyanite grades; and braunite + bixbyite + quartz and braunite + rhodonite + quartz at sillimanite grade. Progressively higher temperatures resulted in braunite coexisting with more reduced manganese oxides and ultimately with rhodonite or pyroxmangite. A proven assemblage involving braunite and tephroite in nature is not known to us, but we note a report of hausmannite + braunite + tephroite of unknown composition and textural relationship (Abs-Wurmbach et al., 1983). Huebner (1967, 1969) suggested that steep  $f_{O_2}$  gradients must have existed between these braunite-bearing assemblages and surrounding Mn-poor, Fe<sup>2+</sup>-rich country rocks: the braunite-bearing assemblages had the capacity to maintain, and the ability to record, the relatively high O potentials of the sedimentary environments in which the Mn was originally deposited. Subsequently, Dasgupta et al. (1985) confirmed the hypothesis.

Rhodonite and pyroxmangite are pink to red and easily noticed; for this reason, there are many reported occurrences. Most rhodonite appears to form in one of three environments: hydrothermal, pegmatitic, and (regional or contact) metamorphic. Volumetrically, the most important occurrences are found in hydrothermal (where the manganese silicate forms a gangue) and regional metamorphic environments. These rhodonite-forming environments lie beneath the surface of the Earth's crust; the occurrence and preservation of rhodonite records a continuous history of low to moderate oxidation state. If exposed to atmospheric weathering processes, the manganese silicate rapidly transforms to quadrivalent oxide.

In regional terranes, the metamorphic grade at which rhodonite appears depends upon the bulk composition or mineral assemblage. In Mn-oxide-rich metasediments assemblages containing pyrolusite, bixbyite, braunite, hausmannite, or vredenburchite, rhodonite is absent in

greenschist and biotite grades but common in garnet and higher grades (see Dasgupta and Manickavasagam, 1981). In the absence of manganese oxides, rhodonite and pyroxmangite occur at greenschist facies (Peters et al., 1973; Abrecht, 1989). [Flohr and Huebner (1992) described a zeolite-facies deposit in which rhodonite and hausmannite occur but never in the same assemblage.] Thus, it would appear that rhodonite and braunite occur in equilibrium only at relatively high temperatures, >675 K.

Huebner (1967) noted that at low metamorphic grades rhodochrosite (MnCO<sub>3</sub>) can occur with either braunite or rhodonite, but not both phases. He presented evidence that at relatively low  $f_{O_2}$  and temperature, the assemblage MnCO<sub>3</sub> + SiO<sub>2</sub> reacts to rhodonite + CO<sub>2</sub>. Although braunite and rhodochrosite coexist in apparent equilibrium (Huebner and Flohr, 1990), no direct evidence for a comparable reaction, rhodochrosite + quartz + O<sub>2</sub> = braunite + CO<sub>2</sub>, is known to us. Nevertheless, given appropriate bulk compositions, it is clear that rhodochrosite + quartz is a low-temperature assemblage relative to assemblages that contain rhodonite, and a low  $f_{O_2}$  assemblage relative to assemblages that contain braunite.

#### CRYSTAL CHEMISTRY AND PHASE EQUILIBRIA OF RHODONITE AND BRAUNITE

The mineralogical end-member composition of rhodonite is CaMn<sub>4</sub>Si<sub>3</sub>O<sub>15</sub>, but the solid-solution range of the rhodonite structure extends to MnSiO<sub>3</sub>, the composition that is the subject of the present paper. This composition can also have the pyroxmangite structure. Maresch and Mottana (1976) determined the rhodonite + pyroxmangite equilibrium at 3–30 kbar H<sub>2</sub>O pressure and extrapolated the curve to 1 bar, ~670 K. Pyroxmangite is the low-temperature form. Nevertheless, Huebner (1986) found that mixtures of SiO<sub>2</sub> (quartz or silica glass) and MnCO<sub>3</sub> or Mn<sub>1-x</sub>O in H<sub>2</sub>O (1–2 kbar) invariably crystallized as pyroxmangite at <1123 K. Rhodonite was obtained only if the reaction was conducted in fused MnCl<sub>2</sub>·4H<sub>2</sub>O at pressure.

Previous measurements of the thermodynamic properties of MnSiO<sub>3</sub> were made by Kelley (1941), who measured  $C_p^0$  at 27 temperatures between 52.6 and 294.8 K. Kelley's sample was prepared by dry sintering of a mixture of precipitated MnCO<sub>3</sub> and silica in a Ni cartridge heated to 1323 K for 5 d under flowing H gas. We presume that the sample crystallized as rhodonite, rather than pyroxmangite. Southard and Moore (1942) determined the heat content,  $H_T^0 - H_{298}^0$ , of this same sample of MnSiO<sub>3</sub> between 488.5 and 1508.7 K. King (1952) determined the enthalpy of the reaction



at 298.15 K (25 °C) by HF<sub>aq</sub> solution calorimetry also using Kelley's sample. Other studies are summarized in Table 1.

The compositions of the braunite minerals are related to the composition of bixbyite, (Mn > Fe)<sub>8</sub><sup>3+</sup>O<sub>12</sub>, by means of the substitutions Mn<sup>2+</sup> + Si<sup>4+</sup> = 2(Mn<sup>3+</sup>, Fe<sup>3+</sup>) to form

**TABLE 1.** Enthalpy of formation of MnSiO<sub>3</sub> calculated from various sources of calorimetric and equilibrium measurements

Type of measurement	Enthalpy $\Delta_f H_{298.15}^\circ$ (kJ/mol)	Reference
HF <sub>aq</sub> solution calorimetry	-1319.4	King (1952); Hemingway and Robie (1977)
Activity-composition relations in Fe-Mn-Si-O at 1423 K	-1324.5	Schwerdtfeger and Muan (1966)
Activity-composition relations in Co-Mn-Si-O at 1473 K	-1327.7	Biggers and Muan (1967)
MnCO <sub>3</sub> + SiO <sub>2</sub> = MnSiO <sub>3</sub> + CO <sub>2</sub> at 2000 bars CO <sub>2</sub> , 781 K	-1324.0	Peters (1971)
MnCO <sub>3</sub> + SiO <sub>2</sub> = MnSiO <sub>3</sub> + CO <sub>2</sub> at 500 bars CO <sub>2</sub> , 746 K	-1318.2	Candia et al. (1975)
Molten salt calorimetry in 2PbO-B <sub>2</sub> O <sub>3</sub> at 986 K	-1320.8	Navrotsky and Coons (1976)
MnCO <sub>3</sub> + SiO <sub>2</sub> = MnSiO <sub>3</sub> + CO <sub>2</sub> at 1000 bars CO <sub>2</sub> , 758 K	-1321.2	Abrecht (1988)
MnO + SiO <sub>2</sub> = MnSiO <sub>3</sub> emf at 950-1300 K	-1323.1	Rog and Pycior (1987)

braunite, Mn<sup>2+</sup>Mn<sub>6</sub>SiO<sub>12</sub>, and Ca<sup>2+</sup> + Si<sup>4+</sup> = 2(Mn<sup>3+</sup>, Fe<sup>3+</sup>) to form braunite II, Ca<sub>0.5</sub>Mn<sub>7</sub>Si<sub>0.5</sub>O<sub>12</sub>, and neltnerite, CaMn<sub>6</sub>SiO<sub>12</sub>. Most samples of natural braunite and neltnerite have nearly "end-member" compositions (with 10% SiO<sub>2</sub> and either 0 or 9% CaO by weight), indicating that either of these substitutions can be dominant. However, plots of the compositions of some braunite define an irregular field extending toward neltnerite and braunite II (Baudracco-Gritti, 1985), indicating that both substitutions can occur simultaneously. Additional substitutions in braunite are minor Mg<sup>2+</sup>, Fe<sup>3+</sup>, and Al<sup>3+</sup> for Mn<sup>3+</sup> (Bhattacharya et al., 1984; Baudracco-Gritti, 1985). The ratio (Mn + Ca + Mg)/Si is insensitive to the compositions of the coexisting minerals or peak metamorphic grade. Abs-Wurmbach et al. (1983) analyzed 24 samples of braunite from a wide range of metamorphic grades; the minimum and maximum SiO<sub>2</sub> concentrations were 9.50 and 11.08 wt% (0.96 and 1.09 Si cations per eight-cation formula unit). Similarly, Bhattacharya et al. (1984) present 19 braunite analyses; the range in SiO<sub>2</sub> was 9.25-10.41 wt% (0.93-1.04 Si cations per 12-O formula unit). Thus, the Si content of ideal braunite, Mn<sup>2+</sup>Mn<sub>6</sub>SiO<sub>12</sub>, should be a good approximation to that of naturally occurring braunite.

Early laboratory investigations of phase equilibria in the system MnO-SiO<sub>2</sub>-O<sub>2</sub> indicated that "Mn<sub>2</sub>O<sub>3</sub>" could accommodate from 0 to at least 40 wt% SiO<sub>2</sub> and that a single phase containing at least 40 wt% SiO<sub>2</sub> could be synthesized at 1367-1493 K from quenched Mn-Si-O melt (Muan, 1959a, 1959b). Muan proposed that the operative substitution was Si<sup>4+</sup> for Mn<sup>4+</sup> in Mn<sup>2+</sup>Mn<sup>4+</sup>O<sub>3</sub> and that the observed limit of ≥40 wt% SiO<sub>2</sub> supported the presence of Mn<sup>4+</sup>. In a brief subsequent report (Ito, 1961), bementite [Mn<sub>8</sub>Si<sub>6</sub>O<sub>15</sub>(OH)<sub>10</sub>] was said to oxidize at low temperatures to SiO<sub>2</sub>-rich braunite. Thus, the seemingly

variant composition of natural braunite with 10% SiO<sub>2</sub> by weight (neltnerite and braunite II were not yet known) was surprising. The early experimental results were not confirmed by Abs-Wurmbach (1980), who was unable to synthesize braunite with Mn/Si > 7/1 or < 6.8/1.2, corresponding to Mn<sub>1.0-1.2</sub><sup>2+</sup>Mn<sub>6.0-5.6</sub><sup>3+</sup>Si<sub>1.0-1.2</sub>O<sub>12</sub>. More Mn-rich compositions in the system MnO-SiO<sub>2</sub>-O<sub>2</sub> yielded braunite and either bixbyite (1073 K) or hausmannite (≥1288 K); more siliceous compositions yielded braunite and silica or a pyroxenoid. Dasgupta et al. (1986) performed experiments in the system MnO-FeO-SiO<sub>2</sub>-O<sub>2</sub>. Microprobe analyses of Fe-bearing braunite from nine different experiments had 0.797-1.125 Si cations per formula unit, averaging 0.994 Si, close to the ideal value. Because the Si content does not correlate with the presence of quartz or jacobsite, the range is probably experimental error. Recently, de Villiers and Buseck (1989) predicted the occurrence of 21 polysomes, having 0-10 wt% SiO<sub>2</sub>, in the bixbyite-braunite group. In addition to bixbyite, braunite II, and neltnerite, they observed three new polysomes, using high-resolution transmission electron microscopy methods. Their work suggests that there may be many ordered states having compositions between the now familiar species bixbyite, braunite, braunite II, and neltnerite. Although their results provide an explanation for the observed 0-10 wt% range in the SiO<sub>2</sub> contents of the braunite-group minerals, there is neither experimental confirmation nor a modern structural explanation for the reported SiO<sub>2</sub> contents of braunite that exceed 10% by weight.

