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$MgSiO_3$ ilmenite: calorimetry, phase equilibria, and decomposition at atmospheric pressure

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Abstract

From a combination of transposed temperature drop calorimetry and oxide melt solution calorimetry on a 15 mg sample of $MgSiO_3$ (ilmenite), the enthalpy of the transition $MgSiO_3$ (pyroxene → ilmenite) was found to be 17163 ± 750 cal mol^{-1}. Combining this value with recent calorimetric data for α, β, and γ-Mg_2SiO_4 and SiO_2 (stishovite), one obtains thermodynamic parameters which are used to calculate the phase diagram. The direct transition px → il is metastable except possibly above 1700 K. The transition γ + st → 2 il has a definitely negative dP/dT and the transition β + st → 2 il may also have a negative dP/dT. Three triple points (px, γ + st, β + st), (il, β + st, γ + st) and (il, px, β + st) are predicted. Upon heating at 973 K for an hour, $MgSiO_3$ (il) decomposes to a mixture of phases, including glass and perhaps an intermediate phase of unknown structure.

Introduction

Formation of dense post-spinel phases (ilmenite, perovskite, or stishovite plus rocksalt) of ferromagnesian silicates represents an important set of reactions determining the mineralogy of the lower mantel. Because such reactions occur at pressures near and above 20 GPa, their direct study necessitates the use of shock waves, diamond anvil pressure cells, or multianvil high pressure devices. Each of these methods involves considerable problems in pressure and temperature calibrations and in the attainment of equilibrium, resulting in substantial uncertainties in the experimental location of P–T–X boundaries and, at times, serious discrepancies among the work of different investigators. Independent thermodynamic characterization of the high pressure phases is therefore desirable but is made difficult by the very small amounts of samples which can be prepared at high P and T and quenched to ambient conditions for further study. This paper reports a calorimetric determination of the enthalpy of the reaction $MgSiO_3$ (pyroxene) → $MgSiO_3$ (ilmenite) based on a combination of transposed temperature drop calorimetry and oxide melt solution calorimetry on a sample of $MgSiO_3$ (ilmenite) weighing about 15 mg. Combination of this datum with recently obtained data for β- and γ-Mg_2SiO_4 and SiO_2 (stishovite) (Akaogi et al., 1984; Akaogi and Navrotsky, 1984) permits the calculation of P–T relations involving these phases, the results of which are relatively consistent with the available high pressure data.

Synthesis and characterization of $MgSiO_3$ (ilmenite) and $MgSiO_3$ (opx)

The $MgSiO_3$ (opx) crystals grown in a flux of MoO_3–Li_2O_2–V_2O_5 were kindly offered by M. Ozima of the Institute for Solid State Physics, University of Tokyo. The colorless transparent crystals had euhedral rod-shapes with a typical size of 100 × 150 × 300 μm. Microprobe analysis and lattice parameters for the crystals confirmed that the composition was very close to stoichiometry (Takei et al., 1984). The $MgSiO_3$ (opx) sample was used for calorimetric study and served as the starting material for the ilmenite synthesis.

The $MgSiO_3$ ilmenite samples, synthesized in two slightly different procedures, were combined (totally 15.52 mg) and used for the calorimetric study. The synthesis was performed employing a uniaxial split-sphere apparatus (Ito and Yamada, 1982). The $MgSiO_3$ (opx) crystals were put into a cylindrical tantalum heater with fine NaCl powder. The sample was subjected to 23 GPa and 1823 K for 40 min. After recovery to ambient conditions, the run product was rinsed with water to remove the attached NaCl. The particles were found to keep the original shapes of the orthoenstatite crystals. The particles in the central portion of the heater became opaque, whereas those in the end portions remained transparent. Micro X-ray diffraction of the opaque particles demonstrated complete conversion to ilmenite. Most of the $MgSiO_3$ ilmenite sample (~90%) in the present study was obtained in this manner in several runs. The remainder was synthesized as follows. Finely pulverized $MgSiO_3$ (opx) was put into the tantalum heater without NaCl and converted to the ilmenite phase at 23 GPa and 1823 K. The $MgSiO_3$ ilmenite thus obtained was a loosely cemented aggregate of platy crystals of 50–100 μm in size.

