

Liquid Immiscibility and the Evolution of Basaltic Magma

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This experimental study examines relationships between alternative evolution paths of basaltic liquids (the so-called Bowen and Fenner trends), and silicate liquid immiscibility. Synthetic analogues of natural immiscible systems exhibited in volcanic glasses and melt inclusions were used as starting mixtures. Conventional quench experiments in 1 atm gas mixing furnaces proved unable to reproduce unmixing of ferrobasaltic melts, yielding instead either turbid, opalescent glasses, or crystallization of tridymite and pyroxenes. In contrast, experiments involving in situ high-temperature centrifugation at 1000g ($g = 9.8 \text{ m/s}^2$) did yield macroscopic unmixing and phase separation. Centrifugation for 3–4 h was insufficient to complete phase segregation, and resulted in sub-micron immiscible emulsions in quenched glasses. For a model liquid composition of the Middle Zone of the Skaergaard intrusion at super-liquidus temperatures of 1110–1120°C, centrifugation produced a thin, silicic layer (64.5 wt% SiO_2 and 7.4 wt% FeO) at the top of the main Fe-rich glass (46 wt% SiO_2 and 21 wt% FeO). The divergent compositions at the top and bottom were shown in a series of static runs to crystallize very similar crystal assemblages of plagioclase, pyroxene, olivine, and Fe–Ti oxides. We infer from these results that unmixing of complex aluminosilicate liquids may be seriously kinetically hampered (presumably by a nucleation barrier), and thus conventional static experiments may not correctly reproduce it. In the light of our centrifuge experiments, immiscibility in the Skaergaard intrusion could have started already at the transition from the Lower

to the Middle Zone. Thus, magma unmixing might be an important factor in the development of the Fe-enrichment trend documented in the cumulates of the Skaergaard Layered Series.

KEY WORDS: liquid immiscibility; Skaergaard; layered intrusions; experimental petrology

INTRODUCTION

Very few ideas in the history of igneous petrology have experienced such dramatic turns in acceptability as the concept of igneous petrogenesis by liquid immiscibility. A popular idea at the dawn of modern petrology (e.g. Daly, 1914), it fell into disrepute in late 1920s (Greig, 1927; Bowen, 1928), was revived by new evidence in the 1970s and 1990s (Roedder & Weiblen, 1970, 1971; De, 1974; McBirney & Nakamura, 1974; Philpotts, 1976, 1982; Dixon & Rutherford, 1979; Roedder, 1979), and has remained largely ignored during the last two to three decades. Nevertheless, a modern re-evaluation of petrogenetic and geochemical aspects of silicate immiscibility has been attempted recently (e.g. Jakobsen *et al.*, 2005; Bogaerts & Schmidt, 2006; Schmidt *et al.*, 2006; Veksler *et al.*, 2006). Observations reported in some of the recent papers imply that the phenomenon of melt unmixing may hold a key to a number of major, long-standing problems of igneous petrology.

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One early recognized and hotly debated problem of igneous petrology has been the Bowen–Fenner controversy. The controversy dates back to the classical works by Bowen (1928) and Fenner (1929), and it deals with the general chemical trend of evolution of sub-alkaline basaltic magma. Simply put, Fenner and his followers since that time have advocated a liquid differentiation trend towards strong enrichment in Fe-oxides at constant or slightly decreasing silica content. Bowen led proponents of the alternative claim that the content of Fe-oxides in basaltic liquids never achieves the concentrations inferred from the Fenner trend, and the liquid evolution is characterized rather by silica enrichment. The trends, which are also called tholeiitic and calc-alkaline, both exist in nature and result in the formation of distinct volcanic rock associations and plutonic complexes (e.g. Wager & Deer, 1939; Yoder & Tilley, 1962; Carmichael, 1964). The processes behind these opposing trends have been traditionally explained in terms of fractional crystallization, with particular emphasis on (1) the onset of magnetite crystallization, which depends on the oxidation state of magma (e.g. Osborn, 1979), and (2) cotectic proportions of olivine, plagioclase and clinopyroxene (Grove & Baker, 1984). Others have stressed the effects of melt chemistry; for example, the role of alkalis (Irvine, 1976; Shi, 1993).

Silica and Fe-oxides, the definitive components of the Bowen and Fenner trends, are also key players in the occurrence of silicate liquid immiscibility (Roedder, 1951). During the last surge of interest in silicate melt unmixing 20–30 years ago, it was established that certain ferrobasaltic liquids were unstable, unmixing to form two contrasting liquid compositions, one with a SiO_2 content of less than 45 wt% and very high total iron [$\text{FeO}(\text{t}) = \text{FeO} + \text{Fe}_2\text{O}_3$] at 25–30 wt% or more, and the other with SiO_2 contents at or exceeding 55–60 wt%, and $\text{FeO}(\text{t})$ at about 5–10 wt% (e.g. Philpotts, 1976, 1979, 1982). Observations both in natural rocks and in laboratory experiments have confirmed the stable coexistence of certain silicic and Fe-rich liquids with gabbroic mineral assemblages (Roedder & Weiblen, 1970; De, 1974; McBirney & Nakamura, 1974; Dixon & Rutherford, 1979; Philpotts, 1979; Roedder, 1979; Longhi, 1990). Silicate liquid immiscibility in ferrobasaltic melts results in the formation of (1) extremely Fe-rich, and (2) silicic conjugate liquids. Thus, it has the potential to place the Bowen vs Fenner debate on a new basis, possibly linking the divergent liquid evolution trends. In the presence of immiscibility, the trends of $\text{FeO}(\text{t})$ and silica enrichment do not appear as mutually exclusive alternatives, but rather as complementary evolution paths of immiscible conjugate liquids in a heterogeneous magma. In this debate experimental evidence is crucial. It should be pointed out that reliable experimental demonstrations of immiscibility in basaltic compositions have been restricted so far to

temperatures below 1050°C, and very advanced stages of crystallization. As a consequence, immiscibility has been relegated to a minor role in igneous petrogenesis. Unless it is proven that immiscibility in natural ferrobasaltic melts can start earlier (i.e. at about 50–60% crystallization of a common tholeiitic liquid, and temperatures around 1070–1100°C), unmixing will remain insignificant in the Bowen vs Fenner debate.

In this study, we examine the experimental evidence for and against earlier unmixing of ferrobasaltic liquids. We revisit the thermodynamic and phase equilibria constraints on the Bowen and Fenner types of liquid evolution. We present new results for static and dynamic (centrifuge) experiments, which demonstrate that unmixing of multi-component basaltic liquids appears to be seriously experimentally hampered by a nucleation barrier, formation of colloidal emulsions, and metastable crystallization. Our results show that conventional static experiments on small melt droplets or rock chips in metal wire loops may be unable to correctly reproduce the onset of liquid immiscibility in evolved, Fe-rich basaltic or dacitic liquids. The onset of macroscopic immiscibility may be pushed to lower temperatures by metastable crystallization, especially in charges with high initial volume proportion of crystals (e.g. in experiments on rock chips). In some cases, a second immiscible liquid phase may not nucleate at all, or not grow beyond the sub-micron, colloidal stage, and after hours and days it may remain unrecognizable in final glasses from fine exsolutions formed during quenching. High-temperature *in situ* centrifugation is, however, capable of separating immiscible emulsions, and thus revealing stable, super-liquidus immiscibility even when the result is a very fine emulsion. In light of our centrifuge experiments, we propose that unmixing of natural ferrobasaltic liquids may in fact start at a much earlier stage of crystallization than was previously thought. Our starting mixtures were based on compositions of natural immiscible glasses, and so we begin with a brief overview of those natural melt inclusions that appear to record the early stages of unmixing. In conclusion, we examine the petrogenetic implications for tholeiitic magmas, mostly using the classical example of the Skaergaard intrusion, East Greenland, and propose that the existence of the divergent trends primarily stems from the strong non-ideality of ferrobasaltic and ferrodacitic liquids.

SILICATE LIQUID IMMISCIBILITY IN MAGMAS AND SELECTION OF EXPERIMENTAL COMPOSITIONS Volcanic glasses and melt inclusions

Droplet exsolution textures in natural volcanic glasses have been traditionally regarded as the strongest evidence

Table 1: Examples of natural immiscible liquids (quenched glasses) in mesostasis of basaltic lavas, and in melt inclusions (wt% oxides)

	Groundmass glasses		Melt inclusions in plagioclase						Inclusions in native iron	
	<i>Lfe</i> ¹	<i>Lsi</i> ¹	<i>Lfe</i> ²	<i>Lsi</i> ²	<i>Lfe</i> ²	<i>Lsi</i> ²	<i>Lfe</i> ³	<i>Lsi</i> ³	<i>Lfe</i> ⁴	<i>Lsi</i> ⁴
SiO ₂	41.5	73.3	52.8	71.8	49.4	79.7	48.47	68.42	39.33	72.18
TiO ₂	5.8	0.8	1.2	0.7	4.0	0.6	4.33	1.55	2.82	0.60
Al ₂ O ₃	3.7	12.1	7.4	10.2	3.4	10.6	2.85	8.1	7.52	13.38
FeO	31.0	3.2	19.3	4.0	22.6	3.5	21.45	7.26	19.78	4.10
MnO	0.5	0.0	0.2	0.0	0.4	0.0	0.6	0.06	1.60	0.26
MgO	0.9	0.0	8.3	1.1	9.6	0.6	6.6	1.92	6.28	1.06
CaO	9.4	1.8	9.0	6.5	10.0	1.2	9.68	2.84	14.23	2.90
Na ₂ O	0.8	3.1	1.0	2.2	0.0	2.2	1.9	2.33	0.60	0.75
K ₂ O	0.7	3.3	0.8	3.5	0.4	1.6	0.93	2.84	0.21	1.40
P ₂ O ₅	3.5	0.07	0.0	0.0	0.2	0.0	1.0	0.0	7.53	0.37
Total	97.8	97.67	100.0	100.0	100.0	100.0	97.81	95.32	99.90	97.01

References: ¹Philpotts (1982); ²Philpotts (1981); ³Krasov & Clocchiatti (1979); ⁴Ryabov (1989). *Lfe*, Fe-rich glass; *Lsi*, silicic glass.

supporting silicate liquid immiscibility. Classical examples were presented by Philpotts (1982), who carried out a detailed study of the mesostasis of basalts and andesites from numerous localities worldwide, and described glassy, or partly crystallized spherical droplets dispersed in a second glass of a different composition. The compositions of the droplets and matrix glasses were shown to compare well with experimental Fe-rich and silica-rich immiscible conjugate melts, consistent with an origin by liquid immiscibility. The average compositions of the coexisting phases in the mesostasis of tholeiitic lavas according to Philpotts (1982) are listed in the first two columns of Table 1. Both phases are notably depleted in MgO, and imply equilibration at low temperature. Experiments on similar basaltic compositions (Roedder & Weiblen, 1970; McBirney & Nakamura, 1974; Dixon & Rutherford, 1979; Philpotts, 1979; Philpotts & Doyle, 1983; Longhi, 1990), confirmed the late-stage, low-temperature origin of the groundmass phase assemblages forming the immiscible globules. According to those experiments, immiscibility in terrestrial basaltic lavas probably occurs below 1020°C.

Significantly less evolved, more refractory compositions have been reported, however, in glassy melt inclusions hosted by olivine and plagioclase phenocrysts (Roedder & Weiblen, 1970; Krasov & Clocchiatti, 1979; Roedder, 1979; Fujii *et al.*, 1980; Philpotts, 1981, 1982; Shearer *et al.*, 2001). Philpotts (1981, 1982) argued that the more primitive glass compositions in plagioclase-hosted inclusions may be due to metastable unmixing. He proposed that early exsolution of pyroxenitic, Fe-rich liquid in plagioclase-hosted melt

inclusions could be a consequence of arrested crystallization of clinopyroxene in small inclusion cavities because of the absence of suitable sites for nucleation. Such an explanation is, however, difficult to apply to the case studied by Krasov & Clocchiatti (1979). Those workers attempted to homogenize inclusions in An₇₀ plagioclase phenocrysts from subduction-related andesite-dacitic lava of the Karymsky volcano, Kamchatka, Russia, and observed two conjugate silicate liquids at temperatures of up to 1250–1280°C. Importantly, some of the immiscible inclusions had been originally crystallized to fine-grained daughter crystal assemblages, and immiscibility was shown to be reversible in heating-cooling experiments around 1280°C. The compositions of the quenched immiscible glass phases reported by Krasov & Clocchiatti (1979) are also presented in Table 1. The glasses are characterized by elevated MgO contents, and a lower contrast in SiO₂ and Fe-oxide contents. These features are consistent with the equilibration of immiscible liquids at higher temperatures.

Perhaps the most convincing example of high-temperature silicate liquid immiscibility is provided by melt inclusions in native iron, which, although exotic in terrestrial environments, do occur in a few basaltic sills and lava flows. Grains, nuggets, and large blocks of native iron and minor cohenite (Fe₃C) have been reported in basaltic lavas on Disco island, West Greenland (Bird *et al.*, 1981), and in the roof endocontact zone of the Khutungunsky sill of the Siberian trap province (Ryabov, 1988, 1989). The occurrences of native iron are believed to

result from reduction of basaltic magma by carbon at the contact with organic-bearing sediments. Some iron nuggets contain numerous inclusions of rock fragments, single silicate crystals, and spherical glass droplets showing clear, classical immiscibility textures, as can be seen in Fig. 1. The photograph shows that the Fe-rich and silica-rich glasses are very distinct, and, in those inclusions where low-temperature devitrification is minor, the interfaces between the glasses are razor-sharp. Representative electron microprobe data on the glasses in the Siberian samples from Ryabov (1989) are also presented in Table 1. Very similar compositions have been reported from Disco island (Bird *et al.*, 1981). The elevated MgO contents of the glasses are similar to those of the plagioclase-hosted melt inclusions studied by Krasov & Clocchiatti (1979; see also Table 1), and imply a high-temperature origin.

