John R. Sowerby · Hans Keppler

The effect of fluorine, boron and excess sodium on the critical curve in the albite–H$_2$O system

Abstract Experiments to define the critical curve for a series of silicate melts in equilibrium with a hydrous fluid were carried out in a hydrothermal diamond anvil cell. Silicate compositions studied were albite with several wt% excess Na$_2$O, B$_2$O$_3$ and F$_2$O$_{-1}$. Complete miscibility between melt and water was observed at lower pressure and temperature conditions compared to pure albite for all compositions. For albite + excess Na$_2$O, the critical curve had been lowered by 143 and 247 °C at 10 kbar for 5 and 10 wt% excess Na. For albite + 5 and 10 wt% F, the difference at 10 kbar was 147 and 246 °C respectively, and for albite + 5 and 10 wt% B differences of 168 and 262 °C were found. These results are likely to be additive, with the presence of more than one of the components depressing the critical curve to even lower temperatures and pressures. The results suggest that in complex pegmatitic systems, complete miscibility between melt and fluid may be important in the final stages of crystallisation. The unusual properties of fluid phases under conditions close to the critical curve in a silicate melt–water system may be essential for the enrichment of trace elements in pegmatites as well as for the formation of typical pegmatite textures.

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Introduction

Pegmatites are among the most enigmatic of the rocks exposed at the Earth's surface. Indeed, Hess (1933) described pegmatites as being "undoubtedly the most bizarre, the most contradictory, the most complex and altogether the most interesting group of rocks known. ... They may be as simple in composition as a granite, or a list of the minerals from a complex pegmatite may look like a page from the index of Dana's System of Mineralogy". Added to this complexity is the fact that many of these minerals are enriched in such elements as Li, B, F, Nb, Zr, U, Th and the REE. This has resulted in pegmatites being extensively studied in the past, and a number of different models have been proposed to explain their formation. Of these, the Jahns and Burnham model (1969) is widely used. This uses a three-stage process to explain the features seen in pegmatites:

1. Crystallisation from a hydrous silicate melt, producing anhydrous solid phases and possibly OH-bearing phases.
2. Crystallisation from the silicate melt and from a co-existing exsolved aqueous fluid, yielding giant textured pegmatite. Constituents partition between these two phases, and this is accompanied by rapid diffusion of constituents through the fluid phase, and gravitational rising of the fluid to the top of the intrusion, forming pods and lenses.
3. Crystallisation in the absence of silicate melt, yielding a number of late-stage products, including such things as "pocket minerals" and mineral aggregates formed through the exchange of material between the fluid and previously formed minerals.

Jahns and Burnham (1969) considered that the appearance of the fluid phase was the most important step, as there were fundamental changes in the style of crystallisation after this point.

London et al. (1989), however, proposed that all the features seen in pegmatites could be explained through an alternative crystallisation path. The further that an

intrusion cooled below the equilibrium liquidus, before the onset of crystallisation, the more likely it was to form a pegmatite rather than granite, with the crystallisation controlled by the bulk composition of the melt, and by the degree of undercooling. London (1992, 1996) suggested that pegmatites do not need to be vapour saturated at any point in their cooling history, and that the role of any fluid phase is likely to be secondary. The role of the fluid was investigated further by London (1999), who suggested that in a cooling pegmatitic intrusion, the advancing crystal–melt interface will be preceded by a boundary layer of highly evolved and highly fluxed melt, which will be very different in composition to the bulk composition of the pegmatite. For example, crystal-rich inclusions from the Tanco Pegmatite, Manitoba, were produced from an alkaline, sodic and highly fluxed silicate–H_2O fluid (London 1986).

The nature of such a highly fluxed fluid is an important question as Niggli (1920) proposed that, under the correct conditions, complete miscibility between silicate melt and aqueous fluid could occur. This concept received some attention in the geological literature (e.g. Paillat et al. 1992 for the system albite–H_2O; Kennedy et al. 1962 for the system SiO_2–H_2O; Bailey 1977), and recently has been examined by a number of groups. Shen and Keppler (1997) reported the first in situ observation of complete miscibility in the albite–H_2O system, using a hydrothermal diamond anvil cell, and defined a critical curve for the system. This work was extended to other compositions by Bureau and Keppler (1999). These studies have shown that complete miscibility between melt and water would be important at upper mantle pressures and temperatures, and that the resulting supercritical phase could affect mass transport of elements, as it would have properties between that of a hydrous melt and a fluid. However, Stalder et al. (2000) proposed that for the system albite–H_2O, true supercritical behaviour only occurs above 15 kbar and 700 °C, the position of the second critical end point. They concluded that for felsic systems, supercritical behaviour would not occur in the crust. In contrast, Thomas et al. (2000) examined melt inclusions in pegmatite quartz from the Ehrenfriedersdorf complex, Germany (which is fluorine, boron and phosphorus rich), and found evidence for complete miscibility between fluid and melt at a pressure of 1 kbar.