Calorimetry

The Calvet-type twin microcalorimeter, operating at 973 K, has been described elsewhere (Navrotsky, 1977). $MgSiO_3$ (ilmenite) is of course metastable at ambient conditions and the crucial question for high temperature calor-

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imetry is: how fast does it decompose at 973 K and atmospheric pressure, and to what phase assemblage? A preliminary experiment consisted of heating a small grain of the sample (~100 μm across) in a platinum sample holder for one hour at 973 K and examining it by optical microscopy which showed complete transformation to a material of much lower index of refraction and lower (but still observable) birefringence than the original ilmenite. There was not enough of this sample for X-ray diffraction. Based on this observation, the appropriate first calorimetric experiment was chosen to be transposed temperature drop calorimetry, in which 15.52 mg of the ilmenite in a platinum capsule was dropped from room temperature into the calorimeter at 973 K and the heat effect measured. The capsule was retrieved and weighed. A loss of 0.18 mg, which may represent H_2O or C in the original sample, was observed. Because this weight loss was small and could not be studied in detail, it was considered in the calculations simply as a correction to the weight of sample. The capsule was dropped a second time into the calorimeter. The difference between the first and second drops gives the enthalpy of transformation at 298 K of $MgSiO_3$ from the ilmenite structure to the phase assemblage, "X", formed at 973 K, (see Table 1).

$$\mathrm{MgSiO_3}\ (\mathrm{il}) \rightarrow \mathrm{MgSiO_3}\ (\text{“X”}) \qquad (1)$$

$$\Delta H^\circ_{298} = 11165 - 17441 = -6276 \text{ cal mol}^{-1}$$

The enthalpy of the second drop, 17441 cal mol^{-1}, is the heat content, H°_{973}–H°_{298}, of $MgSiO_3$ ("X"). This is slightly lower than the value of H°_{973}–H°_{298} we measured by analogous drop experiments (see Table 1) for $MgSiO_3$ (opx), 17610 cal mol^{-1}. The latter value is in excellent agreement with the H°_{973}–H°_{298} of 17670 cal mol^{-1} tabulated by Robie et al. (1978) for $MgSiO_3$ (cpx).

The material from the drop experiments, which had been in the calorimeter for a total of about 2 hours, was then removed from the capsule. 13.26 mg was loaded into a platinum solid-bottomed sample holder for solution calorimetry in molten $2PbO \cdot B_2O_3$, while the remainder was used for characterization of phase assemblage "X", see below. Solution calorimetry carried out by our usual procedures (Navrotsky, 1977; Akaogi et al., 1984), gave $\Delta H_{\mathrm{sol},973} = -2202$ cal mol^{-1}. The length of time the sample was equilibrated in the calorimeter before dissolution was minimized to about 2 hours. Since the enthalpy of solution of $MgSiO_3$ (opx) was measured to be 8685 ± 228 cal mol^{-1} (see Table 2), in good agreement with previous work (Charlu et al., 1975), we conclude that "X" represents an assemblage intermediate in enthalpy between ilmenite and pyroxene. Subsequent characterization of this material, see below, supports that interpretation.

From the solution calorimetry,

$$\mathrm{MgSiO_3}\ (\text{“X”}) = \mathrm{MgSiO_3}\ (\mathrm{opx}), \qquad (2)$$

$$\Delta H^\circ_{973} = -10887 \text{ cal mol}^{-1}$$

Combining the drop and solution calorimetry and neglecting any heat capacity differences between $MgSiO_3$ (il) and $MgSiO_3$ ("X"), we get

$$\mathrm{MgSiO_3}\ (\mathrm{opx}) = \mathrm{MgSiO_3}\ (\mathrm{il}), \qquad (3)$$

$$\Delta H^\circ = 17163 \text{ cal mol}^{-1}$$

Table 1. Results of transposed temperature drop calorimetry on $MgSiO_3$

Phase	weight (mg)	H_{973}-H_{298} (kcal mol^{-1})
ilmenite	15.52	11165[a]
"X"	15.34	17441[b]
opx	40.88	17681[c]
opx	21.13	17439
opx	40.88	17811
opx	21.13	17507

[a] Includes contribution from transformation to "X"
[b] Second drop on capsule initially containing ilmenite
[c] Average (4 expts) = 17610 ±290

The error in this value is hard to judge because only one sample was run, but, since the calorimetric experiments appeared perfectly normal, we can probably assume that the usual statistical uncertainty observed in calorimetery holds here. This would suggest a standard deviation of about ±750 cal mol^{-1} for the ΔH of reaction (3).