Petrogenetic (*T-f<sub>O2</sub>*) grids for the system Mn-Si-C-O containing braunite were first presented by Huebner (1967), who noted that Si-rich and Si-poor braunite compositions led to topologically distinct multibundles of invariant points. Si-rich braunite samples plot on the Si-rich side of the join Mn<sub>2</sub>SiO<sub>4</sub>-O<sub>2</sub> in the subsystem MnO-SiO<sub>2</sub>-O<sub>2</sub>. The invariant point experimentally delineated by Muan (1959b) involves Si-rich braunite and results in the coexistence of braunite and tephroite (Mn<sub>2</sub>SiO<sub>4</sub>) (Fig. 1A). Chemographic analysis indicates that a vapor-absent (condensed) reaction with suggested braunite stoichiometry Mn<sub>3</sub><sup>2+</sup>Mn<sub>3</sub><sup>3+</sup>Si<sub>3</sub>O<sub>12</sub> + Mn<sub>2</sub>SiO<sub>4</sub> = 4MnSiO<sub>3</sub> + Mn<sub>3</sub>O<sub>4</sub>, not shown by Muan, must originate at the invariant point. The equilibria of Muan (1959b) that are relevant to the present work are the reactions of tephroite + vapor to form rhodonite + hausmannite and of rhodonite + hausmannite + vapor to form braunite.

Compositions of Si-poor braunite plot on the Mn-rich side of the tephroite-vapor join; the multibundle for silica-poor braunite (Fig. 1B), in which braunite cannot be in equilibrium with tephroite, is consistent with natural assemblages. Huebner (1967, 1976) incorporated this multibundle in a petrogenetic grid for the system Mn-Si-O-C. This grid was modified by Peters et al. (1974) and Abs-Wurmbach et al. (1983). Dasgupta and Manickavasagam (1981) added Fe to the grid. Despite these refinements, great uncertainties still surround the placement of braunite equilibria in *T-f<sub>O2</sub>* space.

## SAMPLE PREPARATION

The preparation of the sample of rhodonite used for our measurements was described by Robie et al. (1989). The rhodonite crystals are transparent, brownish red to rose pink, and have well developed faces. Rhodonite X-ray diffraction patterns were recorded with a Guinier-Hagg camera, using  $\text{CrK}\alpha$  radiation and Si standard; preliminary unit cell dimensions were reported in Robie et al. (1989). Following remeasurement of the films, all observed diffraction lines were indexed by comparison with a powder pattern calculated from the structure of Peacor and Niizeki (1963) but using the formula unit  $\text{Mn}_3\text{Si}_5\text{O}_{15}$ . The results are given in Table 2. Electron microprobe analysis of our crystals yielded  $\text{MnO} = 54.52 \pm 0.2$  wt% and  $\text{SiO}_2 = 46.14 \pm 0.45$  wt%. These values are the average and standard deviation based on 19 analyses. This composition corresponds to the formula unit  $\text{Mn}_{1.00}\text{Si}_{1.00}\text{O}_3$ . The probe standards used were synthetic  $\text{Mn}_2\text{SiO}_4$  for Mn and Kakanui hornblende for Si, Al, Ca, and Fe (see Huebner and Woodruff, 1985).

Braunite with  $\text{Mn}/\text{Si} = 7$  is stable at relatively high  $f_{\text{O}_2}$  but decomposes if the temperature exceeds about 1433 K in air (Muan, 1959a; Abs-Wurmbach, 1980; Abs-Wurmbach et al., 1983). We prepared braunite from a mix of analyzed-reagent-grade  $\text{MnO}_2$  (Baker lot no. 30740) and silica glass (Corning no. 7904) that had been used previously by Robie and Hemingway (1985) and by Huebner (1986). A 50 g mix was ground and heated ten times in air in a large, initially covered Pt dish, for a total of 2417 h at an average temperature of 1298 K. After the second heating, the cover was removed to promote reaction (see Abs-Wurmbach, 1980). Reaction progress was monitored by examining the experiment products in immersion oil and by using X-ray powder diffraction patterns [particularly the intensities of the (624) and (123) reflections of braunite, compared with the (400) and (122) reflections of hausmannite]. The proportion of braunite increased, and that of hausmannite decreased, systematically with time. Virtually no isotropic glass, or weakly anisotropic cristobalite or tridymite, was detected. Only in the early stages could a possible silica phase be resolved by X-ray diffraction: a very weak, poorly defined peak in the position of the (101) reflection of cristobalite. Strong hausmannite and braunite reflections together with a weak silica peak might indicate initial formation of Si-rich braunite. At no stage was any other phase detected. If we were to synthesize braunite in the future, we would use cristobalite rather than silica glass, so that the silica phase might be better monitored with X-ray diffraction. The final product consisted of braunite and  $\ll 0.1\%$  by volume hausmannite (under crossed nicols, minute grains of the highly anisotropic, brilliantly orange to red grains of hausmannite are clearly discernable against the braunite).

The X-ray powder diffractometer peaks were exceedingly sharp. Unit cell dimensions were determined using a combination of 11 small splits of braunite and Si [ $a =$

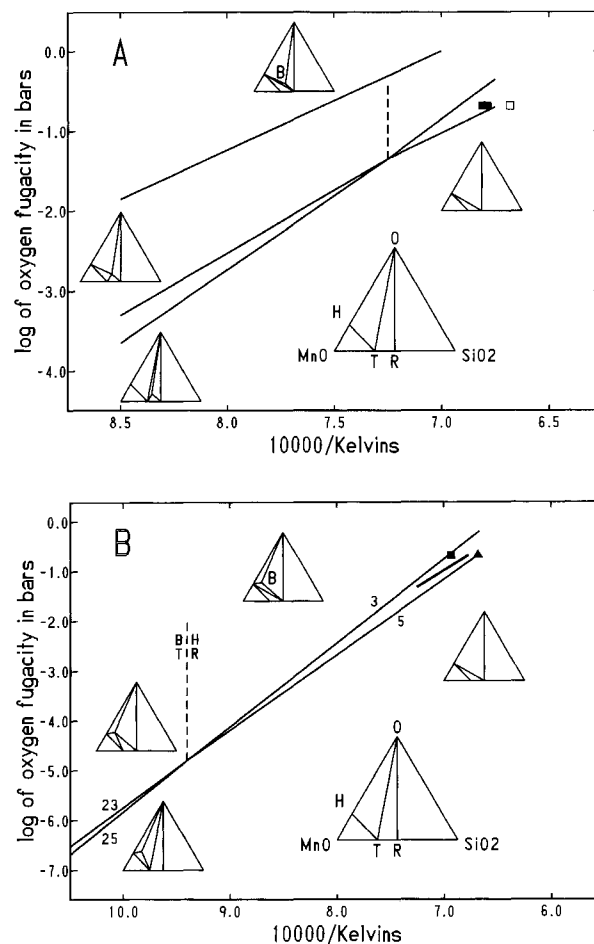


Fig. 1. Topology about invariant points involving the phases braunite (B), hausmannite (H), rhodonite (R), tephroite (T), and vapor (V) in the system  $\text{MnO-SiO}_2\text{-O}_2$  at 1 bar total pressure. Lines are calculated from the thermodynamic properties listed in Table 10; dashed lines are metastable (vapor-absent) reactions. (A) Topology involving Si-rich braunite with reactions as positioned by Muan (1959b). The reaction of rhodonite + vapor to form Si-rich braunite + silica is shown even though it is not involved with the invariant point. Also shown are new experiments (this paper) bracketing Reaction 5. (B) Topology involving Si-poor braunite, following the results presented in this paper. The heavy solid line corresponds to Muan's (1959b) determination of Reaction 5,  $2\text{Mn}_3\text{O}_4 + 6\text{MnSiO}_3 = 6\text{Mn}_2\text{SiO}_4 + \text{O}_2$ . Symbols represent bracketing experiments from Table 4. The metastable extensions of Reactions 4 and 6 would fall outside of the region bounded by Reactions 23 and 25, were the extensions to be shown.