Previous work has shown that the addition of F, B_2O_3 and excess Na_2O all increase the solubility of water in silicate melts (Holtz et al. 1993; Dingwell et al. 1997), aiding the development of complete miscibility. Presented here are the results of a study on the effect of these additional components on the critical curve of albite, and the possible importance of this for the evolution of pegmatitic melts.

Experimental method

A series of albite glasses, doped with several wt% of excess Na_2O or B_2O_3, were prepared from commercially available oxides and carbonates, which had been heated to 1,200 °C for 24 h to decarbonate the starting materials, and then crushing the product. Two albite + F glasses, with fluorine replacing the stoichiometrically equivalent amount of oxygen (i.e. as component F_2O_{-1}), were prepared by producing a glass deficient in Na or Al, and then adding the fluorine as either NaF or as AlF_3 after crushing. An albite glass ("Peg. 1") was also made for a pilot study, which contained all three of the components. Following this, hydrous glasses with either 3.5 wt% water or 5 wt% water (for the Peg. 1 composition) were prepared by weighing appropriate amounts of distilled water and anhydrous powder into Pt capsules, which were sealed using an electrical arc. These were then placed into an oven at 150 °C overnight, and their weight checked the next day to ensure no water had been lost. The doped, hydrous glasses were synthesised using rapid quench TZM autoclaves at 1,100 °C and pressures of 1.5 kbar for 7 days. After quenching, the capsules were torn apart yielding glass fragments for the in situ experiments. Final glass compositions are shown in Table 1.

In situ experiments were performed in a hydrothermal diamond anvil cell (Bassett et al. 1993), as modified by Shen and Keppler (1995). Two Mo heaters were employed, produced by winding Mo wire around the tungsten carbide supports for the type I diamonds. Temperatures were measured by chromel–alumel thermocouples attached to the diamonds, and calibrated by measuring the melting points of NaCl, $NaNO_3$ and CsCl. To prevent oxidation of the diamonds and the Mo heaters, the cell was purged with a 98 vol% Ar/2 vol% H_2 mixture during high temperature experiments.

For the experiments, a Re gasket (initial hole diameter 500 μm, thickness 250 μm) was prepared by filling the cell with water of close to the desired bulk density and cycled several times through the temperature interval of interest. This process has been shown to produce an isochoric system in the cell (Bassett et al. 1993). If water is used as the pressure medium, the pressure at any temperature can then be determined from the equation of state of water, provided that the bulk density of the fluid phase in the cell is known. This can be determined from the homogenisation temperature of a bubble and the fluid, assuming that there is zero excess volume on mixing of melt and fluid. The cell was then opened, cleaned, and the sample chamber refilled with about equal

Table 1. Glass compositions as wt% oxide

	Peg. 1	Ab + 5% Na[a]	Ab + 10% Na[a]	Ab + 5% F[b]	Ab + 10% F[b]	Ab + 5% B[a]	Ab + 10% B[a]
SiO_2	47.68[b]	65.72	62.15	64.07	62.25	57.97	51.49
Al_2O_3	12.23[b]	16.47	15.39	18.33	16.25	16.56	15.27
Na_2O	20.26[b]	14.31	18.96	9.89	9.07	8.29	7.97
B_2O_3	9.53[a]	–	–	–	–	13.67	21.77
F	10.69[b]	–	–	4.52	9.04	–	–
H_2O	4.5	3.5	3.5	3.5	3.5	3.5	3.5
–O = F	4.50	–	–	1.90	3.81	–	–
Sum	100.39	100	100	98.41	96.30	99.99	100

