

Liquid immiscibility and its role at the magmatic–hydrothermal transition: a summary of experimental studies

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Abstract

Several types of fluid immiscibility may affect the evolution of volatile-rich magmatic systems at the magmatic–hydrothermal transition. The topology of silicate–salt–H₂O systems implies that three-fluid immiscibility (silicate melt + hydrosaline melt + vapour) should be stable in a broad range of compositions and *P–T* conditions. The most important factor controlling the immiscibility appears to be the Coulombic properties (electric charges *Z* and ionic radii *r*) of the main network-modifying cations and the capacity for immiscibility appears to decrease in the following sequence: Mg>Ca>Sr>Ba>Li>Na>K. Liquid immiscibility is enhanced in peralkaline compositions and in the presence of nonsilicate anions such as F[−], Cl[−], CO₃^{2−} and BO₃^{3−}. In volatile-rich magmatic systems, the H₂O is likely to react with the chloride, fluoride, borate and carbonate species and the chemical effects of high-temperature hydrolysis may be greatly enhanced by phase separation in systems with multiple immiscible fluid phases. Natural granitic magmas can thus exsolve a range of chemically and physically diverse hydrosaline liquids and the role of these fluid phases is likely to be especially significant in pegmatites and Li–F rare-metal granites.

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1. Introduction

The magmatic–hydrothermal transition can be defined as a stage in evolution of magmatic systems when, in the process of cooling, aluminosilicate melt—the major liquid of the magmatic stage—approaches a terminal multiple-saturated eutectic and the leading role in element transport and further (subsolidus) evolution of the system is taken over by other fluid phases: vapours and hydrothermal liquids. In the melt-phase components compatible

with the main liquidus minerals become extremely depleted, while incompatible ones (including volatiles) are enriched. Almost a century of extensive experimental studies provided robust constraints on crystallisation of silicate melts, especially at pressures below 1 GPa. In dry and volatile poor silicate systems, we now have a good idea about the main crystallisation trends and the parameters of the terminal eutectic points. There is, however, a range of alkali-rich compositions, where melts are characterised by very high solubility of H₂O and other volatiles and show complex behaviour. Few experimental studies have dealt with such compositions and the results, although sketchy and incomplete, indicate that with high contents of volatiles, some silicate melts can persist down

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to very low temperatures and that melts and hydrothermal fluid phases coexist and interact over a broad range of P – T conditions. The compositions are such that precise definitions are difficult and the distinction between melts, brines and silicate colloids become unclear. To avoid terminological confusion in the following text, I am using the word “fluid” as a general term that includes liquids and vapours at subcritical P – T conditions and also a single mobile phase at supercritical conditions, where the liquid–vapour phase transitions disappear.

The main topic of this review is immiscibility phenomena between various types of fluids that can be present in natural magmatic–hydrothermal systems. For dry silicate melts, again, there is a large body of experimental data on this issue and good understanding of the mechanisms and principles of phase separation. To a large extent, the progress is due to the importance of the immiscibility for technology and the glass industry. Immiscibility between aqueous fluids and silicate melts at pressures and temperatures above the critical point of water so far has little, if any, technological importance and thus has not attracted the attention of material scientists and chemists. These types of phase equilibria are, however, of prime interest for igneous petrologists dealing with the magmatic–hydrothermal transition, and in this paper, I compile and examine experimental information on the properties of extremely volatile-rich silicate liquids, their relationships to other hydrous fluids and implications for natural processes.

Since the early days of igneous petrology, the importance of magma degassing and aqueous magmatic fluids has been recognised through numerous geologic observations. The chemical role of fluid separation has been further revealed by studies of melt and fluid inclusions in magmatic minerals. It is in the inclusions that very concentrated aqueous solutions and extreme enrichment of melts and fluids in some components (F, Cl, Sn and B_2O_3) have been observed (e.g., Roedder, 1992; Webster et al., 1997; Thomas et al., 2000; Kamenetsky et al., 2003, 2004). Classical models of late stage magma evolution, e.g., pegmatite formation (Jahns and Burnham, 1969), emphasized the role of exsolution of aqueous fluid from silicate melt, and the evidence from inclusions (Roedder, 1992) implied that other types of fluid

immiscibility may also be important at the magmatic–hydrothermal transition.

However, the petrologic importance of the aqueous fluid phase and fluid immiscibility has been challenged recently by experimental studies showing the possibility of supercritical behaviour in volatile-rich silicate systems (e.g., Bureau and Keppler, 1999; Sowerby and Keppler, 2002) and some petrogenetic models downplay the role of magmatic hydrothermal fluids (e.g., London, 1992). In view of the diversity of models and interpretations, there is a need to examine the possible natural scenarios in a broader context of phase equilibria established for a wide range of synthetic systems. Much of the information compiled here comes from sources with relatively poor accessibility, and citations from Russian literature are especially abundant. This reflects the intense research in volatile-related aspects of magma evolution by Russian petrologists. Fragmental or incomplete information has been treated with due caution and on several occasions not only were the authors contacted for clarification of their results, but original samples were re-examined.