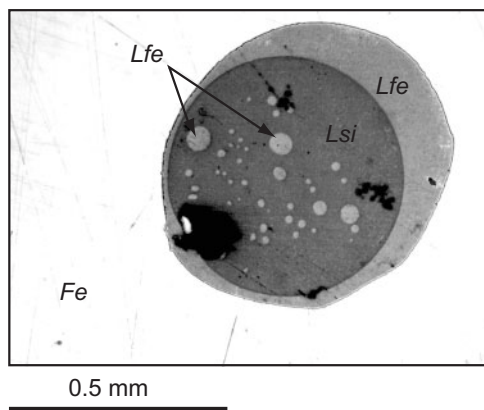


Fig. 1. Natural inclusions of immiscible Fe-rich (*Lfe*) and silica-rich (*Lsi*) glasses in native iron, Siberian Traps; reflected light. The Fe-rich glass forms a rim around the silica-rich glass, and there are also a few smaller spherical droplets of *Lfe* inside the *Lsi*. Glass compositions reported by Ryabov (1989) are given in Table 1.

Two of our starting mixtures were based on the average compositions of the immiscible glasses of the iron-hosted melt inclusions. The compositions RY40 and RY20 (Table 2) were calculated as mixtures between the average Fe-rich (*Lfe*) and silica-rich (*Lsi*) iron-hosted glasses published by Ryabov (1989) (Table 1) in mass proportions of 3:2 and 4:1. In other words, the composition RY40 upon complete melting should theoretically yield 40 wt% of the conjugate liquid *Lsi*, and 60 wt% *Lfe*, whereas the composition RY20 should give 20 and 80 wt% respectively of the same liquids.

Three other starting mixtures were designed in a similar way from compositions of other immiscible glasses listed in Table 1. The composition SF-1 is based on the analyses of low-temperature immiscible groundmass globules and glasses published by Philpotts (1982), and compiled in the two leftmost columns of Table 1. Accordingly, the composition has the lowest MgO content among the mixtures used in this study. The mixture SF-1 has been used in previous centrifuge experiments (Veksler *et al.*, 2006), where it produced roughly equal proportions of *Lfe* and *Lsi* immiscible phases. The composition KC is based on electron microprobe analyses of the Fe-rich and silica-rich glasses of the plagioclase-hosted melt inclusions published by Krasov & Clocchiatti (1979). The mass proportion of the *Lfe* and *Lsi* (see the analyses in Table 1) is 7:3. The mixture FJ is based on electron microprobe analyses of immiscible glassy inclusions in plagioclase phenocrysts from an olivine-bearing andesite of the Akita-Komagatake volcano, Japan, which were published by Fujii *et al.* (1980). The analyses were carried out using defocused beam, and the composition FJ represents an average mixture of the Fe-rich and silica-rich immiscible liquids in unidentified proportions. Notably, the MgO content in the bulk of the inclusions is the highest ever reported among immiscible liquids.

Table 2: Compositions of synthetic starting mixtures normalized to 100 wt%

	SF-1	KC	FJ	FJ20	RY40	RY20	MZ-1	MZ-2	MZF	MZS
SiO ₂	56.6	56.1	49.94	55.45	53.13	45.22	50.0	48.0	45.66	64.56
TiO ₂	2.0	3.6	2.01	1.61	1.96	2.96	5.1	4.9	5.41	1.80
Al ₂ O ₃	6.0	4.56	3.39	5.29	9.99	9.6	10.0	9.6	9.78	13.25
FeO	24.0	18.16	23.16	18.53	14.77	16.9	17.2	20.51	21.0	7.39
MgO	1.4	5.35	9.61	7.68	4.24	5.48	4.0	3.84	4.15	2.32
CaO	6.0	7.86	10.27	8.22	9.82	11.48	10.0	9.60	10.65	6.34
Na ₂ O	0.5	2.09	0.81	1.50	0.67	1.38	2.8	2.69	2.44	2.81
K ₂ O	2.0	1.55	0.32	1.34	0.69	0.58	0.6	0.58	0.48	1.37
P ₂ O ₅	0.0	0.72	0.49	0.39	4.73	6.4	0.3	0.29	0.43	0.15
Total	98.5*	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

*The remaining 1.5 wt% comprises a mixture of more than 30 trace elements [see Veksler *et al.* (2006) for details].

By their very nature, plagioclase-hosted melt inclusions must be saturated in their host plagioclase. The compositions KC and FJ are, however, surprisingly low in alumina, and, as we learned from our experiments on these mixtures (see below), do not produce plagioclase on the liquidus. To compensate for possible post-entrapment modification as a result of precipitation of plagioclase on inclusion walls [see Veksler (2006) for discussion], we prepared another mixture FJ20, which has been derived from the composition FJ by the addition of 20 wt% of pure anorthite.

Liquids of the Skaergaard intrusion

Since the study by Wager & Deer (1939), the Skaergaard intrusion of layered gabbros has been the prime example of the Fenner, tholeiitic, or Fe-enrichment trend. Thus, Skaergaard has remained for decades at the centre of the Bowen–Fenner controversy. The intrusion is located in East Greenland, and after many years of comprehensive research was once termed ‘the most intensely studied body of rock on Earth’ (McBirney & Naslund, 1990). Numerous attempts have been made to reconstruct liquid lines of descent in the intrusion by: (1) mass-balance calculations (Wager & Brown, 1968; Hunter & Sparks, 1987; Nielsen, 2004); (2) experimental simulation of crystallization or partial melting of Skaergaard rocks (McBirney & Naslund, 1990; Toplis & Carroll, 1995; Thy *et al.*, 2006); (3) tracing specific elements using mineral–melt partition coefficients (Tegner, 1997; Jang *et al.*, 2001); (4) geochemical thermometry of cumulus mineral assemblages (Ariskin, 1999, 2002); (5) studies of crystallized melt inclusions in cumulus minerals (Hanghøj *et al.*, 1995; Jakobsen *et al.*, 2005, 2007); (6) comparisons with compositions of coeval and spatially associated dykes (Brooks & Nielsen, 1978, 1990).

The disparate results of these reconstructions are illustrated in Fig. 2. In general, one may conclude that the disagreement among researchers is the strongest when it comes to the late stages of magma evolution, especially after the onset of ilmenite and magnetite crystallization. The disagreement between the models is, however, not so dramatic regarding the starting composition of the Skaergaard parental magma (see also Nielsen, 2004), and the models also agree reasonably well at the early stages of magma evolution, up to about 50–60% crystallization. This stage corresponds roughly to the transition from the Lower to the Middle Zone of the Layered Series marked by the disappearance of olivine from the liquidus mineral association and the appearance of liquidus pigeonite [see Wager & Brown (1968) and McBirney (1989) for a detailed description of the Skaergaard stratigraphy]. The liquid composition at this stage has been well constrained by detailed experimental studies (McBirney & Naslund, 1990; Toplis & Carroll, 1995; Thy *et al.*, 2006), thermodynamic modelling (Ariskin, 2002), and mass-balance calculations (Nielsen, 2004). Our starting mixtures MZ-1 and MZ-2 (Table 2) are based on estimates of the liquid composition at the top of the Lower Zone. The composition MZ-1 is very similar to the glasses produced in experiments by Toplis & Carroll (1995) at temperatures close to 1100°C. The composition MZ-2 differs from MZ-1 only by its somewhat higher FeO content, which brings it closer to the mass-balance estimation of the Middle Zone liquid by Nielsen (2004). The remaining two starting mixtures in Table 2, the Fe-rich composition MZF and silica-rich composition MZS, are explained below, where we describe the results of our centrifuge experiments.

EXPERIMENTAL AND ANALYTICAL METHODS

Preparation of starting mixtures

All the starting mixtures listed in Table 2 were synthesized by fusion in Pt crucibles of carefully weighed and mixed reagent-grade chemicals [SiO_2 , Al_2O_3 , MgO , TiO_2 , CaCO_3 , Na_2CO_3 , K_2CO_3 and $\text{Ca}_3(\text{PO}_4)_2$]. To avoid strong oxidation and Fe losses to the Pt crucibles, Fe-free glasses were first prepared by repeated fusions in an electric furnace once at 900°C, and then twice at 1350°C. The Fe-free glasses were then crushed to a fine-grained powder (grain size less than 3 μm) and mixed and ground with reagent-grade FeO in an agate mortar under acetone. Fine powders of the glass–FeO mixtures were used for the experimental charges.

Static experiments

Static experiments were conducted in a 1 atm vertical tube furnace in which $f\text{O}_2$ was controlled by CO–CO₂

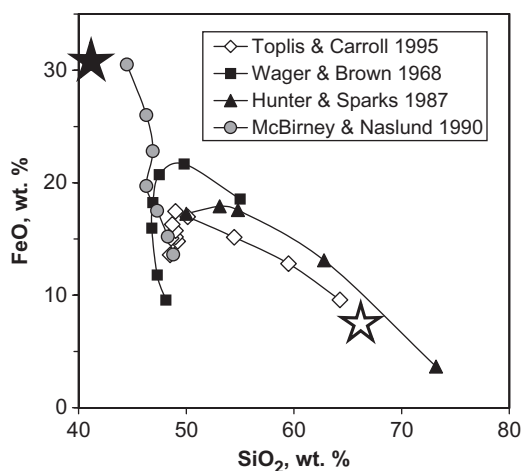


Fig. 2. Liquid lines of descent in the Skaergaard intrusion in terms of total iron (FeO) vs silica (SiO_2) variations. Average compositions of immiscible Fe-rich and Si-rich melt inclusions in apatite reported by Jakobsen *et al.* (2005) are shown by filled and open stars.

gas mixtures. A PtRh₆–PtRh₃₀ (type B) thermocouple was employed for temperature measurements. The uncertainties of cited log f_{O_2} values and temperature do not exceed ± 0.2 and $\pm 2^\circ\text{C}$, respectively. In most cases, silicate melts were suspended from Re loops, prepared from commercially available Re ribbon (Rhenium Alloys, Inc.). Rhenium has been shown to be an excellent loop material, preventing iron loss from a charge even at very reducing conditions (Borisov & Jones, 1999). The samples were either (1) directly placed in a pre-heated furnace at the required temperature or (2) first over-heated by 50–150°C and then cooled to run temperature at a rate of 10–50°C per hour. After sufficient dwell exposure at constant temperature, the samples were quenched in air within a few seconds.

Centrifuge experiments

The experimental equipment and Fe–Pt double containers for the centrifuge experiments have been described in detail previously (e.g. Dorfman *et al.*, 1996; Veksler *et al.*, 2006). Briefly, the equipment represents a small cylindrical wire-wound electric furnace mounted on a centrifuge, which provides acceleration of up to 1000g ($g = 9.8 \text{ m/s}^2$) over maximal run durations of 5 h. Temperature is controlled by three Pt–PtRh₁₀ (type S) thermocouples at the top, bottom and the middle of the container, respectively. Comparisons between the thermocouple readings imply that ‘top to bottom’ temperature gradients in the samples did not exceed $\pm 2^\circ\text{C}$. Inner containers made of ‘iron’ (more precisely, low-carbon steel with C concentration of less than 0.6 wt%), wrapped and sealed inside platinum foil (Veksler *et al.*, 2006) were used in most of the runs. However, a few runs were carried out in nickel or graphite containers. At the start of centrifuge runs, starting mixtures were first completely melted and homogenized at high, super-liquidus temperatures and the slowest rotation speed (50g) for at least 30 min, but usually for 1 h or more. The purpose of the rotation at this stage was to prevent melts from creeping up the container walls by capillary forces. Complete melting and homogenization was checked by a few test runs in which containers were opened and the glasses were examined after the heating at slow rotation. The main centrifugation stage at 1000g and experimental temperature followed after the homogenization and lasted for a few hours. Quenching was performed in air by turning off the heating, while the centrifuge rotation continued at a constant speed. During quenching, temperature inside the sample dropped from 1200 to 1100°C in 10 s, from 1100 to 1000°C in 15 s, and further cooling of the sample to 800°C took about 1.5–2 min.

Electron microprobe analyses

Run products were mounted in epoxy, ground and polished and studied by electron microprobe at the GeoForschungsZentrum Potsdam using a Cameca SX50

instrument in wavelength-dispersive spectrometry (WDS) mode at 15 kV accelerating voltage and 15 nA beam current with spot sizes ranging from 1 to 3 μm depending on the properties and compositions of the analyzed materials. Counting time for all the elements was set to 20 s on peak and 10 s on background. The following synthetic and natural standards were used for the calibration: orthoclase (Al and K), rutile (Ti), wollastonite (Si and Ca), albite and jadeite (Na), apatite (P), hematite (Fe), diopside and periclase (Mg).

Transmission electron microscopy (TEM)

TEM was carried out using a FEI TecnaiTMG² F20 X-Twin electron microscope operated at 200 kV. Focused ion beam milling (FIB) was applied to cut site-specific TEM-foils from the area of interest. FIB preparation was performed under ultrahigh vacuum conditions in an oil-free system FEI FIB200TEM. TEM-ready foils with dimensions 20 $\mu\text{m} \times 10 \mu\text{m} \times 0.1 \mu\text{m}$ were cut directly from microprobe epoxy mounts using a gallium-ion beam. The TEM foils were placed on a perforated carbon film on a copper grid. Carbon coating to prevent charging of the TEM samples was not applied.

RESULTS

Static experiments on synthetic analogues of natural immiscible glasses

The results of the static experiments are summarized in Tables 3 and 4. The most important result in the context of this study is that none of the products of the conventional static runs showed unambiguous, macroscopic signs of liquid immiscibility. The composition SF-1 that had repeatedly unmixed at almost identical T and f_{O_2} conditions in our previous centrifuge runs (Veksler *et al.*, 2006) quenched in the loops to beads of turbid, milky glass, occasionally with trace amounts of small (3–10 μm), dendritic tridymite crystals. Over-heating to 1400°C (run L-34) did not result in any visible changes in the optical appearance of the glass. TEM images of foils cut from one of the turbid glasses (Fig. 3b) revealed sub-micron heterogeneity comprising silica- and Fe-rich amorphous phases. Compositional TEM scans and profiles showed sharp co-variations in Fe, Ca and K at the sub-micron scale with areas enriched in Fe and Ca being depleted in K, but a more uniform distribution of Al and Si. The Fe-rich and Si-rich phases form 3D sponge-like interconnected textures that are usually interpreted as products of spinodal phase separation (Vogel, 1985; Shelby, 2005). Thus, it appears that although the composition SF-1 did not produce macroscopic immiscible liquid (glass) segregations in static runs, it falls within the spinodal region of the liquid miscibility gap, and consequently cannot be quenched to a homogeneous glass.

