Magma chamber–scale liquid immiscibility in the Siberian Traps represented by melt pools in native iron

Vadim S. Kamenetsky[1]*, Bernard Charlier[2], Liudmila Zhitova[3,4], Victor Sharygin[3,4], Paul Davidson[1], and Sandrin Feig[5]
[1]ARC Centre of Excellence in Ore Deposits and School of Earth Sciences, University of Tasmania, Hobart, TAS 7001, Australia
[2]Institut für Mineralogie, Leibniz Universität Hannover, Callinstrasse 3, 30167 Hannover, Germany
[3]Novosibirsk State University, Novosibirsk 630090, Russia
[4]V.S. Sobolev Institute of Geology and Mineralogy SB RAS, Novosibirsk 630090, Russia
[5]Central Science Laboratory, University of Tasmania, Hobart, TAS 7001, Australia

ABSTRACT

Magma unmixing (i.e., separation of a homogeneous silicate melt into two or more liquids) is responsible for sudden changes in the evolution of common melts, element fractionation, and potential formation of orthomagmatic ore deposits. Although immiscible phases are a common phenomenon in the mesostasis of many tholeiitic basalts, evidence of unmixing in intrusive rocks is more difficult to record because of the transient nature of immiscibility during decompression, cooling, and crystallization. In this paper, we document a clear case of liquid immiscibility in an intrusive body of tholeiitic gabbro in the Siberian large igneous province, using textures and compositions of millimeter-sized silicate melt pools in native iron. The native iron crystallized from a metallic iron liquid, which originated as disseminated globules during reduction of the basaltic magma upon interaction with coal-bearing sedimentary rocks in the Siberian craton. The silicate melts entrapped and armored by the native iron are composed of two types of globules that represent the aluminosilicate (60–77 wt% SiO_2) and silica-poor, Fe-Ti-Ca-P–rich (in wt%: SiO_2, 15–46; FeO, 15–22; TiO_2, 2–7; CaO, 11–27; P_2O_5, 5–30) conjugate liquids. Different proportions and the correlated compositions of these globules in individual melt pools suggest a continuously evolving environment of magmatic immiscibility during magma cooling. These natural immiscible melts correspond extremely well to the conjugate liquids experimentally produced in common basaltic compositions at <1025 °C. Our results show that immiscibility can occur at large scale in magma chambers and can be instrumental in generating felsic magmas and Fe-Ti-Ca-P–rich melts in the continental igneous provinces.

INTRODUCTION

Magmatic immiscibility (unmixing of melt phases) begins when a melt reaches a composition where its Gibbs free energy is higher than that of paired melts whose compositions equal the precursor homogeneous melt. This process results in major petro- and geochemical differentiation, because the compositional divergence between unmixed phases can be extreme (e.g., Charlier et al., 2013; Kamenetsky and Kamenetsky, 2010; Roedder, 1992; Thompson et al., 2007; Veksler et al., 2007). Even though the physical amounts of one of the immiscible phases may be small, its separation and transport can be important, especially with respect to formation of some rock types and orthomagmatic ore deposits (e.g., Charlier et al., 2013; De, 1974; Philpotts, 1967; Roedder, 1992; Thompson et al., 2007; Veksler, 2004; Veksler et al., 2007). For example, volumetrically significant immiscibility between high-Si and Fe-Ti-Ca-P–rich conjugate melts has been suggested to explain compositional bimodality of some intrusive layered rocks (Charlier et al., 2011, 2013) and the origin of certain magnetite-apatite deposits (Philpotts, 1967).

Documenting immiscible liquids (e.g., silicate, oxide, phosphate, chloride, etc.) in common silicate magmas proved to be difficult, largely because of the transient nature of the phases involved. The existing record of the silicate-silicate liquid immiscibility is supported by observations in matrix glasses and melt inclusions (Charlier et al., 2011; De, 1974; Jakobsen et al., 2005; Kamenetsky and Kamenetsky, 2010; McBirney and Nakamura, 1974; Philpotts, 1978, 1981, 1982; Roedder and Weiblen, 1970). However, the compositional evolution of immiscible melts with cooling is unknown and the small size (<10 μm) and disequilibrium state of coexisting immiscible liquid and crystal phases render much of the evidence controversial. Here we describe a suite of compositionally diverse conjugate melt globules fortuitously entrapped and preserved by native iron, demonstrating unmixing during crystallization of Siberian flood basalt magmas over a large temperature interval.