The key ideas examined in this paper can be briefly formulated as follows:

- (1) At pressures below 1 GPa and temperatures less than 900 °C, aluminosilicate melts may exsolve not one but two conjugate aqueous fluids of contrasting density and salinity. To distinguish between them, the dilute one with lower density is typically called vapour; the other, a concentrated liquid phase of higher density, is called hydrosaline melt.
- (2) At a microscopic scale and in terms of melt structure, the main factors controlling immiscibility phenomena in silicate melts appear to be the Coulombic properties of network-modifying cations (in natural compositions represented predominantly by alkalis and alkaline earths) and their relationships to Al. Immiscibility is favoured in peralkaline compositions, and the role of nonsilicate anions (e.g., F^- , Cl^- , CO_3^{2-} and BO_3^{3-}) is important, but not decisive.
- (3) Phase equilibria in salt–water systems and studies of physical and chemical properties of hydrothermal aqueous solutions imply a fundamental difference between dilute fluids and concentrated

liquids (hydrosaline melts). The difference is so great that the phases are often not miscible with each other.

- (4) Water in silicate and hydrosaline melts, as well as in dilute high-temperature vapour, cannot be regarded as a single H₂O component nor does it act as an inert solvent. Reactions of high-temperature hydrolysis appear to be very effective, especially when vapour and hydrosaline melt coexist.

2. Special experimental techniques in volatile-rich systems

High reaction rates and the unstable nature of the key aqueous phases in volatile-rich systems require unconventional experimental methods. Before discussing the results, it seems worthwhile to briefly introduce those special methods by which the results have been obtained and to catalogue the main experimental approaches used for characterisation of unstable phases and unquenchable equilibria.

2.1. Monitoring P – T – x relationships

Much information on phase composition and phase transitions in synthetic systems can be obtained by quantitative monitoring of P – V , P – T , P – x and other relationships between extensive and intensive parameters. Thus, it is desirable to use experimental devices that not only control pressure and temperature but also enable measurements of at least one extensive parameter such as volume. Two such autoclaves have been developed and extensively used by Ravich (1974) and his group for solubility studies in salt–water systems. Both designs are essentially cold-seal pressure vessels partially filled with liquid mercury and placed inside an electric tube furnace. Mercury serves as a hydraulic lock, which enhances pressure measurements, regulates volume and, in some experiments, isolates system components at the start of the run. One type of these autoclaves, used at pressures up to 30–35 MPa, enables controlled releases of vapour and thus simultaneous changes of volume and bulk composition. The second type, designed for pressures up to 200–250 MPa, enables controlled volume changes by release of carefully measured amounts of mercury. In both techniques, components of the systems should

not react with Hg and it is assumed that the influence of Hg vapour on the system is negligible. In the salt–water systems studied by Ravich et al., both requirements were fulfilled.

2.2. Direct sampling of fluids during the run

Pressure vessels that allow sampling of liquids and vapours during experiments are very diverse and have a long history of successful employment (e.g., see review by Valyashko, 1990 and references therein). There are numerous types of the sampling devices. The simplest designs basically represent two pressure vessels separated by a valve and a metal filter (Ravich, 1974), while some of the more complicated ones employ in situ centrifuge separation of solid and liquid phases. As discussed in the Section 6.1, Kravchuk and Valyashko (1979) used the sampling technique developed by Ravich (1974) for chemical analyses of fluid phases in the Na₂O–SiO₂–H₂O system. More recently, Shmulovich et al. (2002) used a modernized sampling equipment in a study of REE partitioning between NaCl melt and aqueous vapour. The techniques work best for unsaturated, dilute fluids because crystallisation of solid phases in tubes and capillaries is a major obstacle for fluid sampling.

2.3. Visual control on phase transitions and in situ measurements

Thick-wall sealed glass tubes were the earliest and simplest vessels that allowed visual control on the system, but they are not strong enough to withstand pressures higher than 15–25 MPa nor chemically resistant. A breakthrough in the technique came about with the development of the hydrothermal diamond cell (HDAC, Bassett et al., 1993). In the classical design of the cell solid and liquid substances under investigation are put inside a metal gasket and squeezed between two diamond anvils placed inside a small vertical electric tube furnace. Run conditions are limited by mechanical and thermal stability of the anvils. Normally, pressure does not exceed 2–2.5 GPa and the temperature limit is 1200 °C. The HDAC technique has been widely used in studies of critical phenomena in hydrated silicate systems (Shen and Keppler, 1997; Bureau and Keppler, 1999; Sowerby and Keppler, 2002). The modern cells allow not only

the visual observation of phase transitions under a microscope but enable *in situ* infrared and Raman spectroscopy for insights into speciation of key components in melts and fluids (e.g., Zotov and Keppler, 2000; Veksler et al., 2002b). Experimental studies with HDAC is an active and expanding field of research, and the latest developments include, for example, *in situ* analyses of trace element concentrations (Schmidt and Rickers, 2002) and speciation (Anderson et al., 2002) in fluids by synchrotron radiation XRF and the X-ray absorption fine structure.