Table 3: Conditions of static runs and phase composition of the run products

Run no.	Mixture	Over-heating, T (°C)	T (°C)	log fO_2	Duration (h)	Run products
L-1	SF-1	1200	1145	-12.8	32	L + trace tr
L-4	SF-1	1200	1123	-11.7	63	L + trace tr
L-5	FJ	1200	1123	-11.7	63	L + pig + aug
L-6	SF-1	1200	1123	-10.6	61.5	L + trace tr
L-7	FJ	1200	1123	-10.6	61.5	L + pig + aug
L-8	SF-1	1240	1203	-10.6	23.5	L
L-9	FJ	1240	1203	-10.6	23.5	L + pig
L-10	SF-1	none	1156	-11.2	48	L + trace tr
L-11	FJ	none	1156	-11.2	48	L + pig + aug
L-13	KC	none	1200	-10.6	15.5	L
L-14	FJ20	none	1200	-10.6	15.5	L + pig
L-15	RY40	none	1200	-10.6	15.5	L + tr
L-16	KC	none	1249	-10.0	9	L
L-17	FJ20	none	1249	-10.0	9	L
L-18	FJ	none	1249	-10.0	9	L
L-19	RY40	none	1249	-10.0	9	L + tr
L-20	KC	1200	1151	-11.3	14	L + pig
L-21	RY40	1200	1151	-11.3	14	L + tr
L-22	RY40	none	1280	-9.6	6	L + tr
L-23	FJ20	none	1280	-9.6	6	L
L-24	RY40	none	1200	-7.8	16	L + tr
L-25	FJ20	none	1200	-7.8	16	L + pig
L-26	KC	none	1200	-7.8	16	L
L-27	RY40	none	1169	-11.1	17	L + tr
L-29	KC	none	1169	-11.1	17	L + pig + tr
L-30	RY40	none	1319	-9.2	5	L + trace tr
L-31	RY40	1200	1098	-12.1	35.5	L + tr
L-33	KC	1200	1098	-12.1	35.5	L + pig + aug + tr
L-34	SF-1	none	1400	-8.3	1.5	L
L-35	SF-1	none	1153	-11.3	18	L + trace tr
L-36	SF-1	none	1153	-12.6	26.5	L + trace tr
L-62	MZF	none	1081	-11.2	27	L + aug + plag + ilm
L-63	MZS	none	1081	-11.2	27	L + aug + plag + tr + mt
L-64	MZF	1080	1022	-12.2	96	L + aug + ol + plag + ilm + mt
L-65	MZS	1080	1022	-12.2	96	L + aug + ol + plag + tr + mt
L-66	MZF	none	1062	-11.6	26	L + aug + plag + ilm + mt
L-67	MZS	none	1062	-11.6	26	L + aug + plag + tr + mt
L-69	MZF	none	1043	-11.9	64	L + aug + ol + plag + ilm + mt
L-70	MZS	none	1043	-11.9	64	L + aug + ol + plag + mt

Static experiments on mixing between MZF and MZS

L-51	MZF-MZS	1350	1113	-11.5	27	Lfe + Lsi
L-52	MZF-MZS	1350	1113	-11.5	27	Lfe + Lsi
L-56	MZF-MZS	1350	1114	-11.5	75	Lfe + Lsi
L-57	MZF-MZS	1350	1114	-11.5	75	L
L-58	MZF-MZS	1350	1090	-11.9	64	Lfe + Lsi + aug
S-141	MZF-MZS	1270	1110	<IW	72	Lfe + Lsi + ol + aug

IW, iron-wüstite buffer. Crystal phases: aug, augite; ilm, ilmenite; mt, magnetite; ol, olivine; pig, pigeonite; plag, plagioclase; tr, tridymite.

Table 4: *Electron microprobe analyses of glasses and crystal phases in products of static loop experiments*

Run	Mixture	T (°C)	Phase	SiO ₂	TiO ₂	Al ₂ O ₃	MgO	FeO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Total
L-9	FJ	1203	glass	50.92	2.31	3.66	7.64	23.06	10.85	0.86	0.29	0.49	100.08
			pig	53.08	0.23	0.15	23.57	18.93	3.56	0.03	0.00	0.01	99.56
L-11	FJ	1156	glass	49.17	2.55	4.25	5.96	25.11	9.81	2.32	0.33	0.52	100.00
			pig	51.64	0.33	0.19	18.25	21.38	8.02	0.10	0.01	0.03	99.95
			aug	52.99	0.02	0.00	20.45	0.58	24.41	0.01	0.01	0.02	98.50
L-5	FJ	1123	glass	48.11	3.23	5.43	4.23	24.35	9.75	1.37	0.42	0.63	97.52
			pig	51.08	0.329	0.21	19.54	18.65	8.25	0.04	0.03	0.0	98.14
			aug	50.72	0.53	0.40	14.64	17.27	14.91	0.10	0	0.0	98.57
L-25	FJ20	1200	glass	55.64	1.79	5.34	6.88	18.38	8.74	1.53	1.19	0.35	99.82
			pig	55.11	0.15	0.20	26.95	15.20	3.15	0.04	0.00	0.01	100.82
L-29	KC	1169	glass	57.36	3.57	4.39	5.41	18.21	8.17	1.79	1.37	0.36	100.65
			pig	55.24	1.16	1.21	17.99	19.75	5.30	0.45	0.36	0.10	101.54
L-33	KC	1098	glass	58.22	4.35	5.55	2.66	19.21	6.62	1.78	1.77	0.42	100.60
			pig	53.62	1.62	1.63	13.59	21.84	7.26	0.48	0.49	0.12	100.64
			aug	51.73	0.96	0.24	14.13	19.28	14.36	0.11	0.01	0.02	100.85
L-30	RY40	1319	glass	53.05	2.07	10.02	4.33	15.25	9.91	0.49	0.39	4.62	100.13
			tr	98.65	0.27	0.38	0.02	0.49	0.13	0.09	0.05	0.01	100.07
L-22	RY40	1280	glass	52.00	2.07	10.38	4.31	14.97	10.01	0.60	0.50	4.88	99.74
			tr	97.38	0.01	0.02	0.00	0.26	0.02	0.01	0.01	0.00	97.71
L-19	RY40	1250	glass	49.10	2.15	10.60	4.50	15.58	10.44	0.71	0.59	5.49	99.15
			tr	98.45	0.30	0.60	0.00	0.44	0.11	0.12	0.11	0.02	100.15
L-24	RY40	1200	glass	48.63	2.20	10.67	4.55	15.48	10.53	0.72	0.65	5.81	99.23
			tr	98.18	0.31	0.68	0.03	0.47	0.14	0.11	0.11	0.02	100.04
L-27	RY40	1169	glass	48.45	2.25	10.86	4.70	16.11	10.65	0.68	0.65	5.87	100.21
			tr	98.21	0.14	0.70	0.18	0.86	0.50	0.08	0.05	0.18	100.88
L-21	RY40	1150	glass	47.95	2.33	11.08	4.54	15.72	10.69	0.73	0.70	6.21	99.93
			tr	98.92	0.03	0.00	0.00	0.30	0.01	0.03	0.00	0.00	99.29
L-31	RY40	1098	glass	46.80	2.26	11.18	4.66	16.87	10.81	0.75	0.70	6.24	100.27
			tr	98.04	0.30	0.82	0.01	0.45	0.17	0.19	0.18	0.04	100.19
L-62	MZF	1081	glass	44.58	5.94	9.77	3.60	21.66	10.06	2.49	0.51	0.46	99.08
			cpx	49.24	2.43	3.08	11.27	13.84	19.43	0.43	0.06	0.06	99.83
			plag	53.34	0.48	27.54	0.15	1.33	11.54	4.87	0.21	0.03	99.49
L-66	MZF	1062	glass	47.02	4.53	9.54	2.56	22.56	8.97	2.62	0.78	0.82	99.40
			cpx	48.54	2.77	4.84	7.35	18.64	15.44	1.15	0.32	0.31	99.36
			plag	54.94	0.70	25.77	0.35	2.60	10.27	5.51	0.31	0.09	100.53
			ilm	0.07	50.40	0.12	2.65	43.83	0.43	0.00	0.01	0.00	97.52
			mt	0.13	28.16	1.94	2.19	65.37	0.23	0.01	0.01	0.01	98.04
L-69	MZF	1043	glass	50.22	3.68	9.70	2.03	21.51	8.21	2.59	1.08	1.16	100.18
			ol	32.45	0.61	0.05	12.93	53.52	0.62	0.01	0.00	0.08	100.26
			cpx	50.00	1.72	2.77	8.86	18.22	17.79	0.68	0.17	0.18	100.39
			plag	57.21	0.51	24.95	0.22	2.48	8.85	6.13	0.50	0.08	100.93
			mt	0.14	26.48	2.32	1.52	68.20	0.15	0.01	0.01	0.01	98.85
L-64	MZF	1022	glass	52.82	2.67	10.29	1.41	19.19	7.44	2.45	1.40	1.73	99.39
			ol	31.80	0.46	0.04	10.66	56.13	0.62	0.02	0.01	0.13	99.87
			cpx	48.65	1.85	2.49	9.18	20.78	16.96	0.32	0.01	0.03	100.28
			plag-1	53.59	0.44	27.98	0.14	1.74	11.69	4.73	0.32	0.09	100.72

(continued)

Table 4: Continued

Run	Mixture	<i>T</i> (°C)	Phase	SiO ₂	TiO ₂	Al ₂ O ₃	MgO	FeO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Total
L-63,	MZS	1081	plag-2	43.16	1.07	35.19	0.27	0.90	19.11	0.64	0.02	0.13	100.47
			mt	0.28	27.40	1.76	1.23	67.65	0.24	0.02	0.01	0.01	98.59
			glass	67.51	2.19	12.47	1.80	6.23	5.16	2.20	1.75	0.29	99.60
			cpx	50.82	0.71	2.53	14.42	15.76	15.55	0.21	0.03	0.04	100.06
L-67	MZS	1062	plag	49.37	0.57	31.16	0.61	1.32	13.49	2.82	0.19	0.06	99.59
			glass	68.30	1.85	11.87	1.50	6.83	4.71	2.30	1.97	0.24	99.56
			cpx	49.62	0.54	1.45	12.89	19.39	15.50	0.15	0.02	0.02	99.56
			plag	54.49	0.10	27.28	0.33	1.01	11.83	4.30	0.19	0.02	99.55
L-70,	MZS	1043	tr	96.44	0.23	1.03	0.22	0.37	0.37	0.08	0.12	0.05	98.91
			glass	72.44	1.69	11.94	0.80	4.53	2.94	2.50	2.60	0.30	98.14
			ol	32.88	0.86	0.27	13.82	50.10	0.54	0.01	0.02	0.25	98.74
			cpx	50.63	0.59	1.96	10.94	22.63	13.11	0.23	0.17	0.05	100.30
L-65	MZS	1022	plag	62.71	0.88	20.41	0.46	2.55	7.38	3.58	1.24	0.15	99.36
			mt	0.57	6.57	4.64	1.69	79.63	0.14	0.00	0.02	0.01	93.26
			glass	70.57	1.16	13.09	0.69	5.44	3.67	3.00	2.64	0.43	100.68
			ol	32.18	0.12	0.11	12.35	54.17	0.61	0.00	0.02	0.17	99.73
L-51	MZS	1022	cpx	51.04	0.66	1.89	9.89	23.10	11.74	0.22	0.18	0.03	98.74
			plag	63.09	0.70	19.93	0.51	3.30	6.97	3.72	1.53	0.14	99.89
			mt	0.33	7.25	4.25	0.91	81.81	0.08	0.00	0.00	0.00	94.64
			tr	98.83	0.17	1.01	0.01	0.22	0.07	0.27	0.04	0.04	100.66
L-52	MZS	1113	Fe-glass	53.80	3.82	11.55	3.65	14.36	8.73	2.47	0.79	0.30	99.45
			Si-glass	62.79	2.16	12.74	2.72	8.92	6.40	2.37	1.37	0.18	99.65
L-56	MZS	1114	Fe-glass	54.31	3.82	11.51	3.64	13.96	8.63	2.44	0.79	0.29	99.38
			Si-glass	63.19	1.99	13.17	2.81	8.41	6.48	2.44	1.39	0.16	100.04
L-57	MZS	1114	Fe-glass	54.51	3.67	11.72	3.29	13.68	8.28	2.41	0.86	0.29	98.71
			Si-glass	64.92	1.97	12.50	2.37	8.36	5.77	2.15	1.54	0.15	99.75
L-58	MZF/S	1114	glass	53.58	3.95	11.51	3.41	14.58	8.63	2.51	0.82	0.27	99.26
L-58	MZS	1090	Fe-glass	54.31	3.85	11.90	3.33	13.88	8.46	2.49	0.82	0.30	99.34
			Si-glass	65.18	1.89	13.21	2.02	7.76	5.57	2.17	1.59	0.16	99.55
			cpx	52.30	1.11	1.58	16.71	12.91	14.98	0.13	0.02	0.03	99.77
			Fe-glass	45.37	5.08	10.19	3.92	20.25	9.90	2.57	0.48	0.50	98.26
S-141	MZS	1110	Si-glass	61.61	2.20	12.38	2.10	10.39	5.86	2.29	1.44	0.21	98.48
			ol	34.78	0.29	0.15	23.14	40.45	0.70	0.06	0.01	0.10	99.68
			cpx	51.78	1.59	1.53	15.03	10.05	18.85	0.29	0.02	0.02	99.14

Oxide concentrations are in wt%.