$5.4307(2) \text{ \AA}$ ] or  $\text{BaF}_2$  [ $a = 6.1971(1) \text{ \AA}$ ] as internal standards, using digital methods (Huebner, 1986). Each reflection was indexed by comparison with the calculated pattern of Smith and Anderson (1979), which showed good agreement with our observed intensities, and refined using the program of Evans et al. (1963). Each data set was processed a second time, using relaxed criteria for peak resolution (so that more, and possibly insignificant,

**TABLE 2.** Unit cell parameters and molar volumes of synthetic rhodonite and pyroxmangite forms of  $MnSiO_3$  and of braunite,  $Mn_7Si_2O_{12}$ 

a (Å)	b (Å)	c (Å)	$\alpha$ (°)	$\beta$ (°)	$\gamma$ (°)	cell V (Å <sup>3</sup> )	mol V (cm <sup>3</sup> )	References
<b>Rhodonite</b>								
7.62	11.84	6.70	92.67	94.40	105.5	579	34.87	Ito (1972)
7.627(2)	11.853(3)	6.709(1)	92.47(2)	94.42(2)	105.70(2)	580.9(2)	34.98(1)	Momoi (1974)
7.616(3)	11.851(5)	6.707(2)	92.55(10)	94.35(10)	105.67(10)	579.8(5)	34.92(3)	Narita et al. (1977)
7.614(3)	11.856(6)	6.703(2)	92.40(4)	94.25(4)	105.73(4)	579.6(3)	34.91(1)	Huebner (1986)
7.620(1)	11.852(2)	6.704(1)	92.48(2)	94.38(1)	105.65(1)	580.0(1)	34.93(1)	Huebner (1986)
7.624(2)	11.852(4)	6.710(1)	92.32	94.47	105.68	580.8(3)	34.98(2)	Abrecht (1988)
7.616(1)	11.853(2)	6.706(1)	92.44(2)	94.40(2)	105.70(1)	579.8(1)	34.92(1)	Robie et al. (1989)
7.613(2)	11.849(2)	6.701(1)	92.49(2)	94.36(2)	105.64(2)	579.1(1)	34.87(1)	(42 refl., Si std)
7.615(2)	11.857(3)	6.703(1)	92.46(3)	94.45(2)	105.62(2)	579.8(2)	34.92(1)	(32 refl., Si std)
7.610(4)	11.845(5)	6.697(2)	92.52(4)	94.31(5)	105.56(4)	578.6(3)	34.84(2)	(27 refl., Si std)
<b>Pyroxmangite</b>								
6.722(2)	7.600(2)	17.461(5)	113.80(2)	82.27(2)	94.77(2)	808.2(4)	34.76(2)	Momoi (1974)
6.717(2)	7.603(1)	17.448(5)	113.83(2)	82.35(3)	94.72(2)	807.5(3)	34.74(1)	Maresch and Mottana (1976)
6.721(2)	7.603(3)	17.455(6)	113.17(10)	82.27(10)	94.13(10)	812.4(8)	34.95(3)	Narita et al. (1977)
6.717(2)	7.601(2)	17.429(11)	113.79(3)	82.35(5)	94.73(3)	806.5(5)	34.70(2)	Huebner (1986), expt. 67
6.718(1)	7.598(1)	17.469(7)	113.80(2)	82.28(3)	94.68(2)	808.1(3)	34.76(1)	Huebner (1986), expt. 130
6.718(1)	7.598(1)	17.469(7)	113.80(2)	82.28(3)	94.68(2)	808.1(4)	34.76(2)	Huebner (1986)
6.707(3)	7.594(2)	17.405(11)	113.38	82.43	94.65	804.4(6)	34.60(3)	Abrecht (1988)
6.711(3)	7.582(4)	17.417(12)	113.74(5)	82.27(8)	94.69(5)	803.5(6)	34.55(3)	Peters (1971), reindexed
<b>Braunite</b>								
9.4267(3)		18.6995(18)				1661.7(2)	125.09(2)	(25 refl., BaF <sub>2</sub> std.)
9.4261(4)		18.6986(16)				1661.4(2)	125.06(2)	(35 refl., BaF <sub>2</sub> std.)
9.4269(6)		18.6982(16)				1661.6(2)	125.08(2)	(25 refl., Si std.)
9.4262(5)		18.7046(22)				1661.2(2)	125.05(2)	(42 refl., Si std.)
9.428(1)		18.701(2)				1662.3(3)	125.13(2)	Abs-Wurrmbach (1980)
9.4248(2)*		18.6989(9)				1661.0(1)	125.03(8)	de Villiers (1980)
9.44(0.05)*		18.76(1)				1671.8(15)	125.84(11)	de Villiers and Herbstein (1967)
9.432(2)*		18.703(7)				1663.9(8)	125.25(6)	de Villiers (1975)
9.408(16)*		18.668(32)				1652.3(49)	124.37(37)	Moore and Araki (1976)

\* Naturally occurring material.

maxima in the data could be resolved) with the result that more peaks could be indexed and were accepted in the refinement, but that the overall quality of the least-squares fit was reduced slightly (Table 2). There is no evidence (such as peak broadening or additional reflections) for a phase with other than an ordered 18.699(1) Å repeat distance.

To gage the level of contamination in the laboratory, we obtained instrumental neutron activation analyses (see Baedeker and McKown, 1987) and some semiquantitative, DC-arc emission spectrographic (see Golightly et al., 1987) analyses of the reagents and synthesis products (Table 3). The only significant impurities detected in the reagents were about 500 ppm Ca in the  $MnO_2$  and increases in Cr and Fe following crushing (in a hardened steel mortar) and acid leaching of the  $SiO_2$  glass. For comparison, typical analyses of uncontaminated  $SiO_2$  (Hetherington and Bell, 1967) reveal Cl (10–100 ppm), Ti (0.1–10 ppm), and Fe (0.01–5 ppm), and all other elements (<1 ppm each). Replicate INAA analyses of the braunite reveal that Fe and Cr increased by 240 and 400 ppm, respectively, probably from the furnace windings, and that Ir increased 41 ppm, probably from the Pt-ware crucible. Splits of the rhodonite sample, taken after calorimetric measurements, showed no evidence of contamination during synthesis; the 140 ppb Au is probably from the calorimeter.

In Table 2, we compare unit cell parameters for our calorimetric samples together with a number of recent values for synthetic rhodonite and pyroxmangite and for both synthetic and natural braunite. We did not include the values of Dasgupta et al. (1986) because their samples of synthetic braunite and pyroxmangite were ferruginous. The braunite and rhodonite unit cell parameters are in excellent agreement. Furthermore, the parameters for rhodonite prepared anhydrously by flux growth (Robie et al., 1989) and by hydrothermal synthesis (Huebner, 1986) agree excellently. As a best value for the molar volume of the ten samples of synthetic rhodonite we adopt  $34.91 \pm 0.05$  cm<sup>3</sup> and for the five samples of synthetic braunite  $125.08 \pm 0.03$  cm<sup>3</sup>.

For pyroxmangite the agreement between reported investigations is not as good. The pyroxmangite cell dimension published by Peters (1971) is anomalously small ( $V = 779$  Å<sup>3</sup>). Following reindexing of his pattern by comparison with a pattern calculated from the structure of Pinckney and Burnham (1988), but with composition  $Mn_7Si_2O_{21}$ , we could account for all observed lines. Revised dimensions based on 37 unambiguously indexed lines are reported in Table 2 and are now consistent with other reports. The cell dimension for experiment 130 in Table 2 is for the same material measured by Huebner (1986), but now 27 lines were refined, decreasing the standard errors. Based on the results summarized in Ta-

TABLE 3. Trace element analyses of reactants and products

	SiO <sub>2</sub> *	SiO <sub>2</sub> **	MnO <sub>2</sub> †	Braunite‡	Rhodonite§
Na (ppm)	20	30	60	30	30
Ca		20	520		
Cr	0.3	39.0	6	243	8.6
Fe	20	200	30	370	40
Co	0.01	0.08	3.4	4.2	5.2
Ni	<1	<2	4	<17	10
Zn	0.4	0.6	5.3	9	2.4
Mo	<0.3	1.1	4.3	<6	0.7
Au	1.5	<0.5	3.2	12	140
Ir (ppb)	<0.4	<0.6	<0.3	41400	6.7

Note: Sc, As, Rb, Sb, Cs, Hf, Ta, Th, and U were analyzed and found to be <1 ppm each; K, Sr, Zr, and Ba were also analyzed and found to be below the detection limit, which exceeds 1 ppm. REE below the limit detection or <1 ppm, whichever is greater.

\* Lumps from broken disk of SiO<sub>2</sub> glass.

\*\* SiO<sub>2</sub> glass from same disk, crushed to pass 100 mesh and acid leached.

† MnO<sub>2</sub>, reagent grade (Baker lot no. 30740).

‡ Braunite synthesized from SiO<sub>2</sub>\*\* and MnO<sub>2</sub>† in Pt-ware dish open to furnace. Average of two analyses.

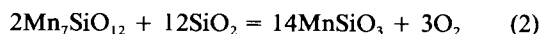
§ Rhodonite synthesized from SiO<sub>2</sub>\*\* and MnO<sub>2</sub>†.

|| Semiquantitative DC-arc emission spectroscopy.

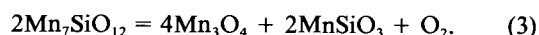
ble 2, the average value for the molar volume of the eight samples of synthetic pyroxmangite is  $34.73 \pm 0.12 \text{ cm}^3$ . The volume change for the phase transition rhodonite = pyroxmangite is  $-0.18 \pm 0.13 \text{ cm}^3$  per mole of MnSiO<sub>3</sub>. This change is consistent with pyroxmangite being the high-pressure, low-temperature polymorph of MnSiO<sub>3</sub>.

#### PHASE EQUILIBRIUM EXPERIMENTS

Knowledge of the phase equilibria of reactions involving braunite, rhodonite, and other phases serves to (1) provide high-temperature free energies of reaction, which, when combined with the heat capacity (entropy) data, will yield free energies of formation of braunite and rhodonite as a function of temperature; and (2) provide some  $T$ - $f_{\text{O}_2}$  values with which to position the high-temperature, high- $f_{\text{O}_2}$  portion of the petrogenetic grid. The only previous attempt to locate reactions that bound the high-temperature, low  $f_{\text{O}_2}$  side of the braunite field is by Abs-Wurmbach et al. (1983). Although they emphasized the possible compositional range of braunite solid solution and braunite oxidation reactions, four unreversed experiments, in air, are relevant: rhodonite → braunite + cristobalite at 1288 K, braunite + quartz → rhodonite at 1436 and 1502 K, and braunite → rhodonite + hausmannite at 1459 K. These experiments deal with two reactions, shown on the grid of Huebner (1967, 1976, and to which the reader is specifically referred), that bound the high-temperature, low  $f_{\text{O}_2}$  side of the braunite stability field



and, at higher temperatures,



On the basis of chemography, Huebner (1967, 1976) showed that these reactions should intersect such that, at

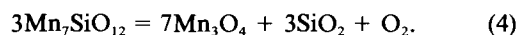
TABLE 4. Results of experiments in air

Reactants	T (°C)	T (K)	t (h)	Products*	Stable
1	1025	1298	771	BCR	B
1	1050	1323	263	RBC	?
1	1075	1348	991	BRC	?
1	1100	1373	263	R	R
1	1150	1423	263	R	R
2	1050	1323	261	BHR	B
2	1100	1373	261	BHR	B
2	1150	1423	261	B(H)	B
2	1171	1444	171	BRH	B
2	1196	1469	656	HR	HR
2	1224	1497	354	HT	HT
3	1025	1298	771	BH(C?)	B
3	1050	1323	261	BH	?
3	1100	1373	261	BH(R?)	?
3	1150	1423	261	BH(R?)	?
3	1171	1444	171	BHR	BR
4	1196	1469	656	HR	HR
4	1201	1474	429	HR	HR
5	1201	1474	429	HR	HR

Note: 1 = braunite (B), cristobalite (C), and rhodonite (R) in the proportions of Eq. 2; 2 = braunite, hausmannite (H), and rhodonite in the proportions of Eq. 3; 3 = braunite, hausmannite, and cristobalite in the proportions of Eq. 4; 4 = hausmannite + tephroite (T) synthesized from Mix 2; 5 = braunite.

