Spinodal decomposition of supercritical fluid forms melt network in a silicate-H₂O system

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Abstract

Supercritical fluid in silicate-H₂O systems, with composition intermediate between silicate melt and aqueous fluid, has distinctive physicochemical properties and can be an important agent of mass transfer in Earth’s interior. Decreasing temperature and pressure drive supercritical fluid to a miscibility gap and cause unmixing into coexisting melt and fluid. With a hydrothermal diamond anvil cell, we observed that unmixing of a supercritical fluid with 37 to 51 wt. % aluminosilicate formed a silicate melt network, a phenomenon never documented before. The melt network was stable over a range of cooling rates, although further cooling led to disintegration of the network to dispersed melt droplets. The melt network was unlikely to be formed by nucleation-growth at discrete sites, but probably derived from an early stage of spinodal decomposition characterised by high phase interconnectivity. Also key to the stabilisation of melt network was elastic stress supported by polymerised silicate component. The occurrence of a silicate melt network with uneven fluid-melt boundaries may facilitate heterogeneous entrapment of melt and fluid. Spinodal decomposition and formation of melt network provide an efficient mechanism for fluid-melt separation and mineralisation in magmatic-hydrothermal systems.

Introduction

With increasing pressure and temperature in Earth’s interior, the miscibility gap between silicate melt and aqueous fluid diminishes, and single phase supercritical fluid with an intermediate composition (both silicate solute and H₂O are in the range of 30–70 wt. %) can form, most likely in deep subduction zones (Manning, 2004; Frezzotti and Ferrando, 2015; Ni et al., 2017) and in pegmatite systems (Sowerby and Keppler, 2002). Supercritical fluid can be an important agent of mass transfer because it can carry large amounts of elements (Kessel et al., 2005; Schmidt and Poli, 2014) while keeping low viscosity (Audétat and Keppler, 2004). The stability field of supercritical fluids is largely determined by the critical curves of silicate-H₂O systems, which were found by experiments to be generally above 1 GPa with negative P-T slopes (Shen and Keppler, 1997; Bureau and Keppler, 1999; Sowerby and Keppler, 2002; Mibe et al., 2007, 2008, 2011). Coexisting melt and fluid inclusions with a wide range of silicate to H₂O ratios in pegmatites (Zajacz et al., 2008) imply that decreasing temperature and pressure (to <700 °C and <1 GPa) can drive supercritical fluid to a miscibility gap, and cause its unmixing into coexisting melt and fluid. Unmixing of supercritical fluid is important for unravelling fluid differentiation and melt/fluid inclusion records in both subduction zone and pegmatite settings, but this unmixing process has not been well documented and understood (all previous experiments focused on mixing of silicate and H₂O and the locus of critical curves). Here, we report some novel results from direct observation of unmixing of supercritical fluid in a silicate-H₂O system at conditions pertinent to peralkaline aluminosilicate systems.

Methods

Experiments (see Supplementary Information for details) were carried out in a Bassett-type hydrothermal diamond anvil cell (HDAC) (Bassett et al., 1993). Sample chamber was initially filled with a piece of sodium aluminosilicate glass (Na₃Al₂Si₅O₁₄ with 1.5 wt. % H₂O), distilled water, and an air bubble, with the mass ratio of silicate to H₂O (S/H) ranging from 0.47–1.69 (32 to 63 wt. % silicate; Table S-1). This peralkaline silicate composition was chosen because its complete miscibility does not require extremely high pressure and temperature that would pose serious challenges to HDAC. This heterogeneous solid-liquid-gas system was homogenised into a supercritical fluid upon heating to ~720 °C and concomitant pressurisation to ~1 GPa. During cooling to ~650 °C with cooling rates of 0.001–2 °C/s, unmixing of supercritical fluid was observed by an Olympus BX53 optical microscope with 20x magnification objective (numerical aperture = 0.25) equipped with a camera recorder. Raman spectra of supercritical fluids, silicate melts and aqueous fluids were collected in situ with a Horiba Jobin-Yvon LabRam HR Evolution spectrometer.

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Results

A summary of experimental conditions and results is presented in Table S-1, and the videos of selected experiments are available in Supplementary Information. When a supercritical fluid was subjected to cooling, a variety of phenomena were observed depending on the S/H ratio of the Na₃AlSi₅O₁₃-H₂O system. For S/H less than 0.54, silicate melt droplets were nucleated at discrete sites (Fig. 1a,b), followed by droplet growth and coalescence (Fig. 1c,d). When S/H increased to ~0.57, silicate melt droplets formed homogeneously with a high number density (Fig. 1e–h), and the coalescence of droplets became more prominent. For greater S/H such as 0.68, a spectacular network of silicate melt, with multiple threads and nodes, developed during cooling (Fig. 1i–l). Increasing image contrast between silicate melt network and aqueous fluid (both phases are continuous)
reflected increasing difference in their composition. Melt subsequently retreated toward a number of nodes (Fig. 1m,n), leading to disruption to the network (Fig. 1o). The bicontinuous texture was converted to melt droplets dispersed in the fluid (Fig. 1p). With an increase of S/H from 0.58 to 1.05 (37 to 51 wt. % silicate), melt threads became stronger, alongside less congregation of melt at the nodes (Fig. S-2). At the highest S/H of 1.69 being investigated, instead of a melt network we observed large pockets of aqueous fluid (Fig. 1q–t).

