

# MnO exsolution in periclase from Långban, Sweden: an evaluation of the activity-composition relations in the system MgO–MnO

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## ABSTRACT

The occurrence of MnO exsolution in periclase host crystals from Långban, Sweden, is described. The composition of the periclase is  $\text{Mg}_{0.942}\text{Mn}_{0.046}\text{Zn}_{0.012}\text{O}$ , and it coexists with exsolved manganosite crystals with a composition of  $\text{Mn}_{0.909}\text{Mg}_{0.082}\text{Zn}_{0.008}\text{O}$ . Crystals of hausmannite are also present, indicating  $f_{\text{O}_2}$  conditions approaching the MnO–Mn<sub>3</sub>O<sub>4</sub> equilibrium.

Activity-composition data for the system MgO–MnO is critically reviewed. The data obtained from solid electrolyte measurements are rejected because of the unrealistic calculated equilibration temperatures and the large deviations from the gas equilibration Mn–Pt activity measurements. The large errors associated with the gas equilibration measurements, especially at large  $X_{\text{MnO}}$ , also introduces uncertainties associated with the asymmetric interaction parameters. The non-parametric 'jack-knife' method was used to determine the asymmetric interaction parameters and their standard deviations from the data of Wood *et al.* (1994) and Tsai and Muan (1992). These were calculated as  $W_{\text{MnO}} = 21.2$  kJ/mol,  $\sigma W_{\text{MnO}} = 2.5$  kJ/mol and  $W_{\text{MgO}} = 8.2$  kJ/mol,  $\sigma W_{\text{MgO}} = 3.3$  kJ/mol.

Using the asymmetric interaction parameters,  $W_{\text{MnO}} = 19.9$  kJ/mol and  $W_{\text{MgO}} = 13.7$  kJ/mol for the system MgO–MnO as determined by Wood *et al.* (1994) and the equations for two-phase equilibrium as formulated by Thompson (1967), equilibration temperatures of 334°C and 466°C were calculated. The difference between the calculated temperatures is ascribed to inaccuracies in the experimentally determined interaction parameters.

**KEYWORDS:** manganosite, periclase, exsolution, system MgO–MnO, calculated solvus.

## Introduction

THE thermodynamic properties of oxide solid solutions are of critical importance in both petrology and metallurgy since the mixing properties of many silicates have been derived from their equilibrium compositions with co-existing oxide solid solutions (Muan, 1967). Recently, Wood *et al.* (1994) determined and

used the activity-composition data of MgO–MnO solid solutions to determine activity coefficients for olivine solid solutions co-existing with the monoxide solid solutions. These activity coefficients of olivine were then used to determine mixing properties of garnet solid solutions. Clearly, the mixing parameters determined for many silicate solid solutions depend on accurate mixing parameters for the oxide solid solutions.

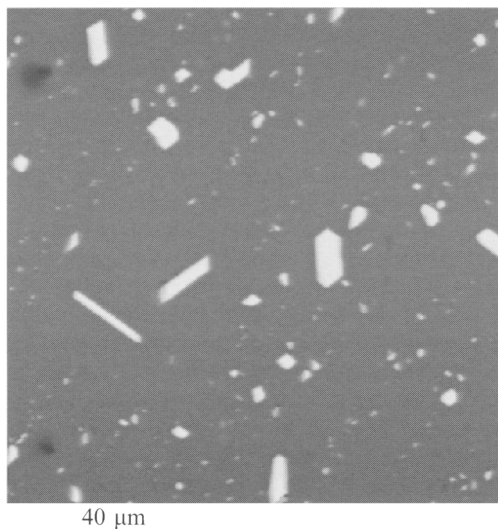


FIG. 1. Electron backscatter image of crystallites of manganosite in a matrix of periclase. The manganosite shows up as the bright phase.