2.4. Methods of prequench and postquench phase separation

These methods include double-capsule modifications of the quench method (Ryabchikov et al., 1989), synthetic fluid inclusions (Bodnar and Sterner, 1985) and high-temperature centrifuge phase separation in miniature internally heated pressure vessels (Dorfman et al., 1997). The methods are designed to prevent mixing of phases in quenched run products and to minimise their mutual contamination and reequilibration. Double-capsule and centrifuge techniques were extensively used in studies of element partitioning between immiscible melts and fluids (e.g., Veksler and Keppler, 2000; Veksler et al., 1998b, 2002a). Synthet-

ic fluid inclusions in quartz proved to be effective for preservation of silica-saturated hydrosaline and hydrosilicate quench products in the $\text{SiO}_2\text{--K}_2\text{CO}_3\text{--H}_2\text{O}$ and $\text{SiO}_2\text{--NaF--H}_2\text{O}$ systems (Wilkinson et al., 1996; Kotelnikova and Kotelnikov, 2002).

2.5. Problems of identification of immiscible phases in quench run products

Finally, a word of caution about conventional quench methods. Crystallisation and liquid immiscibility do not only compete but often mimic each other. Experiments in several seemingly unrelated immiscible systems reported crystallisation of solids with unusual spherical and oval shapes that looked very much like immiscible liquid globules. Brooker and Hamilton (1990) were probably the first to misinterpret round calcite crystals in a silicate–carbonate system as droplets of a second immiscible carbonate liquid (see also Lee et al., 1994). Formation of round crystals and other deceptive textures have caused much controversy in studies of liquid immiscibility in various fluoride–silicate systems. It appears that Gramenitskiy and Shekina (1994, 2001) mistook oval and rounded cryolite grains in their experiments for droplets of immiscible fluoride melt and only the Li-bearing compositions studied by these authors (Gra-

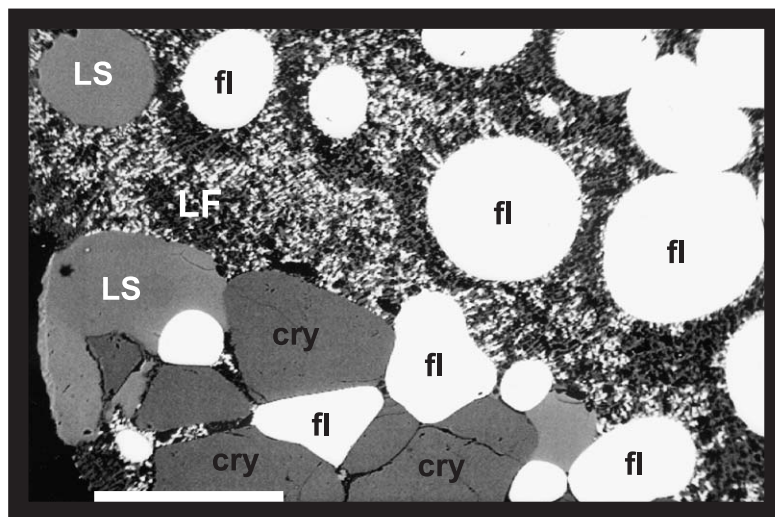


Fig. 1. Back-scatter electron image of run products in a fluoride–silicate system at 800 °C and 100 MPa showing spherical and oval fluorite and cryolite crystals (see text for details). LS—aluminosilicate granitic melt, LF—fluoride melt, fl—fluorite, cry—cryolite. The scale bar is 0.2 mm long.

menitskiy et al., 1993) produced true silicate–fluoride liquid immiscibility (Gramenitskiy, 2003, personal communication). My own recent experiments with silicate–fluoride compositions gave spectacular examples of such deceptive textures (Fig. 1). The starting composition was haplogranitic glass mixed with 18% NaF, 12% CaF₂, 12% AlF₃, 4.5% LiF and 10% H₂O (by weight) and the run was carried out in a rapid-quench cold-seal pressure vessel at 800 °C and 100 MPa. In this particular case, liquid immiscibility took place, but in addition to the silicate and fluoride liquids and an aqueous fluid phase, large and perfectly round crystals of fluorite precipitated and they resembled the real liquid droplets. Oval cryolite crystals also formed in this run.

Spherical single crystals and quenched globules of salt melts usually can easily be distinguished optically in transmitted light because the crystals are transparent, while the globules normally quench to fine-grained opaque aggregates. The fine-grained textures of quenched salt melts are also visible under scanning electron microscope, or in electron microprobe images (Fig. 1). Compositionally, the crystals tend to be stoichiometric, while the globules vary broadly from run to run. One could speculate that the formation of oval and spherical single crystals in the presence of immiscible melts may be caused by preferential wetting of solids by melts of similar composition and decrease of the excess surface energy, which otherwise would enhance euhedral crystal shapes. However, the exact mechanism of such crystal growth is not yet known.

