The free energy of formation of Mg_2TiO_4 (synthetic qandilite), an inverse spinel with configurational entropy

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Abstract: Synthetic qandilite (Mg_2TiO_4) is an inverse spinel in which random mixing of Mg and Ti on the octahedral site should give rise to a configurational entropy of 11.5 J K^{-1} mol^{-1}. The free energy of formation of Mg_2TiO_4 has been determined from the location of the univariant reaction $MgTiO_3 + MgO = Mg_2TiO_4$ in pressure-temperature space between 0 and 20 kbar; together with literature data for $MgTiO_3$ and MgO, the results give $S^o_{(298K)}= 111.2 \pm 0.6$ J K^{-1} mol^{-1} for Mg_2TiO_4. This entropy is only 7.6 ± 0.9 J K^{-1} mol^{-1} more than the calorimetrically determined value of 103.6 ± 0.7 J K^{-1} mol^{-1}. The discrepancy implies either considerable short-range order of Mg and Ti in Mg_2TiO_4, or perhaps an error in the high-temperature heat-capacity data for $MgTiO_3$ caused by disordering in this substance.

Key-words: spinel, thermodynamic data, order-disorder, phase equilibria.

Introduction

A recent experimental investigation of the significance of Ti substitution into forsterite (Mg_2SiO_4) in the system $MgO-SiO_2-TiO_2$ (Hermann *et al.*, in press) has raised the need for accurate thermodynamic data for Mg_2TiO_4 spinel (the mineral qandilite). At present there exist some calorimetric data for this substance (reviewed by Eriksson & Pelton, 1993), but these data are insufficient to give the free energy of formation, as Mg_2TiO_4 is an inverse spinel which is expected to have configurational entropy from mixing of Mg and Ti on the octahedral sites of the spinel structure (O'Neill *et al.*, 2003b). Full development of this configurational entropy would contribute 11.5 J/K.mol in Mg_2TiO_4, but this may be reduced if there is short-range ordering. Since Mg_2TiO_4 with the usual cubic spinel structure ($Fd\bar{3}m$) is known to undergo a phase transition on cooling at ~ 1000°C to a tetragonal modification ($P4_122$), in which Mg and Ti are ordered onto distinct octahedral sites (Wechsler & Navrotsky, 1984; Millard *et al.*, 1995), some short-range ordering is a possibility.

Akimoto & Syono (1967) found that Mg_2TiO_4 breaks down to $MgTiO_3$ (geikielite) plus MgO (periclase) with increasing pressure, according to the univariant reaction:

$$Mg_2TiO_4 = MgTiO_3 + MgO \qquad (1).$$
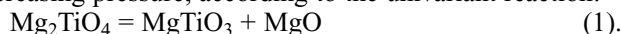
Since this reaction occurs in an experimentally easily accessible region of P-T space, and since there are complete calorimetric data for $MgTiO_3$ and MgO (which are both nearly pure, stoichiometric phases in the system $MgO-TiO_2$), this reaction provides an excellent means of

determining the free energy of formation of Mg_2TiO_4, which moreover can be done over an adequate temperature span to test whether the full configurational entropy of Mg-Ti mixing is developed. However, the study of Akimoto & Syono (1967) is really only reconnaissance work, in that their results do not bracket the reaction particularly snugly (see Fig. 1). Hence the purpose of this study is to reinvestigate reaction (1), applying modern piston-cylinder methods to obtain reversals that bracket the reaction with better precision than that achieved by Akimoto & Syono (1967), and probably also with better accuracy as regards temperature and pressure measurement.

Experimental

Starting materials consisted of synthetic Mg_2TiO_4 (material from the study of O'Neill *et al.*, 2003b) and $MgTiO_3$, synthesised, similarly to Mg_2TiO_4, from a stoichiometric mixture of MgO and TiO_2, ground under acetone in an agate mortar, pressed into pellets, and reacted at 1400°C in air in a box furnace. MgO was from BDH (Analar grade), fired at 1200°C in air before use. A starting mixture consisting of all three phases in the molar ratio of 1 Mg_2TiO_4 to 1 $MgTiO_3$ to 2 MgO (*i.e.* MgO in excess of that required by the stoichiometry of reaction 1) was then prepared.

Experiments at atmospheric pressure were made in a vertical tube furnace in air with a type B thermocouple positioned directly above the sample, ensuring that the
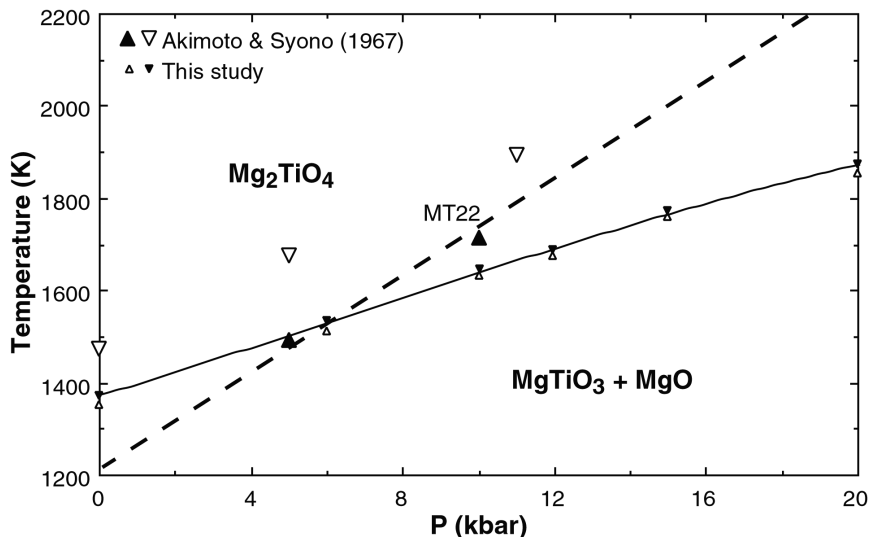
Fig. 1. Pressure-temperature brackets on the univariant reaction $MgTiO_3$ + MgO = Mg_2TiO_4 from this study, and from Akimoto & Syono (1967). Only the results from the experiments defining the curve are shown. The solid curve is an empirical 4th order polynomial drawn through the brackets of this study (note that this univariant reaction is not linear in P-T space). The dashed line is the equation quoted by Akimoto & Syono (1967), P (kbar) = –18 + 0.019 T (°C). Although their equation is in poor agreement with the results of this study, only one of their defining half-brackets (MT22 at 10 kbar) violates the curve of this study.