A sample of a natural occurrence of unmixing of manganosite in a periclase host provided an opportunity to test the validity of the mixing parameters of the system MgO–MnO, as well as to evaluate the different experimentally determined activity–composition relations. The solvus calculated from the experimentally derived interaction parameters can thus be compared with the measured compositions of naturally occurring samples. In synthetically prepared samples, exsolution was never found to occur, but Wood *et al.* (1994) predicted exsolution to occur below the critical temperature of 1077 K (804°C). In natural samples, manganosite intergrowths in periclase from Långban, Sweden was described by Frondel (1940), and the sample described in this study is from the same occurrence.

## Experimental

Samples of manganese-containing oxides were obtained from the Transvaal Museum and are labelled: Manganosite — Långban, Sweden. These samples were examined petrographically, by X-ray diffractometry, and by scanning electron microscopy.

The samples contain hausmannite and calcite, together with minor intergrown grains of periclase

and green manganosite. The grains of the periclase-manganosite intergrowth were isolated by dissolving the sample in dilute hydrochloric acid. Both the carbonates and the hausmannite were dissolved, leaving the intergrown green monoxide phases as a residue. Figure 1 shows the crystals of manganosite of varying size in a matrix of periclase.

The co-existing phases were carefully analysed by electron microprobe. Standards used were experimentally prepared MnO/Mn mixtures sintered at 1500°C to ensure that the MnO is stoichiometric, (Keller and Dieckmann, 1985), synthetic MgO, ZnO and hematite.

## Results

The *d*-spacings shown in Table 1, derived from the X-ray diffraction data of the periclase–manganosite intergrowth also indicate the presence of solid solution in the two phases. No other peaks are present in the X-ray data of the green residue. The unit cell values show reasonable correspondence with those calculated using Vegard's Law.

The results of the microprobe analyses are given in Tables 2 and 3. Inspection of the mean values and their standard deviations show a small variation in composition regardless of the size of the manganosite crystals. Average detection limits for MnO, ZnO, MgO, and FeO are 0.06%, 0.13%, 0.07%, and 0.05% respectively. FeO is below the detection limit and is not included in the Tables.

## Discussion

Evaluation of the microprobe analyses reveals that the phases have consistent compositions with low standard deviations. These values will be used to calculate temperatures of exsolution using experimental thermodynamic interaction parameters from several sources.

Several sources of data were consulted in order to obtain the most reliable set of interaction parameters for the solid solution. These will be discussed separately below. In all calculations the subregular model as used by Thompson (1967) was used. The expression describing the activity coefficient of MnO is:

$$RT \ln \gamma_{\text{MnO}} = \frac{W_{\text{MnO}} + 2X_{\text{MnO}}(W_{\text{MgO}} - W_{\text{MnO}})(X_{\text{MgO}})^2}{(W_{\text{MnO}} + 2X_{\text{MnO}}(W_{\text{MgO}} - W_{\text{MnO}})(X_{\text{MgO}})^2)}$$

The data of Raghavan *et al.* (1985) were derived from solid electrolyte electrochemical

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TABLE 1. X-ray diffraction data for a periclase–manganosite intergrowth

Periclase		Manganosite	
<i>d</i> -spacing (Å)	JCPDS (Å)	<i>d</i> -spacing (Å)	JCPDS (Å)
2.442	2.431	2.560	2.568
2.114	2.106	2.217	2.223
1.494	1.489	1.567	1.571
1.274	1.270	1.336	1.340
1.220	1.216		

Unit cell size of manganosite and periclase (Å)			
Phase	<i>a</i> (Experimental)	<i>a</i> (Vegard's Law)	<i>a</i> (Pure phases)
Manganosite	4.432	4.424	4.445
Periclase	4.226	4.224	4.213

measurements in the temperature range 1163 to 1318 K. These activity–composition data were considered by Wu *et al.* (1993) to be the preferred values.