[a]Analysis performed by ICP-AES
[b]Analysis obtained by electron microprobe, 10 kV, 15 nA, 30 μm spot size
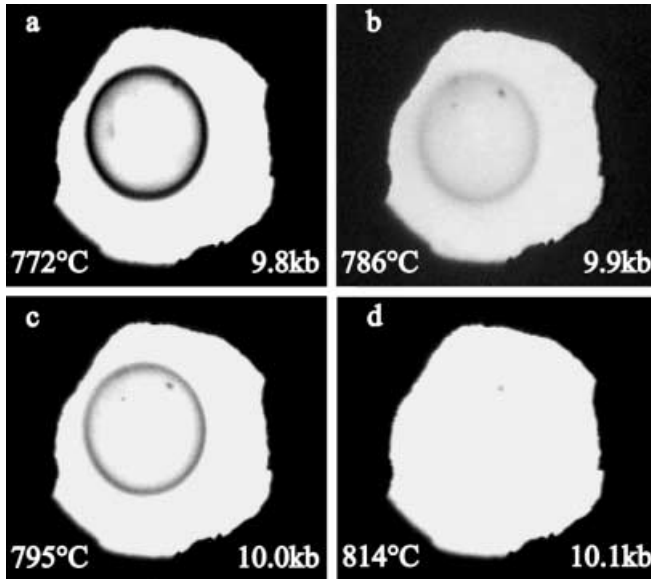
Fig. 1. The system albite–B_2O_3–H_2O (5 wt% B in anhydrous melt) as seen in a diamond cell from 772 °C and 9.8 kbar to 814 °C and 10.1 kbar. The size of the gasket hole is around 200 μm. The density of the fluid medium was 0.88 g/cm^3
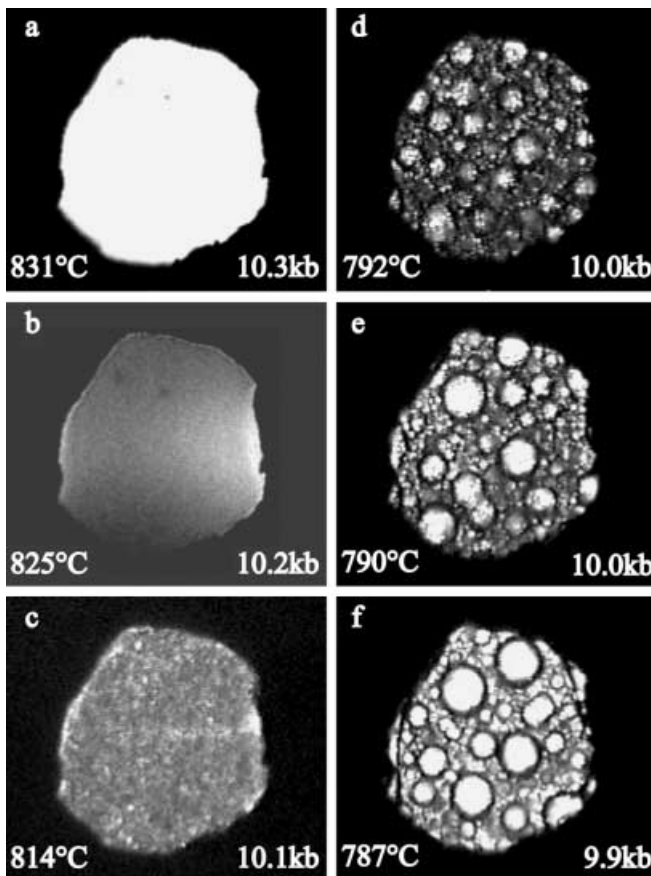

Fig. 2. The system albite–B_2O_3–H_2O (5 wt% B in anhydrous melt) as seen in the diamond anvil cell from 831 °C and 10.3 kbar to 787 °C and 9.9 kbar, showing the events that occur on passing from a supercritical fluid back into separate fluid and melt phases. Dimensions and density of the fluid are the same as in Fig. 1
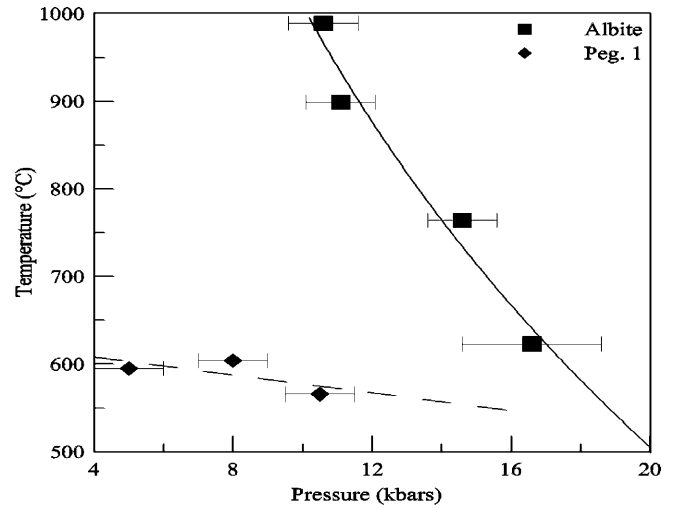