temperature of the experiment was measured accurately to ± 1°C. The thermocouple was checked against the melting point of gold, with results within 0.5°C of the recommended value of 1064.18°C (ITS-90). Previous work on Mg_2TiO_4 has shown that the kinetics of reaction (1) are too sluggish for any perceptible reaction to occur at atmospheric pressure in the simple system $MgO-TiO_2$ (Wechsler & Navrotsky, 1984), hence a flux of $Na_2B_4O_7$ (dehydrated borax) was added. The charge was run in a Pt capsule (5 mm diameter) sealed at one end and crimped closed at the other to minimize loss of Na_2O by volatilization. This flux proved less than completely ideal, as it reacts with MgO to produce a Mg-Ti-borate phase, thus the direction of reaction cannot be inferred simply from a change in proportions of the phases. Nevertheless, the results are strongly suggestive, in that abundant euhedral Mg_2TiO_4 is observed at 1100°C, but is completely absent at 1070°C. The formula of the Mg-Ti-borate is $Mg_3TiB_2O_8$ from electron microprobe determination of MgO and TiO_2, with B_2O_3 estimated by difference. Trials of a number of other possible fluxes (78 wt% BaO + 22 wt% B_2O_3, K_2CO_3, Na_2WO_4) were unsuccessful due to their incompatibility with one or more of Mg_2TiO_4, $MgTiO_3$ or MgO.

Experiments at high pressure (6 to 20 kbar) were conducted either in a 30 mm (at 12 kbar) or a 5/8" (other pressures) piston-cylinder apparatus with a NaCl-pyrex assembly surrounding a cylindrical graphite heater. The lengths of the cells were 60 mm for the 30 mm diameter cell and 1.5" (38 mm) for the 5/8" cell, and both cells used a graphite heater of 9.5 mm OD by 7 mm ID. In order to allow initial friction to decay, the run was first taken to 800°C and the pressure of interest, where it was held for ~24 hours; see Bose & Ganguly (1995) for a discussion of friction decay in the piston-cylinder apparatus with NaCl as the pressure medium. The run was then heated to the final desired temperature and the pressure adjusted to the final desired value. Samples were held in sealed Pt capsules, with dimensions 2.3 mm OD, 1.7 mm ID, 5 mm long. Temperature was controlled and measured with a type B

thermocouple positioned directly above the capsule. Thermocouples were made from the same batches of wire as those used in the 1-bar experiments. Temperatures in the piston-cylinder runs were not corrected for any effect of pressure; apart from this, the reported temperatures, which were controlled to ± 1°C, are thought to be accurate to ± 5°C at T ≤ 1400°C, the uncertainty being caused by small deviations in sample position within the thermal profile of the piston-cylinder cell. The thermal profile of the 30 mm cells should have a larger constant-temperature zone, lessening this source of error. Temperatures are probably more uncertain at T > 1400°C due to greater temperature gradients, and also to several other factors to do with thermocouple calibration and performance. Pressures, which are reported without any correction for friction, are precise to ± 0.2 kbar, and probably to ± 0.1 kbar in the 30 mm assembly.

Following the quenching of each run, the sample was mounted in epoxy, sectioned and polished for examination using the electron microprobe (CAMECA SX100) for back-scattered electron imaging and quantitative analysis by wavelength dispersive spectrometry. The starting material and selected run products were also examined by powder X-ray diffraction, using a STOE STADIP diffractometer in the transmission mode, with monochromatic $CoK\alpha_1$ radiation (λ = 1.78897 Å), scanning from 10 to 130°C. An internal standard of NIST 640c Si (a_0 = 5.4312 Å) was used, and the lattice parameters were extracted by Rietveld refinement of the whole pattern using the program LHPM-Rietica (Hunter & Howard, 2000).

Results

Results are reported in Table 1 and the defining brackets are plotted in Fig. 1. Experiments at ≥ 10 kbar are at a sufficiently high temperature that the reaction takes place rapidly and no flux is needed. The results are straightforward reversals, which bracket the reaction to within a

Table 1. Experimental results.

