

Some experiments pertaining to the magnetite-ulvöspinel miscibility gap

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Abstract

Hydrothermal experiments on the join $\text{Fe}_3\text{O}_4\text{-Fe}_2\text{TiO}_4$ are consistent with—but do not conclusively prove—the existence of a miscibility gap having a consolute temperature of $565 \pm 15^\circ\text{C}$ and composition near $\text{Mt}_{55}\text{Usp}_{45}$ 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 $\sim 600^\circ\text{C}$ (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 ($565 \pm 15^\circ\text{C}$) and a slightly asymmetric composition (probably near $\text{Mt}_{55}\text{Usp}_{45}$, mole percent) for the pure $\text{Fe}_3\text{O}_4\text{-Fe}_2\text{TiO}_4$ 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 Usp_{10} , Usp_{33} , Usp_{48} , Usp_{60} , and Usp_{80} ; 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.% H_2O in $\text{Ag}_{80}\text{Pd}_{20}$ capsules. Most of these capsules were then sealed with wüstite-magnetite (WM) or iron-magnetite (IM) buffer + H_2O in Au capsules. The WM buffer (IM below 570°C) was chosen because Mt-Usp solutions ranging from Usp_0 to Usp_{80} 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 H_2O) 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- H_2 mixture at 1 kbar; the H_2 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 $0.125^\circ 2\theta/\text{min.}$ or through step-scans at $0.01/2\theta$ 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.

Table 1. Experiments pertaining to the Mt-Usp miscibility gap

Run #	Starting material Bulk Phases	Temp. °C	Buffers; medium	Duration days	Products	Remarks	
572	Usp ₅₀	2-ph	600	WM*	77	Usp ₄₈₋₅₃	Broad peaks, but virtually homogenized; no ilm.
575	Usp ₅₀	2-ph	580	WM;CH ₄	51	Usp ₄₅₋₅₅	Broad peaks, but nearly homogenized; no ilm or relic Usp ₁₀ .
576	Usp ₅₀	2-ph	560	IM;CH ₄	66	Usp _{32±4} ; Usp _{52±4}	Much relic Usp ₁₀ ; minor ilm.
577	Usp ₅₀	2-ph	540	IM;CH ₄	66	Usp _{33±4} ; Usp _{58±4}	Much relic Usp ₁₀ ; minor ilm.
578	Usp ₄₈	1-ph	580	IM;CH ₄	151	Usp _{48±1}	Peaks indistinguishable from starting material
579	Usp ₄₈	1-ph	560	IM;CH ₄	132	Usp _{48±2}	Peaks are broader, and α_1 - α_2 separation less distinct
580	Usp ₄₈	1-ph	540	IM;CH ₄	115	Usp _{48±2}	Peaks are broader, and α_1 - α_2 separation less distinct
621	Usp ₃₅	2-ph	600	WM;CH ₄	118	Usp _{33±2}	Still some Usp ₁₀ , Usp ₆₀ ; no ilm.
623	Usp ₃₅	2-ph	580	WM;CH ₄	118	Usp _{36±3} ; Usp _{63±4}	Much relic Usp ₁₀ ; no ilm.
624	Usp ₃₅	2-ph	570	WM;CH ₄	121	Usp _{36±3} ; Usp _{60±4}	Much relic Usp ₁₀ ; possible minor ilm.
630	Usp ₃₁	3-ph	560	IM;Ar+H ₂	321**	Usp _{36±2} ; Usp _{53±4}	Minor relic Usp ₁₀ ; contains Fe ^o
631	Usp ₃₃	1-ph	560	Ar+H ₂	240	Usp _{38±1} ; Usp _{60±4}	Run was reduced; contains Fe ^o

Except as noted, all runs were made at 1 kbar total pressure. Two-phase (2-ph) mechanical mixtures (of the bulk compositions indicated) were made by grinding together Usp₁₀ and Usp₈₀ for one hour in an agate mortar. The three-phase (3-ph) mixture was equimolar amounts of Usp₁₀, Usp₃₃, and Usp₆₀. Compositions of run products were estimated using (440), (620), and (622) peak positions on x-ray diffractograms. "Broad peaks" indicates a single maximum but with a broad width-at-half-height interpreted as residual zoning in an essentially homogenized material.

*Pressure medium, 2 kbar H₂O.

**Initially 81 days with IM buffer in 1 kbar CH₄ medium; remaining 240 days in Ar + H₂ at P_{Tot} = 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 mixtures (#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 Usp_{36±3} 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 Usp₈₀, both were ground for the same length of time, and both appear to have similar grain sizes (all grains < 10 μ m, most less than 5 μ m).

Homogenization experiments at 540–570°C all yielded results similar to those of #623: two new spinels (approx. Usp₃₂₋₃₈ and Usp₅₅₋₆₀) formed; the initial Usp₈₀ 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 Usp₅₇ 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

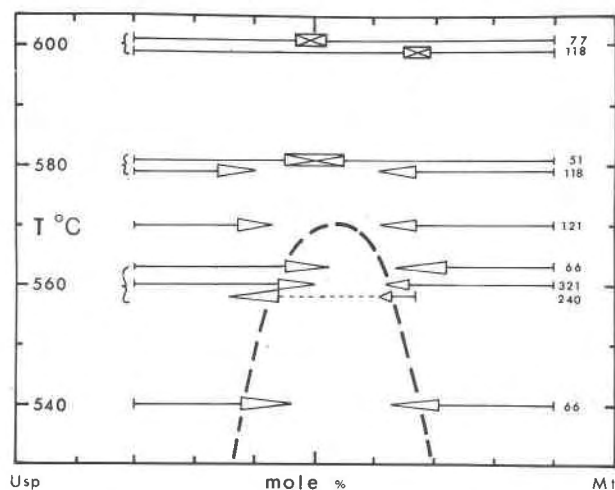


Fig. 1. Results of experiments on the Mt-Usp miscibility gap. Inward-pointing arrows show the results of dissolving experiments on mechanical mixtures of U_{sp10} and U_{sp80} . Crossed rectangles show essential homogenization. The pair of arrows pointing toward Usp at 560° results from an exsolution 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 (U_{sp48} at 560° and 540°C , respectively) still show peaks centered around those for U_{sp48} , but the peaks are slightly broader and the $K\alpha_1$ and $K\alpha_2$ 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 (U_{sp33}) 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 U_{sp33} . But the Ar plus the 30–50% H_2 pressure medium employed in lieu of an oxygen buffer reduced the charge, producing some Fe^0 and driving the bulk composition of the remaining spinel to approximately $U_{sp40-42}$. Most of this new spinel is a homogeneous phase with X-ray peaks corresponding to $U_{sp38\pm 1}$; but there are also smaller amounts of a spinel with composition $U_{sp61\pm 4}$. Because both product spinels were formed by reaction from one direction (*i.e.*, from an Fe_3O_4 -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_3O_4 – Fe_2TiO_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_2O_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_3O_4 – Fe_2TiO_4 join. The consolute point would appear to lie at $565\pm 15^\circ\text{C}$ and at approximately $\text{Mt}_{55}\text{Usp}_{45}$. However, there are no unequivocal exsolution experiments to prove this suggestion, and the results at 540 – 570° 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.

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