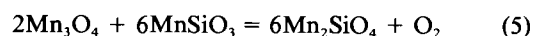
\* In order of estimated abundance.

lower  $f_{\text{O}_2}$  and temperatures, there would be only one reaction bounding the lower  $f_{\text{O}_2}$ , high-temperature side of the braunite field:



The metastable extension of Reaction 4 should lie sub-parallel to Reaction 3 and at lower  $f_{\text{O}_2}$  (higher temperature) values; if rhodonite failed to nucleate, we should be able to locate this reaction, even though metastable.

Cristobalite was synthesized by heating SiO<sub>2</sub> glass in a covered Pt crucible, contained in a high-purity alumina muffle tube, at 1788 K for 22 h. Synthetic hausmannite (Huebner and Sato, 1970) and rhodonite (Robie et al., 1989) have been described previously. Mixtures of reactants and products in the molar proportions specified by the reaction were heated in air. Reactants and products were identified by X-ray powder diffraction and oil-immersion methods to determine which phases grew at the expense of other phases. Results are tabulated in Table 4. Reaction 2 lies between 1298 and 1373 K. Reaction 3 lies between 1444 and 1469 K. We were not successful in locating Reaction 4. Using mixtures of braunite + hausmannite + rhodonite and of hausmannite + tephroite, we were also able to determine that the reaction



lies between 1474 and 1497 K.

#### CALORIMETRIC MEASUREMENTS

The calorimeters and techniques used for measuring heat capacities from 5 to 1000 K in our laboratory have been described previously [see for example Robie (1987), Hemingway et al. (1981)]. Our experimental measure-

**TABLE 5.** Molar heat capacities of rhodonite\* determined by adiabatic calorimeter

<i>T</i> (K)	Heat capacity [J/(mol·K)]	<i>T</i> (K)	Heat capacity [J/(mol·K)]	<i>T</i> (K)	Heat capacity [J/(mol·K)]
<b>Series 1</b>		<b>Series 3</b>		<b>Series 4 (cont.)</b>	
301.65	87.63	59.34	20.97	239.96	76.63
306.50	88.51	64.38	22.87	245.28	77.50
311.83	89.46	69.44	23.63	250.64	78.53
317.16	90.89	74.77	25.09		
322.48	91.02	80.50	27.47	<b>Series 5</b>	
327.79	91.90	86.02	29.81		
333.05	93.08	91.59	32.28	255.78	79.54
338.31	93.91	97.20	34.64	261.64	80.61
343.59	94.75	102.68	36.88	267.13	81.64
348.91	95.24	108.06	39.01	272.64	82.75
354.23	95.69	113.36	41.06	278.13	83.65
		118.59	43.03	283.61	84.73
<b>Series 2</b>		123.74	44.97	289.07	85.86
4.46	6.674	128.83	46.88	294.53	86.92
5.42	5.333	133.87	48.67	299.98	87.61
6.42	5.161	138.87	50.46	305.41	88.57
7.03	5.159	143.84	52.04	310.83	89.50
7.83	5.205	148.77	53.76		
8.78	5.437	153.68	55.09	<b>Series 6</b>	
9.77	5.567			51.37	15.56
10.77	5.553	<b>Series 4</b>		55.07	17.91
11.74	5.668	150.30	54.42	58.56	20.76
13.09	5.538	155.75	55.98	62.27	22.11
14.82	5.540	160.84	57.46	66.36	23.51
16.57	5.611	165.96	59.00	70.30	23.90
18.72	5.520	170.77	60.32	74.13	25.06
21.14	5.524	175.55	61.69	77.84	26.56
23.51	5.674	180.35	62.91		
25.92	5.994	185.14	64.30	<b>Series 7</b>	
28.82	6.747	189.94	65.56		
32.19	7.468	194.76	66.74	51.50	15.64
35.67	8.578	199.59	67.94	53.54	16.86
39.74	10.57	204.45	69.09	55.50	18.23
44.34	11.97	209.34	70.31	57.52	20.42
49.01	14.12	214.28	71.31	59.70	20.64
		219.26	72.42	61.86	21.95
		224.32	73.45	63.97	22.92
		229.46	74.42	66.04	23.52
		234.68	75.54		

\* Formula weight 131.022 g/mol.

**TABLE 6.** Molar heat capacities of braunite\* determined by adiabatic calorimeter

<i>T</i> (K)	Heat capacity [J/(mol·K)]	<i>T</i> (K)	Heat capacity [J/(mol·K)]	<i>T</i> (K)	Heat capacity [J/(mol·K)]
<b>Series 1</b>		<b>Series 5</b>		<b>Series 7 (cont.)</b>	
302.39	382.8	88.49	181.9	213.17	314.7
307.66	386.5	89.24	186.7	219.53	320.3
313.15	389.0	90.01	189.4	226.03	326.0
318.61	393.0	90.88	197.6	232.75	331.8
324.03	396.1	91.71	203.5	239.64	337.2
329.44	398.8	92.54	213.2	246.60	342.7
334.86	400.2	93.36	229.6	253.62	348.4
340.26	404.2	94.19	213.7	260.69	353.8
345.68	407.2	95.09	181.9	267.80	359.1
		95.97	180.3		
<b>Series 2</b>		96.77	180.3	<b>Series 8</b>	
38.74	37.15	97.59	181.0		
43.16	46.39	98.43	180.1	275.03	364.4
		99.27	180.6	282.30	368.9
		100.11	181.6	289.34	375.1
<b>Series 3</b>		100.95	182.5	296.40	379.1
47.92	56.78	101.78	182.9	303.48	384.0
52.86	68.50				
57.21	79.59	<b>Series 6</b>		<b>Series 9</b>	
62.07	92.37	97.01	180.4	5.20	0.6279
67.37	107.0	101.95	182.9	5.37	0.3846
72.36	121.9	106.89	188.6	5.49	0.3686
		111.88	194.6	5.76	0.5700
<b>Series 4</b>		116.75	200.6	6.05	0.6029
77.30	137.4	121.64	207.2	6.64	0.9568
81.76	152.8	126.48	213.8	7.20	1.149
86.03	170.5	131.28	220.1	8.15	1.946
90.54	195.9	136.04	226.4	9.39	2.447
95.05	197.2	140.78	232.4	10.61	2.973
99.76	181.2	145.50	238.3	11.85	3.587
104.36	185.7	150.20	244.8	12.96	4.327
108.59	190.8	154.88	250.1	14.25	5.115
		159.55	255.7	15.80	6.178
		164.22	261.2	17.49	7.457
				19.38	9.122
		<b>Series 7</b>		21.50	11.12
		169.68	267.6	23.87	13.61
		175.93	275.3	26.53	16.78
		182.13	282.0	29.51	20.86
		188.40	289.7	32.87	26.18
		194.50	295.9	36.61	33.75
		200.68	302.3	40.80	41.68
		206.89	308.4	45.41	50.99
				50.36	62.22

\* Formula weight 604.644 g/mol.

ments are listed in Tables 5, 6, and 7 in their chronological order of measurement.

The heat capacity of rhodonite was measured between 5 and 354 K. The mass of the calorimetric sample was 16.834 g. The contribution of the sample to the total measured heat capacity ranged from 97% at 5.4 K to a minimum of 20% at 80 K. Although we had anticipated finding a  $\lambda$ -peak in  $C_p^\circ$  at low temperatures, none was observed. However, in the temperature range 5–30 K,  $C_p^\circ$  was essentially constant with a value of approximately 5.4 J/(mol·K), as shown in Figure 2. The magnetic susceptibility of  $MnSiO_3$  was measured between 4.2 and 300 K by Sawaoka et al. (1968), who report a Néel temperature of 7 K. Our  $C_p^\circ$  data suggest that if  $MnSiO_3$  orders antiferromagnetically it must do so at a temperature below 6 K.

The heat capacity of braunite ( $Mn_7SiO_{12}$ ) was measured by adiabatic calorimetry between 5.2 and 345.6 K.

Braunite exhibits a  $\lambda$ -point in  $C_p^\circ$  with a Néel temperature (i.e., paramagnetic to antiferromagnetic transition temperature,  $T_N$ ) between 93.4 and 94.2 K, in good agreement with Abs-Wurmbach et al. (1981), who reported 93 K on the basis of the magnetic susceptibility of synthetic powdered braunite. The heat capacity of braunite between 75 and 110 K is shown in Figure 3. The braunite sample had a mass of 43.923 g and ranged from 71 to 40% of the measured total heat capacity. The heat capacity of braunite was also measured between 340 and 900 K by differential scanning calorimetry. For these measurements the sample mass was 21.041 mg, the heating rate was 10 K/min, and the sensitivity was 0.0084 J/s.

We are unaware of any previous calorimetric measure-

**TABLE 7.** Differential scanning calorimeter measurements of braunite

$T$ (K)	$C_p^0$ [J/(mol·K)]	$T$ (K)	$C_p^0$ [J/(mol·K)]
338.7	400.1	459.4	449.7
348.8	406.0	469.5	451.1
358.8	410.6	479.6	453.5
368.9	415.7	489.6	454.0
379.0	420.0	499.7	455.7
389.0	424.4	509.7	458.8
399.1	428.3	519.8	459.2
409.1	432.4	529.9	461.3
419.2	435.7	539.3	476.0
429.3	439.1	549.2	492.2
439.3	442.7	800.5	506.3
449.4	445.9	899.5	521.2

ments on braunite. Miyano and Beukes (1987) estimated values for  $C_p^0$ ,  $S_{298}^0$ , and  $\Delta_f H_{298}^0$  of braunite.