The neglect of a heat capacity correction for reaction (1), $\int_{298}^{973}(C_p\ (\text{“X”}) - C_p\ (\mathrm{il}))\,dT$, can be justified as follows. Watanabe (1982) measured the heat capacity of $MgSiO_3$ (il) from 350 to 500 K by differential scanning calorimetry. Above 500 K the ilmenite presumably began to decompose but in the measured range it had a heat capacity about 1 cal K^{-1} mol^{-1} less than that of $MgSiO_3$ (cpx). If that difference holds to higher temperature, and assuming that the heat capacities of $MgSiO_3$ (opx) and $MgSiO_3$ (cpx) are very similar, then H_{973}–H_{298} of $MgSiO_3$ ("X") would be intermediate between those of $MgSiO_3$ (il) and $MgSiO_3$ (opx), the entire spread of H_{973}–H_{298} values being less than 700 cal mol^{-1}.

It is interesting that the enthalpy of solution of $MgSiO_3$ ("X") is similar to (actually about 900 cal mol^{-1} more exothermic than) that of $MgSiO_3$ (glass). We show below that the assemblage "X" may contain significant amounts of

Table 2. Results of solution calorimetry of $MgSiO_3$

Phase	$\Delta H_{\mathrm{sol},\ 973}$ (kcal mol^{-1})
"X"	-2202 (1 expt., 13.26 mg)
orthoenstatite	8685 ± 228 (9 expts.)
orthoenstatite	8780 ± 130 (Charlu et al., 1975)
glass	-1311 ± 56 (Hervig and Navrotsky, in preparation)

glass which would be supported by the above observation.

Phase equilibria at $MgSiO_3$ stoichiometry

The reaction

$$Mg_2SiO_4\ (\gamma) + SiO_2\ (\text{stishovite}) = 2MgSiO_3\ (\text{ilmenite}) \quad (4)$$

occurs at approximately 19.5 GPa and 1373 K (E. Ito, unpublished data). The enthalpy of this transition, using our new calorimetric data for $MgSiO_3$ (il) (this work), Mg_2SiO_4 (γ) (Akaogi et al., 1984) and SiO_2 (stishovite) (Akaogi and Navrotsky, 1984), is 10456 cal mol^{-1}. Neglecting compressibility and thermal expansion (since these are unknown for $MgSiO_3$ (il) and poorly known for Mg_2SiO_4 (γ), we get

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -P\Delta V^\circ \quad (5)$$

Thus if one knows ΔH° and ΔV° for a reaction, and one point on the P, T boundary, ΔS° and the entire P, T boundary can be calculated.

Three sets of such calculated thermochemical parameters, marked A, B, C, are shown in Table 3. Each represents an internally consistent data set based on somewhat different assumptions and input data. Ito and Matsui (1984, unpublished) have new accurate powder refinements of well crystallized β- and γ-Mg_2SiO_4 giving molar volumes of 40.58 and 39.48 cc mol^{-1}, respectively, compared to earlier "best" values of 40.54 and 39.65 cc mol^{-1} (Jeanloz and Thompson, 1983). Calculation A and C use these new values, calculation B, the old ones. All calculations use molar volumes of $MgSiO_3$ (px) $MgSiO_3$ (il) and SiO_2 (st) of 31.29, 26.35 and 14.01 cc mol^{-1}, respectively (Jeanloz and Thompson, 1983, Ito and Matsui, 1977), ignore the very small differences in measured thermochemical properties between $MgSiO_3$ ortho and clinopyroxene, and neglect the effects of compressibility and thermal expansion, to keep all calculations at the same level of approximation. This approximation probably introduces uncertainties of 0.5–1 GPa in most cases, which are small compared to uncertainties in pressure calibration in the 15–25 GPa range. The uncertainty is largest for the reaction with the smallest ΔH° and ΔV°, namely Mg_2SiO_4 ($\beta \rightarrow \gamma$) and Mg_2SiO_4 (γ) + SiO_2 (st) $\rightarrow$ $2MgSiO_3$ (il), see below. Calculation A uses a point on the $\beta \rightarrow \gamma$ boundary (16.8 GPa, 1273 K), (Suito, 1977) and on the 2px $\rightarrow \beta$ + st boundary (15.2 GPa, 1273

