Some experiments pertaining to the magnetite–ulvöspinel miscibility gap

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Abstract

Hydrothermal experiments on the join Fe₃O₄–Fe₂TiO₄ are consistent with—but do not conclusively prove—the existence of a miscibility gap having a consolute temperature of 565±15°C and composition near Mt₃₅Usp₄₁, for the pure magnetite–ulvöspinel join. These results appear to conflict with the conclusion of Price (preceding paper) that the consolute point for natural magnetite–ulvöspinel intergrowths lies at or below 490°C. The experiments can be reconciled if (a) the presence of several percent MgO in the natural specimens depresses the consolute point, or (b) the experiments reported here failed to attain equilibrium—a real possibility since they have not been strictly reversed.

Introduction

In the preceding paper, Price (1981) argues strongly that the consolute temperature of the magnetite–ulvöspinel (Mt–Usp) miscibility gap lies below 490°C, that is, more than 100°C below the generally accepted value of ~600°C (Vincent et al., 1957). In 1967–68, I made a series of experiments on the Mt–Usp join. The results, while not conclusive, seemed generally compatible with those of Vincent et al., so I never completed or published them. Price’s manuscript prompted a careful review of these old experiments; they do not disprove Price’s low consolute temperature, but they do provide permissive evidence for a consolute point at a higher temperature (565±15°C) and a slightly asymmetric composition (probably near Mt₃₅Usp₄₁, mole percent) for the pure Fe₃O₄–Fe₂TiO₄ join. The discrepancy between our results may reflect the effect of minor constituents such as Mg in Price’s natural samples or it may reflect a failure of my experiments to reach equilibrium—a very real possibility since they are not reversed in a strict sense.

Experimental details

The starting materials for the experiments were single-phase powders of synthetic Usp₁₀, Usp₃₃, Usp₅₅, Usp₇₀, and Usp₉₀; for most runs, two of these spinels were ground together (under ethanol in an agate mortar for one hour) to provide a two-phase mechanical mixture of the desired bulk composition. Other runs were made on single phases of intermediate composition. Approximately 100 mg of powder was sealed with 5–10 wt.% H₂O in Ag₉₆Pd₄₀ capsules. Most of these capsules were then sealed with wustite-magnetite (WM) or iron-magnetite (IM) buffer + H₂O in Au capsules. The WM buffer (IM below 570°C) was chosen because Mt–Usp solutions ranging from Usp₉₀ to Usp₅₀ are stable at the oxygen fugacity it imposes (Lindsley, 1962). I hoped that the hydrothermal environment would enhance reaction rates. The external pressure medium for most experiments was methane (rather than H₂O) so as to extend the life to the buffers. Some buffers still did not last for the duration of the experiment, and minor amounts of ilmenite formed in them (Table 1). Two capsules without buffer were run in an Ar–H₂ mixture at 1 kbar; the H₂ content was maintained at 300–500 bars through a Pt membrane.

Compositions of run products were estimated from the positions of the (440), (620), and (622) peaks on X-ray diffraction patterns, which were obtained either at a scan rate of 0.125°2θ/min. or through stepscans at 0.01°2θ per 100 sec. The calibration curves were based on the unit-cell values (Lindsley, 1965) as modified by some additional points. The rather large uncertainties reported for many compositions (Table 1) reflect the lack of sharpness in the corresponding X-ray peaks.
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Table 1. Experiments pertaining to the Mt-Usp miscibility gap

<table>
<thead>
<tr>
<th>Run #</th>
<th>Starting material</th>
<th>Bulk Phases</th>
<th>Temp. °C</th>
<th>Buffers: medium</th>
<th>Duration days</th>
<th>Products</th>
<th>Remarks</th>
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<tr>
<td>572</td>
<td>Usp₅₀</td>
<td>2-ph</td>
<td>600</td>
<td>WM*</td>
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<td>560</td>
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<td>66</td>
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<tr>
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<td>WM₂₃₋₄CH₄</td>
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<tr>
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<td>560</td>
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<td>Ar+H₂</td>
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*Pressure medium, 2 kbar H₂O.
**Initially 81 days with IM buffer in 1 kbar CH₄ medium; remaining 240 days in Ar + H₂ at Ptot = 1 kbar, with 300-500 bH₂.

Results

Most of the experiments (Table 1) were of the dissolving (homogenization) type, that is, mechanical mixtures of phases (whose individual compositions lie outside the miscibility gap) are allowed to dissolve mutually. Complete homogenization shows that the bulk composition chosen lies outside the miscibility gap. Partial reaction shows that either (a) equilibrium was not attained or (b) the bulk composition lies within the two-phase field, in which case the compositions of the run products place outer limits on the width of the miscibility gap at the temperature of the experiment. Results of exsolution experiments—in which a single phase lying within the two-phase field is allowed to exsolve—may aid in distinguishing between cases (a) and (b).

The experiments at 600°C appear essentially to have reached equilibrium. Both mechanical mixtures (nos. 572, 621) have virtually homogenized. The results at 580°C are less clear-cut: the near-homogenization of the Usp₅₀ mechanical mixture (#575) and the persistence of Usp₄₈ (#578) strongly suggest that those compositions lie outside the miscibility gap at 580°C. But the Usp₃₅ mechanical mixture (#623) failed to homogenize after 121 days. The formation of considerable amounts of Usp₃₆₋₃₃ suggests that eventually this experiment might homogenize. The reasons for the more sluggish reaction rate (compared to #575) are unclear: both mechanical mixtures were made from the same batches of Usp₁₀ and Usp₅₀, both were ground for the same length of time, and both appear to have similar grain sizes (all grains < 10 μm, most less than 5 μm).