3. Chemical bonds, liquid immiscibility and crystallisation

Liquid phases have no long-range ordering on the atomic and molecular scale and are characterised by much greater structural tolerance than crystalline solid solutions. Phase separation in the liquid state often results from fundamental differences in the nature of chemical bonds and immiscible fluid phases can be classified by their dominant types of bonding: ionic, covalent, metallic or intermolecular.

Silicate melts are characterised by an interplay of covalent and ionic forces and both types of chemical bonds are important in the melt structure. Consequently,

components of silicate melts are subdivided into network formers (covalent) and network modifiers (ionic). Network-forming components of natural melts, as well as most common technological compositions are predominantly SiO₂ and Al₂O₃. Four coordinated Si⁴⁺ and Al³⁺ cations tend to form a three-dimensional network of corner-shared SiO₄ and AlO₄ tetrahedra held together by strong covalent bonds. Network modifiers, mostly mono- and divalent cations (alkalis, alkaline earths, Fe²⁺), bond to the network by ionic forces. As discussed below, it is the weaker ionic forces that are crucial for the unmixing of silicate melts.

With the exception of borates and phosphates, other geologically relevant salts (chlorides, fluorides, sulphates, carbonates, etc.) do not form strong, covalently bonded network structures and their melts are purely ionic. On the other hand, liquids and vapours of H₂O, CO₂, CH₄ and other C–O–H species are typical molecular fluids. Because of the abundance and exceptional role of H₂O in natural hydrothermal fluids, hydrogen bonds, a peculiar type of intermolecular forces typical for water and some other polar molecules, are of special interest. The strong intermolecular bonds result in anomalous physical and chemical properties of pure water and aqueous solutions. The strength of hydrogen bonds decrease with temperature and above 200–250 °C at pressures of vapour saturation, ice-like molecular structures in liquid water are effectively destroyed (Valyashko, 1990 and references therein). Nevertheless, hydrogen bonds do not disappear completely and are believed to affect some properties of water and aqueous fluids to temperatures up to at least 400 °C. The relationships between ionic hydrosaline melts and molecular fluids (dilute aqueous solutions and vapours) and their implications for liquid immiscibility are discussed below.

Finally, most natural sulphides are characterised by metallic bonds and sulphide melts have very limited miscibility with all the other types of fluid phases. Sulphide–silicate liquid immiscibility is common in natural magmas and responsible for the formation of certain types of Ni–Cu–Co ores (e.g., Peach and Mathez, 1993). A similar type of immiscibility (in terms of the bond types involved) is operated on a cosmic scale and apparently led to formation of Fe–Ni cores in the interiors of terrestrial planets. However,

this type of liquid immiscibility has little bearing on the evolution of residual magmas at the magmatic–hydrothermal transition and thus is not discussed in this paper.

In the next sections, I shall review and examine the main chemical and structural factors that are believed to be responsible for immiscibility phenomena in various silicate–salt–H₂O systems starting from relatively simple binaries and moving to complex multicomponent analogues of natural magmas. To achieve the necessary broad coverage, examples include some components at concentrations not common in nature. With few exceptions, the pressures considered are not higher than 1–1.5 GPa and thus petrologic implications are restricted to the Earth's crust.

4. Dry silicate systems

Unmixing in dry silicate melts and its possible implications to igneous petrology have been thoroughly reviewed by Greig (1927), Bowen (1928) and Roedder (1979). There is also a vast experimental and theoretical literature on liquid immiscibility in technological silicate melts and glasses. It appears that immiscibility, rather than being exceptional, is likely to be a common feature of silicate melts and glasses. Experimental studies reported numerous cases of stable and metastable (subliquidus) immiscibility in silicate systems. In all the cases, network-forming and network-modifying components are strongly fractionated between the conjugate liquids, and immiscibility theories usually seek explanations in structural models of silicate melts (e.g., Roedder, 1979; Hess, 1995; Hudon and Baker, 2002a). Although little can be added to the excellent previous reviews on this subject, it seems necessary to outline briefly the main statements, starting with the well-established features of simple systems before considering more complex compositions and more controversial issues.

4.1. Oxide binaries and the role of network-modifying cations

Metal oxide–silica binaries are key for understanding the driving forces of liquid immiscibility in silicate melts because it is in the simple binaries that the leading role of network-modifying cations is

revealed most fully and vividly. Elements of the first two columns of the periodic table—alkalis and alkaline earth elements—are the classical network modifiers, and large miscibility gaps exist in the SiO₂-rich parts of the alkaline earth oxides–silica systems MO–SiO₂, where M = Mg, Ca, and Sr (Fig. 2). All the gaps are located within stability field of cristobalite; they have similar asymmetric shapes and one of the immiscible melts is extremely silica-rich (97–99 wt.% SiO₂). The asymmetry can be removed by a proper choice of the components, and this may hint at the stoichiometry of actual species that dominate the structures of the silica-rich and silica-poor melts on the opposite sides of the gaps (Hess, 1995). Even more remarkable is the systematic decrease in consolute (critical) temperatures of the immiscibility domes with increasing atomic numbers of the elements, so that in the BaO–SiO₂ system, liquid immiscibility becomes metastable and hidden below the S-shaped liquidus of silica polymorphs. The same