Table 3. Thermochemical data for reactions relevant to $MgSiO_3$ transitions

	Data Set	ΔH°	ΔS°	ΔV°
$MgSiO_4\ (\beta) \rightarrow Mg_2SiO_4(\gamma)$	A	1630^{a}	-2.23^{b}	-1.10^{c}
	B	1630^{a}	-1.50^{d}	-0.89^{d}
	C	1630^{a}	-2.23^{b}	-1.10^{c}
$2MgSiO_3(px) = Mg_2SiO_4(\beta) + SiO_2(st)$	A	22240^{a}	-5.63^{e}	-7.99^{c}
	B	22240^{a}	-5.20^{d}	-8.03^{d}
	C	22240^{a}	-5.63^{e}	-7.99^{c}
$2MgSiO_3(px) \rightarrow Mg_2SiO_4(\gamma) + SiO_2(st)$	A	23870^{a}	-7.86^{e}	-9.09^{c}
	B	23870^{a}	-6.70^{d}	-8.92^{d}
	C	23870^{a}	-7.86^{d}	-9.09^{d}
$Mg_2SiO_4(\gamma) + SiO_2(st) = 2MgSiO_3(il)$	A	10456^{a}	$+4.90^{g}$	$-0.79^{c,f}$
	B	10456^{a}	$+4.31^{h}$	$-0.96^{d,f}$
	C	7456^{k}	$+2.71^{k}$	$-0.79^{c,f}$
$Mg_2SiO_4(\beta) + SiO_2(st) = 2MgSiO_3(il)$	A	12086^{a}	$+2.67^{g}$	$-1.89^{c,f}$
	B	12086^{a}	$+2.87^{h}$	$-1.85^{d,f}$
	C	9086^{k}	$+0.48^{k}$	$-1.89^{c,f}$
$MgSiO_3(px) \rightarrow MgSiO_3(il)$	A	17163^{a}	-1.48^{i}	-4.94^{f}
	B	17163^{a}	-1.17^{i}	-4.94^{f}
	C	15663^{j}	-2.58^{k}	-4.94^{f}

a. Calculated from calorimetric data, this work, Akaogi et al., 1984, Navrotsky et al., 1979, cal $mol^{-1}K^{-1}$.
b. Calculated from ΔH°, ΔV°, and P=16.8 GPa at 1273 K, Suito, 1977, cal $mol^{-1}\ K^{-1}$.
c. Using new volume data for β and γ of Ito and Matsui, (unpublished), cc mol^{-1}.
d. Calculated as in Akaogi et al., 1984; Navrotsky et al., 1979. Volume of β and γ as in Jeanloz and Thompson, 1983. ΔS° values from entropy changes tabulated in Akaogi et al., 1984 for α-β-γ relations in Navrotsky et al., 1979, for $\alpha \rightarrow$ 2px + q, and in Akaogi and Navrotsky, 1984 for q $\rightarrow$ st.
e. ΔS° calculated from ΔH°, ΔV°, and observation that 2px $\rightarrow \beta$ + st occurs at 15.2 GPa and 1273 K, E. Ito (recent unpublished data).
f. Volume of $MgSiO_3$(il) from Ito and Matsui, 1977.
g. Calculated from ΔH°, ΔV°, and observation (Ito and Matsui, unpublished, that γ + at $\rightarrow$ 2 il occurs at 19.5 GPa and 1373 K.
h. Using values in (g) and $\beta \rightarrow \gamma$ values above.
i. Consistent with values above.
j. Lower limit on calorimetric ΔH° (two standard deviations).
k. Consistent with ΔH°(px $\rightarrow$ il) = 15663 cal, and all other data as in data set A.