A plot of  $\ln \gamma_{\text{MnO}}/(1 - X_{\text{MnO}})^2$  vs.  $X_{\text{MnO}}$  is shown in Fig. 2 for the 1163, 1213, and 1318 K data of Raghavan *et al.* (1985). If the measurements at  $X_{\text{MnO}} = 0.1$  are omitted, then this plot shows symmetric behaviour with  $W_{\text{MgO}} = W_{\text{MnO}} = 10$  kJ/mol.

The solvus and chemical spinodal calculated with the symmetric  $W_{\text{MnO}}$  value of 10 kJ/mol is shown in Fig. 3.

As can be deduced from inspection of the solvus, unrealistically low exsolution temperatures of around 400 K (or 127°C) result if the experimentally measured  $X_{\text{MnO}}$  values are used. We therefore concluded that the activity–composition data of Raghavan *et al.* (1985) are not as reliable as the gas equilibration data, since

TABLE 2. Microprobe analyses for manganosite. Figures in bold are the means and standard deviations

MnO	ZnO	MgO	Totals	$X_{\text{MnO}}$	$X_{\text{ZnO}}$	$X_{\text{MgO}}$
94.47	0.87	5.1	100.45	0.907	0.007	0.086
94.17	0.95	5.13	100.25	0.905	0.008	0.087
94.49	0.82	5.36	100.70	0.903	0.007	0.09
94.24	0.95	4.65	99.85	0.913	0.008	0.079
94.55	0.92	4.9	100.37	0.909	0.008	0.083
94.10	1.04	4.85	100.00	0.909	0.009	0.082
94.48	1.13	4.81	100.44	0.909	0.009	0.081
93.69	1.13	4.89	99.72	0.907	0.01	0.083
94.60	0.98	4.72	100.30	0.912	0.008	0.08
93.69	1.04	5.01	99.74	0.906	0.009	0.085
94.10	1.00	4.49	99.59	0.915	0.008	0.077
95.25	0.94	4.13	100.31	0.922	0.008	0.07
94.34	1.10	4.23	99.69	0.918	0.009	0.072
95.06	1.05	4.35	100.5	0.917	0.009	0.074
93.80	1.09	5.48	100.36	0.899	0.009	0.092
93.96	0.86	5.47	100.29	0.901	0.007	0.092
<b>94.31</b>	<b>0.99</b>	<b>4.85</b>	<b>100.16</b>	<b>0.909</b>	<b>0.008</b>	<b>0.082</b>
<b>0.44</b>	<b>0.1</b>	<b>0.41</b>	<b>0.34</b>	<b>0.006</b>	<b>0.001</b>	<b>0.007</b>

TABLE 3. Microprobe analyses for periclase. Figures in bold are the means and standard deviations

MnO	ZnO	MgO	Totals	$X_{MnO}$	$X_{ZnO}$	$X_{MgO}$
7.91	2.14	90.38	100.43	0.047	0.011	0.942
8.02	2.29	89.16	99.47	0.048	0.012	0.94
7.72	2.41	89.62	99.75	0.046	0.013	0.941
7.86	2.56	89.76	100.18	0.047	0.013	0.94
8.34	2.39	89.31	100.03	0.05	0.012	0.938
8.37	2.38	89.28	100.03	0.05	0.012	0.938
7.19	2.26	90.94	100.38	0.042	0.012	0.946
7.50	2.25	90.47	100.21	0.044	0.012	0.944
7.28	2.26	90.59	100.12	0.043	0.012	0.945
7.55	2.31	90.85	100.71	0.045	0.012	0.944
7.92	2.39	90.32	100.64	0.047	0.012	0.941
8.00	2.41	90.61	101.02	0.047	0.012	0.94
7.89	2.34	89.33	99.55	0.047	0.012	0.941
7.96	2.5	89.96	100.42	0.047	0.013	0.94
8.06	2.17	89.75	99.98	0.048	0.011	0.941
8.15	2.26	88.97	99.38	0.049	0.012	0.939
7.90	2.34	90.01	100.25	0.047	0.012	0.941
8.02	2.24	89.67	99.93	0.048	0.012	0.941
7.20	2.39	90.91	100.49	0.043	0.012	0.945
7.47	2.43	89.94	99.83	0.044	0.013	0.943
7.31	2.25	90.05	99.61	0.044	0.012	0.945
7.47	2.29	89.62	99.38	0.045	0.012	0.943
<b>7.78</b>	<b>2.33</b>	<b>89.98</b>	<b>100.08</b>	<b>0.046</b>	<b>0.012</b>	<b>0.942</b>
<b>0.35</b>	<b>0.10</b>	<b>0.59</b>	<b>0.45</b>	<b>0.002</b>	<b>0.001</b>	<b>0.002</b>