Bennington et al. (1987) reported  $C_p^0$  data for two natural manganese silicates, pyroxmangite of composition  $(\text{Mn}_{0.93}\text{Ca}_{0.056}\text{Mg}_{0.01}\text{Fe}_{0.010})\text{SiO}_3$  from Butte, Montana, and zincian rhodonite of composition  $(\text{Mn}_{0.632}\text{Ca}_{0.21}\text{Zn}_{0.09}\text{Mg}_{0.05}\text{Fe}_{0.02})\text{SiO}_3$  from Franklin, New Jersey. They reported a  $\lambda$ -like transition in  $C_p^0$  of pyroxmangite at  $-272.1$  K and Schottky anomalies in the heat capacities of pyroxmangite and zincian rhodonite at 11 and 8 K, respectively. The temperature of the  $\lambda$ -like transition in their pyroxmangite coupled with the large amount (0.37 wt%) of  $\text{H}_2\text{O}+$  in the analysis strongly suggests that the cause of the peak in  $C_p^0$  at 272.1 K is due to the melting of ice in fluid inclusions in the pyroxmangite and is not a property of  $\text{MnSiO}_3$ . Furthermore, neither our sample of rhodonite nor the  $\text{MnSiO}_3$  of Kelley (1941), both of which were synthesized anhydrously, nor the zincian rhodonite sample of Bennington et al. (1987), which has only 0.02 wt%  $\text{H}_2\text{O}+$ , exhibits the transition that the pyroxmangite shows. We believe this transition is due to the enthalpy of fusion of ice. This phenomenon has been observed previously in materials that contain significant numbers of fluid inclusions, e.g., euclase (Hemingway et al., 1986).

The absence of a  $\lambda$ -peak in  $C_p^0$  of rhodonite is somewhat surprising for such a magnetically concentrated compound. A large-scale plot of the  $C_p^0$  data of Bennington et al. (1987) for pyroxmangite and zincian rhodonite, of Kelley's (1941) values for synthetic  $\text{MnSiO}_3$ , and our own flux-grown synthetic rhodonite, all reduced to the same mass, shows systematic differences. Below approximately 130 K our values and those of Kelley (1941) are always greater than those for pyroxmangite and very much greater than those for the zincian rhodonite sample, and the percentage difference increases with decreasing temperature. We believe that this is a reflection of the replacement of the paramagnetic  $\text{Mn}^{2+}$  by diamagnetic Ca and Zn ions in the natural mineral samples, and, further, that this implies that the magnetic contribution of the  $\text{Mn}^{2+}$  ion to the heat capacity is still significant at temperatures of the order of 100 K. Note that approximately 5 and 35% of the  $\text{Mn}^{2+}$  has been replaced by diamagnetic ions in the pyroxmangite and zincian rhodonite samples

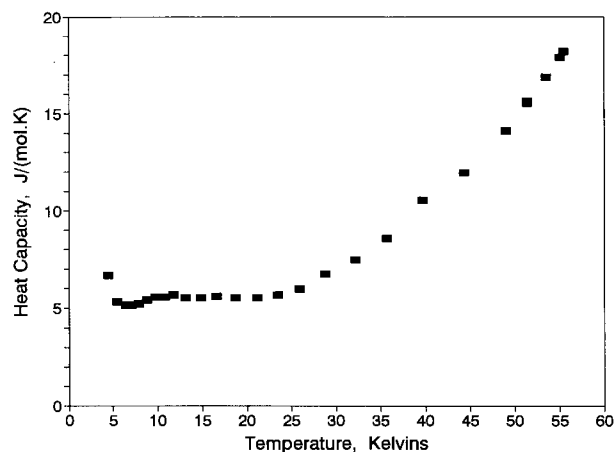


Fig. 2. Molar heat capacity  $C_p^0$  of synthetic rhodonite ( $\text{MnSiO}_3$ ) between 5 and 55 K. Note the absence of a pronounced  $\lambda$  transition.

of Bennington et al. (1987), respectively, and, furthermore, that both samples contain appreciable amounts of  $\text{Fe}^{2+}$ .

The crystal structure of rhodonite has been refined by Peacor and Niizeki (1963), by Ohashi and Finger (1976), and by Narita et al. (1977). The  $\text{SiO}_2$  tetrahedra form zig-zag chains with a repeat unit of five tetrahedra (fünferketten) separated by bands of edge-linked Mn coordination polyhedra. The important feature of the structure is that the ten  $\text{Mn}^{2+}$  of the unit cell ( $Z = 10$ ) occupy five different equipoints. The M1, M2, and M3 Mn are coordinated by fairly regular octahedra, whereas M4 is four-fold-fivefold coordinated and M5 is sevenfold coordinated. This irregularity in the coordination polyhedra may be the reason that  $\text{MnSiO}_3$  does not exhibit a sharp  $\lambda$ -transition above 6 K as do  $\text{Mn}_2\text{SiO}_4$  ( $T_N = 47.4$  K; Robie et al., 1982) or  $\text{MnCO}_3$  ( $T_N = 34.3$  K; Robie et al., 1984). Antiferromagnetic ordering of the  $\text{Mn}^{2+}$  presumably takes place by the superexchange mechanism (see, for example, White and Geballe, 1979), and this is sensitive to both the interionic spacing and to the cation-anion angle ( $\text{Mn}^{2+}\text{-O}^{2-}\text{-Mn}^{2+}$ ), which is presumably different for each pair because of the nonequivalence of the  $\text{Mn}^{2+}$  equipoints.

The observed behavior of  $C_p^0$  could arise from the persistence of short-range magnetic order above a cooperative magnetic transition at some temperature below our lowest measurement. A neutron diffraction study of the spin structures of rhodonite and pyroxmangite at He temperatures (4.2 K) and also of their magnetic susceptibilities at temperatures below 20 K would be most helpful for understanding the cause of the anomalous behavior of  $C_p^0$  of rhodonite below 20 K.

#### THERMODYNAMIC PROPERTIES OF RHODONITE AND BRAUNITE

The low-temperature  $C_p^0$  measurements were extrapolated to 0 K using the customary plot of  $C_p^0/T$  against



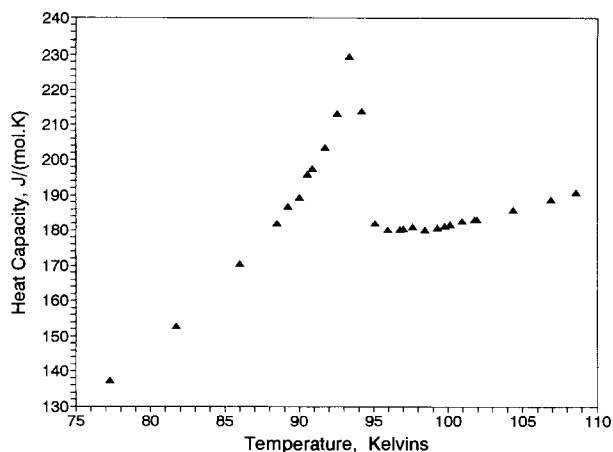


Fig. 3. Molar heat capacity  $C_p^\circ$  of braunite ( $\text{Mn}_7\text{SiO}_{12}$ ) between 75 and 110 K, showing the  $\lambda$  transition at a Néel temperature of 94 K. This point is associated with the antiferromagnetic-paramagnetic transition (discussed in text).

$T^2$ . For braunite the entropy arising from this extrapolation is only 0.4 J/(mol·K). This value may be slightly low. Westerholt et al. (1986) observed a maximum in the magnetic susceptibility of braunite at 1 K. The process yielding this maximum could also cause a heat capacity anomaly and increase in entropy. For rhodonite, however, the very large values for  $C_p^\circ$  at the lowest measured temperatures give rise to a significant amount of entropy below 6 K and accordingly increase the uncertainty in  $S_{298.15}^\circ$  considerably.

Tables of the thermodynamic properties at integral temperatures were obtained by spline smoothing of the experimental  $C_p^\circ$  data. Properties for rhodonite and braunite are listed in Tables 8 and 9, respectively.

The entropies at 298.15 K derived from our low-temperature measurements are  $100.5 \pm 1.0$  and  $416.4 \pm 0.8$  J/(mol·K) for rhodonite and braunite, respectively. Our  $C_p^\circ$  data for rhodonite were combined with the high-temperature relative enthalpy data of Southard and Moore (1942) to generate values for  $C_p^\circ$  up to 1500 K. For braunite we extrapolated our combined adiabatic and DSC measurements (6–900 K) graphically to 1500 K and generated a three-term Maier-Kelley equation to represent  $C_p^\circ$  between 300 and 1500 K. The equation  $C_p^\circ$  (braunite) =  $4.301 \times 10^2 + 1.110 \times 10^{-1} \times T - 7.325 \times 10^6/T^2$  fits the observed (300–900 K) data to 0.9%.

The available data for the enthalpy of formation of  $\text{MnSiO}_3$  (rhodonite) are summarized in Table 1. There are two direct calorimetric measurements of the enthalpy change for Reaction 1. King (1952) used aqueous HF solution calorimetry at 298.15 K, whereas Navrotsky and Coons (1976) used the molten salt technique at 986 K. The equilibrium



has been studied by Peters (1971), Candia et al. (1975),

TABLE 8. Standard molar thermodynamic properties of rhodonite,  $\text{MnSiO}_3$

$T$ (K)	Heat capacity $C_p^\circ$	Entropy $S_p^\circ - S_0^\circ$	Enthalpy function $(H_p^\circ - H_0^\circ)/T$	Gibbs energy function $-(G_p^\circ - H_0^\circ)/T$
10	5.49	6.49	3.72	2.78
20	5.68	10.37	4.66	6.77
30	6.98	12.80	5.12	7.68
40	10.16	15.20	5.94	9.26
50	14.91	17.93	7.21	10.72
60	18.21	20.85	8.69	12.16
70	22.58	23.99	10.36	13.62
80	26.96	27.29	12.16	15.12
90	31.24	30.71	14.05	16.67
100	35.41	34.22	15.97	18.24
110	39.43	37.78	17.93	19.86
120	43.28	41.38	19.88	21.50
130	46.96	44.99	21.82	23.17
140	50.46	48.60	23.74	24.86
150	53.76	52.20	25.64	26.56
160	56.87	55.77	27.49	28.27
170	59.80	59.30	29.31	30.00
180	62.58	62.80	31.08	31.72
190	65.21	66.26	32.81	33.45
200	67.70	69.66	34.49	35.17
210	70.08	73.02	36.13	36.90
220	72.33	76.34	37.72	38.61
230	74.48	79.60	39.27	40.33
240	76.53	82.81	40.78	42.03
250	78.48	85.98	42.25	43.72
260	80.35	89.09	43.68	45.41
270	82.15	92.16	45.07	47.08
280	83.89	95.18	46.43	48.75
290	85.58	98.15	47.75	50.40
300	87.23	101.1	49.04	52.04
310	88.86	104.0	50.30	53.67
320	90.46	106.8	51.53	55.29
330	92.03	109.6	52.73	56.89
340	93.59	112.4	53.91	58.48
350	95.13	115.1	55.07	60.06
273.15	82.70	93.11	45.51	47.61
298.15	86.93	100.5	48.80	51.74

Note: units are joules per mole kelvin.