K), (E. Ito, unpublished data) to calculate ΔS° from ΔH° and ΔV° (Eq. 5). Calculation B uses the thermochemical data for the α–β–γ Mg_2SiO_4 transitions derived by Akaogi et al. (1984). Calculation C uses the same data set as calculation A except that the enthalpy of the transition $MgSiO_3$ (px → il) is decreased by 1500 cal mol^{-1} (two estimated standard deviations of the calorimetric data). These three calculations give some insight into the effect of uncertainties in the data on the calculated phase relations.

The calculated phase relations corresponding to data sets A, B, and C are shown in Figure 1A, B, C. They show several common features. (a) The direct transition of $MgSiO_3$ (px) to $MgSiO_3$ (il) is metastable at temperatures of 1000–1700 K. The single phase field (px) is separated from the single phase field (il) by one of two phase fields (γ + st) or (β + st). The thermochemical data suggest a triple point (px, il, β + st) to occur near 16–17 GPa and a temperature between about 1700 and 1900 K. At higher temperatures pyroxene could transform to ilmenite directly (unless melting occurred first). (b) A triple point (β + st, γ + st, px) is suggested to occur near 1000 K and 14 GPa. Its exact location is sensitive to the precision position of the β–γ boundary. (c) Another triple point (β + st, γ + st, il) is suggested near 1400 K and 18 GPa. The triple points of course are related and can not be moved independently of each other in P–T space by varying the thermodynamic parameters. (d) The boundary γ + st → il appears to have a strongly negative P–T slope, corresponding to the large position ΔS° (2.7 to 4.9 cal K^{-1} mol^{-1}) shown in Table 3. The boundary β + st → il also appears to have a somewhat negative slope. It is these negative slopes which lead to the predicted (px, il, β + st) triple point mentioned above. Other phase boundaries have positive P–T slopes, with the β–γ boundary being the steepest (and probably most uncertain). We believe that the topology of the phase relations is constrained by the thermochemical data although the exact location of the triple points is subject to relatively large error limits.

The calculated phase diagram may be compared to experimental data. The $\beta - \gamma$ boundary is in reasonable agreement with that found by Suito (1977) which is somewhat different from that of Kawada (1977) as discussed in our previous paper (Agaogi et al., 1984). Liu (1976) observed, in a laser-heated diamond cell at 1273–1673 K, that $MgSiO_3$ clinoenstatite began to decompose to β-Mg_2SiO_4 plus stishovite at about 17.5 GPa (where some ilmenite was also claimed to be present), and that at 19.0 GPa β-Mg_2SiO_4, stishovite, and clinoenstatite were observed in roughly equal amounts. Given the problems with equilibration and pressure gradients in a laser heated cell and the difficulty of determining or controlling the temperature, Liu's results are consistent with our calculations. At 22 GPa, Liu observed γ-Mg_2SiO_4, stishovite, and ilmenite. Our calculations suggest that ilmenite should be the stable phase under those conditions and that Liu's samples may not have been totally transformed.

Recently, E. Ito (1984, unpublished) has performed synthesis experiments on this system, using a uniaxial split sphere apparatus. The results are shown in Figure 1D. Two possible sets of phase boundaries are sketched in. The solid