For experimentally practical cooling rates, a silicate melt network always formed as long as the S/H was in the intermediate range of 0.58 to 1.05. When the cooling rate decreased from 2 °C/s to 0.02 °C/s, melt network became sparse, and the size of domains (mainly as pentagonal and hexagonal sections in 2D) increased correspondingly (Fig. 2a–d). Melt network was fairly stable – when cooling rate decreased to 0.001 °C/s, melt network could persist for more than 60 min (Fig. 2e,f). The reversibility of texture evolution is also worth noting: upon heating, dispersed melt droplets reconnected into a network before homogenisation into a supercritical fluid occurred.

Raman spectra of supercritical fluids, silicate melts, and aqueous fluids are presented in Figure 3. For supercritical fluid (Fig. 3a), the band at ~770 cm⁻¹, assigned to the vibration of silica monomers (Zotov and Keppler, 2000), weakened with an increase of S/H from 0.5 to 0.82. Concomitantly, the intensities of the broad bands at 400–700 cm⁻¹, 790–960 cm⁻¹ and ~1050 cm⁻¹ (Fig. 3a), related to polymerised aluminosilicate species (i.e. dimers and trimers) (Mibe et al., 2008; Dalou et al., 2014), appeared to increase. After unmixing of supercritical fluid with S/H = 0.82, the 770 cm⁻¹ band in the spectra of aqueous fluids indicated significant presence of monomers (Fig. 3b). By contrast, the spectra of silicate melts suggested the dominance of polymerised aluminosilicate species.

**Discussion**

Experimental results demonstrate the primary control of bulk composition, as indexed by the S/H ratio, over the mechanism and process of unmixing of supercritical fluid in silicate-H₂O systems (Fig. 4). A H₂O-rich supercritical fluid with S/H = ~0.5 (composition A in Fig. 4) contains predominantly Si and Al monomers (Fig. 3a). Assembling these monomers to clusters would exhaust silicate solute in the local environment, leading to nucleation of silicate melt droplets at discrete sites (Fig. 1a–d). This nucleation-growth mechanism needs to overcome interfacial energy, and is essentially similar to the exsolution of fluid
bubbles from a hydrous magma (composition C in Fig. 4), except that the roles of silicate and H$_2$O are exchanged.

By contrast, the observed melt network for S/H in the range of 0.58–1.05, was unlikely to be formed by nucleation-growth, but probably derived from an early stage of spinodal decomposition throughout the supercritical fluid. According to theories of thermodynamics and phase separation (Cahn, 1965; Debenedetti, 2000), when a homogeneous solution falls between the binode (solubus) and the spinode of a miscibility gap, it would either stay metastable or unmixed by nucleating a daughter phase with a different composition. But when the solution falls inside the spinode, concentration fluctuation would produce droplets structure, but a melt network is unique to viscoelastic spinodal decomposition involving dynamic asymmetry.

Further cooling enlarged the compositional difference between silicate melt and aqueous fluid and hence interfacial tension. After outweighing the elastic stress, interfacial tension eventually caused disintegration of the melt network, and the structure was relaxed into dispersed melt droplets. In principle, the relaxation rate should be controlled by interfacial tension and melt viscosity (Tanaka and Araki, 2006), although we still lack the essential parameters to verify this relationship quantitatively.

The development of a stable silicate melt network during unmixing of supercritical fluid can have important implications for magmatic-hydrothermal systems. Some granitic pegmatites contain fluid/melt inclusions with a spectrum of silicate to H$_2$O ratios (Zajacz et al., 2008; Thomas et al., 2012), which could be attributed to heterogeneous entrapment of coexisting silicate melt and aqueous fluid. Compared to a droplets structure with smooth spherical fluid-melt phase boundaries, a silicate melt network with uneven phase boundaries would increase the likelihood of trapping melt and fluid together in different proportions. Furthermore, unmixing by spinodal decomposition and formation of an extensive melt network, in contrast to nucleation of fluid/melt droplets at discrete sites, can promote the efficiency of separating aqueous (hydrothermal) fluid from silicate melt. This, in turn, can contribute to the extraction of metals by hydrothermal fluid, and hence to mineralisation.

Conclusions

Our experimental observations demonstrate that the mechanism and process of unmixing of supercritical fluid in silicate-H$_2$O systems are primarily controlled by its composition. Spinodal decomposition of supercritical fluid with 37 to 51 wt.% silicate developed into a stable silicate melt network due to elastic stress supported by the polymerised silicate component. The occurrence of silicate melt network could facilitate heterogeneous entrapment of coexisting silicate melt and aqueous fluid, and promote the efficiency of melt-fluid separation and mineralisation in magmatic-hydrothermal systems.

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Additional Information

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