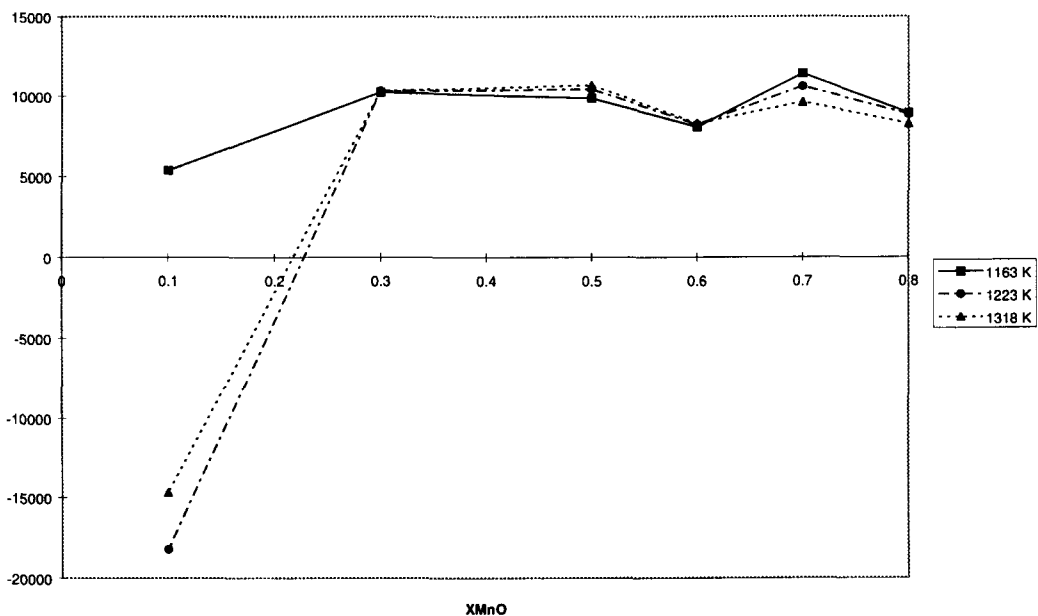


FIG. 2. Asymmetric plot of  $\ln \gamma_{MnO} / (1 - X_{MnO})^2$  vs.  $X_{MnO}$  for 1163, 1223, and 1318 K data as determined by Raghavan *et al.* (1985).

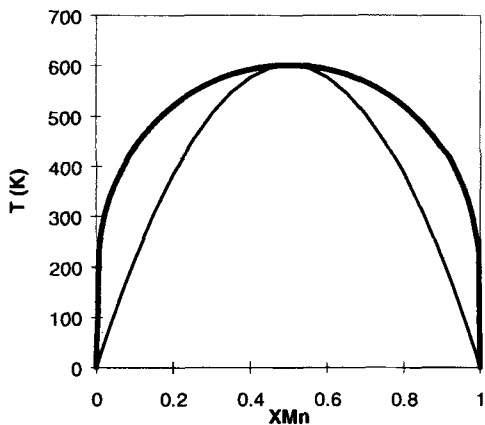


FIG. 3. Calculated solvus and chemical spinodal of the system MgO–MnO using a symmetric interaction parameter  $W = 10$  kJ/mol.

diffusion would probably cease at appreciably higher temperatures than 127°C. No exsolution should occur at these low temperatures.