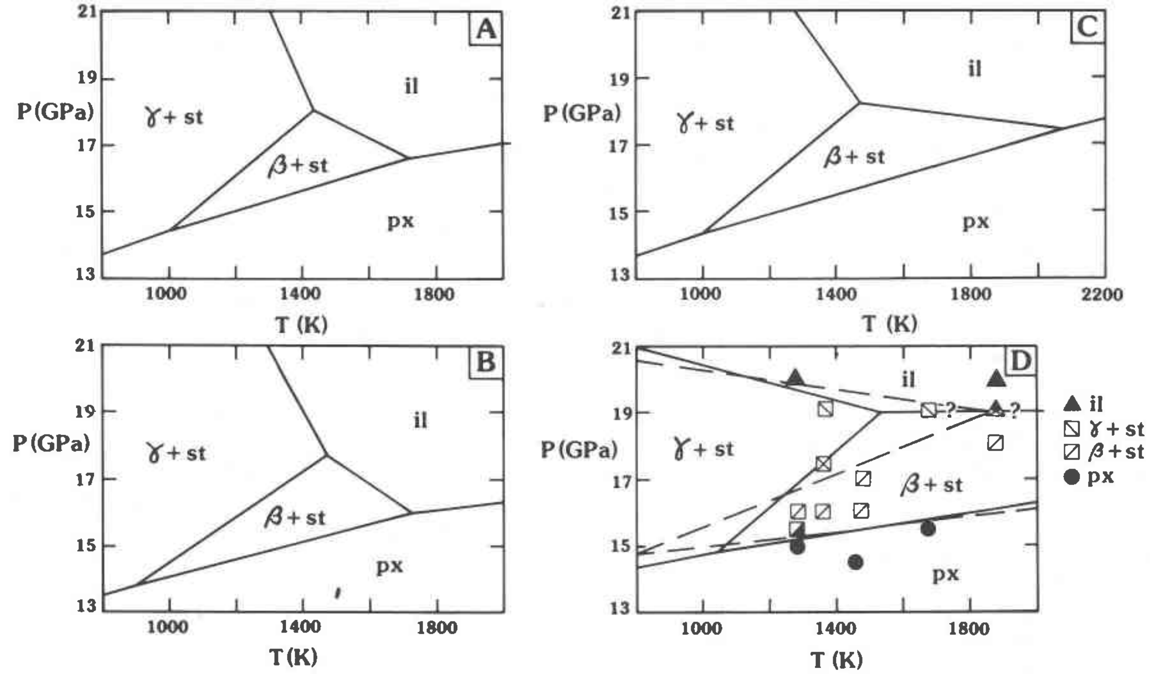

Fig. 1. Calculated $MgSiO_3$ phase relations. Fig. 1A, B, C represents calculations based on thermochemical data sets A, B, C in Table 3, respectively. Fig. 1D shows the experimental synthesis data of E. Ito (1984, unpublished). See text for discussion of boundaries.

lines represent boundaries consistent with the β–γ boundary we calculated in Figure 1A, which is consistent with Suito's (1977) data. The dashed lines show a β–γ boundary consistent with Ito's synthesis data but having a slope much shallower than found in previous studies. The two points which suggest the shallower slope are annotated with question marks.

A comparison of Ito's experimental data and our calculations show them to be generally consistent with respect to overall topology. The only significant discrepancy is the following. Although Ito suggests a slightly negative dP/dT for the transition $\gamma + \mathrm{st} \rightarrow \mathrm{il}$, the calculations suggest a much more strongly negative slope. Therefore the experimental data would suggest that the triple point (px, il, β + st), if it exists at all, would lie at much higher temperatures than the calculations imply. Thus, although both high pressure synthesis and calorimetry suggest that ilmenite is a phase of relative high entropy, the exact value of the positive $\Delta S°$ of its formation from low pressure phase assemblages is in doubt.

This discrepancy may have several sources. In the experimental high pressure runs, problems of pressure and temperature calibration may both change absolute values of P and T and distort P–T slopes. Additionally, short synthesis runs may not represent complete equilibrium, especially when they involve both β- and γ-Mg_2SiO_4. In the calculations, the neglect of thermal expansion and compressibility may introduce substantial uncertainty in the relatively small volume charge (~ -1 cc mol^{-1}) of the transition $\gamma + \mathrm{st} \rightarrow 2$ il. Because thermal expansion and compressibility affect the volume in opposite directions, their effects partially compensate each other, but the net effect on the calculated phase boundary depends on actual numerical values and can not be predicted, even as to sign. Accurate measurements of these parameters, especially for $MgSiO_3$ (il) are needed. In view of all these uncertainties, we consider the general agreement between thermochemical calculation and high pressure experiment to be very encouraging. Given the uncertainties in both the high pressure work and the thermochemical calculations, we can not say whether the experimental or the calculated phase relations are likely to be quantitatively closer to the "real" phase diagram.

The fact that $MgSiO_3$ (il) has a higher entropy than the corresponding low pressure assemblage (γ + st) probably reflects the change in bonding and silicon coordination (4-fold to 6-fold). The changes are reflected in the vibrational spectrum of $MgSiO_3$ ilmenite (Ross and McMillan, 1984) which shows the absence of high frequency tetrahedral Si–O stretching modes and the concentration of modes at lower frequencies compared to vibrations of tetrahedral silicates. This leads to higher vibrational entropies as described qualitatively by Navrotsky (1980). We are presently applying to $MgSiO_3$ (il) the lattice vibrational models developed by Kieffer (1979a, b, c, 1980) and used by Akaogi et al. (1984) for the α–β–γ Mg_2SiO_4 transitions. These calculations (N. Ross, in progress) support the conclusion that the transition $\gamma + \mathrm{st} \rightarrow 2$ il has a positive $\Delta S°$, but exact numerical values are sensitive to parameters (dispersion of low frequency modes, compressibility and thermal expansion needed to convert C_v to C_p) which are poorly known.