The composition FJ quenched at 1249°C to clear, dark brown, optically homogeneous glass. At 1203°C, it produced a similar glass with a few elongated, euhedral crystals of low-Ca pyroxene corresponding to pigeonite (sample L-9; see analyses in Table 4). As the temperature was brought further down to 1156 and 1123°C, the size and the bulk volume proportion of the pyroxene crystals increased. A strong compositional zoning developed in the crystals, with low-Ca, pigeonitic compositions in the cores, and progressively Ca-rich, augitic compositions at the rims (samples L-11 and L-5). Glass compositions

retained very high FeO(t) contents of about 24–25 wt%, but no signs of liquid unmixing have been observed in the run products. The liquid clearly remained under-saturated in plagioclase down to at least 1123°C. The addition of 20 wt% of plagioclase components (mixture FJ20) also failed to stabilize plagioclase. Pigeonite remained the only liquidus phase in the samples L-14 and L-25 produced from the mixture FJ20 at 1200°C, and the mixture completely melted at and quenched to clear, optically homogeneous brownish glass from 1249 and 1280°C (samples L-17 and L-23).

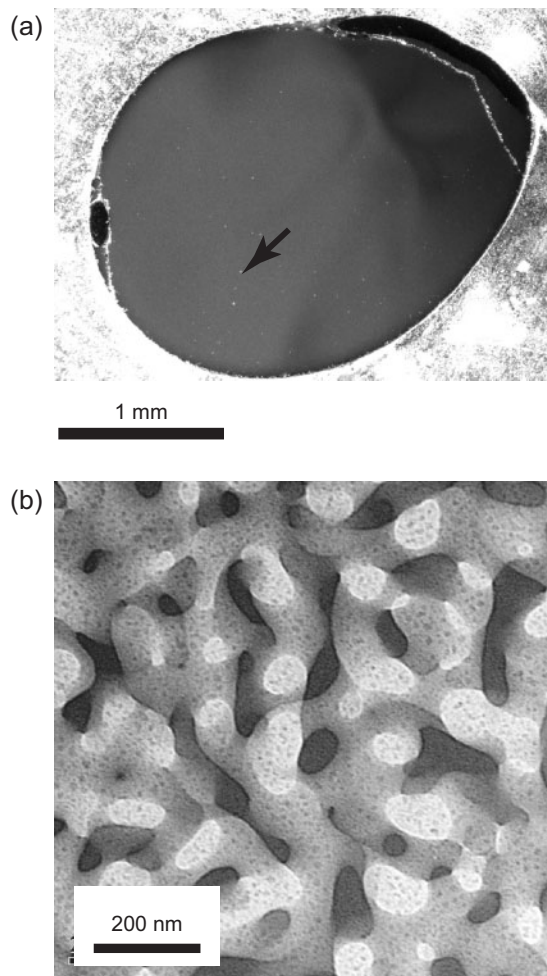


Fig. 3. Products of a static experiment at atmospheric pressure, 1123°C and $\log f_{\text{O}_2} = -10.6$ on starting composition SF-1 (sample L-6). The charge quenched to a bead of turbid glass. (a) General view of the polished epoxy mount in reflected light. The location of the fragment studied by TEM is indicated by an arrow. (b) TEM image showing sub-micron heterogeneity in the glass fragment. The high-absorption, Fe-rich amorphous phase is darker. The lightest areas are those where the low-absorption silica-rich phase goes through the whole thickness of the foil.

Static experiments on starting mixture KC produced homogeneous, very dark brown glass at 1200 and 1249°C, and liquidus assemblages comprising low-Ca pyroxene at 1169 and 1098°C (samples L-29 and L-33). The pyroxene crystals are similar to those produced in the experiments on the mixtures FJ and FJ20, and they also showed a strong compositional zoning from pigeonitic cores to sub-calcic and high-Ca rims (Table 4). A few smaller tridymite crystals were found in sample L-33 quenched at 1098°C. Plagioclase did not crystallize, and no signs of liquid unmixing were observed in the samples. The absence of plagioclase from the products of mixtures FJ, FJ20 and KC is not consistent with the fact that the original natural

glasses occur as inclusions in plagioclase, but it is not entirely unexpected in view of the low Al_2O_3 contents in the bulk compositions as well as quench partial liquids. As noted above, the original natural plagioclase-hosted melt inclusions may have been modified by post-entrapment diffusion and crystallization of host plagioclase on inclusion walls (see also Veksler, 2006).

Eight static experiments on the mixture RY40 at temperatures 1098–1319°C and $\log f_{\text{O}_2}$ ranging from -7.8 to -12.1 all produced tridymite crystals suspended in clear, dark brown glass, and no signs of liquid immiscibility. Unlike the sample L-33 (see above), where tridymite formed tiny, micron-sized needles, and small (2–10 μm) elongated euhedral crystals, in the products of mixture RY40 it mostly formed strange-looking oval blebs or crystal aggregates measuring up to 0.4 mm in diameter. The bulk mass fraction of tridymite in the samples varied from 2% at 1319°C (sample L-30) to 13% at 1098°C (sample L-31), and tridymite showed no visible resorption at run durations of up to 35 h. Crystallization of tridymite as a single liquidus phase over such a broad temperature interval from a melt with SiO_2 content of only 53.3 wt% is remarkable, and is discussed in more detail below. The absence of liquid immiscibility is no less remarkable, as the failure of melt droplets to unmix starkly contrasts with spectacular immiscibility textures of the natural iron-hosted melt inclusions, on which the mixture RY40 was based (Fig. 1).

Centrifuge experiments

Optical and electron microscope images of centrifuge run products are presented in Figs 4–8, and experimental conditions and results are summarized in Tables 5 and 6. As mentioned above, the mixture SF-1 has previously been studied and described in detail by Veksler *et al.* (2006). In this study, we present the results of centrifuge experiments on new starting compositions KC, FJ, FJ20, RY20, RY40, MZ, and MZ-2.

Our first pilot centrifuge run on starting mixture KC lasted for a total duration of 90 min (sample C-101 in Table 5), and was probably not long enough to equilibrate the charge. Olivine, which was never observed in static runs, formed at the bottom of the container, whereas tridymite crystallized at the top in a turbid, brownish glass. Glass at the bottom, just above the olivine crystals, was darker and more transparent than at the top. Vertical electron microprobe (EMP) profiles of the glass over the height of the sample revealed strong, semi-linear compositional gradients with top-to-bottom variations in SiO_2 content from 72.6 to 45.5 wt%. However, when the total duration of the centrifuge runs was increased to 180 min, and initial heating to 1180°C was performed at a slower rotation speed, the mixture KC quenched to a uniformly turbid, non-transparent brownish glass, which showed no detectable compositional gradients in vertical electron

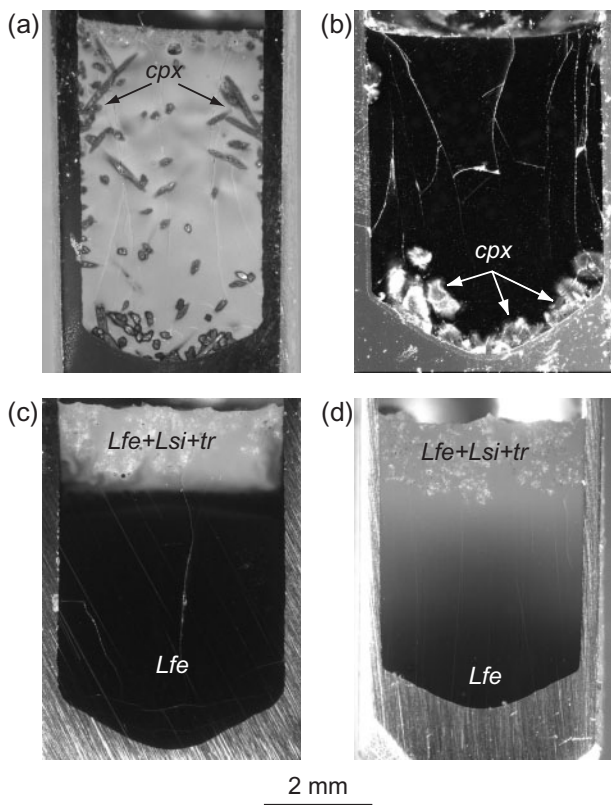


Fig. 4. Examples of centrifuged run products. (a) Sample C-117, mixture KC at 1150°C. Pyroxene crystals (cpx) in a turbid glass. (b) Sample C-106, mixture FJ and 1200°C. Large clinopyroxene crystals in a dark brown glass. (c) Sample C-114, mixture RY20 in iron container at 1150°C. Emulsion of two liquids *Lfe* and *Lsi* and suspended tridymite crystals (tr) separated at the top of the clear Fe-rich glass *Lfe*. (d) Sample C-116, mixture RY20 in nickel container at 1170°C. Poorly separated emulsion of two liquids and suspended tridymite crystals.

microprobe profiles (see the analyses at the top and bottom of sample C-105 in Table 6). At 1150°C (sample C-117), the mixture produced abundant crystals of low-Ca pyroxene, and tridymite grains fractionated to the top of the sample in a brownish-greenish, turbid glass (Fig. 4c). Vertical electron microprobe profiles revealed significant variations in glass composition, with higher FeO contents at the bottom and more silicic compositions at the top (Table 6). Thus, we conclude that the composition KC showed some signs of unmixing (probably metastable) in the centrifuge runs, but the results were obscured by crystallization and were not reproducible at run durations shorter than 2 h.

Centrifuge experiments on mixture FJ at 1200°C produced clear, brown glasses with large, elongated crystals of low-Ca pyroxene (samples C-106 and 108). Mixture FJ20 quenched at 1200°C to turbid, greenish glass with no detectable compositional gradients in the vertical cross-section (see analyses in Table 6). In a static run (sample L-25), the mixture quenched at the same temperature

to clear glass, and small amounts of low-Ca pyroxene. Thus, for mixtures FJ and FJ20 the results of centrifuged runs are generally in good agreement with static experiments at similar conditions (Tables 3 and 4). No signs of liquid immiscibility have been detected by either method.

At different run durations and 1200°C, the centrifuged products of the mixture RY40 retained, in agreement with isothermal static runs, variable amounts of tridymite, but showed also unequivocal signs of liquid immiscibility and phase separation. Longer run durations resulted in a better phase separation. However, immiscibility led to formation of *Lfe*–*Lsi* emulsions, and at the exposures of 2 and 3 h liquid segregation was still incomplete. Vertical cross-sections of the quenched samples featured three distinct zones (Figs 5–7): (1) a bottom zone of dark brown Fe-rich glass; (2) a middle creaming zone of tridymite crystals suspended in semi-transparent, milky glass with plumes and clouds representing quenched emulsion of silica-rich and Fe-rich liquids (Fig. 7); (3) a thin (2–3 mm) layer of yellowish, honey-coloured, transparent silica-rich glass at the very top of the sample (Figs 5 and 6). According to the TEM image of a glass foil cut from the creaming zone of the sample C-110 (Fig. 7b), the *Lsi*–*Lfe* emulsions are characterized by drop-in-matrix morphology, which implies immiscibility in the nucleation regime (Shelby, 2005), and a mean droplet size of about 100–150 nm. Some droplets appear to merge by flocculation and coalescence. In addition to the silicate unmixing, a small amount of Fe–P liquid metal alloy (FeP) accumulated at the bottom of the container in most of the runs. The formation of the alloy liquid probably resulted from P_2O_5 reduction by C residing in the inner low-carbon steel container. The formation of the Fe–P alloy had a negligible effect on the FeO content of the silicate liquids, but resulted in a significant drop of P_2O_5 concentrations from 4.7 wt% in the starting charge to an average of less than 4 wt% in some of the centrifuged glasses. The increase of run duration, and the decrease in the proportion of silica-rich components (mixture RY20) visibly improved phase separation. Tridymite crystals are virtually absent from some of the products of the RY20 mixture (e.g. sample C-112 in Fig. 5), and a narrow but clear and distinct layer of silicic glass formed at the top. The compositions of the Fe-rich and silica-rich experimental glasses at 1200°C are, however, not so contrasting as those in the natural iron-hosted melt inclusions (Table 1), upon which the starting mixtures RY40 and RY20 were originally based. To increase fO_2 to the level of the Ni–NiO buffer, and completely block the formation of the Fe–P alloy, we carried out a few runs in nickel containers. Two experiments on mixture RY20 (samples C-116 and C-118) produced poorly separated *Lfe*–*Lsi* emulsions, which quenched to turbid, non-transparent glasses, and small amounts of tridymite crystals that floated to the top.