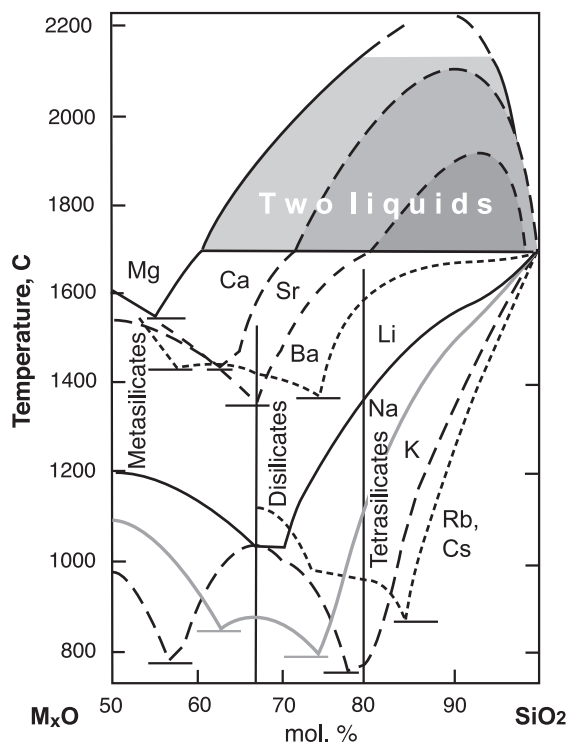


Fig. 2. Silica-rich portions of alkali and alkaline earth oxides binaries with two liquid fields (after Levin et al., 1964). See text for discussion.

trend continues in the binaries of alkali oxides (M_2O-SiO_2 , where $M=Li, Na, K, Rb$ and Cs), in which immiscibility is either metastable or not revealed at all. In general, within the first two columns of the periodic table the tendency for unmixing decreases in the following sequence: $Mg > Ca > Sr > Ba > Li > Na > K > Rb, Cs$ (Hess, 1995).

Miscibility gaps exist not only between silica and typical network modifiers but in many other oxide binaries (Levin et al., 1964; Hudon and Baker, 2002a,b). For quantitative comparisons the miscibility gaps can be measured either by the heights of two liquid domes along the temperature axis or the widths of the gaps along the compositional axis measured at some specific temperature (Fig. 2). Hudon and Baker (2002a) provided a detailed discussion of the merits and drawbacks of both methods. In short, the method of consolute temperatures is universally applicable to stable and metastable domes, but precise measurements of the consolute temperatures are hampered by quench problems and other experimental difficulties, so that large uncertainties exist in the experimental data. The widths of the gaps are well constrained at monotectic temperatures, at which immiscible melts become saturated with cristobalite (Fig. 2), but such method of quantification is not applicable to metastable immiscibility (e.g., $BaO-SiO_2$, Fig. 2) and for systems in which stable gaps are located outside the cristobalite crystallisation field (e.g., $V_2O_3-SiO_2$, Hudon and Baker, 2002a).

It was noticed long ago (see reviews by Hess, 1995; Hudon and Baker, 2002a and references therein) that the consolute temperatures of the two-melt fields correlate with Coulombic properties of the metal cations, such as ionic potential—the ratio of Z/r , where Z is the nominal charge and r —atomic radius of the cation. Many explanations were offered and a great number of models designed to account for the correlation. Summarising them, Hess (1995) concluded that the correlation can be viewed as an indication that the main forces at the atomic scale responsible for the phase separation were Coulombic in character and repulsive. In his view, bridging oxygen ions of highly polymerised silica networks provide poor shielding of network-modifying cations, and this results in substantial Coulombic repulsions between the cations, and may eventually lead to phase separation. The higher the ionic potential of modifier cations, the

greater are the Coulombic repulsions between them, and the larger are the two-liquid fields in oxide–silica binaries.

Recently, Hudon and Baker (2002a,b) carried out a detailed revision of liquid immiscibility phenomena in the binaries. They accepted the general mechanism of phase separation proposed by Hess (1995) but revealed more complex relationships between ionic potentials and $T-x$ dimensions of the miscibility gaps and proposed that other factors, mostly related to configurations of electron shells of ions, affected liquid immiscibility. A detailed plot of the consolute temperatures vs. Z/r constructed by the authors (Fig. 3a) demonstrates that the relationships are not linear but parabolic, and homovalent cations (mono-, di-, trivalent, etc.) can be fitted by separate parabolae. In relation to liquid immiscibility Hudon and Baker (2002a,b) subdivided cations into four groups. The first group which includes large cations ($r > 87.2$ pm in octahedral coordination), which have coordination numbers 5 and higher, cannot enter tetrahedral sites and can act in melt structures only as network modifiers. The typical representatives of the group are alkalis from Na to Cs, alkaline earths from Ca to Ba, light rare-earth elements, U and Th. The second group consists of amphoteric cations (e.g., $Li^+, Mg^{2+}, Ga^{3+}, Al^{3+}, Ti^{4+}$ and Nb^{5+}), which have ionic radii larger than that of Si^{4+} (26 pm, Shannon, 1976) but smaller than about 87.2 (in sixfold coordination) or 78.6 pm (in fourfold coordination). Bonds formed by those cations with O^{2-} are characterised by substantial degree of covalency. This results in a better shielding of the cations and lower consolute temperatures than expected from the Z/r values. The third group includes cations with variable crystal field stabilisation energies (VCFSE). They are formed by elements that occupy the first row of transition elements in the periodic table (Fe, Co, Ni, Cu, V and Cr) and characterised by five d -electron orbitals. The orbitals are known to poorly shield the atomic nucleus (Hudon and Baker, 2002a,b and references therein), and the miscibility gaps associated with the cations in the binaries are larger than expected from simple Z/r relationships. Finally, highly polarizable cations with a lone pair of electrons ($Pb^{2+}, Sn^{2+}, Bi^{3+}, Tl^{2+}$ and Te^{4+}) show better compatibility with polymerised silica, borate and germanate networks and reduced miscibility gaps (Hudon and Baker, 2002b).