Ilmenite decomposition at 973 K and 1 atm

A fragment approximately 100 microns on a side of $MgSiO_3$ ilmenite contaminated with Ta from the furnace element was heated for 1 hour at 973 K in the calorimeter. The Ta apparently oxidized completely to a white fluffy powder while the grain of ilmenite remained intact. It was broken in an agate mortar and mounted in oil of index of refraction 1.700. The grains had a lower index of refraction than the liquid indicating that a transformation from ilmenite ($n > 1.7$) had occurred. Individual fragments were mostly polycrystalline with a yellowish tinge and very low birefringence. Individual particles within a fragment often appeared isotropic. Another sample of annealed ilmenite, phase assemblage "X" from the drop calorimetric experiment, showed $n > 1.6$ and extremely low birefringence. Two colored grains were polycrystalline and appeared similar to the initial test fragment. Thus, there is evidence for some inhomogeneity, including minor, yellowish, low birefringent material and more abundant, colorless material with extremely low birefringence. Both materials have $1.7 > n > 1.6$. For comparison, orthoenstatite has $n \sim 1.61$ and enstatite glass has $n < 1.6$.

Two small portions were separated from the 973 K drop calorimetric decomposition product of $MgSiO_3$ ilmenite for analysis by X-ray diffraction. One was yellowish in color, one colorless, as described above. Powder patterns for both samples were recorded with a Guinier focusing camera using $CuK\alpha_1$ radiation.

Table 4 reports approximate ($\pm 0.05°$) 2θ values and corresponding d spacings for sample A (white) and sample B (yellowish) along with previously reported d spacings for $MgSiO_3$ ilmenite (Ito and Matsui, 1977). The film recorded sharp diffraction lines but even after 30 hours of exposure all lines were very faint, suggesting that part of the sample may have been amorphous. Both samples revealed similar diffraction patterns. However, one strong line present in B ($d = 2.247$Å) was not observed in A. Other weaker lines present in B may not have been observed in A due to the overall faintness of pattern A compared to B.

All but one of the strong diffraction lines which could be assigned to $MgSiO_3$ ilmenite are seen in both samples, but the absence of the ilmenite 003 reflection indicates that ilmenite as such is no longer present, although a distorted or disordered structure related to ilmenite is a strong possibility. Attempts to index all the lines seen in the pattern using a hexagonal or C-centered orthorhombic unit cell proved unsuccessful. The pattern is definitely not that of any known $MgSiO_3$ pyroxene polymorph.

Raman spectroscopy was carried out with an Instruments S.A. U-1000 micro-Raman system using the 488 or 514 nm lines of a Coherent Innova 90-4 Ar^+ laser. The original ilmenite and the Ta-contaminated large grain heated for 1 hour at 973 K gave similar spectra. Various small grains of the calorimetric run product (assemblage

Table 4. X-Ray powder data for phase(s) "X" and $MgSiO_3$ ilmenite

$MgSiO_3$ ilmenite			phase(s) "X" Sample A		phase(s) "X" Sample B	
hkl	d	I	d	I	d	I
003	4.522	55				
001	3.922	5				
012	3.507	70	3.520	S	3.520	S
104	2.611	100	2.609	M	2.616	M
110	2.364	30			2.382	W
			2.378	W	2.369	M
015	2.263	15			2.247	VW
113	2.094	70	2.095	M	2.098	M
021	2.026	<5				
					2.073	S
			1.892	W	1.897	M
107	1.7524	25	1.750	VW	1.755	W
024	1.7524		1.700	W	1.702	W
			1.665	W	1.666	W
116	1.6335	65	1.632	M	1.635	M
			1.481	VW	1.482	VW
					1.469	W
					1.463	VW
018	1.5661	5				
214	1.4078	15			1.407	VW
030	1.3651	20	1.363	M	1.364	M
1010	1.2869	10				
119	1.2705	10				
220	1.1820	5				

"X") showed different spectra, confirming the multiphase nature of this material. No portion of assemblage "X" gave a spectrum similar to that of the initial ilmenite. The larger (10–100 μm), yellowish aggregates showed spectra suggestive of the presence of Mg_2SiO_4 (forsterite), SiO_2 (coesite) and glass near $MgSiO_3$ in composition. The smaller (5–10 μm) transparent grains gave spectra which could not be readily assigned and which may belong to a new phase.