\* Formula weight 131.022 g/mol.

and Abrecht (1988). Their data were combined with the thermal functions for  $\text{MnCO}_3$  of Robie et al. (1984), for  $\text{MnO}$ ,  $\text{CO}_2$ , and  $\text{SiO}_2$  of Robie et al. (1978), and  $f_{\text{CO}_2}$  calculated using the program of Kerrick and Jacobs (1981), to generate enthalpies for Reaction 6 at 298.15 K.

Schwerdtfeger and Muan (1966) give  $\Delta_r G_{1473}^\circ = -24.68 \pm 1.26$  kJ for Reaction 1 based upon the extrapolation of their activity measurements on  $(\text{Mn,Fe})\text{SiO}_3$  to the pure Mn end-member. Biggers and Muan (1967) obtained  $\Delta_r G_{1473}^\circ = -27.20$  kJ for this reaction on the basis of activity measurements for  $(\text{Mn,Co})\text{SiO}_3$  and  $(\text{Mn,Co})_2\text{SiO}_4$ , extant values for  $\Delta_r G_{1473}^\circ$  for  $\text{CoSiO}_3$  and  $\text{Co}_2\text{SiO}_4$ , and the equilibrium



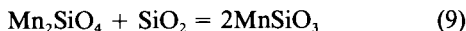
Both of these investigations were made in the temperature region where the deviation of  $\text{MnO}$  from exact stoichiometry becomes significant. We used the values listed in Robie et al. (1978) for  $\text{MnO}$  and  $\text{SiO}_2$  to convert these to  $\Delta_r G_{298.15}^\circ$  and to  $\Delta_r G^\circ$  ( $\text{MnSiO}_3$ , 298.15 K) assuming that the  $\text{SiO}_2$  in both high temperature studies was tridy-

mite, but because these compounds depart from system MnO-SiO<sub>2</sub>-O<sub>2</sub> composition (Table 1), we excluded these values when generating Table 10.

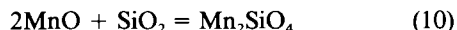
Rog and Pycior (1987) obtained the Gibbs free energy change for the reactions



and



using solid-electrolyte galvanic cells with manganese- $\beta$ -alumina as the electrolyte, between 950 and 1300 K. Adding their  $\Delta_r G^\circ$  values for Reactions 8 and 9 yields  $-27.21 \pm 1.22$  kJ for  $\Delta_r G^\circ$  of Reaction 1, at the intermediate temperature, 1150 K. Using our thermal functions to reduce this to  $\Delta_r H^\circ(\text{MnSiO}_3, 298.15 \text{ K})$  gives  $-1323.1 \pm 1.6$  kJ/mol. Rog and Pycior's (1987) values show a drift of  $\approx 0.5$  kJ in the calculated value of  $\Delta_r H^\circ(298.15 \text{ K})$  as a function of measurement temperature (1000–1300 K). We can also use Rog and Pycior's (1987) data to calculate the Gibbs free energy change for the reaction



since  $2\Delta_r G^\circ(\text{Reaction 8}) + \Delta_r G^\circ(\text{Reaction 9}) = \Delta_r G^\circ(\text{Reaction 10})$ . This calculation yields  $-47.92 \pm 1.95$  kJ (at 1000 K) which is 3.6 kJ more negative than the value adopted by Robie et al. (1982). Unfortunately, the  $\Delta_r G^\circ$  values for MnSiO<sub>3</sub> and Mn<sub>2</sub>SiO<sub>4</sub> obtained from Rog and Pycior's (1987) data are not independent of one another inasmuch as both Reactions 8 and 9 involve MnSiO<sub>3</sub> and Mn<sub>2</sub>SiO<sub>4</sub>. At best we can say that the emf measurements are not in serious disagreement with our selected values. The slope of Rog and Pycior's (1987)  $\Delta_r G^\circ(T)$  for Reaction 9 is  $-8.2$  J/K whereas that calculated from the calorimetric entropy data is  $-6.4$  J/K. Similarly, for Reaction 10 the slope obtained from the emf measurements is 4.0 J/K whereas that from the calorimetric entropies is 7.0 J/K. If we exclude the two high-temperature activity studies the average for  $\Delta_r H^\circ(\text{MnSiO}_3, 298.15 \text{ K})$  is  $-1321.6 \pm 2.0$  kJ/mol, which we adopt. This yields  $\Delta_r G^\circ(\text{MnSiO}_3, 298.15 \text{ K}) = -1244.7 \pm 2.0$  kJ/mol.

The value which we have adopted for braunite,  $-4260$  kJ/mol, was obtained by attempting simultaneously to satisfy our experimental brackets for Reaction 3, while also requiring the curves for Reactions 3 and 5 to intersect within the field outlined by Reactions 24, 6, and 17 (described below) as suggested by the absence of natural assemblages in which braunite coexists with tephroite and as required by the resulting chemography. We assumed that  $\Delta_r H^\circ(\text{Mn}_7\text{SiO}_{12}, 298.15 \text{ K})$  was the only variable quantity, i.e., the entropy changes for Reactions 3, 5, 6, 17, and 24, and the enthalpies of formation of all other phases (listed in Table 10) were exact. If we use  $-4260$  kJ/mol as the enthalpy of formation of braunite together with the ancillary data from Table 10 we get  $T_{\text{eq}}$  for Reaction 3 of  $\approx 1415$  K at  $f_{\text{O}_2} = 0.21$  bar (i.e., air), which is 24 K less than the lowest temperature allowed by our

TABLE 9. Standard molar thermodynamic properties of braunite,\* Mn<sub>7</sub>SiO<sub>12</sub>

T (K)	Heat capacity C <sub>p</sub>	Entropy S <sub>p</sub> - S <sub>g</sub>	Enthalpy function (H <sub>p</sub> - H <sub>g</sub> )/T	Gibbs energy function -(G <sub>p</sub> - H <sub>g</sub> )/T
5	0.39	0.124	0.092	0.032
10	2.70	0.984	0.734	0.250
15	5.67	2.60	1.85	0.75
20	9.72	4.76	3.29	1.47
25	14.91	7.46	5.07	2.39
30	21.57	10.74	7.24	3.50
35	30.38	14.69	9.88	4.81
40	40.16	19.40	13.06	6.34
45	50.23	24.70	16.62	8.08
50	61.50	30.56	20.54	10.02
60	86.85	43.98	29.44	14.54
70	114.6	59.41	39.59	19.82
80	147.0	76.75	50.91	25.84
90	188.7	96.38	63.83	32.55
93	222.4	103.04	68.30	34.72
100	181.4	116.8	76.82	40.01
110	193.1	134.7	86.85	47.85
120	205.4	152.0	96.21	55.79
130	218.2	168.9	105.1	63.81
140	231.1	185.6	113.6	72.0
150	243.9	201.9	121.9	80.0
160	256.3	218.1	129.9	88.2
170	268.3	234.0	137.7	96.3
180	279.8	249.6	145.3	104.3
190	290.9	265.1	152.7	112.4
200	301.4	280.3	159.8	120.5
210	311.3	295.2	166.8	128.4
220	320.6	309.9	173.6	136.3
230	329.4	324.4	180.2	144.2
240	337.7	338.6	186.6	152.0
250	345.7	352.5	192.8	159.7
260	353.3	366.2	198.8	167.4
270	360.7	379.7	204.7	175.0
280	367.8	392.9	210.4	182.5
290	374.7	406.0	215.9	190.1
300	381.3	418.8	221.3	197.5
310	387.9	431.4	226.6	204.8
273.15	363.0	383.9	206.5	177.4
298.15	380.1	416.4	220.3	196.1

Note: units are joules per mole kelvin.

\* Formula weight 604.644 g/mol.

experimental brackets. The  $\Delta_r S^\circ(298.15 \text{ K})$  for Reaction 3 has an uncertainty of  $\pm 2.7$  J/K, and accordingly within the uncertainty in the entropy change we could have adjusted  $\Delta_r H^\circ(298.15 \text{ K})$  of braunite, as derived from the single equilibrium bracket at  $\approx 1440$  K, by  $\pm 3.8$  kJ/mol. Similarly, the uncertainty in  $\Delta_r S^\circ$  of Reaction 5 is  $\pm 6.5$  J/K, and therefore the position of the intersection of Reactions 3 and 5 is only poorly constrained. The very limited amount of equilibrium data involving braunite, coupled with the fact that the data are all at the same  $f_{\text{O}_2}$ , make unwarranted any attempt to adjust the thermodynamic data of any of the other phases in the two reactions. Until more extensive temperature-dependent equilibrium data for Reaction 3 are available, we believe that  $-4260.0 \pm 3.8$  kJ/mol is the current best value for the enthalpy of formation of braunite at 298.15 K. Combining this value with our entropy we calculate  $\Delta_r G^\circ(\text{Mn}_7\text{SiO}_{12}, 298.15 \text{ K}) = -3944.7 \pm 3.8$  kJ/mol. An error in the equilibrium temperature of 10 K corresponds

TABLE 10. Summary of thermodynamic properties of phases in the MnO-SiO<sub>2</sub>-CO<sub>2</sub>-O<sub>2</sub> system