NATIVE IRON IN SIBERIAN THOLEIITES

Native iron occurs in the Khungtukun intrusion (Ryabov, 1989; Ryabov and Lapkovsky, 2010; Ryabov et al., 1985) belonging to the Maimecha-Kotui magmatic province in the northern part of the ca. 250 Ma Siberian large igneous province. The magmatic body, exposed over an area of 900 km², intruded Carboniferous coal-bearing terrigenous sedimentary rocks (see Ryabov and Lapkovsky [2010, their figures 1–3] for location, geological map, and cross-section of the Khungtukun intrusion). The main rock types are weakly differentiated tholeiitic gabbro-dolerites (45–53 wt% SiO_2, 1.5–5 wt% $Na_2O + K_2O$) (Ryabov and Lapkovsky, 2010). Native Fe (α-Fe with <0.5 wt% Ni and inclusions of cohenite Fe_3C, troilite, wüstite, native Cu, and organic matter) occurs as disseminated individual and partly coalesced globules throughout the rocks, variably shaped "sponges", spherical and ovoid inclusions in the silicate minerals (Figs. 1A and 1B), and massive accumulations (Fig. 1C) up to tens of centimeters in size. The contacts between native Fe and silicates are often decorated by wüstite rims.

The textural evidence (drop- and bleb-like shape, Fig. 1) unambiguously indicates that native Fe crystallized from a metallic liquid at the temperature of the basaltic liquid, i.e., well below the solidus of pure iron (1538 °C). By analogy with the metallurgical process in iron smelting, we infer the role of natural chemical fluxes that reduced the magma-derived iron and depressed the liquidus temperature. In this particular case the main fluxing and reducing agent was carbon, provided by assimilated host coal-bearing sedimentary rocks (Iacono-Marziano et al., 2012; Ryabov and Lapkovsky, 2010).

IMMISCIBLE LIQUIDS: OCCURRENCE AND COMPOSITION

The metallic iron liquid coexisted with cooling and crystallizing tholeiitic melt that underwent significant unmixing, as recorded by the silicate melt pools in massive accumulations of iron (Figs. 1C–1E and 2; Ryabov, 1989; Ryabov and Lapkovsky, 2010; Ryabov et al., 1985). The melt pools are typically up to several hundred microns in diameter, and commonly almost spherical (Figs. 1D and 2), but curved and irregular forms (Fig. 1E) are also found. Most pools have a smooth contact with their host, but some have a very thin rim (1–5 μm) of very fine globules of native Fe. Cohenite exsolutions in native Fe are often draped over the outside of the pools (Figs. 1D and 1E). The pools contain two distinct fine-grained (formerly glass) silicate
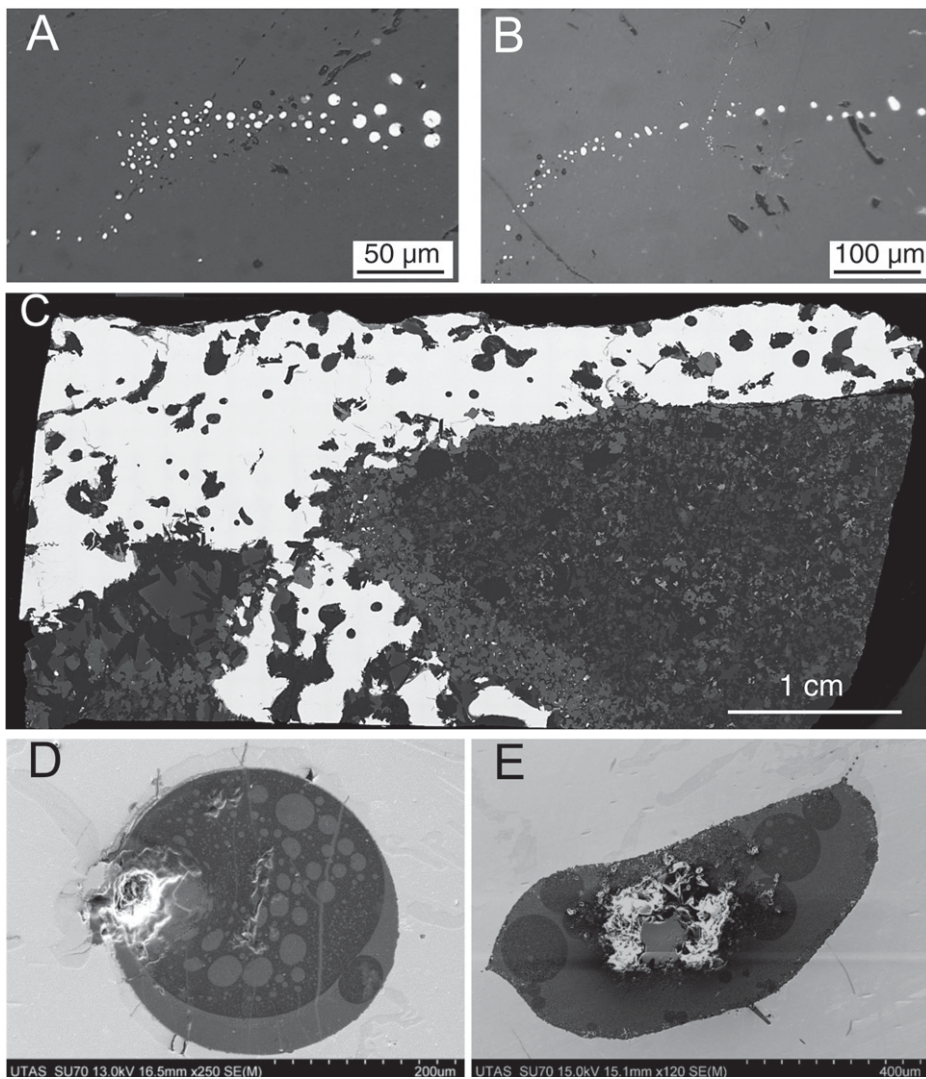
*E-mail: Dima.Kamenetsky@utas.edu.au.

