The solubility of water in NaAlSi$_3$O$_8$ melts: a re-examination of Ab–H$_2$O phase relationships and critical behaviour at high pressures

Olivier Paillat$^1$, Stephen C. Elphick$^2$, and William L. Brown$^1$

$^1$ Centre de Recherches Pétrographiques et Géochimiques, BP 20, F-54501 Vandœuvre-lès-Nancy Cedex, France
$^2$ Department of Geology and Geophysics, Grant Institute, University of Edinburgh, West Mains Road, Edinburgh EH9 3JW, Scotland

Received January 17, 1992 / Accepted July 27, 1992

Abstract. The solubility of water in melts in the NaAlSi$_3$O$_8$–H$_2$O system at high P and T was deduced from the appearance of quenched products and from water concentrations in the quenched glasses measured by ion probe, calibrated by hydrogen manometry. Starting materials were gels with sufficient water added to ensure saturation of the melts under the run conditions. Experiments were carried out for 10–30 h in an internally heated argon pressure vessel (eight at 1400°C and 0.2–0.73 GPa and three at 0.5 GPa and 900–1200°C) and for 1 h in a piston-cylinder apparatus (three at 1200°C, 1–1.3 GPa). No bubbles were observed in the glasses quenched at P<0.5 GPa or from T<1300°C at 0.5 GPa. Bubble concentration in glasses quenched from 1400°C was low at 0.5, moderate at 0.55 GPa and very high at 0.73 GPa and still higher in glasses quenched in the piston cylinder. Water concentration was measured in all glasses, except for the one at 0.55 GPa, for which it was only estimated, and for those at ≥0.73 GPa because bubble concentration was too high. Inferred water solubilities in the melt increase strongly with increasing P at 1400°C (from 6.0 wt% at 0.2 GPa to ~15 at 0.55 GPa) and also with increasing T at 0.5 GPa (from 9.0 wt% at 900°C to ~12.9 at 1400°C). The T variation of water solubility is fundamental for understanding the behaviour of melts on quenching. If the solubility decreases with T at constant P (retrograde solubility), bubbles cannot form by exsolution on isobaric quenching, whereas if the solubility is prograde they may do so if the cooling rate is not too fast. It is inferred from observed bubble concentrations and from our and previous solubility data that water solubility is retrograde at low P and prograde at and above ~0.45 GPa; it probably changes with T from retrograde below to prograde above ~900°C at 0.5 GPa. Moreover, the solubility is very large at higher pressures (possibly > ~30 wt% at 1.3 GPa and 1200°C) and critical behaviour is approached at ~1.3 GPa and 1200°C. The critical curve rises to slightly higher P at lower T and intersects the three-phase or melting curve at a critical end point near 670°C and 1.5 GPa, above which albite coexists only with a supercritical fluid.

Introduction

Water concentration is one of the main parameters for understanding the properties and behaviour of silicate magmas and melts. The effects of water on phase relationships, especially the large shift to lower T of the solidi and liquidi are now well established (Goranson 1931, 1938; Yoder et al. 1957; Tuttle and Bowen 1958; Yoder 1965; Kushiro and Yoder 1969; Goldsmith and Jenkins 1985; Goldsmith and Jenkins 1985; Goldsmith and Peterson 1990). Water also affects the properties of silicates melts, the drastic decrease of viscosity being one of the most well-studied effects (Persikov et al. 1990), but diffusion coefficients and rates of nucleation and growth of crystals are also strongly affected. A first step in a study of hydrous melts is to determine the solubility of water as a function of temperature (T), pressure (P) and composition (X), the solubility being defined as the equilibrium concentration of H$_2$O in the liquid (L) which coexists with vapour (V). The solubility of water in a melt of a simple single-component silicate such as albite as a function of P and T is given by the position of the surface which separates the fields of L and (L+V) in the silicate-H$_2$O phase diagram. This solubility surface (in a P, T, X diagram) is part of the (L+V) extended loop, which, because of the very large difference in T between the melting points of the silicate and H$_2$O, normally intersects the silicate–H$_2$O phase diagram. This solubility surface (in a P, T, X diagram) is part of the (L+V) extended loop, which, because of the very large difference in T between the melting points of the silicate and H$_2$O, normally intersects the silicate liquidus giving rise to a univariant three-phase surface (S+L+V), where S is the crystalline silicate. This surface projects as the familiar curved line with negative slope, the hydrothermal melting curve often improperly called the solidus, which begins at the silicate triple point on a P–T diagram and extends finally to the invariant binary eutectic (S+ice+L+V) at low T. The three-phase surface may have a maximum in P and may inter-
Fig. 1a-c. Possible high-T phase relationships between liquid and vapour at three different P for a binary silicate-water system, assuming congruent melting and boiling. Tg is the glass-transition temperature but its position is only approximately known. a At low P the solubility curve QB of water in the silicate melt intersects the vapour at the congruent boiling point B of the silicate. The solubility of water in the melt is retrograde, so that a melt L becomes undersaturated on cooling and cannot exsolve microbubbles of vapour. b At intermediate P the L–V loop no longer intersects the silicate side line, but has a maximum T at a critical point C’ where liquid and vapour are identical (L = V). Solubility is a minimum at M’ and there are two segments, one Q’M’ being retrograde, the other M’C’ prograde. On cooling a melt L first becomes oversaturated and then undersaturated when it cuts the segment M’Q’. c At high P the point of minimum solubility M” is metastable, so that Q”C’ is entirely prograde.