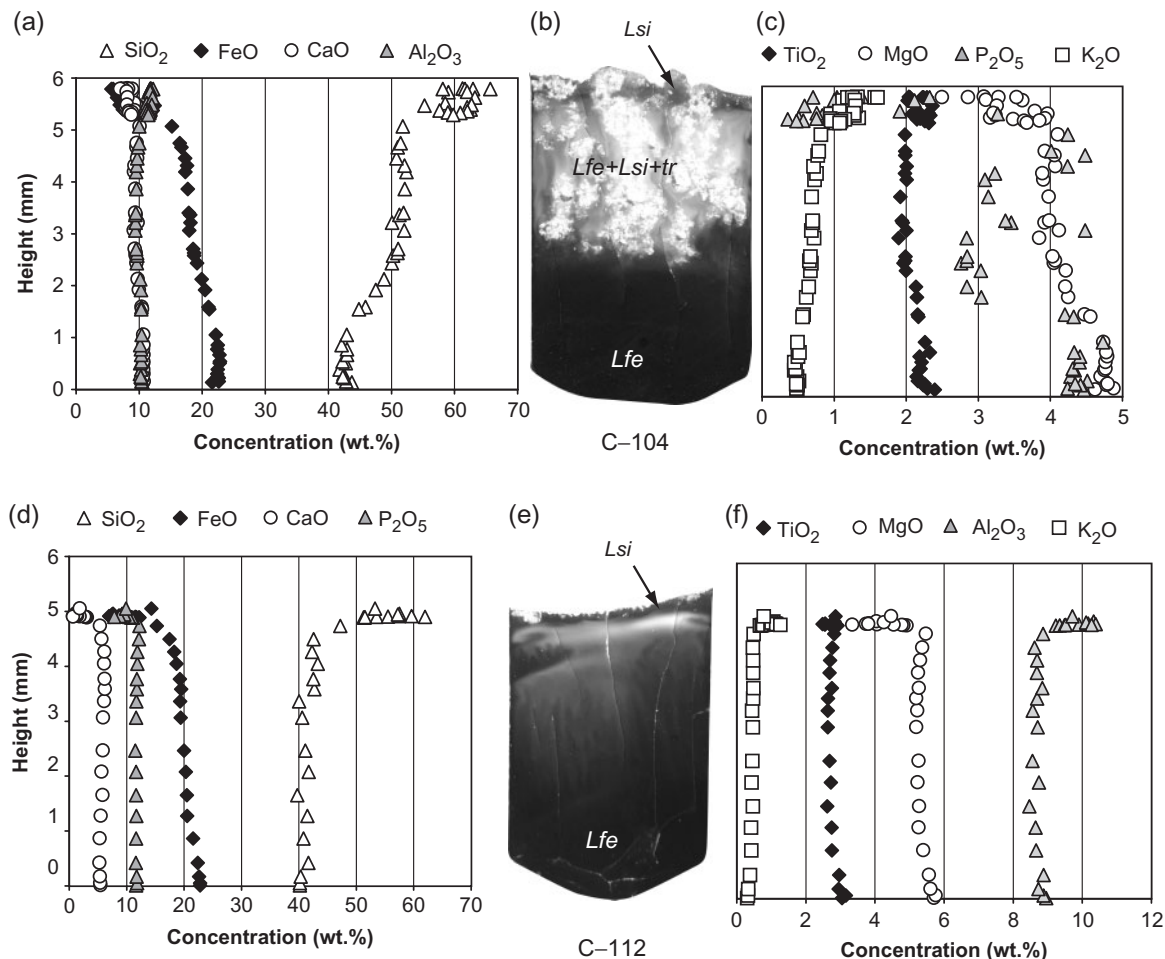


Fig. 5. Phase separation and vertical compositional gradients in products of centrifuge experiments on mixtures RY40 and RY20 analogous to the bulk compositions of the iron-hosted melt inclusions (Fig. 1). (a)–(c) represent compositional plots and a photograph of sample C-104; (d)–(f) represent analogous plots and a photograph of sample C-112. Run conditions and electron microprobe analyses of the phases are given in Tables 5 and 6. Abbreviations for phases are as in Fig. 4.

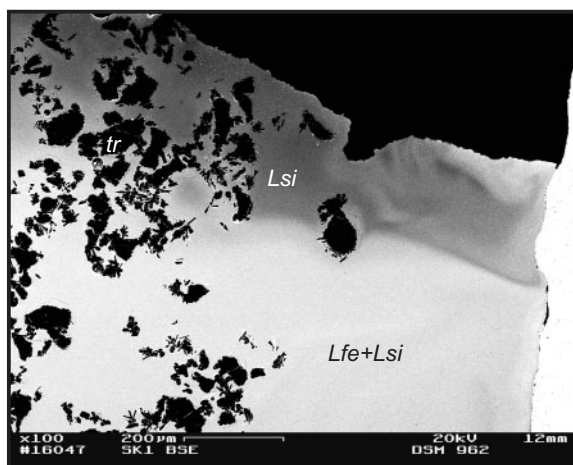


Fig. 6. Back-scattered electron image of a small area at the upper right corner of sample C-104 (see Fig. 5) showing tridymite crystals (tr) and the diffuse transition between the Fe-rich (*Lfe*) and silicic (*Lsi*) glasses.

The model Skaergaard mixture MZ-1 at 1110–1120 °C was, as expected, slightly super-liquidus, and quenched in iron containers to very dark brown glass, which looked optically homogeneous. Electron microprobe profiles revealed, however, steep vertical compositional gradients for all the major oxides in a narrow layer at the very top of the samples (Fig. 8). The profiles of the components are consistent with element partitioning between Fe-rich and silica-rich immiscible liquids (e.g. Schmidt *et al.*, 2006; Veksler *et al.*, 2006, and references therein), and imply stratification by liquid immiscibility. As in the other ferrobasaltic compositions, liquid unmixing apparently started at a sub-micron, colloidal scale, and emulsion coalescence and creaming after 2 or 3 h of centrifugation remained incomplete. TEM line scans of foils cut at the top of the sample C-111 immediately below the thin silica-rich layer revealed fine-grained chemical heterogeneity of the glass at a sub-micron scale. Peaks in the Fe scan, with a characteristic

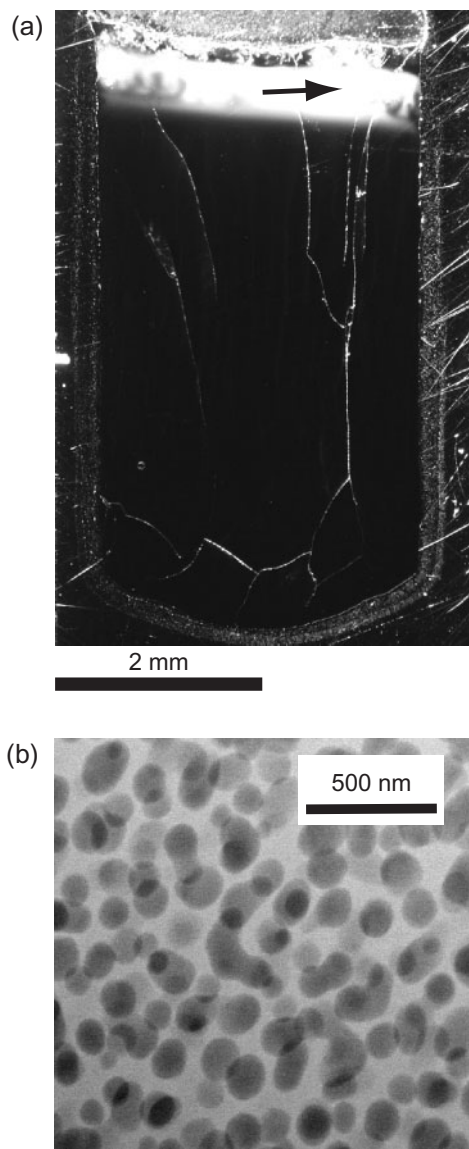


Fig. 7. Centrifuged products of the starting mixture RY20 at 1200°C (sample C-110). (a) General view of the polished epoxy mount in reflected light. The location of the fragment studied by TEM is indicated by an arrow. (b) TEM image of the glass fragment showing sub-micron globular heterogeneity. High-absorption, Fe-rich amorphous phase is darker.

width of 20–30 nm and a magnitude at least two times greater than background noise, corresponded to depressions in the Si scan, implying the nucleation of Fe-rich and silica-rich amorphous phases. The total proportion of silica-rich liquid *Lsi* in centrifuged products of the mixture MZ-1 was small, and the consolidated *Lsi* layer, which formed on the top, is a mere 0.2 mm thick. Longer durations apparently enhance phase separation. Experiments were also performed in nickel and graphite containers (samples C-113 and C-122). Unfortunately, both containers

reacted with the melt, and changed the liquid composition. Glass in the nickel container was contaminated at 1120°C by 0.8–1.2 wt% NiO, and the charge precipitated small amounts of Ni-rich olivine and magnetite (see Tables 5 and 6). Vertical compositional gradients in the quenched glass were not so pronounced as in the iron containers, but still significant (Table 6). In the graphite container, FeO reduction resulted in crystallization of metallic iron on the container walls, and an overall drop in the FeO concentration in the melt to below 15 wt%. A slight increase in the silica content in the glass at the very top (Table 6) may indicate incipient liquid phase separation, but the gradient is even less pronounced than in the Ni container, and probably insignificant.

Centrifuge experiments on the second, more Fe-rich Skaergaard model mixture MZ-2 did not show significant compositional gradients or any other signs of liquid unmixing. In an iron container at 1110°C, melt quenched to dark brown homogeneous glass (sample C-120). The homogeneity of the glass at a sub-micron scale was confirmed by TEM study, which did not reveal any compositional heterogeneity above the background noise. In the nickel container (sample C-121), the liquid dissolved 0.8–1 wt% NiO and precipitated Ni-rich magnetite at the bottom and on the container walls. The glass showed no systematic compositional gradients, and appeared to be homogeneous to sub-micron scale.

In Fig. 9 the compositions of the glasses from the centrifuge experiments (Table 6) are plotted on the olivine–feldspar–silica projection, and compared with the position of the liquid miscibility gap in the $\text{Fe}_2\text{SiO}_4 - \text{KAlSi}_3\text{O}_8 - \text{SiO}_2$ system (Roedder, 1951, 1979). For the projection, molar fractions of oxides (X_{MO}) calculated from the analyses in Table 6 were combined into normative components: $\text{Fo} = X_{\text{MgO}}/2$; $\text{Fa} = (X_{\text{FeO}} - X_{\text{TiO}_2})/2$; $\text{Ab} = 2X_{\text{Na}_2\text{O}}$; $\text{Or} = 2X_{\text{K}_2\text{O}}$; $\text{An} = X_{\text{Al}_2\text{O}_3} - 2(X_{\text{Na}_2\text{O}} + X_{\text{K}_2\text{O}})$; $\text{Qz} = (X_{\text{SiO}_2} + X_{\text{TiO}_2})/2 + 3X_{\text{P}_2\text{O}_5} - (X_{\text{MgO}} + X_{\text{FeO}})/2 - 5X_{\text{Na}_2\text{O}} - 5X_{\text{K}_2\text{O}} - X_{\text{Al}_2\text{O}_3} - X_{\text{CaO}}$. Although the projection excludes important normative components such as wollastonite, apatite and ilmenite, the compositions of the immiscible *Lsi* and *Lfe* glasses from the centrifuge experiments plot well inside the immiscibility gap of the simplified synthetic system. The compositions of homogeneous glasses tend to lie to the left of the two-liquid field.

Static mixing experiments

The conflicting results of static and centrifuge experiments on mixtures RY40, RY20 and SF-1, as well as the unexpected unmixing of the Skaergaard model composition MZ-1, call for a critical examination of the experimental techniques, and a careful check of equilibrium. Equilibrium is normally checked by reversal experiments, and to perform those, we prepared mixtures and synthesized glasses of the compositions MZF and MZS (Table 2),

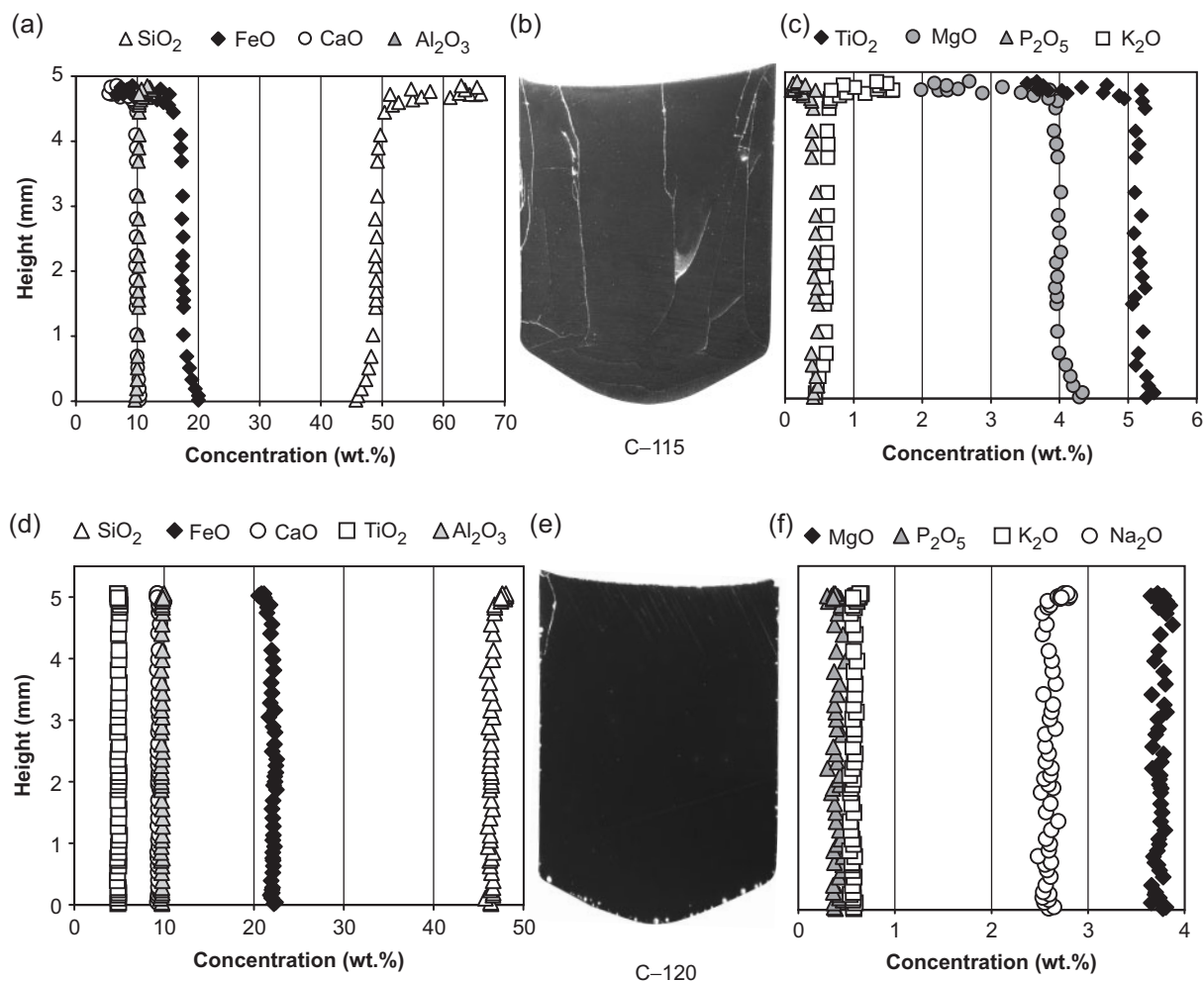


Fig. 8. Vertical compositional gradients in centrifuged products of mixtures MZ-1 and MZ-2. (a)–(c) represent compositional plots and a photograph of sample C-115; (d)–(f) represent analogous plots and a photograph of sample C-120.

which correspond to the end-member glass compositions produced at the bottom and at the top in centrifuge runs on mixture MZ-1 and believed to represent conjugate immiscible liquids *L_{Fe}* and *L_{Si}*. Because the duration of our centrifuge experiments was limited to a few hours, we carried out a series of control reversal experiments in a static setup. For that purpose, pairs of MZF and MZS melt droplets were loaded in Re loops, and Fe–Pt double containers identical to those that were used in centrifuge experiments. The idea was to see whether the liquids, which had been produced in the centrifuge, would mix back when kept in contact in a loop for a sufficient time.