Run#	P (kbar)	T (°C)	Time (h)	Result
C19/5/03[a]	0.001	1050	48	MgTiO3, MgO, Mg-Ti-borate, quenched flux; many crystals of $MgTiO_3$ contain MgO inclusions
C8/4/04[b]	0.001	1070	46	$MgTiO_3$, MgO, Mg-Ti-borate, quenched flux
C21/7/03[b]	0.001	1080	24	Euhedral Mg_2TiO_4, $MgTiO_3$, corroded MgO, Mg-Ti borate, quenched flux
C26/3/04[b,e]	0.001	1088	66	Large euhedral Mg_2TiO_4 poikilitically enclosing some euhedral $MgTiO_3$ and MgO, $MgTiO_3$ and corroded MgO, Mg-Ti-borate, quenched flux
C26/5/03[a]	0.001	1090	23.5	Mg_2TiO_4,$MgTiO_3$,MgO, Mg-Ti-borate, quenched flux; reaction direction ambiguous
C14/7/03[b]	0.001	1100	48	Euhedral Mg_2TiO_4, $MgTiO_3$ and Mg-Ti-borate, corroded MgO, quenched flux
D366	6.0	1240	168	$MgTiO_3$ + MgO, 100% reaction, "eutectoid"
C1922[c]	6.0	1250	6	Mg_2TiO_4, $MgTiO_3$ with holes, quench carbonate
D362[d]	6.0	1250	48	No discernible reaction
D369	6.0	1260	192	MgO + Mg_2TiO_4, 100% reaction
D350	10.0	1340	50	$MgTiO_3$ + MgO, 100% reaction, "eutectoid"
C1918	10.0	1360	6	$MgTiO_3$ + MgO, 100% reaction, "eutectoid"
D354	10.0	1370	6	MgO + Mg_2TiO_4, some unreacted $MgTiO_3$
D343	10.0	1380	6	MgO + Mg_2TiO_4, 100% reaction
D342	10.0	1420	6	MgO + Mg_2TiO_4, 100% reaction
D340	10.0	1460	6	MgO + Mg_2TiO_4, 100% reaction
D338	10.0	1500	7	MgO + Mg_2TiO_4, 100% reaction
R204[e]	12.0	1405	6	$MgTiO_3$ + MgO, 100% reaction, "eutectoid"
R193[e]	12.0	1410	20	MgO + Mg_2TiO_4, some unreacted $MgTiO_3$
D361	15.0	1480	6	$MgTiO_3$ + MgO, 100% reaction, "eutectoid"
D364	15.0	1490	6	$MgTiO_3$ + MgO, 100% reaction, "eutectoid"
D358	15.0	1500	6	MgO + Mg_2TiO_4, some unreacted $MgTiO_3$
D363	20.0	1580	3	$MgTiO_3$ + MgO, 100% reaction, "eutectoid"
D360	20.0	1600	6	MgO + Mg_2TiO_4, few grains unreacted $MgTiO_3$
D359	20.0	1640	3	MgO + Mg_2TiO_4, 100% reaction

[a] +50% $Na_2B_4O_7$ (dehydrated borax);
[b] +20% $Na_2B_4O_7$;
[c] +20% oxalic acid;
[d] +10% oxalic acid
[e] 30 mm cell; all other high pressure runs in 15.875 mm cells; [e] no Mg_2TiO_4 in starting mix.

nominal 10 K at 10 and 15 kbar and 20 K at 20 kbar. At 12 kbar in the 30 mm pressure assembly, where the control of both temperature and pressure is sufficiently good to warrant the attempt at greater precision, the bracket is only 5 K in width.

There is a remarkable asymmetry in the textures produced on either side of the reaction in these fluxless experiments. On the high temperature side (Mg_2TiO_4 stable) there is extensive recrystallization to the typical granular texture expected for textural equilibrium, although in several runs close to the reaction boundary residual grains of $MgTiO_3$ persist, but completely surrounded by Mg_2TiO_4 and isolated from MgO (Fig. 2a). By contrast, on the low temperature side of the reaction there is little recrystallization of the original $MgTiO_3$ and MgO grains, while what were originally grains of Mg_2TiO_4 have decom-posed to a eutectoid-like intergrowth of $MgTiO_3$ and MgO (Fig. 2b). Despite this textural disequilibrium, the extent of reaction is complete in all cases, with no residual Mg_2TiO_4 persisting in any experiment.