Figure 1. Native iron and iron-hosted melt pools in the Khungtukun intrusion (Siberia). A,B: Native Fe globules along fractures in plagioclase and clinopyroxene phenocrysts, respectively (reflected-light optical microscope). C: Back-scattered electron image of the polished fragment of gabbro with a large mass of native Fe (white), containing solidified melt pools (black). D,E: Secondary electron images of melt pools with two immiscible phases (L_{Fe}—bright; L_{Si}—dark) in native Fe with exsolved cohenite Fe_3C (slightly darker than Fe).

Immiscible phases in the melt pools were measured using the electron microprobe (see Methods and Table DR1 in the GSA Data Repository[1]). The compositions of coexisting L_{Fe} and L_{Si} phases are distinct and essentially uniform within a given melt pool (Fig. 2), but vary systematically between pools. The L_{Fe} phase is low in SiO_2 (48.5–15.5 wt%) and has high FeO_{tot} (14.8–21.9 wt%) and highly elevated P_2O_5 (4.8–30.2 wt%), whereas the L_{Si} phase is characteristically Si rich (59.3–76.5 wt% SiO_2,) but depleted in other elements (e.g., 0.8–9.1 wt% FeO_{tot}, and 0.5–1.7 wt% P_2O_5). Al_2O_3, Na_2O, and K_2O are enriched in the L_{Si}, while TiO_2, MgO, and CaO partition in the L_{Fe} (Figs. 2 and 3; Fig. DR1 in the Data Repository).

DISCUSSION AND CONCLUSIONS

The compositions of coexisting L_{Fe} and L_{Si} in individual silicate melt pools correspond well to experimental immiscible melts from common tholeiitic systems (Charlier and Grove, 2012; Dixon and Rutherford, 1979; Philpotts and Doyle, 1983) (Fig. 3; Fig. DR1). The observed partitioning of SiO_2 between coexisting L_{Fe} and L_{Si} melts ($D_{L_{Fe}/L_{Si}}^{SiO_2}$) is used as a proxy for equilibration temperature (Fig. 3). Indeed, because the two-liquid field broadens with decreasing equilibration temperature, $D_{L_{Fe}/L_{Si}}^{SiO_2}$ decreases with cooling (Fig. 3). Data on immiscible melts in Siberian basaltic magmas extend the trend of the binodal defined by experimental melts (Fig. 3; Table DR1; Fig. DR1), which supports a larger range of equilibration temperatures compared with experimental conditions (1020–940 °C; Dixon and Rutherford, 1979; Charlier and Grove, 2012). Using a linear regression with available experimental data (Fig. DR2), we suggest a minimum equilibration temperature of 850 °C for the most evolved immiscible melt compositions.