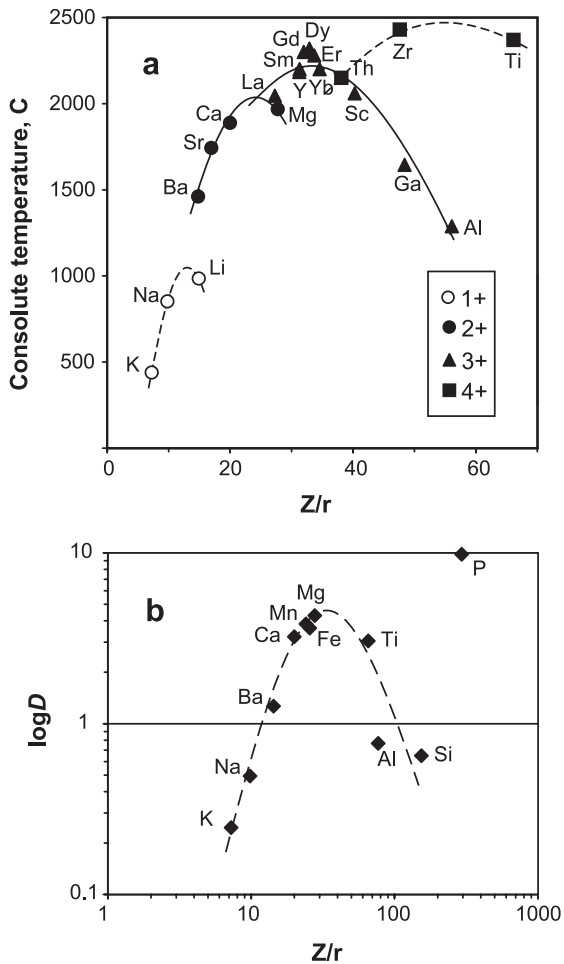


Fig. 3. Effects of network-modifying cations on liquid immiscibility in dry silicate systems. (a) Consolute (critical) temperatures of the miscibility fields in the metal oxide–silica binaries as a function of the Coulombic properties of the metal cations (after Hudon and Baker, 2002a,b). See text for discussion. (b) Partition coefficients (D) of elements between dry immiscible ferrobasic and granitic melts at the atmospheric pressure. Experimental data by Longhi (1990) and Ryerson and Hess (1978). Dashed curve is a reference curve emphasising the general trend of the data points. Z —nominal electric charge, r —ionic radii in nanometres from Shannon (1976).

4.2. The role of Al

As discussed in the previous section, Al^{3+} falls into the category of amphoteric cations and plays a dual role in the structure of silicate melts. At low pressures, Al mostly forms a four coordinated species and joins Si in corner-shared aluminosilicate

tetrahedral networks, but it may also act as a network modifier in sixfold octahedral coordination. All the low-pressure liquidus phases of the Al_2O_3 – SiO_2 binary—cristobalite, mullite and corundum—are very refractory. There is a metastable immiscibility dome beneath the mullite liquidus (Maddowell and Beall, 1969; see also discussions by Hudon and Baker, 2002a,b). Even small additions (a few mole percent) of typical network modifiers (e.g., alkali oxides or alkaline earth elements) strongly suppress or totally eliminate the metastable immiscibility in alumina–silica glasses (Maddowell and Beall, 1969). In a similar way, the consolute temperatures of the two-liquid fields in the alkaline (and alkaline earth)–silica binaries dramatically decrease with the addition of small amounts of Al_2O_3 , and at about 5 mol% Al_2O_3 , the stable miscibility gaps close up in all the MO – Al_2O_3 – SiO_2 ternaries (Levin et al., 1964). In terms of melt structure, these effects can be explained by formation of very strong feldspathoid aluminosilicate complexes, in which tetrahedrally coordinated Al^{3+} and mono- or divalent network modifiers charge-balance each other (Hess, 1995). Thus, the molar ratio of typical network modifiers (Na, K, Ca, etc.) to Al emerges as a very important chemical parameter controlling immiscibility in silicate systems. It appears that liquid immiscibility should be enhanced in peralkaline compositions, where the sum of molar fractions of alkalis and alkaline earth elements exceeds that of Al because the excess of network modifiers, as demonstrated by the oxide binaries, will tend to form a separate liquid phase. On the other hand, peraluminous compositions are likely to precipitate refractory crystalline phases, such as corundum or mullite from a single homogenous melt, and not to show stable immiscibility.