For runs at 6 kbar, a small pinch (20 wt%) of oxalic acid was added to the first run (C1922, at 1250°C). A considerable amount of MgO dissolved in the CO_2-H_2O fluid produced by the decomposition of the oxalic acid, driving the starting composition off the target stoichiometry, which makes the result in terms of reaction direction difficult to ascertain. The $MgTiO_3$ contains carbonate/vapour "holes" while the Mg_2TiO_4 does not (Fig. 2c), which may perhaps indicate that Mg_2TiO_4 is stable; alternatively, this texture could be due to growth of the $MgTiO_3$ trapping the inclusions. Hence we regard this run as completely ambiguous. For the next run at 6 kbar and 1250ºC (D362) some extra
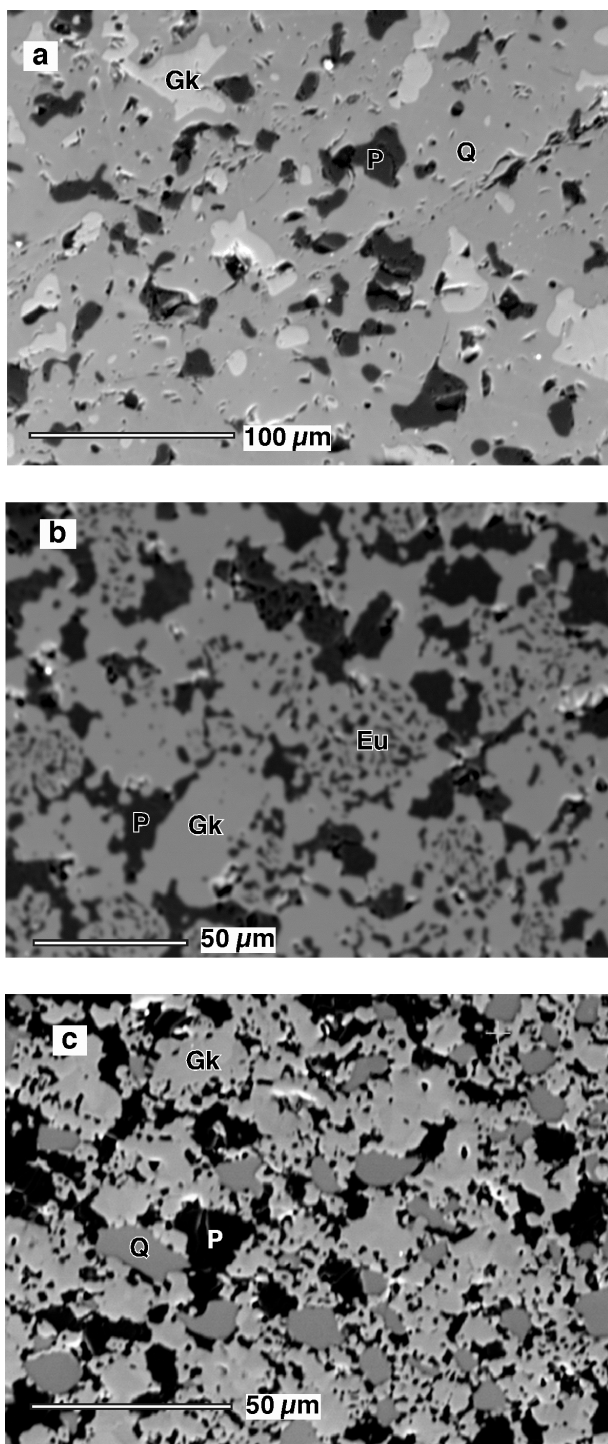
Fig. 2. Electron back-scattered images of run products from high-pressure experiments. The lighter the area, the higher the mean atomic number. Contrast has been adjusted to illuminate optimally the textures discussed in the text. a) run R193, showing residual MgTiO$_3$(Gk) surrounded by Mg$_2$TiO$_4$ (Q), with no contact with MgO (P); b) run D364, showing typical "eutectoid-like" intergrowths of MgTiO$_3$ + MgO (labelled "Eu") replacing original Mg$_2$TiO$_4$, plus original grains of MgTiO$_3$ (Gk) and MgO (P); c) Run C1922, showing MgTiO$_3$ (Gk) trapping vapour (or quench carbonate), now present as holes; the Mg$_2$TiO$_4$ (Q) does not contain these holes. What this means for the direction of reaction is equivocal.

MgO was added and the amount of oxalic acid reduced to 10 %. This run produced no discernible reaction direction, and the use of oxalic acid was abandoned. The two subsequent runs at 6 kbar produced an unambiguous bracket between 1240 and 1260°C.

The bracket at atmospheric pressure is placed between the run at 1070°C (C8/4/04), which produced euhedral MgTiO$_3$ plus MgO with no Mg$_2$TiO$_4$ (Figure 3a); and at 1080°C (C21/7/03), which contained Mg$_2$TiO$_4$ and MgTiO$_3$ with MgO, but with the Mg$_2$TiO$_4$ showing good crystal faces, while the MgO appears somewhat corroded (Fig. 3b). However, no reaction direction could be inferred from a run at 1090°C, in which all three phases were present but none show good crystal faces. An additional run at 1088°C (C26/3/04), which used a starting mix of MgTiO$_3$, MgO and flux only (*i.e.*, no Mg$_2$TiO$_4$), produced large, euhedrally faceted crystals of Mg$_2$TiO$_4$ poikilitically enclosing MgTiO$_3$ and the Mg-Ti-borate phase, with occasional small poorly faceted grains of MgO, interpreted to be residual (Fig. 3c); but the unambiguous growth of Mg$_2$TiO$_4$ in this run implies clearly that it is stable at this temperature. Run C19/5/03, which at 1050°C is well below the breakdown temperature, shows many grains of MgTiO$_3$ enclosing MgO blobs (Fig. 3d), which is somewhat reminiscent of the "eutectoid-like" textures of the high-pressure experiments; and like for these runs, we interpret these grains to be due to decomposition of original Mg$_2$TiO$_4$ grains.

The results are compared to the data of Akimoto & Syono (1967) in Fig. 1. At first sight there appears to be a large difference between the results if ours are compared to the equation for the univariant curve provided by Akimoto and Syono, which is P (kbar) = -18 + 0.019 T (°C). In fact, only one experiment of Akimoto and Syono is actually discrepant, namely their run MT22, in which Mg$_2$TiO$_4$ is reported to break down to MgTiO$_3$ and MgO at 10 kbar and 1440°C (*cf.* our bracket between 1360 and 1370°C at 10 kbar). This is far outside any likely experimental uncertainty in pressure or temperature measurement and we suggest an *ad hoc* experimental malfunction in run MT22 such as piston seizure or thermocouple extrusion.