The natural immiscible system studied is represented by at least four liquids (metallic iron, iron sulfide, silica rich, and silica poor), as demonstrated by spherical globules of each inferred liquid with curved menisci against other phases. The metallic liquid, although unusual for terrestrial rocks, has a renowned analogue in the form of native Fe and Fe carbide in the volcanic rocks of Disko Island, western Greenland (Bird et al., 1981). Both occurrences of strongly reduced Fe have been ascribed to intrusion of basalt magmas into carbon-bearing (graphite, coal) sedimentary country rocks (Bird et al., 1981; Ryabov and Lapkovsky, 2010). The immiscibility between basaltic and metallic iron liquids, recorded in the native Fe inclusions inside silicate minerals (Figs. 1A and 1B), was followed by coalescence of the metallic liquid droplets into larger masses (Fig. 1C) that

phases, one light (L_{Fe}) and the other dark (L_{Si}) under back-scattered electron illumination, with very sharp, curved contacts (Figs. 1D, 1E, and 2). Both phases coexist in any silicate pool with a wide range of phase proportions. Where one phase is volumetrically dominant and occupies the central part of the pool, the other phase is present as a discontinuous rim on the pool's wall and as spherical or elliptical globules inside the dominant phase (Figs. 1D, 1E, and 2). The melt rims and globules may contain dispersed smaller globules of the dominant phase (globule-in-globule texture or microemulsion; Figs. 1D and 1E). The globules are highly variable in size (several to 100 μm) within a given melt pool, and a globule-free space around larger globules (Figs. 1D and 1E) implies their formation by in situ coalescence of smaller globules. Apparent soft-body deformation of the globules in the vicinity of former vapor bubbles (Fig. 1D) suggests their low-viscosity state at the time of entrapment.

The globular, typically near-spherical form of the phases, including globule-in-globule forms, apparent soft-body deformation, and meniscus-like boundaries strongly suggest an origin as two immiscible liquid phases. Both phases have crystallized, typically into fine acicular crystals that radiate from the boundary with a matrix. Crystals of apatite and armalcolite are occasionally noted in these pools, sometimes parallel to and on the pool walls, but commonly on the phase boundaries.
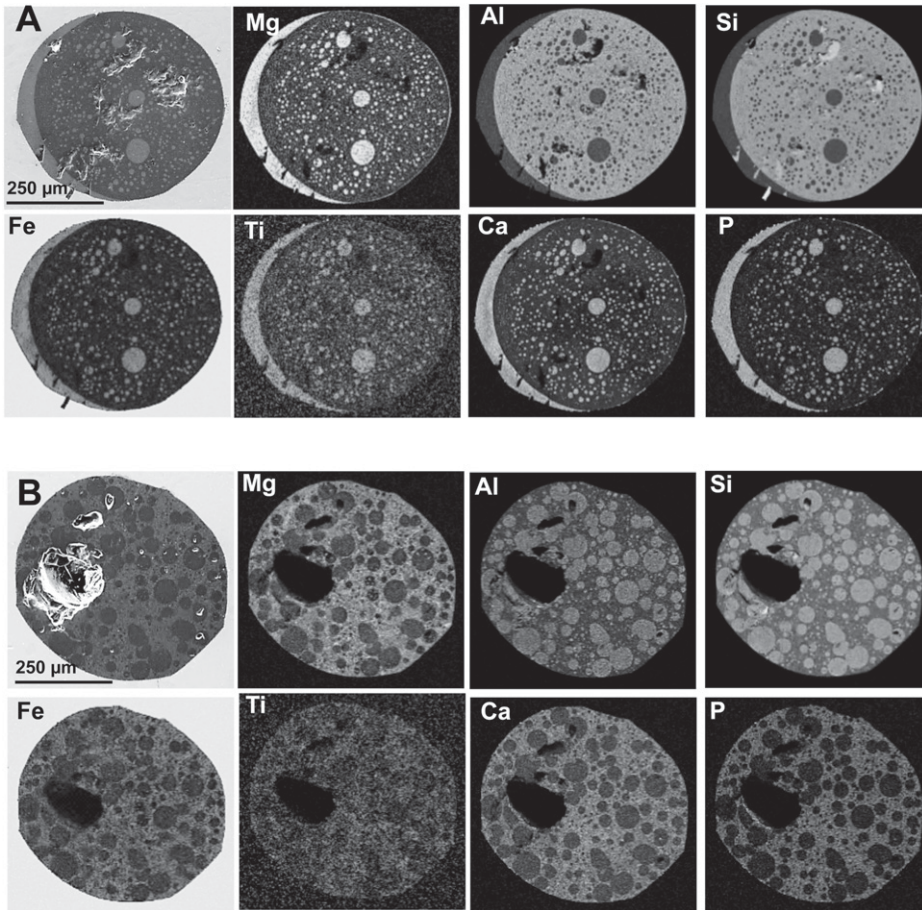
Figure 2. Back-scattered electron images of spherical melt pools in native Fe, and X-ray maps showing distribution of elements between immiscible phases (L_{Fe}—bright; L_{Si}—dark).
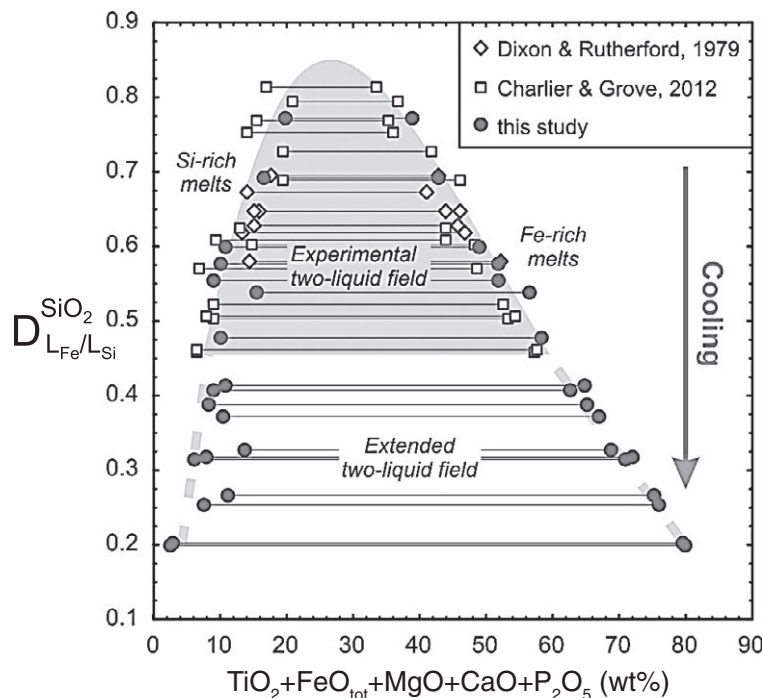