Further characterization of $MgSiO_3$ ("X") was carried out on a Phillips 400 HRTEM equipped with an EDAX energy dispersive X-ray spectrometer. Sample "A" previously characterized by X-ray diffraction was cleaned and mounted on a holely carbon film deposited on a copper grid. The sample was then placed in the microscope and cooled to 77 K in order to minimize beam damage. Subsequent work was carried out with a field emission filament at 100 and 120 kV. Nevertheless some beam damage and charging effects were seen.

Both amorphous and crystalline materials were seen both as separate grains and intimately intergrown. All particles appeared to be cleavage fragments; no clear development of crystal faces was seen.

Microdiffraction indicated two crystalline phases. One was pseudohexagonal with real symmetry orthorhombic. The limited diffraction information obtained allowed measurement of two crystallographic axes of 17.2 and 7.8Å, similar to lattice spacing of orthopyroxene. The error of these measurements is 10–15%. Lattice imaging indicated a major repeat distance to be ~8.2Å, which is not a spacing in pyroxene. Some superlattice development was also apparent. This material was found to be a magnesium silicate with a Mg/Si ratio near unity but with some apparent variation in both bulk composition and impurity levels. Crystalline SiO_2 was also seen. It exhibited four-fold symmetry in one orientation which suggests that it may have been cristobalite or stishovite.

Crystalline material was found to occur as either single crystals or aggregates of smaller randomly oriented crystallites. The single crystals were relatively resistent to beam damage, but the aggregates quickly became amorphous under the electron beam even at 77 K.

The amorphous material ranged in composition from pure SiO_2 glass, to a magnesium silicate with variable Mg/Si ratio. No glass, however, was found corresponding in composition to the $MgSiO_3$ crystalline material. In general the EDAX data suggest that $MgSiO_3$ ilmenite tends to decompose to crystals and glass of variable Mg/Si ratio, with the glass tending to be silica-rich.

We conclude that phase assemblage "X" is definitely a mixture. Its major constituents are a crystalline phase which may be, but is by no means proven to be, a disordered ilmenite-related material, and glass of somewhat variable composition.

The isocompositional decomposition of $MgSiO_3$ ilmenite to glass or to pyroxene obviously would involve a large volume increase and a change of Si coordination from octahedral to tetrahedral. One can speculate that such a transition could occur by keeping the topology of the hexagonal oxygen sublattice relatively intact and disordering the cations, not just over the octahedral sites filled in the ilmenite and corundum structures, but onto tetrahedral sites as well. The disordering process may lead to local intermediate states and possible superstructures (of which the new phase(s) suspected in assemblage "X" may be examples) before a very disordered amorphous state is reached. This transformation may originate at defects, impurities, surfaces, and grain boundaries. Because of the large volume increase, the initial grains may break up into many microcrystalline domains which gradually become amorphous. As time progresses, diffusion may allow the formation of phases of different composition, e.g., $Mg_2SiO_4$and SiO_2.

Because transformation of high pressure phases to glass has been observed in shock and static high pressure experiments and may occur during meteor impact, understanding their mechanisms is interesting. A detailed TTT (time-temperature-transformation) study of the decomposition of $MgSiO_3$ ilmenite, with characterization by all the methods used above, is needed to quantify these preliminary observations.

Conclusions

Calorimetric study of a 15 mg sample of $MgSiO_3$ (il) has provided thermochemical data which enable approximate calculation of high pressure phase relations. Accurate calculations are hampered by the lack of thermal expansion and compressibility data. Useful information on the transformation of ilmenite back to lower pressure metastable and stable assemblages upon heating at one atmosphere can also be obtained using less than 2 mg of sample.

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