The activity–composition data derived from gas equilibration and reaction with platinum seem to give more accurate results, but the precision of the data leaves much to be desired. A plot of  $\ln \gamma_{\text{MnO}} / (1 - X_{\text{MnO}})^2$  vs.  $X_{\text{MnO}}$  is shown in Fig. 4 for the 1300°C activity–composition data of Wood *et al.* (1994) and those of Tsai and Muan (1992) at 1500°C and 1600°C. There is reasonable corre-

spondence between these two sets of data, but the deviations are still large, especially at high  $X_{\text{MnO}}$ .

Also apparent is the increasing error limits as  $X_{\text{MnO}}$  increases towards unity. These were calculated using the method of propagation of errors. Because of the fact that there is a relation between the residuals and  $X_{\text{MnO}}$ , a non-parametric ‘jack-knife’ method was used to calculate the values of  $W_{\text{MnO}}$ ,  $W_{\text{MgO}}$ , and their standard errors. These were calculated as  $W_{\text{MnO}} = 21.2$  kJ/mol,  $\sigma W_{\text{MnO}} = 2.5$  kJ/mol and  $W_{\text{MgO}} = 8.2$  kJ/mol, with  $\sigma W_{\text{MgO}} = 3.3$  kJ/mol. The large asymmetry in the calculated values is not confirmed when the analysed compositions are taken into account, and the actual interaction parameters are more symmetric than the values calculated above.

The calculated solvus and chemical spinodal is shown in Fig. 5. These were calculated by Newton iteration using  $W_{\text{MnO}} = 19.9$  kJ/mol and  $W_{\text{MgO}} = 13.7$  kJ/mol, the most symmetric values used by Wood *et al.* (1994) and the equations for two-phase equilibrium as formulated by Thompson (1967).

If the compositions of the periclase and manganosite, together with the  $W_{\text{MnO}}$  and  $W_{\text{MgO}}$ -values of Wood *et al.* (1994) quoted above, are used to calculate temperatures of exsolution, then the following temperatures are obtained:

Periclase:  $X_{\text{MnO}} = 0.046$   $X_{\text{MgO}} = 0.942$   $T = 334^\circ\text{C}$   
 Manganosite:  $X_{\text{MnO}} = 0.909$   $X_{\text{MgO}} = 0.082$   $T = 466^\circ\text{C}$

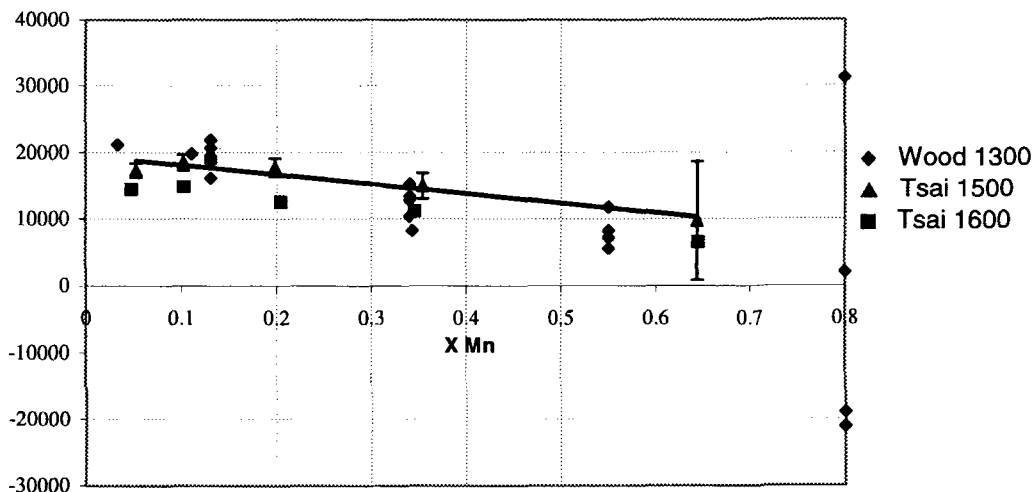


FIG. 4. Asymmetric plot of the data of Wood *et al.* (1994) and Tsai and Muan (1992). The least-squares line is drawn through the 1500°C data of Tsai and Muan.