Fig. 3. Comparison of the critical curves for the albite–H_2O system (Shen and Keppler 1997) and for the "Peg. 1" glass

amounts by weight of water and irregular fragments of the glass of interest. Above the glass transition temperature, this produces one or more round drops of melt surrounded by water, which contains some dissolved melt (Fig. 1a). If the temperature and pressure in the cell approach a critical point, then the phase boundary between the melt and the fluid can be seen to fade, as the compositions of the two phases approach each other (Fig. 1b, c). At the critical point, the phase boundary disappears entirely (Fig. 1d). This behaviour is distinct from dissolution, as the volumes of the two phases remain approximately the same, as opposed to the volume changes that would accompany dissolution. On lowering the temperature to just below the critical point, the homogeneous supercritical phase first turns milky (Fig. 2a, b) in a process known as critical opalescence, due to large density fluctuations in the fluid, then turbulently separates into a fluid phase and a melt phase (Fig. 2c–f), which can be again heated to pass through the critical point. Temperatures obtained from subsequent passes through the critical point are typically within ± 10–15 °C of the first temperature. Altering the bulk density of the fluid, by introducing bubbles of different sizes into the water on loading, allows a series of points along the critical curve to be mapped out in pressure and temperature.

Results

Figure 3 shows the results obtained from the pilot study (a full list of conditions for each experiment are given in Table 2). As can be clearly seen, there are substantial differences between the critical curve for albite from Shen and Keppler (1997) and the curve obtained from the doped glass. The presence of the Na, F and B not only lowers the critical temperature at any one pressure, producing a drop of at least 600 °C at 4 kbar, a reasonable pressure for pegmatite emplacement, but also alters the shape of the curve.

The results from the experiments involving albite + excess Na are shown in Fig. 4. For both the albite + 5 and + 10 wt% excess Na, the critical curve is not only lowered in temperature (by 143 and 247 °C at 10 kbar for 5 and 10 wt% excess Na respectively), but the gradient of the critical curve has changed compared

Table 2. Experimental run conditions

Sample	$T_{homogenisation, avg}$ (°C)	Density (g/cm^3)	$T_{critical, avg}$ (°C)	Pressure (kbar)
Peg. 1	148	0.92	604	8.0
	67	0.97	566	10.5
	242	0.81	595	5.0
Albite + 5 wt% Na	192	0.87	889	10.1
	291	0.73	744	13.4
	291	0.73	952	6.8
	320	0.65	1,110	6.0
Albite + 10 wt% Na	67	0.97	685	11.8
	141	0.92	747	10.3
	126	0.93	774	11.0
	195	0.86	788	9.0
Albite + 5 wt% F	138	0.93	750	11.2
	132	0.93	775	11.3
	252	0.80	1,000	9.4
	221	0.84	870	9.0
Albite + 10 wt% F	282	0.77	980	8.0
	150	0.91	745	10.0
	116	0.95	673	10.4
	–	1.00	597	11.3
Albite + 5 wt% B	209	0.86	862	9.7
	188	0.88	833	10.2
	88	0.96	750	12.0
	179	0.89	810	10.4
Albite + 10 wt% B	338	0.65	949	5.2
	243	0.81	818	7.9
	248	0.80	830	7.7

to that for pure albite. The results for the experiments on albite + F are shown in Fig. 5. In a similar fashion to the albite + Na results, the presence of F lowers the albite–H_2O critical curve by 147 and 276 °C at 10 kbar for 5 and 10 wt% F added to the system. However, unlike the addition of excess Na, no effect on the gradient of the critical curve can be seen. These results are similar to those for albite + B (Fig. 6), with the critical curve at 10 kbar being lowered by 168 and 262 °C for 5 and 10 wt% B in the system, again with no change in the gradient of the curve being seen. For the 10 wt% B albite, no experiments could be performed above 10 kbar, as thin needle-like crystals precipitated in the sample, which were still present when the coexisting melt and fluid had reached a metastable critical point. In the study of Bureau and Keppler (1999), a critical point could be obtained for systems in which similar crystallisation was seen by melting the crystals at temperatures around 1,000 °C, and then observing the critical unmixing on cooling. In this study, this was not possible. Although crystals could be melted at a similar temperature, cooling of the cell resulted in precipitation of further crystals above the critical temperature.