Name and formula	Formula weight (g)	Entropy S <sub>298</sub> <sup>0</sup> [J/(mol·K)]	Enthalpy Δ <sub>f</sub> H <sub>298</sub> <sup>0</sup> (kJ/mol)	Molar V <sup>*</sup> (J/bar)	A1	A2	A3	A4	A5	Range (K)	Reference
Braunite Mn <sub>7</sub> SiO <sub>12</sub>	604.644	416.4 0.8	-4260.0 3.8	12.508 0.005	430.1	0.111	-7325000			298 1700	This study
Rhodonite MnSiO <sub>3</sub>	131.022	100.5 1.0	-1321.6 2.0	3.494 0.005	99.04	0.01915	-3041000	274.5		298 1500	This study
Pyroxmangite MnSiO <sub>3</sub>	131.022	99.4 2.0	-1322.3 3.0	3.472 0.002						298	This study
Pyrolusite MnO <sub>2</sub>	86.937	52.8 0.1	-520.0 0.7	1.661 0.002	290.4	-0.1442	2012000	-3787.0	4.541 × 10 <sup>-5</sup>	298 850	Robie and Hemingway (1985)
Hausmannite Mn <sub>3</sub> O <sub>4</sub>	228.812	164.1 0.2	-1384.5 1.4	4.695 0.006	-7.432	0.09487	-6712000	3396.0		298 1400	Robie and Hemingway (1985) Keller et al. (1991)
Bixbyite Mn <sub>2</sub> O <sub>3</sub>	157.874	113.7 0.2	-959.0 1.0	3.137 0.005	162.4	0.01211	1046000	-1317.0	3.462 × 10 <sup>-6</sup>	325 1400	Robie and Hemingway (1985)
Tephroite Mn <sub>2</sub> SiO <sub>4</sub>	201.96	155.9 0.4	-1731.5 2.9	4.861 0.007	261.3	-0.01378		-22178.0		298 1600	Robie et al. (1982)
Manganosite MnO	70.937	59.7 0.4	-385.2 0.5	1.322 0.0004	60.28	0.0351	0	97.5		298 1800	Robie et al. (1978)
Rhodochrosite MnCO <sub>3</sub>	114.947	98.0 0.1	-892.9 1.2	3.107 0.001	149.7	0.01876	141700	-1314.2		298 600	Robie et al. (1984) This study
Quartz SiO <sub>2</sub>	60.085	41.46 0.16	-910.7 1.0	2.2688 0.0001	81.14	0.01828	-181000	-698.5	5.406 × 10 <sup>-6</sup>	298 844	Hemingway (1987)
Carbon dioxide** CO <sub>2</sub> (ideal gas)	44.01	213.79 0.04	-393.5 0.2	2478.97 0.02	88.11	-0.002698	723200	-1007.0		298 2200	Garvin et al. (1987)
Oxygen O <sub>2</sub> (ideal gas)	31.999	205.15 0.0	0.0 0.02	2478.97 0.02	56.58	-0.005255	685600	-578.0	1.113 × 10 <sup>-6</sup>	298 2500	Garvin et al. (1987)

Note: uncertainties as 2σ. C<sub>p</sub> = A1 + A2 × T + A3/T<sup>2</sup> + A4/T<sup>3</sup> + A5 × T<sup>2</sup>.

\* At standard temperature and pressure.

\*\* The effect of pressure can be calculated from Kerrick and Jacobs (1981).

to a change in the derived value of Δ<sub>f</sub>H<sup>0</sup>(Mn<sub>7</sub>SiO<sub>12</sub>, 298.15 K) of 1.1 kJ/mol.

Our measured value for S<sub>298.15</sub><sup>0</sup> of Mn<sub>7</sub>SiO<sub>12</sub> is 10.4 J/(mol·K) less than the estimated value of Miyano and Beukes (1987), and our value for Δ<sub>f</sub>H<sup>0</sup>(Mn<sub>7</sub>SiO<sub>12</sub>, 298.15 K) is 24.0 kJ/mol more negative than their estimate. Their value for braunite was based in part upon phase equilibrium studies by Muan (1959b), which, as noted above, pertain to Si-rich braunite and which Abs-Wurmbach et al. (1983) did not reproduce.

#### ENTROPY AND FREE ENERGY OF PYROXMANGITE

If we accept the slope of the phase boundary for the rhodonite = pyroxmangite transformation given by Maresch and Mottana (1976), ≈ 50 bar/K, our value for the entropy of rhodonite, and the previously derived difference in molar volumes, then we can calculate an entropy for pyroxmangite at 298.15 K of 99.0–99.5 J/(mol·K). Bennington et al. (1987) give 99.5 ± 0.2 J/(mol·K) for the entropy of pyroxmangite of supposed composition (Mn<sub>0.955</sub>Ca<sub>0.045</sub>)SiO<sub>3</sub>. Bennington et al. (1987) also give -1324.8 ± 4.2 kJ/mol for Δ<sub>f</sub>H<sup>0</sup>(298.15 K) of pyroxmangite after correcting their results to the composition MnSiO<sub>3</sub>. Furthermore, Navrotsky and Coons (1976) have

measured the enthalpy change for the pyroxmangite-rhodonite transition by molten salt calorimetry with the result Δ<sub>f</sub>H<sub>986</sub><sup>0</sup> = 0.25 ± 1.38 kJ. All this is by way of emphasizing that the difference in the molar Gibbs free energies of pyroxmangite and rhodonite is quite small, of the order of 1 kJ/mol.

#### Mn-Si-O-C PHASE DIAGRAM

For convenience, we have assembled the thermodynamic data for the more important phases in the MnO-SiO<sub>2</sub>-CO<sub>2</sub>-O<sub>2</sub> system in Table 10. The values for the enthalpies of formation of the manganese oxides were taken from Robie and Hemingway (1985) except for Mn<sub>3</sub>O<sub>4</sub>, which was modified by the inclusion of the data of Keller et al. (1991), and the elimination of a typographic error (inversion of the last two digits) in the value for Δ<sub>f</sub>H<sup>0</sup>(Mn<sub>3</sub>O<sub>4</sub>, 298.15 K) of Robie and Hemingway (1985).

These values were entered into a spreadsheet to calculate the equilibrium constants, as a function of temperature and pressure, for the reactions indicated below. The RT ln(f<sub>CO<sub>2</sub></sub>) term for those equilibria involving CO<sub>2</sub> was calculated using the f<sub>CO<sub>2</sub></sub> polynomial given by Holland and Powell (1990). The results of the calculations for these reactions helped us develop Figure 4 and are

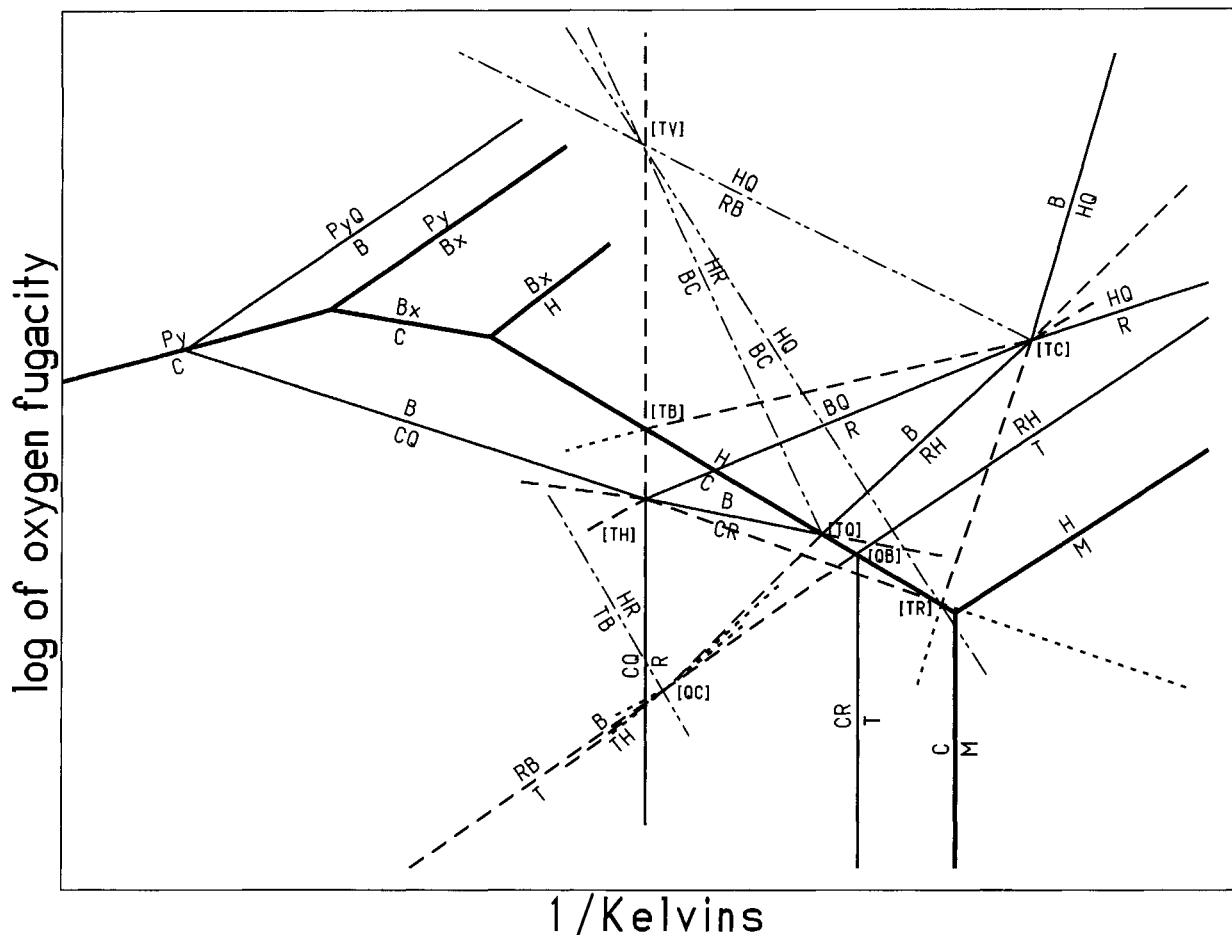
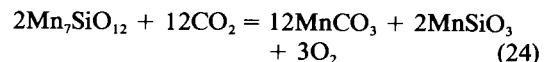
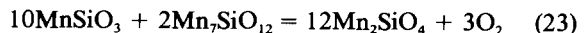
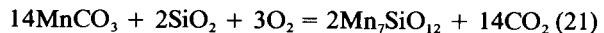
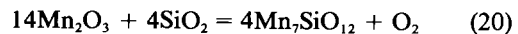
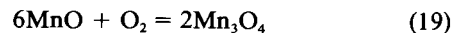
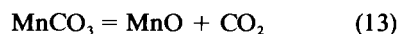
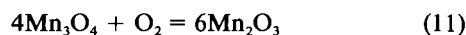
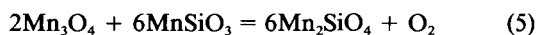
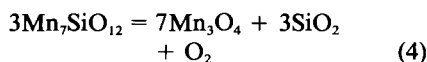
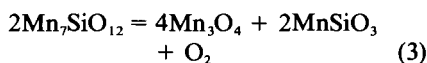
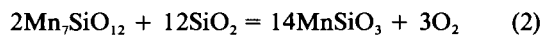