Stoichiometry and composition of the run products

Like many spinels, Mg$_2$TiO$_4$ might be anticipated to show some non-stoichiometry by solid solution towards MgTiO$_3$ at high temperatures (*i.e.*, like MgAl$_2$O$_4$ towards γ-Al$_2$O$_3$). However, electron microprobe analysis showed almost negligible deviations in all runs from Mg$_2$TiO$_4$ stoichiometry (Table 2). It is probable that at atmospheric pressure the temperature at which reaction (1) occurs (*i.e.* 1075 ± 10°C) is not high enough for deviations from stoichiometry to be significant, while higher pressures suppress the non-stoichiometry due to the relatively high partial molar volume of the defect spinel component. Similarly, MgTiO$_3$ was found to be stoichiometric within analytical error in all runs. The observation of small amounts of TiO$_2$ (~ 0.6 wt%, corresponding to a mole fraction of 0.003) in MgO is likely at least in part an analytical artefact due to the "stray electron effect" (this is an issue of
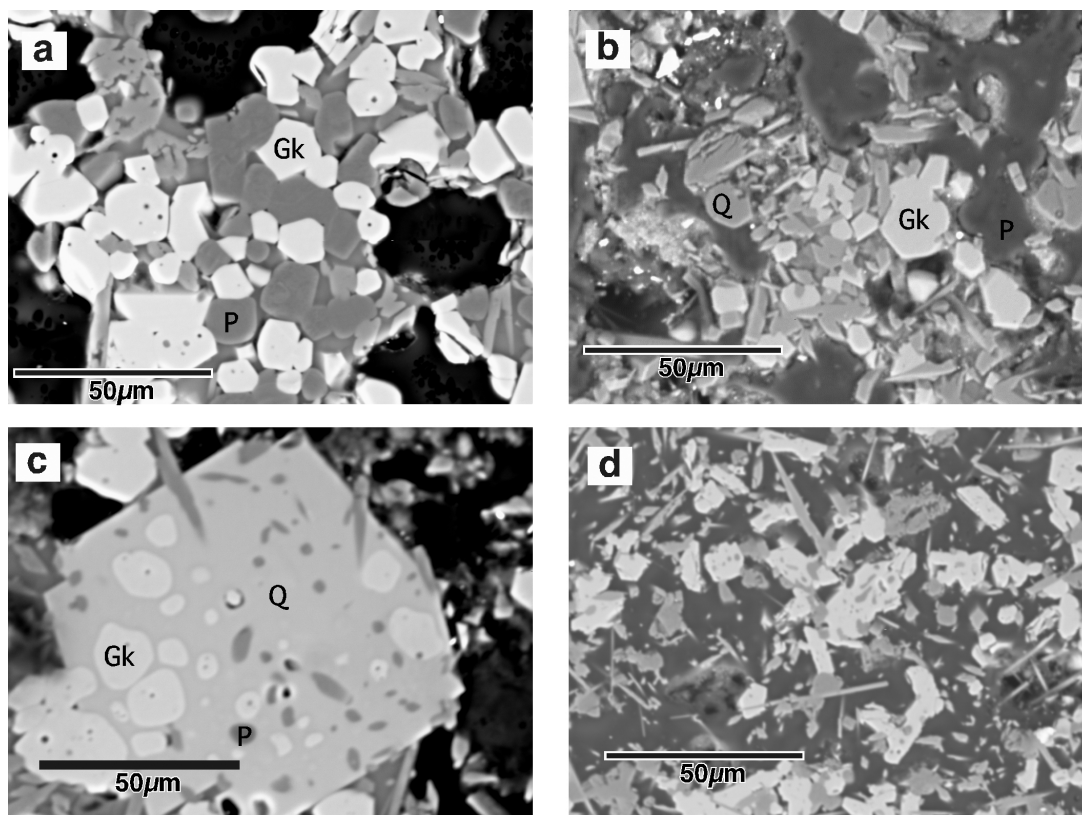
Fig. 3. Electron back-scattered images of run products from experiments at atmospheric pressure using Na$_2$B$_2$O$_4$ flux. All runs contain crystals of a Mg-Ti-borate phase (generally sub-acicular in habit, slightly lighter shade of grey to MgO) and quenched melt rich in Na$_2$O and B$_2$O$_3$ (dark areas, but generally indistinguishable from holes in these micrographs). The euhedral MgTiO$_3$ crystals in these runs are ~ 10 μm in diameter.
a) C8/4/04 (1270°C) showing euhedral MgTiO$_3$ (Gk) and MgO (P), with no sign of any Mg$_2$TiO$_4$. b) C21/7/03 (1280°C), showing euhedral Mg$_2$TiO$_4$ (Q) and MgTiO$_3$, with somewhat corroded MgO; c) C26/3/04 (1288°C) showing a large crystal of Mg$_2$TiO$_4$, which has grown to enclose subhedral to euhedral MgTiO$_3$ and some Mg-Ti-borate, with the occasional microblob of MgO; d) C19/5/03 (1050°C), in which some but not all MgTiO$_3$ contains many inclusions of MgO – cf. Fig. 2b.

experimental interest that is discussed in more detail in Hermann *et al*., in press). However, the jump to 0.9 wt% TiO$_2$ in the highest temperature run analysed (D363, 1580°C, 20 kbar) looks real as the MgO grain size in this run is larger than in the analysed runs with 0.6 wt% TiO$_2$. Pelton *et al*. (1998) report somewhat similar amounts of Ti in MgO in equilibrium with Mg$_2$Ti^{4+}O$_4$-MgTi$_2^{3+}$O$_4$ spinels in the system MgO-Ti-O at 1500°C and atmospheric pressure, the amounts increasing with decreasing oxygen

fugacity, suggesting that the valence state of the substituting Ti is mainly Ti^{3+}.