In the loop set-up, approximately half of the loop was filled first with the silica-rich mixture MZS. The powdered mixture was melted for a few minutes at 1350°C and reducing conditions in a 1 atm gas mixing furnace, and quenched to glass. Then the rest of the loop was filled with the Fe-rich mixture MZF, and the charge was once

again rapidly heated to 1350°C, held at that temperature for a few minutes, and quenched. Finally, the loop with two glasses was placed into gas-mixing furnace pre-stabilized at 1090 or 1114°C, and *f*O₂ conditions indicated in Table 3, annealed for 1 or 3 days, and quenched. Run durations longer than 3 days were deemed not practical, because the losses of more volatile components, such as alkalis or P₂O₅, were expected to become significant, and affect bulk chemistry of the two-liquid charges.

In containers (run S-141 in Tables 3 and 4), the mixture MZF was first fused at the bottom of the inner iron container to a layer of bubble-free, homogeneous Fe-rich glass in the centrifuge furnace at 1110°C. The upper part of the container was then filled with the silica-rich mixture MZS; the outer Pt container was welded shut; the container assembly was placed in a vertical position into a static furnace, heated for 5 h at 1270°C to fuse the MZS mixture, and then kept for 72 h at 1110°C.

Table 5: Run conditions and phase assemblages in products of centrifuge experiments

No.	Mixture	T_1	T_2	Exposure (min)				Inner container	Run products
		(°C)	(°C)	Slow rotation at T_1	Slow rotation at T_2	Fast rotation at T_2	Total		
C-101	KC	$T_1 = T_2$	1180		30	60	90	iron	Emulsion glass + ol + tr
C-102	RY40	$T_1 = T_2$	1200		30	60	90	iron	Lfe + Lsi + tr
C-103	RY40	$T_1 = T_2$	1200		60	none	60	iron	Lfe + Lsi + tr
C-104	RY40	$T_1 = T_2$	1200		60	120	180	iron	Lfe + Lsi + FeP + tr
C-105	KC	$T_1 = T_2$	1180		60	120	180	iron	Emulsion glass
C-106	FJ	$T_1 = T_2$	1200		60	none	60	iron	L + pig
C-107	FJ20	$T_1 = T_2$	1200		60	120	180	iron	Emulsion glass
C-108	FJ	$T_1 = T_2$	1200		60	120	180	iron	L + pig
C-109	RY40	$T_1 = T_2$	1200		120	240	360	iron	Lfe + Lsi + FeP + tr
C-110	RY20	$T_1 = T_2$	1200		60	120	180	iron	Lfe + Lsi + FeP + tr
C-111	MZ-1	1170	1120	30	60	120	210	iron	Lfe + trace Lsi
C-112	RY20	$T_1 = T_2$	1170		120	120	240	iron	Lfe + Lsi + trace tr
C-113	MZ-1	1170	1120	30	30	60	120	nickel	Lfe + trace Lsi + ol + mt
C-114	RY20	$T_1 = T_2$	1150		120	120	240	iron	Lfe-Lsi emulsion + tr
C-115	MZ-1	1150	1100	30	30	180	240	iron	Lfe + trace Lsi
C-116	RY20	$T_1 = T_2$	1170		90	90	180	nickel	Emulsion glass + tr
C-117	KC	$T_1 = T_2$	1150		30	180	210	iron	Emulsion glass + pig + tr
C-118	RY20	$T_1 = T_2$	1200		60	180	240	nickel	Lfe-Lsi emulsion + tr
C-120	MZ-2	1150	1110	30	60	120	210	iron	L
C-121	MZ-2	1150	1110	30	60	120	210	nickel	L + mt
C-122	MZ-1	1150	1120	15	30	135	180	graphite	L + iron
C-123	MZ-1	1150	1120	15	45	360	420	iron	Lfe + trace Lsi

Slow rotation corresponds to the acceleration of 50g ($g = 9.8 \text{ m/s}^2$), except in C-101 and C-102 where it was 160g. Fast rotation corresponds to the acceleration of 1000g.

Despite the simple experimental design, the results appeared not as simple and straightforward as anticipated. In four loop runs L-51, 52, 56 and 58 the *Lfe* and *Lsi* liquid droplets did not mix back (Fig. 10); however, they did mix completely in the run L-57 (Table 3). Furthermore, electron microprobe analyses of quenched glasses (Table 4) revealed a significant partial mixing in all the loop runs. Notably, it mostly affected the Fe-rich liquid. Regardless of the run durations, and initial mass proportions of the two starting droplets, the Fe-rich melts dissolved roughly equal amounts of *Lsi*, whereas the composition of the silicic liquid (provided it did not dissolve completely as in the run L-57) changed only slightly. In all the experiments, including the run L-57, mixing stopped on the Fe-rich side at the same final melt composition characterized by a SiO_2 content of $54 \pm 0.5 \text{ wt\%}$. Electron microprobe profiles across the samples demonstrated that the final *Lfe* glasses were chemically homogeneous, probably because of

effective mixing by convection. The *Lsi* glasses were also homogeneous, and the transition zone between the glasses in most cases was narrow and sharp (Fig. 10b). In a single run at a lower temperature of 1090°C, groups of thin, needle-like, Ca-rich pyroxene crystals nucleated in the silica-rich glass, and the portion of glass near the crystals was further depleted in CaO, MgO, and FeO, and enriched in SiO_2 by about 2 wt%. We interpret the crystals as the first liquidus phase forming in the *Lfe-Lsi* mixtures.

It appears that the outcome of the mixing experiments in loops depended on the mass proportion of the Fe-rich and silica-rich (MZf and MZs) liquid droplets. The masses of the MZf and MZs mixtures were carefully measured in three runs, L-56, L-57 and L-58, and the MZs/MZf mass ratios in those runs were 1.35, 0.77 and 1.2, respectively. Thus, it is not surprising that the *Lsi* glass completely dissolved in the run L-57 in which the initial mass proportion of the silica-rich MZs mixture

Table 6: *Electron microprobe analyses of the products of centrifuge experiments*

No.	<i>T</i> (°C)	Mixture	Phase	SiO ₂	TiO ₂	Al ₂ O ₃	MgO	FeO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	NiO	Total
C-106	1200	FJ	glass	50.20	2.12	3.31	9.54	21.27	10.63	0.86	0.30	0.42	0.01	98.66
			pigeonite	53.24	0.54	0.41	21.97	18.91	4.98	0.02	0.00	0.03	0.02	100.12
C-108	1200	FJ	glass	48.82	2.13	3.44	7.72	22.50	10.57	1.11	0.35	0.44	0.02	99.09
			pigeonite	51.82	0.35	0.19	22.22	18.57	5.05	0.06	0.01	0.02	0.03	98.30
C-107	1200	FJ20	bottom*	54.68	1.72	5.30	7.81	17.56	8.86	1.66	1.33	0.32	0.01	99.26
			top*	55.13	1.69	5.27	7.54	17.18	8.60	1.58	1.30	0.34	0.00	98.61
C-101	1180	KC	bottom*	45.48	3.58	3.39	6.25	28.83	9.24	1.53	0.82	0.37	0.00	99.48
			top*	72.48	1.17	10.22	1.87	4.97	3.37	2.11	3.41	0.01	0.01	99.60
			olivine	34.89	0.16	0.02	23.01	42.42	0.65	0.01	0.01	0.08	0.01	101.24
C-105	1180	KC	bottom*	57.29	3.74	4.54	5.63	16.69	8.32	1.97	1.47	0.36	0.00	100.01
			top*	56.74	3.81	4.45	5.50	16.31	8.24	2.00	1.46	0.35	0.00	98.86
C-117	1150	KC	bottom*	52.37	4.14	4.40	5.68	20.67	9.05	1.85	1.24	0.48	0.00	99.88
			top*	60.09	3.70	5.06	4.43	15.21	7.21	1.95	1.83	0.38	0.00	99.85
			Pigeonite	52.14	1.09	0.38	18.66	18.85	9.40	0.18	0.06	0.02	0.00	100.79
C-104	1200	RY40	<i>Lfe</i>	42.54	2.23	10.27	4.78	22.60	10.64	0.53	0.48	4.36	0.02	98.45
			<i>Lsi</i>	62.33	2.25	11.80	3.19	7.25	8.04	1.11	1.31	0.89	0.01	98.17
C-109	1200	RY40	<i>Lfe</i>	45.04	2.15	10.01	4.53	21.57	10.26	0.59	0.53	3.30	0.01	98.00
			<i>Lsi</i>	64.46	2.24	12.05	3.42	5.51	8.17	1.14	1.32	0.15	0.01	98.46
C-110	1200	RY20	<i>Lfe</i>	42.15	2.76	8.76	5.29	21.97	11.48	0.78	0.43	4.88	0.01	98.51
			<i>Lsi</i>	63.20	2.93	10.79	3.80	6.54	8.48	1.55	1.16	0.44	0.01	98.91
C-112	1170	RY20	<i>Lfe</i>	40.63	2.97	8.82	5.61	22.43	11.69	0.71	0.35	5.38	0.01	98.61
			<i>Lsi</i>	62.97	2.70	10.27	3.34	7.11	7.87	1.58	1.26	0.67	0.00	98.61
C-114	1150	RY20	bottom*	41.77	2.95	9.14	5.88	22.57	11.42	0.67	0.36	5.07	0.00	99.82
			top*	48.18	2.54	9.06	4.90	16.53	10.73	1.08	0.69	6.46	0.00	100.16
C-116	1170	RY20	bottom*	40.06	2.96	9.17	5.66	18.35	11.96	0.74	0.4	8.50	1.10	98.90
			top*	46.50	2.53	9.14	5.31	14.90	11.08	0.95	0.64	7.51	0.90	99.46
C-118	1200	RY20	bottom*	40.46	2.95	9.14	5.73	17.78	11.89	0.75	0.44	8.51	0.90	98.56
			top*	47.27	2.61	8.79	5.14	14.59	10.93	0.95	0.61	7.62	0.85	99.35
C-111	1120	MZ-1	<i>Lfe</i>	47.67	5.05	9.88	3.75	17.84	9.98	2.62	0.56	0.38	0.01	97.76
			<i>Lsi</i>	62.46	4.51	12.01	2.23	7.75	6.40	1.80	1.34	0.16	0.00	98.66
C-115	1100	MZ-1	<i>Lfe</i>	48.15	5.16	10.10	4.04	18.14	10.04	2.58	0.56	0.44	0.00	99.21
			<i>Lsi</i>	64.92	3.77	12.24	2.23	7.28	5.84	2.50	1.49	0.13	0.00	100.39
C-113	1120	MZ-1	bottom*	48.06	5.14	10.06	3.75	16.89	10.16	2.57	0.58	0.37	0.88	98.45
			top*	54.54	4.10	10.70	3.10	13.23	8.68	2.58	0.93	0.29	0.99	99.14
			olivine	34.31	0.19	0.06	17.04	15.62	0.08	0.03	0.01	0.04	32.72	100.10
			magnetite	0.32	19.57	3.25	3.07	53.61	0.00	0.02	0.02	0.01	14.80	94.66
C-122	1120	MZ-1	Bottom*	50.82	5.41	10.64	4.13	14.83	10.41	2.69	0.61	0.42	0.00	99.95
			top*	55.01	5.40	11.34	3.69	11.84	9.42	2.70	0.74	0.29	0.00	100.43
C-120	1110	MZ-2	Bottom*	46.39	4.85	9.77	3.78	22.24	9.42	2.60	0.58	0.39	0.00	100.00
			top*	47.64	4.81	9.96	3.73	21.12	9.25	2.79	0.64	0.38	0.00	100.31

Oxide concentrations are in wt%.

*Glass compositions at the bottom and at the top of the container.

was the lowest. The presence of a massive iron container also seems to play a role in the mixing process, as demonstrated by the static experiment S-141. In that experiment, the MZF and MZS liquids layers did not mix back after

3 days at 1110°C. However, microprobe profiles show that the transition between optically distinct Fe-rich and Si-rich glasses is not razor-sharp. The width of the diffusion zone between the glasses is about 0.2 mm. The diffusion zone

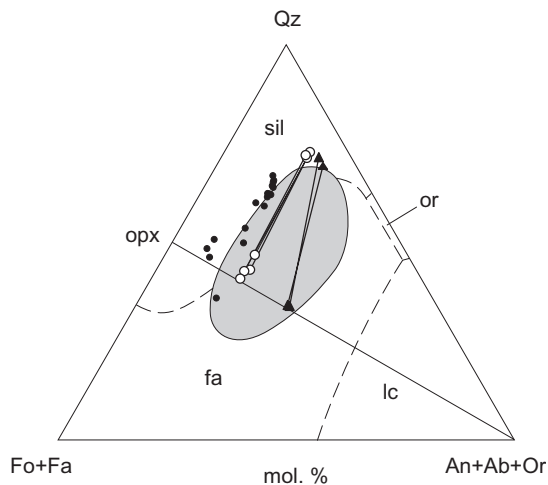


Fig. 9. Glass compositions from centrifuge experiments plotted on the (Fo + Fa)-(An + Ab + Or)-Qz projection. Homogeneous glasses from samples without phase separation are plotted in black circles. Immiscible glasses are shown by open circles (mixtures RY40 and RY20), and black triangles (mixture MZ-1). Pairs of the conjugate *Lsi* and *Lfe* compositions are connected by tie-lines. The gray area and dashed curves represent the miscibility gap and crystallization fields in the system Fa-Or-Qz (after Roedder, 1951). (See text for explanation of the projection method.)

may have formed during the brief heating to 1270°C, and it seems that no further mixing took place during the long exposure at 1110°C. The composition of the bottom Fe-rich layer remained virtually intact (Table 4). In contrast to the centrifuge experiments, minor crystallization took place in the charge. The bottom Fe-rich liquid precipitated small amounts of olivine crystals (Fo_{50}), and a few pyroxenes crystallized in the silicic glass at the container walls, and at the MZF-MZS contact. As discussed in the next section, the iron container may function as a buffer of FeO activity and thus affect the equilibrium between two immiscible silicate liquids.