Figure 3. Compositions of conjugate immiscible liquids in individual melt pools in native Fe are compared to experimental paired melts in tholeiitic systems. $D_{L_{Fe}/L_{Si}}^{SiO_2}$, the partitioning of SiO_2 between the iron-rich and the silica-rich melts, which expresses the compositional gap between the two liquids, is plotted as a function of elements partitioned into the iron-rich melts. Horizontal tie lines indicate conjugate immiscible melt pairs.

gravitationally separated and gradually sank in the magma chamber. Concurrently the basaltic melt was splitting into Si-rich and Si-poor liquids represented by conjugate compositions (L_{Si} and L_{Fe} in this study) at any given temperatures (Figs. 2 and 3; Table DR1; Fig. DR1). With decreasing temperature, the compositions of the conjugate silicate liquids moved further apart along the solvus (Fig. 3). Apparently, the coexisting liquids varied in composition and relative quantities in different parts of the magmatic system, but nevertheless they had specific wetting properties that favored their entrapment by the sinking metallic liquid as the silicate melt pooled. While continued cooling produced more divergent compositions, the metallic iron liquid progressively sampled "snapshots" of the unmixed liquids across the entire magma chamber. Sharply different densities of the metallic liquid and the composite samples of conjugate silicate liquids produced buoyancy of the latter, thus explaining occurrence of texturally and compositionally variable silicate melt pools next to each other on a small scale of a single sample. Notably, the isolation of the silicate melt pools in the metallic iron liquid ensured their unique preservation in pristine form.

The large size of the silicate melt pools, diverse compositions of the conjugate melts, and significant range (>150 °C) in their equilibrium temperatures suggest magma chamber–scale natural liquid immiscibility in the Khungtukun intrusion. The presence of the metallic (reduced) iron and related effects of oxygen fugacity (f_{O_2}) on melt unmixing, coupled with the studies of immiscibility in lunar rocks (Roedder and Weiblen, 1970; Rutherford et al., 1974), seemingly limits applications of this particular case to global processes in crystallizing terrestrial tholeiitic magmas. On the other hand, the two-liquid field has been experimentally shown to expand under oxidizing conditions (Naslund, 1983; Philpotts and Doyle, 1983), although the latter also promote earlier crystallization of magnetite, which decreases the degree of iron enrichment that is necessary to reach the immiscibility field (Philpotts and Doyle, 1983). In the case of the Khungtukun reduced magmas, the separation of the metallic liquid depleted the residual melt in Fe, but nevertheless the Fe-enriched melts (L_{Fe}) were forming. This suggests that immiscibility in terrestrial basalts can occur over a large range of iron contents and f_{O_2}. Thus, the results of our study are applicable to understanding the last-stage evolution of mafic magmas prior to complete solidification at <1025 °C, and related origin of immiscible felsic liquids and Fe-Ti-Ca-P–enriched liquids that can be ultimately involved in the formation of orthomagmatic magnetite-ilmenite-apatite deposits.

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