The accuracy with which lattice parameters can be measured can often make these data sensitive indicators of purity and stoichiometry, especially for phases with high crystallographic symmetry such as the three of interest here. The downside is that it is difficult to interpret the cause of a change in lattice parameter unambiguously; also, it is possible that important changes in purity and stoi-

Table 2. Electron microprobe analysis of selected run products to check for the stoichiometry of the phases.

Run#	P(kbar)	T(°C)	wt% TiO$_2$ in MgO	molar Mg/Ti geikielite	molar Mg/Ti quandilite
D362	6	1250	0.66(3)	1.020(6)	1.982(3)
C1922	6	1250	0.60(6)	1.021(7)	1.991(9)
D369	6	1260	0.64(1)	-	1.980(8)
R204	12	1495	0.69(4)	1.007(3)	-
D364	15	1490	0.68(6)	1.018(6)	1.971(8)
D363	20	1580	0.92(9)	1.009(10)	-

Analytical conditions: WDS, 15 kV, 20 nA, MgO and TiO$_2$ standards, TAP and LPET crystals.

Table 3. Lattice parameters (in Å).

Sample	MgO	Mg_2TiO_4	$MgTiO_3$		
			a	c	V(Å³)
Starting mix	4.2118	8.4418	5.0551	13.8987	307.58
D338	4.2119	8.4430	-	-	-
D343	4.2122	8.4426	-	-	-
D350	4.2128	-	5.0552	13.8977	307.57
D360*	4.2120	8.4433	5.057	13.895	307.7

* Only c.1% $MgTiO_3$ in run products

Estimated uncertainties (one standard deviation) are 0.0001 Å for MgO, 0.0002 Å for Mg_2TiO_4, and 0.01 Å³ for the unit cell volume (V) of $MgTiO_3$ (except D360).

chiometry either do not affect the lattice parameter, or that more than one type change occurs with a net cancelling effect. Here, the lattice parameters of MgO in the run products are consistent with the pure MgO in the starting material (Table 3), except for D350, a run with the "eutectoid-like" intergrowth of $MgTiO_3$ + MgO; here the slightly larger lattice parameter may be caused by strain associated with this texture. The effect on the lattice parameter of MgO from the substitution of Ti is not known, but by analogy with magnesiowüstite in the system MgO-FeO-$FeO_{1.5}$ (e.g., O'Neill et al., 2003a) we expect this substitution to lower the lattice parameter, both because Ti^{4+} is a smaller cation than Mg^{2+}, and because charge-balance is maintained in heterovalent-substituted MgO by cation vacancies, which decrease the lattice parameter.

For Mg_2TiO_4 the lattice parameters in the run products are ~ 0.001 Å larger than in the starting mix (Table 3). Since solid solution towards a defect spinel with cation vacancies would lower the lattice parameter, this is possibly due to the presence of Ti^{3+}, in the form of solid solution towards $MgTi_2^{3+}O_4$ in the moderately low fO_2 environment of the piston-cylinder apparatus (cf. Pelton et al., 1998). The lattice parameter of end-member $MgTi_2^{3+}O_4$ spinel is inferred to be about 8.505 Å (Hohl et al., 1996), hence the observed increase of 0.001 Å corresponds to a mole fraction of 0.015 $MgTi_2^{3+}O_4$. This would imply a molar Mg/Ti ratio of 1.96, in reasonable agreement with the ratio

observed by electron microprobe analysis, 1.98 ± 0.01 (Table 2). For $MgTiO_3$, the lattice parameters of run D350 are identical to those of the starting material, and also to those found by Wechsler & von Dreele (1989), who give $a_o = 5.0548$ (3) Å, $c_o = 13.8992$ (7) Å, V = 307.56 Å³.

Thermodynamic evaluation

The equilibrium condition can be expressed as:

$$\Delta_rG_{(T, P)} = 0 = \Delta_rG^O_{(T, 1 \, bar)} + \int_1^P \Delta_rV^O(T, P)dP + RT \ln K \quad (2),$$

where

$$K = \frac{a^{ilm}_{MgTiO_3} a^{ox}_{MgO}}{a^{sp}_{Mg_2TiO_4}} \quad (3).$$

Following the discussion above on the stoichiometry and purity of MgO, $MgTiO_3$ and Mg_2TiO_4 in the run products, we assume that K = 1, with a probable uncertainty of only ± 0.01, since such minor deviations from stoichiometry and purity that are expected in the run products will tend to cancel out across the reaction. The experimental half-brackets define points in free energy - temperature - pressure space at which $\Delta_rG_{(T, P)} \geq 0$ (low temperature half-bracket) and $\Delta_rG_{(T, P)} \leq 0$ (high temperature half-bracket). Splitting $\Delta_rG^O_{(T, 1 \, bar)}$ into entropy and the enthalpy terms gives:

$$\Delta_rG^O_{(T, 1 \, bar)} = \Delta_rH^O_{(298K)} - T\Delta_rS^O_{(298K)} + \int_{298}^T \Delta_rC_P^O(T)dT$$

$$- T\int_{298}^T \left[\frac{\Delta_rC_P^O(T)}{T}\right]dT \quad (4).$$

Available data for high temperature heat capacities (Table 4) can be used to evaluate the last two terms in eqn. (3) (i.e., the two terms in $\Delta_rC_P^O$). For the $\int_1^P \Delta rV^O(T, P)dP$ term in eqn. 2, we have adopted the equation of state recommended by Holland et al. (1996) and used by Holland & Powell (1998). For MgO and $MgTiO_3$ the heat capacities, molar volumes, thermal expansivities and bulk

Table 4. Thermodynamic data.