If the interaction parameters were correct, then the two calculated temperatures would be identical. However the asymmetry in the parameters is still too large, i.e. the difference between the parameters should be smaller.

It could be argued that the differences in exsolution temperatures could arise from the fact that the  $f_{O_2}$  conditions prevailing in the sample (MnO–Mn<sub>3</sub>O<sub>4</sub> equilibrium) were not the same as in the samples used for the determination of the interaction parameters. This is indeed the case, but this fact should not make any difference to the applicability of the experimental results. If there were an appreciable difference in Mn–O stoichiometry between the natural and synthetic phases, the applicability of the experimental results could be questioned. Fortunately, the composition of natural Mn<sub>1-Δ</sub>O in equilibrium with Mn<sub>3</sub>O<sub>4</sub> at the exsolution temperatures is stoichiometric and is similar to the stoichiometry of the MnO used in the experimental studies at higher temperatures, ( $\log \Delta < -2$ ), (Keller and Dieckmann, 1985).

## Conclusion

In reviewing the accuracy and precision of the interaction parameters in the system MgO–MnO it is clear that the data from Raghavan *et al.* (1985) seem to be less accurate in that unrealistically low exsolution temperatures are predicted. For the gas equilibrium data, large experimental errors cause large uncertainties in the interaction parameters. It is therefore clear that a careful experimental re-assessment of the activity–composition relations is necessary, not only for petrological applications, but also for metallurgically important systems.

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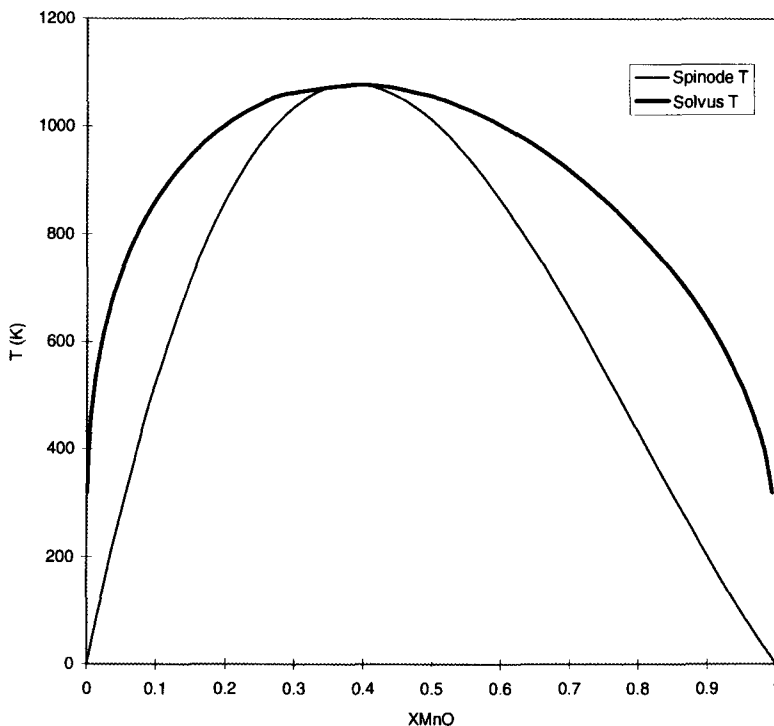


FIG. 5. Calculated solvus and chemical spinodal for the system MgO–MnO using the asymmetric interaction parameters of Wood *et al.* (1994).

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