sect the critical curve which joins the two critical points (see discussion and Fig. 6). However, most silicate–water systems will not be binary at high T and low P because of incongruent boiling of the melt, and may not even be strictly so at lower T because of incongruent dissolution of the silicate in the vapour.

In the high-T part of a T–X diagram, the solubility curve begins at a point Q on an isobaric invariant line (S + L + V) and ends at higher T either (1) at a point B called the isobaric boiling point (Fig. 1a) on the silicate side line where the curve intersects the vapour or (2) at a point C within the diagram called the critical point (Fig. 1b, c) where L = V (see Ricci 1966, Morse 1980, or Dingwell 1986 for further details). In the first case, water solubility in the melt decreases as T increases (retrograde solubility, curve QB, Fig. 1a), whereas in the second case it either increases as T increases (prograde solubility, curve Q’C’, Fig. 1c), or is prograde only near the critical point (curve M’C’, Fig. 1b) after an initial retrograde part (curve Q’M’). If a critical point exists, the solubility curve must have a point of minimum solubility M which is either stable (Fig. 1b) or metastable (Fig. 1c); solubility close to the point M is neutral. We chose the system NaAlSi3O8 (Ab)–H2O for experimental study of water solubility in melts at high T and P, even though data at moderate T are abundant (Goranson 1938; Burnham and Jahns 1962; Kharatov et al. 1963; Orlova 1963; Kadik and Lebedev 1968; Voigt et al. 1981; Day and Fenn 1982; Hamilton and Oxtoby 1986). It is, along with SiO2–H2O, the most extensively studied silicate melt–water system, and has been used as a basis for general thermodynamic models of water solubility in silicate melts (Burnham 1975; Silver and Stolper 1985). Recent studies have focused on water speciation and on the local structure of the melts (McMillan and Holloway 1987; Kohn et al. 1989; Silver and Stolper 1989). Water concentrations in the melts may be determined by chemographic methods (Yoder et al. 1957; Burnham and Jahns 1962; Boettcher and Wylie 1969; Day and Fenn 1982) in which known amounts of water are added and the phases present identified from the quench products. Water analysis can also be done on homogeneous quenched glasses and the different methods were reviewed by Dingwell (1986) and McMillan and Holloway (1987).

Controversy exists, however, about the validity of water solubilities inferred for melts from those determined experimentally on quenched glasses (Burnham and Jahns 1962; Dingwell et al. 1984; Dingwell 1986; Hamilton and Oxtoby 1986). Most measurements were made on glasses by the weight-loss on ignition method (Goranson 1938; Tuttle and Bowen 1958; Kadik and Lebedev 1968) or by a low-T variant thereof (Hamilton and Oxtoby 1986), although others used a manometric method (Dingwell et al. 1984) or infra-red spectroscopy (Newman et al. 1986). Problems arise for glasses with bubbles. Some authors suggested that bubbly glass should not be analyzed for total water, because they considered that the bubbles were trapped in the melt before quenching, i.e. primary bubbles (Tuttle and Bowen 1958; Burnham and Jahns 1962; Dingwell et al. 1984). If the bubbles are primary, the water solubility will be overestimated; this will be serious in viscous melts which free themselves of bubbles only very slowly, but it should be less serious at higher water concentrations because of the lower melt viscosity. Burnham and Jahns (1962) showed that the inferred trapped bubble concentration varied inversely with P at low to moderate P and low T, and they took account of the water in such bubbles, their number and size being estimated by point counting across thin sections of quenched glasses. In order to avoid as far as possible the presence of bubbles...