Fig. 4. Partial net of Schreinemaker bundles for the system  $\text{MnO-SiO}_2\text{-C-O}_2$ , not drawn to scale in order to show topologic relationships. Pressure greater than the vapor pressures of the solid phases; vapor is present and  $P_1 = P_{\text{CO}_2} + P_{\text{CO}} + P_{\text{O}_2}$ . Phases are Py = pyrolusite ( $\text{MnO}_2$ ), Bx = bixbyite ( $\text{Mn}_2\text{O}_3$ ), M = manganosite ( $\text{Mn}_{1-x}\text{O}$ ), C = rhodochrosite ( $\text{MnCO}_3$ ), H = hausmannite, Q = quartz, B = braunite of nominal composition  $\text{Mn}_7\text{SiO}_{12}$ , R = Ca-free rhodonite, T = tephroite, and V = vapor. For simplicity, V is omitted when labeling reactions. Heavy solid lines

represent stable reactions in the system Mn-C-O (Huebner, 1969). All other reactions are a consequence of adding  $\text{SiO}_2$  to the system; those pertaining to the phases C, H, B, R, T, Q, and V are shown. Light solid lines are stable; dashed and dotted lines are metastable. Dash-dot-dot lines are condensed (vapor absent); although they cannot exist, they are shown for completeness. Invariant points are labeled by enclosing the two missing phases in brackets; [TR], [QC], and [TB] are metastable; [TV] is condensed.

summarized in Figure 5 as a plot of  $\log f_{\text{O}_2}$  against  $1/T$  (K) at 2 kbar total pressure. The reactions corresponding to the phase boundaries in Figure 5 are:



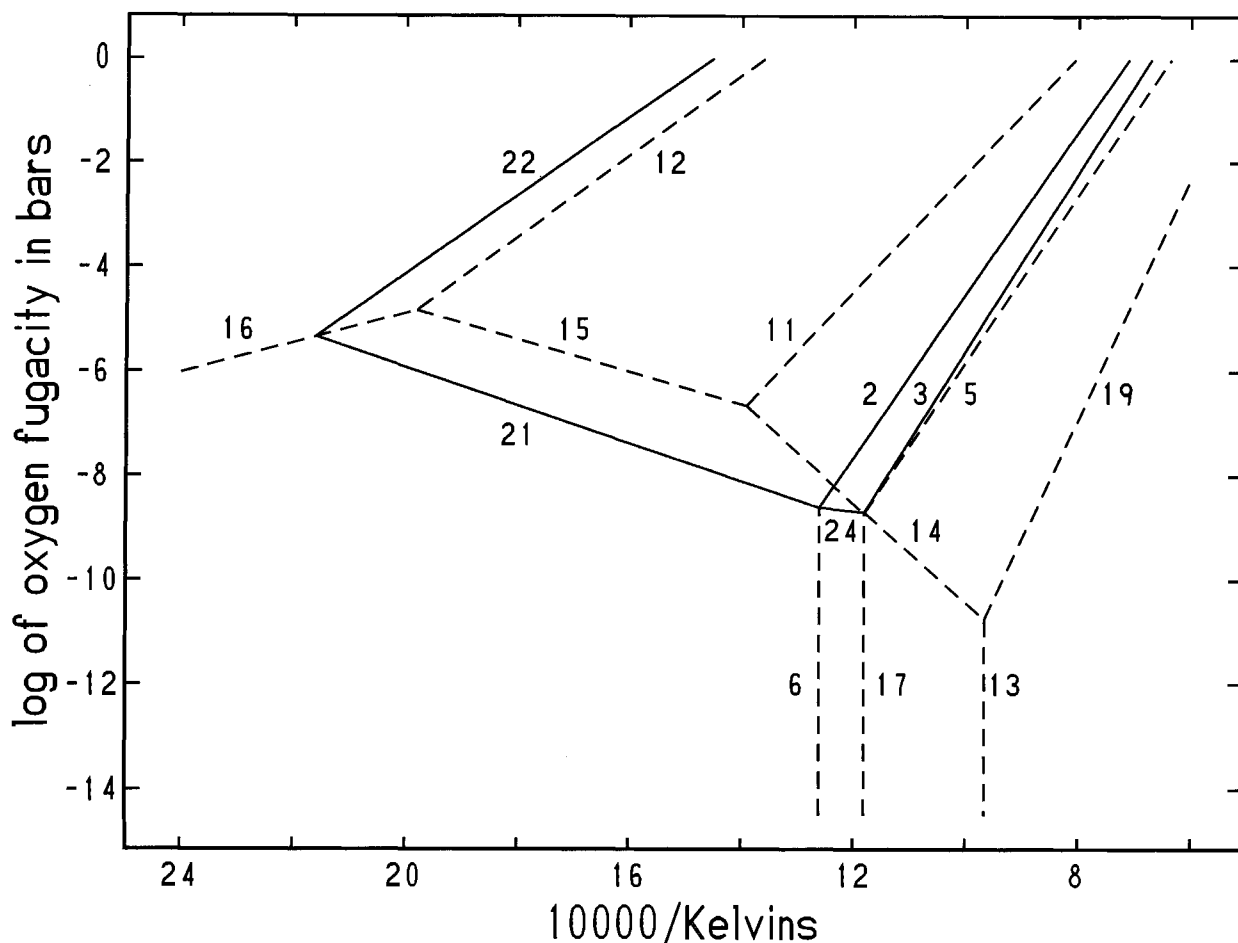
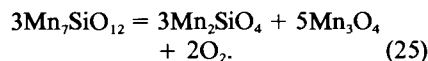


Fig. 5. Net of stable reactions at 2000 bars (0.2 GPa) calculated from the data of Table 10 and emphasizing reactions involving braunite.  $P_i = P_{\text{CO}_2} + P_{\text{CO}} + P_{\text{O}_2}$ , and the vapor is  $\text{CO}_2$ -rich in the temperature- $\log f_{\text{O}_2}$  region shown. Numbered reactions correspond to equations in text. Solid lines correspond to reactions involving braunite. Invariant points [TQ], [QB], and [QC], shown on Fig. 4, cannot be distinguished on this figure so six stable reactions (3, 5, 14, 17, 24, and 14) appear to radiate from a point.



The stoichiometric coefficients for several of the phases, e.g.,  $\text{Mn}_2\text{O}_3$ ,  $\text{MnCO}_3$ ,  $\text{MnSiO}_3$ , and  $\text{SiO}_2$ , are large, specifically in Reactions 20, 21, and 3; and inasmuch as the estimated uncertainties in  $\Delta_r G^\circ$  for these phases are  $\pm 1$ – $2$  kJ/mol, the effect upon the position of the calculated equilibrium arising from these uncertainties can be significant. For example, a change of 1 kJ/mol in  $\Delta_r H^\circ(\text{MnCO}_3, 298.15 \text{ K})$  would change the position of Reaction 21 by 0.49 in  $\log f_{\text{O}_2}$ .

Many of these reactions are shown in Figure 4. The topology of the grid is derived from the petrogenetic grid presented by Huebner (1967, 1976), and the similar grid of Peters et al. (1974), but with two modifications arising from our new thermodynamic data for braunite (summarized in Table 10 and Fig. 5). (1) Reaction 21,  $\text{CQ} = \text{B}$ , by which rhodochrosite + quartz form braunite, now lies at lower  $f_{\text{O}_2}$  values. One consequence of this shift is

that braunite oxidizes to pyrolusite + quartz (Reaction 22,  $\text{B} = \text{PyQ}$ ) rather than to bixbyite + quartz (Reaction 20). This change is in accord with the aforementioned critical assemblage braunite + pyrolusite + quartz but precludes the critical assemblage braunite + bixbyite + quartz. Perhaps solid solution of Fe in braunite lowers the  $f_{\text{O}_2}$  at which braunite oxidizes, so that Fe-rich braunite oxidizes to Fe-rich bixbyite + quartz (similar to Reaction 20), and Fe-poor braunite oxidizes to pyrolusite + quartz (Reaction 22). A second consequence of the shifting of Reaction 21 is to make the reaction of rhodochrosite + rhodonite to form braunite stable (Reaction 24,  $\text{CR} = \text{B}$ ). The critical natural assemblage rhodochrosite + rhodonite + braunite is unknown to us. (2) Invariant points [T,C] and [Q,C] have been modified (such that the stable extensions of the univariant curves have become metastable, and vice versa) and repositioned such that Reaction 2,  $\text{R} = \text{BQ}$ , lies at higher  $f_{\text{O}_2}$  than Reaction 3,  $\text{RH} = \text{B}$ , and these reactions diverge toward lower  $f_{\text{O}_2}$  and temperature, as required by Table 10 and Figure 5.

(As mentioned earlier, the enthalpy of braunite was also adjusted, within the limits of uncertainty, to satisfy the chemography.) The invariant point [Q,C] is now metastable and lies concealed by one of the fields in which carbonate is stable. The result of these changes is that Reactions 3, RH = B, and 5, T = RH now converge as temperature and  $f_{O_2}$  are decreased, consistent with the enthalpies of reaction. When the grid is positioned quantitatively and at the scale of Figure 5 in  $\log f_{O_2} - 1/T$  (K) space at 2000 bars with vapor consisting predominantly of  $CO_2$ , invariant points [TQ], [QB], and [QC] appear to lie on top of each other.

Several features of Figures 4 and 5 merit comment. We are dealing with an isobaric four component system, Mn-Si-O-C; in the absence of graphite, we need only consider the compositional domain MnO-SiO<sub>2</sub>-O<sub>2</sub>-CO<sub>2</sub>. According to the phase rule, an isobaric invariant point has five phases in equilibrium, and an isobaric univariant curve has four phases in equilibrium. Because the grid is an isobaric section with pressure fixed at greater than the vapor pressures of the solids, vapor-absent invariant points, univariant curves, and divariant fields cannot exist. Nevertheless, we show [TV] and its vapor-absent univariant curves for completeness.

In the the seven-phase subsystem rhodochrosite-Si-poor braunite-hausmannite-tephroite-Ca-free rhodonite-quartz-vapor, we show eight (of 21 possible) isobaric invariant points; of these eight, four are stable. The phases TRQ are compositionally colinear and there are two sets of coplanar phases, TQRV and CTRQ. The isobaric univariant curve HCV passes stably through isobaric invariant points [TB], [TQ], [QB], and [TR]; colinearities also occur along RCQV and RHBV. Reactions CHV and RVBQ cross indifferently because the compositional domains of these reactions do not overlap (CHV is silica-free). We know of no precedent for a systematic analysis of a system with four components, seven (or more) phases, and compositional degeneracy. We hope that the availability of consistent thermodynamic data for these phases may stimulate others in a systematic topological analysis.

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