Static mixing experiment S-141 is analogous in design to some experiments performed by Longhi (1990) on Fe-rich and silica-rich immiscible lunar compositions. Those experiments were also performed in iron containers, and different loading methods were used. In some runs, powders of Fe-rich and silica-rich conjugate compositions were loaded in two separate layers, and this is very similar to what we did in the run S-141. Longhi (1990) may well have encountered the same metastability problems as we did in our static runs. He reported extensive crystallization of silicates at the interfaces between glasses of contrasting composition, and noted the absence of a clear sharp meniscus in some of his experimental products. Crystallization of pyroxene in the mixing zone between the MZF and MZS glasses in our run S-141 may be of the same nature.

The reasons why mixing repeatedly stopped (or dramatically slowed down) in loops when SiO_2 concentration in

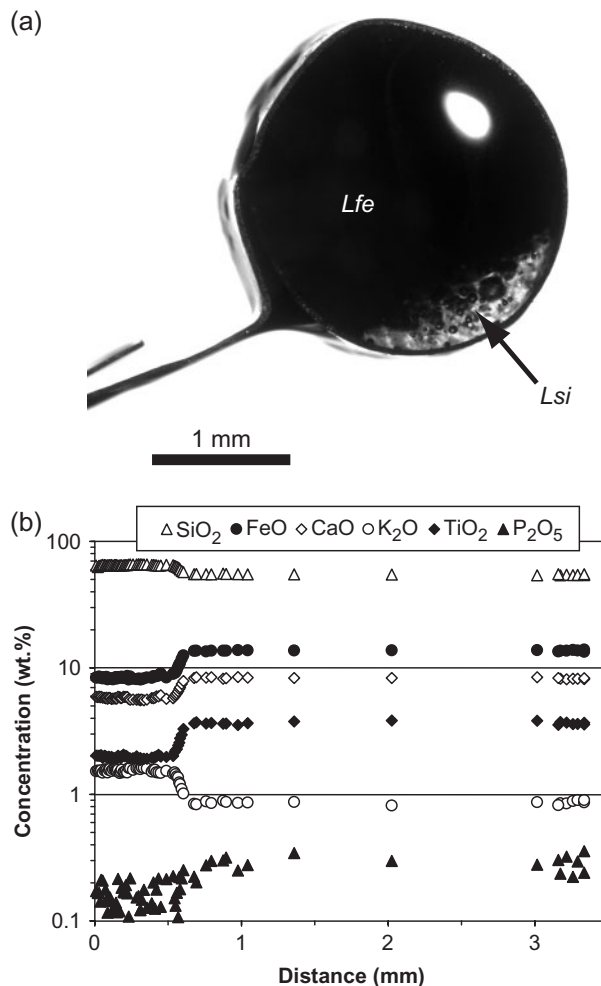


Fig. 10. Products of a static mixing run. (a) General view of sample L-56 in the Re ribbon loop showing incomplete mixing between Fe-rich glass (*Lfe*) and silicic glass (*Lsi*). (b) Electron microprobe profiles across the sample. The interface between the Fe-rich and silicic glasses is manifested by a step in the elemental profiles. (See text for further discussion.)

Lfe reached 54 wt% are not clear. First, the composition may represent a sort of kinetic barrier at which the viscosity of *Lfe* becomes too high for convective mixing, forcing further mixing to proceed at a much slower rate by diffusion only. Alternatively, the composition may represent a true conjugate liquid. If so, the difference from glass compositions formed in the centrifuge may be attributed to incomplete equilibration in shorter centrifuge runs, especially for slowly diffusing network-forming components (see also Veksler *et al.*, 2006). Finally, the composition may correspond to the borders of the spinodal region of the miscibility gap, where further mixing becomes energetically unfavourable. In our view, the first, kinetic explanation is less likely because the run durations were apparently long enough for effective diffusional transport

in even more viscous L_{Si} , and no compositional gradients, which would arise from incomplete diffusion, were observed in the quenched L_{Fe} glasses. With some reservations, we conclude that immiscibility in the MZ-1 liquid is likely to be stable, although chemical equilibration in the centrifuge was probably incomplete, and true conjugate liquids may somewhat differ in composition from the glasses that were analysed at the top and the bottom of centrifuged samples.

Crystallization experiments on the Fe-rich and silica-rich conjugate liquids

Thermodynamics requires that equilibrium immiscible liquids should crystallize identical mineral assemblages. To test this requirement of our putative immiscible liquids, we performed a series of static crystallization experiments on pure compositions MZF and MZS. Run conditions and the results are summarized in Tables 3 and 4. Plagioclase and augite are the main phases crystallizing in both mixtures at 1081 and 1062°C, and compositions of the solid solutions in the products of the MZF and MZS runs are similar (Table 4). The MZF mixture crystallized at 1081°C, plagioclase An_{56} and pyroxene $Wo_{42}En_{34}Fs_{24}$ (sample L-62), whereas the mixture MZS at the same temperature crystallized zoned plagioclase An_{75-65} (average composition An_{72}) and augite $Wo_{32}En_{42}Fs_{26}$ (sample L-63). The crystalline products also include minor amounts of Fe–Ti oxides, and olivine, which appeared in products of both mixtures between 1062 and 1043°C. All the products of the MZS mixture also contain variable amounts of a pure silica phase, probably tridymite. However, this tridymite, as discussed below, may be partly or fully metastable. With falling temperature, plagioclase generally becomes, as expected, more albitic. However, in the low-temperature MZF products at 1022°C (sample L-64) plagioclase crystals showed broad compositional variations clustering around two modes (plag-1 and plag-2 in Table 4). It should be noted that equilibrium is hardly achievable at temperatures below 1050°C, especially in the silicic, viscous liquids of the mixture MZS. Despite these complications at lower temperatures, the main conclusion from the crystallization experiments is that the crystal assemblages formed from the MZF and MZS mixtures above 1050°C are similar, and so the liquids may indeed represent immiscible conjugate phases.

DISCUSSION

Kinetic and thermodynamic limitations

Our results imply that reaching thermodynamic equilibrium in experiments on multicomponent ferrobasaltic compositions at temperatures below 1100°C is a very challenging task. The liquids are strongly non-ideal, and show a clear tendency towards liquid immiscibility. We believe that our results pose serious doubts regarding the

reliability of the conventional static loop technique when it is applied to dry ferrobasaltic, andesitic and dacitic compositions at temperatures below 1100°C. Here, none of the unambiguous cases of immiscibility revealed in natural glasses was reproducible in static experiments.

Centrifuge experiments differed from the static runs not only in their higher acceleration, but also in a significantly greater sample mass, and the presence of massive containers. We used inner containers made of several materials. None of them proved to be perfectly inert. However, iron appears to be the best choice. The main disadvantage of iron is that it sets fO_2 values somewhat below the iron–wüstite buffer [see Veksler *et al.* (2006) for further discussion], and such conditions are too reducing for the vast majority of terrestrial magmatic environments (with the rare exception of the magmas described above that precipitate native iron). Equilibration with an iron container may slightly change the $FeO(t)$ of the silicate charge. However, on the positive side, the dissolution reaction between silicate melt and metal iron regulates not only fO_2 , but also the activity of FeO in the melt. Thus, the FeO component, which is crucial for liquid immiscibility, becomes effectively constrained.

Graphite containers at low pressures are even more reducing than iron and proved to be unsuitable. On the other hand, our experiments in nickel containers and in the presence of the more oxidizing Ni–NiO buffer were hampered, as described above, by Ni contamination and crystallization of Ni-bearing oxides and silicates. It is not clear, however, why liquid immiscibility and phase separation in mixtures RY20 and MZ-1 appear to be slower in nickel than in iron, as evidenced by less pronounced vertical compositional gradients in the centrifuged products. Additions of less than 1 wt% of NiO to the liquid phase(s) are not likely to cause large effects on unmixing, and a greater proportion of the Fe_2O_3 component in more oxidized melts is expected, if anything, to broaden the miscibility gap and enhance the unmixing (Naslund, 1983). However, there may be other, less obvious and indirect effects, of a kinetic nature. If liquid phase separation develops via diffusion-controlled nucleation and growth (and TEM images of quenched glasses, such as that in Fig. 7b, support this view), the process of nucleation and droplet growth may, for example, significantly slow down in liquids with a higher ferric–ferrous ratio, as amphoteric, network-forming Fe^{3+} is likely to diffuse much more slowly than the network-modifying Fe^{2+} .

Metastability and liquid immiscibility

The classical, best-studied example of low-temperature silicate immiscibility in the SiO_2 – Al_2O_3 – FeO – K_2O system is characterized by a flat solvus emerging by maximally 170°C above the liquidus surfaces of tridymite and fayalite (Roedder, 1951; 1979; Schmidt *et al.*, 2006).

The stable miscibility gap along the fayalite–ferrobustamite cotectic in the Fe_2SiO_4 – $\text{CaFeSi}_2\text{O}_6$ – KAlSi_3O_8 – SiO_2 system was reported to be no more than 10°C above the liquidus (Hoover & Irvine, 1978). Numerous other aluminosilicate systems present examples of metastable immiscibility characterized by S-shaped liquidi and liquid–liquid immiscibility domes submerged just below the liquidus surfaces (e.g. Irvine, 1976). Such topological relationships imply that the Gibbs free energy of two immiscible liquids and alternative phase assemblages of a single homogeneous liquid and crystal phase(s) are very close for a broad range of petrogenetically relevant basaltic and dacitic compositions. This situation should be favourable for metastability.

Tridymite as a metastable phase

Unusual crystallization of tridymite in mixtures SF-1, RY20 and RY40 has precedents in other previously published experimental studies. For example, Irvine (1976) reported an unexpected appearance of primary liquidus tridymite inside the plagioclase crystallization field on two pseudo-ternary joins of the Mg_2SiO_4 – Fe_2SiO_4 – $\text{CaAl}_2\text{Si}_2\text{O}_8$ – KAlSi_3O_8 – SiO_2 system. Tridymite crystallization was also reported in the mesostasis of natural tholeiitic basalt at the brink of stable liquid immiscibility (Philpotts & Doyle, 1983). Notably, in the latter case tridymite crystallized at temperatures below 1030 – 1060°C from a homogeneous liquid with only 57–59 wt% SiO_2 . We propose that precipitation of tridymite may in some cases represent a metastable response of silicate liquids to strong interactions between FeO and SiO_2 components at ionic level (Hudon & Baker, 2002), which in a normal, equilibrium state would have led to liquid immiscibility. One could speculate that for complex, multicomponent liquids it may be sometimes easier, from the kinetic point of view, to decrease the instability of melt structure by precipitation of pure crystalline silica than by nucleation of a complex immiscible liquid. Our centrifuge experiments on mixtures RY20 and RY40 demonstrate that better phase separation and a greater volume of the continuous *Lsi* layer at longer run durations also correlate with decreasing proportion of tridymite crystals. In our view, occurrences of sporadic tridymite and quartz precipitation from melts that are high in Fe-oxides and low in SiO_2 deserve a thorough re-examination from the point of view of potential liquid immiscibility.

Immiscible emulsions

Formation of colloidal emulsions is another form of metastability, which was often observed in the products of our centrifuge and static runs. Sub-micron heterogeneities are widespread in silicate glasses, and they have been usually thought to form during quench or to result from metastable liquid immiscibility (Vogel, 1985; Shelby, 2005). Plumes and clouds of colloidal droplets, as well as blurred and diffuse interfaces between immiscible liquid layers, are very

common in our centrifuged run products. Although some turbid glasses in our static and centrifuge experiments may have formed by metastable unmixing during quench (e.g. samples C-107 and C-108), those centrifuged glasses that developed pronounced vertical compositional gradients probably formed from stable immiscible emulsions. The textures of quenched samples, which can be viewed as snapshots of droplet distribution after different centrifugation times, demonstrate that sub-micron droplets were slowly moving during centrifugation over macroscopic distances, and in some samples (e.g. products of the mixtures RY20 and RY40) formed dense clouds, and eventually merged into compact layers of homogeneous liquids (Figs 4c, 5 and 6). Such features cannot form in one or two minutes of quench time, and imply that those fine emulsions of silicate liquids formed by super-liquidus liquid immiscibility, and remained stable for hours. TEM images of quenched glasses allow us to see single droplets at high magnifications, measure their size, and reveal the morphology of emulsions. According to the TEM images, some turbid glasses produced in static runs may result from spinodal decomposition (Fig. 3), but droplets-in-matrix dispersed morphologies, which are typical for centrifuged glasses (Fig. 7b), imply formation and growth in a nucleation regime (Shelby, 2005).

The Bowen and Fenner trends: physicochemical background

Oxygen fugacity, melt non-ideality and magnetite stability

Textbook explanations of the Bowen and Fenner trends (e.g. Morse, 1994) are usually built upon the equation



when the reaction takes place between pure crystalline phases, it defines the fayalite–magnetite–quartz (FMQ) oxygen buffer, and establishes a functional dependence between T and $f\text{O}_2$. Although natural basaltic systems do not crystallize assemblages of pure fayalite, magnetite and silica minerals but rather solid solutions of olivine and Fe–Ti oxides, with silica remaining in a residual melt, the equation is still useful as a simple, shorthand formulation of two key principles: (1) magnetite stability in magmatic systems is a function of $f\text{O}_2$; (2) crystallization of magnetite should lead to a strong increase in the SiO_2 content of the liquid.