Phase	$\Delta_fH^o_{(298K, 1 \, bar)}$	$S^o_{(298 \, K, 1 \, bar)}$	$Cp = a + bT + cT^{-2} + d \, T^{-1/2}$ (in J K⁻¹mol⁻¹)				$V^o_{(298K, 1 \, bar)}$ (J bar⁻¹)	α^o (K⁻¹)	κ (kbar)
			a	b (x10²)	c	d			
MgO periclase	-601.65	26.9	60.5	.0362	-535800	-299.2	1.125	6.2	1650
$MgTiO_3$ geikielite	-1567.42	74.6	151.0	-	-1890400	-652.2	3.086	4.95	1770
Mg_2TiO_4 Qandilite	-2157.41	111.8[a]	161.7[b]	.03286	-2382200	-278.6	4.529[c]	5.48[c]	1890[d]

[a] calorimetrically measured value is 103.6 J K⁻¹ mol⁻¹; from Todd (1952) [b] C_p data from Orr and Coughlin (1952) and Todd (1952), fitted in this study; [c] O'Neill et al. (2003b); [d] value for Fe_2TiO_4 from Holland and Powell (1998).

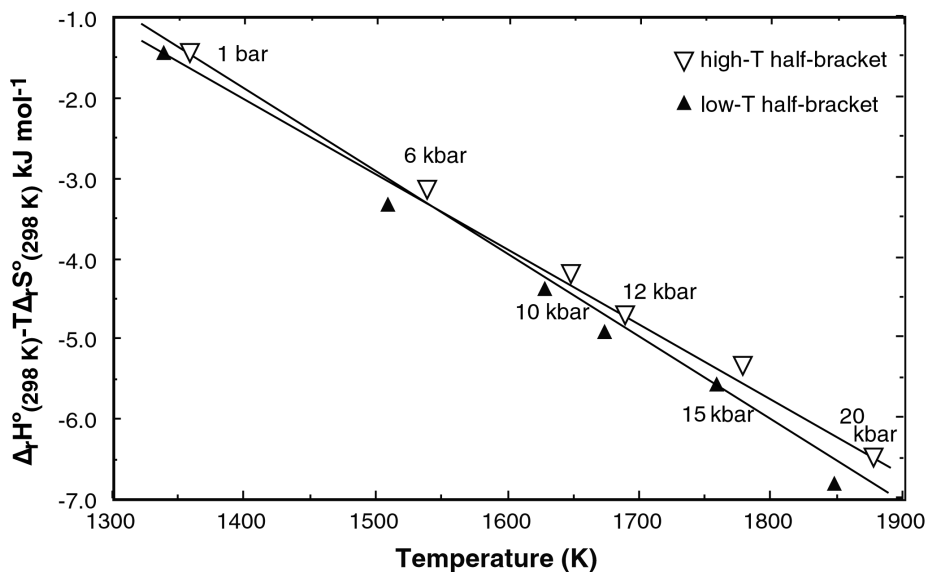Data for MgO and $MgTiO_3$ are from Holland & Powell (1998), for Mg_2TiO_4 from this study except where noted.

Fig. 4. The quantity $\Delta_r H^O_{(298K)} - T\Delta_r S^O_{(298K)}$ vs. T (K) for the defining half-brackets, plotted to allow for experimental uncertainties as discussed in the text. The lines with maximum and minimum slopes are drawn.

moduli are taken from Holland & Powell (1998), as summarized in Table 4. For Mg_2TiO_4, the heat capacity equation is our fit to the heat content measurements of Orr & Coughlin (1952), which extend to 1820 K (31 data). Temperature was corrected from IPTS-48 to ITS-90, and the equation was anchored at low temperature using the adiabatic calorimetric measurements of Todd (1952) in the range 250 to 300 K (5 data). Volume and thermal expansion at 1 bar are from O'Neill *et al.* (2003b), refitted to the equation for thermal expansion of Holland *et al.* (1996). The bulk modulus of Mg_2TiO_4 has not yet been measured, to our knowledge, so we adopt the value listed for Fe_2TiO_4 by Holland & Powell (1998).

With these data, the experimental half-brackets can be used define maximum and minimum values of the quantity ($\Delta_r H^O_{(298K)} - T\Delta_r S^O_{(298K)}$) at each experimental pressure. These values are plotted in Fig. 4 against experimental temperature. To allow for experimental uncertainties in both temperature and pressure measurement in the piston-cylinder apparatus, 5 K has been subtracted from and 0.2 kbar added to the low temperature half-brackets and 5 K added to and 0.2 kbar subtracted from the high temperature half-brackets. For example, the half-brackets nominally at 10 kbar and 1360°C and 1370°C are treated as being at 1355°C and 10.2 kbar and 1375°C and 9.8 kbar respectively. For the experiments at atmospheric pressure, an uncertainty of 5 K in the half-brackets was also adopted.