Discussion

From the results outlined above it can be concluded that the presence of all three of the additional components (Na_2O, B_2O_3 and F_2O_{-1}) strongly affects the critical curve

of the albite–H_2O system. Combined with the results from the pilot study, it can be further seen that the presence of more than one component at the same time is likely to be additive, and produce a greater effect than any one single component. The compositions containing excess Na_2O are peralkaline, as opposed to peraluminous, which is typical of most pegmatitic intrusions. However, some occurrences of peralkaline pegmatites have been reported, including possibly the giant cryolite deposit of Ivigtut, Greenland (Pauly and Bailey 1999), and London (1999) considers that boundary layer melts will be alkaline, and sodic in nature. Peraluminous compositions, which were not investigated in the present study, may in some way behave in a similar way to the peralkaline systems, as the solubility of water in felsic melts increases both with excess alkalis and excess alumina (Behrens and Jantos 2001). Both components may therefore have a similar effect on the position of the critical curve. The compositions of B and F investigated in the present study are very high compared to bulk pegmatite compositions. However, melt inclusions in some pegmatites have been reported to contain up to 8 wt% F (e.g. Breiter et al. 1997) and boron contents in the range of wt% are also common (e.g. London 1992). It is also conceivable that during the final stages of pegmatite crystallisation, these components become enriched to concentrations comparable to those employed in the present study. Indeed, London (1999) found B_2O_3 contents of around 18 wt% in glasses quenched from a highly differentiated "boundary layer" melt that was generated by rapid crystallisation of quartz
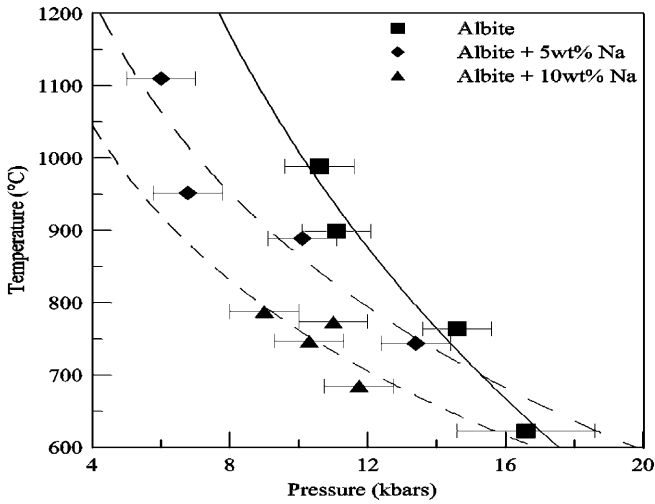
Fig. 4. The effect of excess Na_2O on the critical curve for the albite–H_2O system
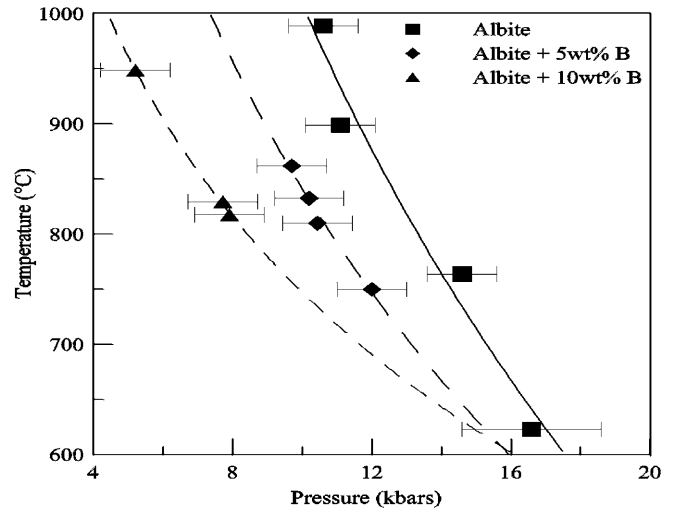