4.3. Immiscibility in multicomponent aluminosilicate compositions

In natural dry aluminosilicate magmas, there is probably only one region where silicate liquid immiscibility surfaces and affects the evolution of natural rocks. This is the range of granitic–ferrobasic compositions enriched in FeO, K_2O and SiO_2 . This type of silicate immiscibility was discovered in lunar basalts and then reported, with various degrees of

certainty, in a number of terrestrial igneous rocks (Roedder, 1979). The system leucite–fayalite–silica, in which a region of stable low-temperature immiscibility emerges along the tridymite–fayalite cotectic, provides a close synthetic model. It demonstrates once again the key role of network modifiers (ferrous iron in this case) and the competitive relationships between immiscibility and crystallisation. High FeO contents are crucial because, firstly, Fe^{2+} belongs to the group of cations with variable crystal field stabilisation energies (Hudon and Baker, 2002a,b) characterised by very poor compatibility with silicate network (as revealed by the broad miscibility gap in the FeO–SiO₂ binary). Secondly, because Fe end-members of Fe–Mg silicate solid solutions have low crystallisation temperatures and pure hypersthene (FeSiO₃) is not stable at low pressures, crystallisation is suppressed, and polymerised silica-rich melt may exsolve a Fe-rich liquid of pyroxenitic composition instead of crystallising Fe-pyroxene.

A number of experimental studies dealt with the ferrobasalt–granite immiscibility in complex, multi-component compositions and provided quantitative data on element partitioning between the immiscible liquids (e.g., Ryerson and Hess, 1978; Longhi, 1990). The studies confirmed that at certain P , T and redox conditions, the immiscible melts can stably coexist with liquidus mineral assemblages common in natural ferrobasalts (fayalite, plagioclase, ilmenite, etc.). As for the element partitioning, it would be reasonable to expect that the most network-incompatible elements showing the highest consolute temperatures of two-liquid fields in Figs. 2 and 3a would show the most contrasting distribution between polymerised granitic melt and immiscible ferrobasaltic liquids. Nernst partition coefficients ($D = C_i^1/C_i^2$, where C_i^1 and C_i^2 are weight concentrations of element i in phases 1 and 2) are the simplest and most straightforward measure of element partitioning. Experimental data on two-liquid D plotted against Z/r (Fig. 3b) resemble indeed the convex trend of the consolute temperatures in Fig. 3a. The number of elements analysed in the ferrobasaltic–granitic system is at the moment very small for detailed comparisons, and it is not clear if the four groups of cations identified in the binaries by Hudon and Baker (2002a,b) retain their specific behaviour in a multicomponent system like this one. Coulombic interactions are obviously much more

complex in multicomponent systems than in the binaries, and the behaviour of elements is affected not only by silica but all the other components. The importance of associations of Na^+ , K^+ and Ca^{2+} with tetrahedral Al^{3+} in stable feldspatoid aluminosilicate complexes was already discussed in the previous section. It is also notable that P^{5+} in Fig. 3b plots way above the main convex trend, despite the fact that no stable immiscibility was reported in the P_2O_5 –SiO₂ binary (Levin et al., 1964) and PO_4 tetrahedra because as such appear to be quite compatible with the silica network. Such distribution of P may be explained by formation of stable phosphate complexes with typical network-modifying cations, especially with Ca^{2+} , Mg^{2+} and Fe^{2+} , which drive P^{5+} into the ferrobasaltic liquid where the network modifiers are concentrated.

4.4. The role of nonsilicate anions (F^- , Cl^- , BO_3^{3-} , CO_3^{2-} and PO_4^{3-})

Minor additions of nonsilicate anions appear to have significant effects on liquid immiscibility. It was argued that P_2O_5 strongly increases the miscibility gap between the ferrobasaltic and granitic compositions (Visser and Koster van Groos, 1979) and the silicate–carbonate liquid immiscibility has been thoroughly discussed and studied in connection to the origin of carbonatites (e.g., Kjarsgaard and Hamilton, 1989 and references therein). Although much has been written about the incompatibilities between the nonsilicate anions and aluminosilicate networks, it seems that in comparison to the network-modifying cations, the effects of the former on liquid immiscibility are subordinate, indirect and secondary. Their role may be better envisaged as fluxing components that suppress crystallisation and thus reveal the tendencies for unmixing in silicate melts that are otherwise hidden below liquidus surfaces. Nonsilicate anions provide means for network modifiers to separate in the form of salt melts, often with very low SiO₂ concentrations. The available experimental data on liquid immiscibility between silicate melts and liquids of fluorides (Kogarko and Krigman, 1970; Gramenitskiy and Shekina, 1994; Gramenitskiy et al., 1993; Veksler et al., 1998a,b), chlorides (Webster and De Vivo, 2002), carbonates (Hamilton et al., 1989; Kjarsgaard and Hamilton, 1989; Jones et al., 1995; Veksler et al.,

1998a,b), borates (Veksler et al., 2002a,b) and phosphates (Krigman and Krot, 1991; Suk, 1998) suggest that the nonsilicate anions may enhance liquid immiscibility, but the general rules and regularities of the salt–silicate unmixing and the decisive role of network-modifying cations are the same as in the pure silicate systems, discussed in the previous sections (Fig. 3).