The link between magnetite crystallization and the Bowen (silica enrichment) trend as a result of fundamental mass-balance principles is undeniable. However, two things should be kept in mind when equation (1) is applied to complex natural basaltic systems. First, $f\text{O}_2$ is surely not the only factor controlling the magnetite stability in multicomponent magmas. In absence of liquidus tridymite or quartz, silica activity (a_{SiO_2}) is not fixed at unity, and becomes a variable, which must be raised to the third

power and incorporated in the equilibrium constant for reaction (1). A detailed analysis of the relationship between silica activity and oxygen fugacity in layered gabbroic intrusions has been carried out by Morse (1980, 1990). Because of the strong non-ideality of silicate liquids, a_{SiO_2} is a complex function of melt composition. The ferrous–ferric ratio in basaltic liquids certainly depends on a_{SiO_2} and the activities of other components, especially alkalis (e.g. Kilinc *et al.*, 1983). In view of the important role of melt chemistry, it is hardly surprising that alkalis have been shown to have a strong effect on magnetite stability, and the general trend of melt evolution in petrologically relevant aluminosilicate systems (Irvine, 1976; Shi, 1993).

The second consideration is also related to the strong non-ideality of ferrobasaltic liquids. Some experimental models show that magnetite crystallization does not necessarily prevent the formation of Fenner-type (Fe-rich) liquids. Furthermore, in those cases where non-ideality takes the extreme form of stable immiscibility, Fe-rich liquids coexist with silicic, Bowen-type liquids, and various assemblages of Fe–Mg silicates, Fe–Ti oxides, and silica minerals. Such relationships have been most vividly demonstrated in simplified synthetic systems where liquidus phases comprise pure fayalite and magnetite, and a_{SiO_2} is fixed at unity by liquidus tridymite (e.g. Naslund, 1983). Naslund (1983) showed that fayalite–tridymite and magnetite–tridymite cotectics in the system $\text{Na}_2\text{O}(\text{K}_2\text{O})\text{–FeO–Fe}_2\text{O}_3\text{–Al}_2\text{O}_3\text{–SiO}_2$ intersected a region of stable liquid immiscibility over a broad range of $f\text{O}_2$ from 10^{-12} to 0.2. As a result, a series of Bowen- and Fenner-type aluminosilicate liquids were shown to coexist regardless of the direction of the magnetite–fayalite reaction (1). This work also showed that the miscibility gap greatly expanded, and the compositions of coexisting liquids diverged at oxidizing conditions and in equilibrium with magnetite. Apparently, this means that the Fe_2O_3 component causes greater non-ideality in aluminosilicate melts than FeO. The main conclusion, however, is that the effect of magnetite crystallization upon the direction of melt evolution may be secondary and subordinate to strong chemical interactions between components and species in the liquid itself. Strong intrinsic non-ideality of ferrobasaltic liquids may be a more important factor in magma evolution than the composition of liquidus mineral assemblages or $f\text{O}_2$ conditions imposed on the system.

Concentration–activity relationships in complex, multicomponent liquids

Unlike the immiscible synthetic systems referred to above, experiments on natural basaltic compositions have seldom produced stable liquid unmixing. Above, we have already expressed our doubts regarding the reliability of conventional static techniques in the vicinity of or inside stable miscibility gaps. Here we would like to point out that non-ideality arising from anomalously strong interactions

Table 7: Liquid compositions and crystal assemblages produced by melting of natural Skaergaard gabbros (sample UB-4145) and crystallization of synthetic glasses

Sample	UB-4145 ¹	L-69 ²	Fe-76 ³	L-70 ²
SiO ₂	46.3	50.22	57.51	72.44
TiO ₂	3.4	3.68	2.62	1.69
Al ₂ O ₃	8.2	9.70	11.13	11.94
MgO	1.9	2.03	1.34	0.80
FeO	26.0	21.51	16.31	4.53
CaO	10.0	8.21	5.99	2.94
Na ₂ O	2.4	2.59	3.25	2.50
K ₂ O	0.5	1.08	1.64	2.60
P ₂ O ₅	1.3	1.16	0.0	0.30
Total	100.0	100.18	99.79	98.14
<i>T</i> (°C)	1056	1043	1050	1043
log <i>f</i> O ₂	–11.1	–11.9	–12.4	–11.9
<i>Compositions of coexisting solid solutions</i>				
Olivine, Fo-no.	34.6	30.1	27.5	33.0
Plagioclase, An-no.	43.4	45.3	43.0	48.0
<i>Pyroxene</i>				
Wo	41.7	40.1	37.9	25.5
En	32.1	27.7	27.5	32.4
Fs	26.2	32.2	34.6	42.1
Other phases	mt, ilm	mt, ilm	ilm	mt, tr

References: ¹McBirney & Naslund (1990); ²this work; ³Toplis & Carroll (1995). Liquid compositions are in wt% oxides; crystal compositions in mol% normative components.

between FeO and SiO₂ components in silicate melts [see Hudon & Baker (2002) for a theoretical discussion] should be universal and reveal itself also in liquid compositions lying outside miscibility gaps. In the case that non-ideality does not result in stable unmixing or metastable phase separation, it reveals itself in broad compositional variations of activity coefficients. Activities in the liquid phase can be assessed from crystal–liquid equilibria. A few examples illustrating this approach are presented in Table 7. Here we compare our samples L-69 and L-70, the products of the MZF and MZS starting mixtures, with two samples published earlier by McBirney & Naslund (1990) and Toplis & Carroll (1995). The data show that very different liquid compositions with SiO₂ concentrations from 46 to 72 wt% can be equilibrated at similar *T* and *f*O₂ with almost identical crystal phase assemblages comprising olivine (Fo_{27–35}), plagioclase (An_{43–48}), clinopyroxene, and Fe–Ti oxides. Notably, the liquids appear to show a strong negative correlation between the SiO₂ and FeO components, and positive

correlations between FeO and CaO, SiO₂ and Al₂O₃, and SiO₂ and alkalis. Also notable is that the spectrum of liquids from silicic to extremely Fe-rich forms in a narrow range of redox conditions, and the presence or absence of magnetite does not seem to be a crucial factor. Importantly, Fenner-type liquids at the Fe-rich side of the spectrum are characterized not only by low silica content, but also by low alkalis and high Ca/Al values. These chemical characteristics appear to arise from activity–composition relationships in complex aluminosilicate liquids where FeO, on the one hand, increases the activity coefficient of SiO₂, whereas alkalis decrease it (e.g. Shi, 1993). A very similar pattern of the activity–composition relationships is revealed by element partitioning between the *Lsi* and *Lfe* immiscible liquids [e.g. Tables 1 and 6; see also Veksler *et al.* (2006) and references therein]. In the process of the formation of immiscible liquids, alkalis partition to the Bowen-type silicic liquids, whereas FeO and alkaline earths partition to the Fenner-type liquids, which are also often characterized by very low alumina contents.

It was also demonstrated that variations of silica content in melts along the pseudo-binary join AnDi–SiO₂ (where AnDi is the eutectic composition in the anorthite–diopside system) have complex, non-linear effects on Fe solubility (Borisov, 2007). The maximum of Fe solubility (that is, a minimum activity coefficient of FeO) was observed in melts with about 55–57 wt% SiO₂, regardless of temperature and oxygen fugacity. Melts on both sides of the maximum show significantly lower Fe solubility and, correspondingly, higher FeO activity coefficients. It is clear that *Lsi* melts should lie on the silica-rich side of the maximum, where increasing silica contents result in decreasing FeO concentrations.

Implications for the Skaergaard intrusion and tholeiitic magmas in general

The most recent major dispute about the Fenner and Bowen trends in the Skaergaard intrusion took place in the late 1980s. It was started by Hunter & Sparks (1987), who argued against the strong Fe-oxide enrichment in the Skaergaard liquid on the basis of mass-balance considerations. A series of papers followed (Brooks & Nielsen, 1990; Hunter & Sparks, 1990; McBirney & Naslund, 1990; Morse, 1990), in which the controversy was examined from different angles, and on the basis of different types of evidence. In the context of the present discussion, we would like to emphasize the thermodynamic and experimental aspects of the debate, and point out that liquid evolution paths at the high- and low-SiO₂ ends of Fig. 2 are directly based on experimental studies. Ferrobasic glasses with FeO(t) well above 26 wt% were produced in a series of partial melting experiments on natural Skaergaard gabbros (McBirney & Nakamura, 1974; McBirney & Naslund, 1990). On the other hand, numerous

crystallization experiments on synthetic glasses and rock powders, which modeled the starting composition of the Skaergaard magma, produced liquids with FeO(t) concentrations of no more than 18–22 wt% (e.g. Toplis & Carroll, 1995; Thy *et al.*, 2006), near the compositional path inflections where Fe–Ti oxides start to crystallize, after which experimental liquids evolve towards silica enrichment. This apparent discrepancy demands an explanation.

Our static experiments on compositions MZF and MZS (Tables 3, 4 and 7) confirm that very different liquid compositions from ferrobasic to rhyolitic can be equilibrated under identical conditions with crystal assemblages typical for cumulates of the Middle Zone (MZ) and Upper Zone (UZ) of Skaergaard. It is also true that very similar mineral assemblages can be found in felsic volcanic rocks (Hunter & Sparks, 1987, 1990; Sparks, 1988) characterized by rhyolitic groundmass, bulk-rock SiO₂ concentrations well above 60 wt% and low FeO(t). Because the compositions MZF and MZS were produced by immiscibility in centrifuge experiments we propose that the diverging liquid evolution paths in Fig. 2 skirt a region of stable liquid immiscibility. Alternatively, immiscibility may be metastable, and the paths may fan out across a flat and broad liquidus plateau. Flat liquidus surfaces are typical for regions above metastable immiscibility domes (e.g. Irvine, 1976). In any case, strong non-ideality rooted in the anomalous incompatibility between Fe-oxide and SiO₂ components in silicate melt structures appears to be the principal reason for the divergent liquid evolution paths.

Silicate liquid immiscibility has been mentioned but previously never as a central issue in debates about the Bowen and Fenner trends (e.g. McBirney, 1975). Immiscibility certainly operated in the Upper Zone of the Skaergaard Layered Series, close to the end of magma crystallization. It has been reproduced in melting experiments on the UZ cumulates (McBirney & Nakamura, 1974; McBirney & Naslund, 1990), confirmed by the discovery of silicic and Fe-rich melt inclusions in cumulus apatite from UZ layered gabbros (Jakobsen *et al.*, 2005; see also Fig. 2) and indicated also by the common occurrence of large-scale, outcrop-sized segregations of melanogranophyre. Our results imply that the process may have started earlier, and demand that the role of silicate liquid immiscibility should be reconsidered.

We propose that the Fe-enrichment trend in Skaergaard was driven at first by fractional crystallization of troctolitic and gabbroic cumulates that formed the lower parts of the Layered Series (the LZa and LZb of the conventional Skaergaard stratigraphy, e.g. McBirney, 1989). This is a classical tholeiitic trend, primarily caused by a high cotectic proportion of plagioclase in the cumulus assemblages, along the lines explained, for example,

by Grove & Baker (1984). Such Fe-enrichment continued until about 60 wt% of crystallization (Nielsen, 2004), which corresponds to crystallization of the upper part of the Lower Zone (LZc), when the magma became saturated in Fe–Ti oxides. Any further significant Fe-enrichment by fractional crystallization would have been impossible, and the liquid would have started to evolve towards silica enrichment. However, in view of our centrifuge experiments on the composition MZ-1, liquid immiscibility may have started in the Skaergaard magma at about the same time. The initial proportion of the immiscible silica-rich liquid *Lsi* in the Fe-rich Skaergaard magma was probably small, at around 15 wt%, but the unmixing and gravitational separation of the conjugate liquids provided a mechanism for continuous Fe enrichment in the denser liquid at the bottom of the magma chamber despite the crystallization of Fe–Ti oxides. In our currently preferred scenario, fractional crystallization coupled with liquid immiscibility continued in Skaergaard until the end of crystallization in the Sandwich Horizon. We believe that the combined effects of crystallization and unmixing may explain many enigmatic features of the Skaergaard rocks and other layered gabbroic intrusions. Studies of plagioclase-hosted melt inclusions (Jakobsen *et al.*, 2007) and pyroxene–plagioclase symplectites (Stripp *et al.*, 2007) have already produced circumstantial evidence in favour of early liquid immiscibility in the Skaergaard intrusion. However, a detailed discussion of the numerous geological implications of this hypothesis is beyond the scope of this paper and will be presented elsewhere.

Immiscible emulsions of silicate melts, which were routinely formed in our experiments, are of special interest for future research. Kinetic and thermodynamic factors regulating the formation and stability of such emulsions in complex aluminosilicate melts are at the moment poorly understood. It is not clear whether such emulsions can be sufficiently stable at the timescale of natural magmatic processes to seriously affect magma dynamics. As discussed above, our results hint at significant effects of melt composition upon the kinetics of unmixing (see also Veksler *et al.*, 2007). Viscosity, interfacial energy and diffusion are likely to be the key factors, and diffusion-driven coarsening of silicate emulsions is expected to be slow.

In general, it is envisaged that the proposed immiscibility between Bowen- and Fenner-type liquids is most likely, and should be most effective in large, slowly cooling basaltic magma chambers, where the proportion of the Fe-rich, low-viscosity liquid is large; where there is enough time for emulsion coarsening as a result of coalescence and/or Ostwald ripening; and where other conditions are met for large-scale gravitational phase separation. The Skaergaard intrusion may represent an example of such a magma chamber. Perhaps the long-standing Bowen–Fenner controversy will

be finally resolved at the location where it has been debated most, the Skaergaard intrusion in East Greenland.

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