Homogenization experiments at 540–570°C all yielded results similar to those of #623: two new spinels (approx. Usp₃₂₋₃₈ and Usp₃₅₋₃₉) formed; the initial Usp₆₀ disappeared completely, whereas the original Usp₁₀ decreased in amount but did not appear to change in composition. This latter aspect of the experiments is very similar to the results of Vincent et al. (1957). In view of the near-consistency of the results—which appear to be independent of run duration—it is tempting to conclude that there is a two-phase field lying between approximately Usp₃₅ and Usp₇₇ at 540–570°C (Fig. 1).

Price has suggested (personal communication, 1981) that the failure of Nos. 576 and 577 to homogenize may be due to kinetic factors rather than to equilibrium. His calculations, based on a simple diffusion model, suggest that 66 days would not be adequate for the attainment of equilibrium at 560 and 540°C. However, the same calculation also suggests that equilibrium should not have been approached in
Fig. 1. Results of experiments on the Mt-Usp miscibility gap. Inward-pointing arrows show the results of dissolving experiments on mechanical mixtures of Usp_{10} and Usp_{80}. Crossed rectangles show essential homogenization. The pair of arrows pointing toward Usp at 560°C results from an exsolution experiment that also underwent reduction. Width of data symbols shows the uncertainty in composition. Uncertainty in temperature is three times the height of the symbols. Numbers at right show duration of the experiments in days. Dashes show the inferred miscibility gap that is permitted—but not strictly required—by the data.

51 days at 580°C—yet #575 nearly homogenized. Thus, the diffusion calculations do not give a definitive answer. Perhaps the presence of minor ilmenite in Nos. 576 and 577 served to inhibit diffusion.

The experiments that attempted to exsolve single-phase spinels at best provide only marginal evidence that the miscibility gap extends as high as 540–570°C. Nos. 579 and 580 (Usp_{88} at 560°C and 540°C, respectively) still show peaks centered around those for Usp_{88}, but the peaks are slightly broader and the Ka_{1} and Ka_{2} separation has become less distinct relative to the starting material. The changes are most unlikely to be due to oxidation, since the buffer assemblage iron + magnetite was maintained throughout these experiments. These X-ray results suggest that either spinodal decomposition or exsolution may have begun—but the changes in the X-ray peaks are too small to be definitive. These samples would appear to be prime candidates for study by transmission electron microscopy!

The remaining exsolution run (#631) provides slightly better, but still not conclusive, evidence for a two-phase field at 560°C. The initial composition (Usp_{33}) was chosen to test the suggestion by Vincent et al. (1957) that the miscibility gap is strongly asymmetric toward magnetite. Had the initial composition been retained, the change would almost certainly have remained a single phase, since homogenization runs at that temperature produced spinels close to Usp_{33}. But the Ar plus the 30–50% H_{2} pressure medium employed in lieu of an oxygen buffer reduced the charge, producing some Fe^{2+} and driving the bulk composition of the remaining spinel to approximately Usp_{40–42}. Most of this new spinel is a homogeneous phase with X-ray peaks corresponding to Usp_{38–39}; but there are also smaller amounts of a spinel with composition Usp_{50–51}. Because both product spinels were formed by reaction from one direction (i.e., from an Fe_{2}O_{3}-rich phase), this run is not strictly an exsolution experiment. Nevertheless, its relatively good agreement with the dissolving experiments supports the suggestion that there is a miscibility gap in the pure Fe_{2}O_{3}–Fe_{2}TiO_{4} system at 560°C (Fig. 1).

Discussion

I am not disputing Price's experimental results; he appears definitely to have homogenized natural Mt-Usp intergrowths down to 490°C. The compositions of his samples project inside the miscibility gap suggested here in Figure 1. The minor constituents in his samples may be the cause of the discrepancy. Much of the Al_{2}O_{3} doubtless remains in the pleonaste lamellae and thus should not affect the Mt and Usp phases. But much of the MgO probably resides in those phases and might affect the miscibility gap.

Conclusions

1. Hydrothermal experiments on the Mt-Usp join suggest—but do not prove—the existence of a miscibility gap for the pure Fe_{2}O_{3}–Fe_{2}TiO_{4} join. The consolute point would appear to lie at 565±15°C and at approximately Mt_{55}Usp_{45}. However, there are no unequivocal exsolution experiments to prove this suggestion, and the results at 540–570°C may simply reflect non-attainment of equilibrium, with the consolute point lying at lower temperatures.

2. Price's homogenization experiments at 490°C can be reconciled with the present results if the several percent MgO in his natural specimens strongly depresses the miscibility gap.

3. The present results support the idea of an asymmetric miscibility gap as advanced by Vincent et al. (1957), although the asymmetry is not so extreme as those authors suggested.

4. It seems clear that more work must be done before we understand the nature of the miscibility gap, either in natural or in synthetic systems.
Acknowledgments

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References


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