The resulting array of limiting values of ($\Delta_r H^O_{(298K)} - T\Delta_r S^O_{(298K)}$) defines a set of lines of slope $-\Delta_r S^O_{(298K)}$ and intercept $\Delta_r H^O_{(298K)}$. By inspection we locate the two limiting values (one from a high-temperature half-bracket, the other from a low-temperature half-bracket) that define the line of maximum slope, and similarly the two that define the line of minimum slope. These lines give maximum and minimum values of $\Delta_r S^O_{(298K)}$ of 10.10 and

9.34 J K^{-1} mol^{-1} respectively, with corresponding values of $\Delta_r H^O_{(298K)}$ of 12.27 and 11.05 kJ mol^{-1}. For a best estimate of $\Delta_r S^O_{(298K)}$ we take the mean of these maximum and minimum slopes, 9.72 J K^{-1} mol^{-1}, with an uncertainty given by half their difference, $\pm$ 0.38 J K^{-1} mol^{-1}. Likewise, $\Delta_r H^O_{(298K)}$ = 11.66 $\pm$ 0.61 kJ mol^{-1}.

Using the values of $\Delta_{f, el}H^O_{(298K)}$ and $S^O_{(298K)}$ for $MgTiO_3$ and MgO from Holland & Powell (1998) in Table 4 gives for Mg_2TiO_4 $\Delta_{f, el}H^O_{(298K)} = -2157.41 \pm 1.35$ kJ mol^{-1} and $S^O_{(298K)} = 111.2 \pm 0.6$ J K^{-1} mol^{-1}. This latter value is 7.6 $\pm$ 0.9 J K^{-1} mol^{-1} more than the calorimetrically determined value of 103.6 $\pm$ 0.7 J K^{-1} mol^{-1} (Todd, 1952). The difference may be ascribed to zero-point entropy, but is somewhat less than the theoretical amount of 2Rln2 or 11.5 J K^{-1}mol^{-1} expected from the random mixing of Mg and Ti on the octahedral site of Mg_2TiO_4 spinel.

One possibility is some short-range ordering of Mg and Ti, which seems plausible given the long-range ordering of Mg and Ti onto distinct octahedral sites at the phase transition from to $Fd\bar{3}m$ $P4_122$ at ~ 1000°C. Unfortunately, as with many hypotheses regarding short-range order in crystal chemistry, this explanation is not really practicable to test with existing experimental methods. It is therefore necessary to eliminate other possibilities, such as error in the calorimetric data for the other phases in reaction (1), *i.e.*, $MgTiO_3$ and/or MgO. For MgO, it is reasonable to assume that the calorimetric data are secure, not only because they have been measured many times, but also because MgO figures in so many other reactions that have been subsumed into the compilation of the Holland & Powell (1998) database. The value $S^O_{(298K)}$ of for $MgTiO_3$ also seems well known, since the low temperature heat capacity measurements of Robie *et al*. (1989) are in good agreement with the earlier measurements of Shomate (1946). However, at high temperatures, the heat-content measurements of $MgTiO_3$ (Naylor & Cook, 1946) leave

some room for doubt, as follows. Firstly, the measurements extend only to 1720 K, with only three data above 1410 K. Refitting the data of Naylor & Cook (1946) to the four-term heat capacity polynomial used by Holland and Powell, (*i.e.*, $C_p = a + bT + cT^2 + dT^{-1/2}$) gives a result very much the same as that listed by Holland & Powell (1998); but adding an extra fifth term to the polynomial, (*i.e.*, the term eT^2), produces a better fit, but one which leads to significantly higher computed values of C_p above ~ 1400K. As an illustration, C_p calculated at 1800 K with the four-term fit is 135.6 J K^{-1} mol^{-1}, whereas that with the five-term fit is 158.9 J K^{-1} mol^{-1}. This would be a large enough change to account for the missing residual entropy in Mg_2TiO_4. Whether this increase in the heat capacity of $MgTiO_3$ is real is difficult to judge, since the extended Maier-Kelley equation for heat capacities is an entirely empirical device for representing the experimental data, in which the inclusion of the term in eT^2 is well known to lead to ambiguities in the extrapolation of the equation to higher temperatures. The value for the four-term fit at 1800 K is in excellent agreement with the Dulong-Petit value ($C_p = 3nR + TV\alpha^2\kappa$), which is calculated to be 136 J K^{-1} mol^{-1} at 1800 K using the data in Table 4. Excess heat capacity could result from disordering of Mg and Ti as the ilmenite structure, in which Mg and Ti are ordered into layers, transforms towards the corundum structure ($R\bar{3} \to R\bar{3}c$). This transition has been observed in $NiTiO_3$ by powder neutron diffraction at ~ 1560 K (Boysen *et al.* (1995), and is inferred at ~ 1673 K in $FeTiO_3$ from extrapolation of the transition in $FeTiO_3$-Fe_2O_3 solid solutions (Harrison *et al.*, 2000). Harrison *et al.* (2000) show that $FeTiO_3$ is ~ 10 % disordered at 1473 K. The occurrence of this transition in $MgTiO_3$ has been discounted by Reynard & Guyot (1994) from their investigation by Raman spectroscopy to 1820 K, on the grounds that the symmetry change would reduce the number of Raman active modes from ten to seven. In fact, the ten modes observable at room temperature could only be tracked to ~ 1400 K due to line broadening and thermal emission, so the possibility of symmetry reduction at higher temperatures remains open, as does the possibility of significant Mg-Ti disordering within the ilmenite structure at temperatures below the putative transition, as has been shown to occur in $FeTiO_3$ by Harrison *et al.* (2000). The question of excess entropy in $MgTiO_3$ could be addressed by more precise high-temperature calorimetry (which would give the data needed to resolve the question of interest here directly), or other methods such as high-temperature powder neutron diffraction.

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