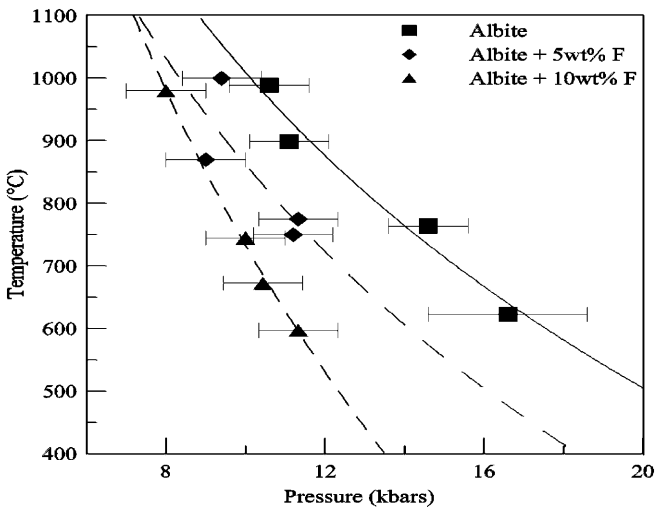**Fig. 6.** The effect of B_2O_3 on the critical curve for the albite–H_2O system

Fig. 5. The effect of fluorine (F_2O_{-1}) on the critical curve for the albite–H_2O system

and feldspar from a melt containing much lower initial boron contents.

The experimental results outlined here suggest, however, that the conditions required to reach complete miscibility between fluid and melt are considerably greater than that reported by Thomas et al. (2000). Their conclusions were based on the existence of two types of melt inclusion in the pegmatite quartz. These two types of melt inclusion, one a H_2O-poor silicate-rich melt and the other a silicate-poor H_2O-rich melt, were considered to have been trapped on the solvus boundary of the melt–water system. Complete miscibility was attained at 712 °C and 21.5 wt% H_2O, at 1 kbar, the pressure at which the intrusive complex was said to have crystal-lised. This is in sharp contrast to the solvus curve determined by Bureau and Keppler (1999) for the hap-logranite–H_2O system, where complete miscibility was

attained at around 825 °C, 16.9 kbar, and close to 60 wt% water.

Two possible explanations can be presented for this discrepancy. The first is that the complex chemistry of the Ehrenfriedersdorf melts dramatically alters the crit-ical curve of the system, producing a much greater effect than that found in the simple model system examined here. This is unlikely, as not all components will have the same effect as Na, F and B. For example, Holtz et al. (1993) showed that the addition of P_2O_5 to haplogranite has a negligible effect on the water solubility. As well as this, Bureau and Keppler (1999) found that increasing silica content increased the critical temperature of a melt. Compared to the simple albite–H_2O system, the parental melt of Thomas et al. (2000) should have a higher critical temperature to start with. The second possible explanation is that the melt inclusions have not acted as a closed system over geological time, and have lost water, as proposed by Sterner et al. (1995), who showed that inclusions in quartz can communicate with an external fluid reservoir when exposed to non-equi-librium conditions. This will have two consequences. The first is that it is possible that the "a" and "b" type inclusions of Thomas et al. (2000) could well be the products of two melts lying on opposite limbs of a melt–fluid solvus, but that the water contents of the two glasses are too low, and should be closer to those found by Bureau and Keppler (1999). The second consequence is that by losing water from the inclusions, they can no longer by considered isochoric, and the pressures ob-tained from them for the crystallisation of the pegmatite complex are too low.

The results suggest that in the complex chemical systems that exist in pegmatitic melts, complete misci-bility between fluid and melt at moderate temperatures and pressures could be important during the final stages of crystallisation. The resulting supercritical phase will have characteristics in between that of a hydrous melt

and a pure fluid, and will persist until the conditions change and the system is below the critical curve. At this point constituents will partition between the now coexisting melt and fluid, but this could well be in an entirely different manner to normal partitioning behaviour due to the nature of the unmixing process from a supercritical phase to the two coexisting phases.

Supercritical fluid–melt systems combine the low viscosity and high diffusivity of aqueous fluids with the high solvent concentrations found in silicate melts. This unusual combination of properties may be responsible for the sharp compositional and textural features and zones found in some highly evolved pegmatites. Small differences in temperature and pressure around the critical point will produce intense density fluctuations in the system, and this will have a dramatic effect on solubilities. Accordingly, small changes in temperature and pressure may induce massive dissolution or precipitation of material. There is also the possibility of interaction between the supercritical fluid and the surrounding country rock. The solvent properties of such a geological fluid are unknown, but supercritical CO_2 has been used for a number of years as an industrial solvent (Leitner 2000). Interestingly, Nowak and Keppler (1998) demonstrated that the environment of trace elements in quenched silicate melts changes abruptly at high water contents. Accordingly, it is conceivable that the environment and the thermodynamic properties of trace elements in supercritical phases may be completely different from ordinary silicate melts. Such effects may therefore be partially responsible for the unusual enrichment of some trace elements frequently found in pegmatites.

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