Silicate–fluoride systems provide the starkest examples in this respect. Consider the composition with the stoichiometry of $\text{KAlSiO}_3\text{F}_2$ (Veksler et al., 1998a). Kalsilite (KAlSiO_4) is one of the most refractory silicates, with a melting temperature above 1700 °C (Levin et al., 1964). The substitution of one O^{2-} by two F^- results in a collapse of the kalsilite structure, and dramatic drop in the liquidus temperature down to about 650 °C. Despite the very high bulk F content in the $\text{KAlSiO}_3\text{F}_2$ composition, no sign of stable or metastable liquid immiscibility has been observed and the melt quenches to perfectly clear, homogeneous glass. However, on the join $\text{KAlSiO}_3\text{F}_2$ – $\text{CaMgSi}_2\text{O}_6$ (Veksler et al., 1998a), even very small amounts of Ca^{2+} and Mg^{2+} , no more than fractions of a weight percent, cause immediate separation of an immiscible fluoride liquid composed mostly of CaF_2 and MgF_2 species. Thus, this example illustrates that F has a strong capacity to destroy aluminosilicate structures, but this does not necessarily result in liquid immiscibility. Fluoride and silicate species can mix very well to form homogeneous melts and glasses, and the crucial factors for phase separation are still the properties of network-modifying cations and their relationships to Al.

4.5. Element partitioning between salt and silicate melts

Silicate–fluoride, silicate–phosphate and silicate–carbonate systems show strong relationship between the experimentally determined two-melt D and Z/r values of network-modifying cations (Fig. 4). Absolute values of D depend on P , T , bulk composition and other conditions, and comparisons between different elements should ideally be done using D measured in the same run. It seems from the available data that the dependence of D on Z/r in the silicate–fluoride, silicate–phosphate and silicate–carbonate systems is not linear, but goes through a

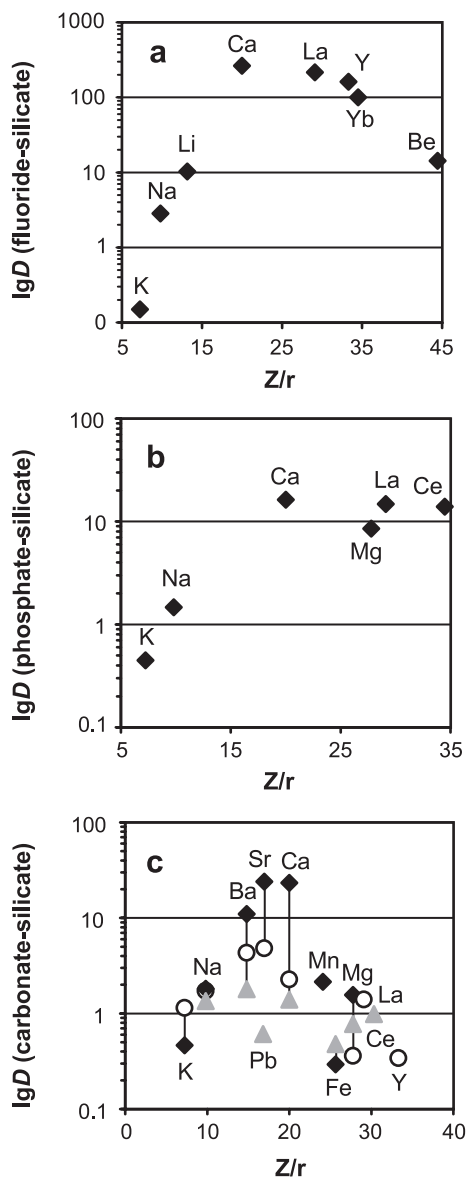


Fig. 4. Partition coefficients (D) of network-modifying elements between silicate and hydrosaline melts. (a) Fluoride–silicate compositions (Gramenitskiy and Shekina, 1994; Gramenitskiy et al., 1993; Veksler, unpublished data). (b) Phosphate–silicate system (Suk, 1998). (c) Carbonate–silicate systems. Solid diamonds—data for 700 °C, 280 MPa (Kjarsgaard et al., 1995); open circles—965 °C, 92 MPa (Veksler et al., 1998a,b); grey triangles—1250 °C, 1 GPa (Jones et al., 1995);). Z/r —the same as in Fig. 2.

maximum somewhere at Ba–Ca (Fig. 4). The general pattern of element partitioning compares well with the oxide binaries (Fig. 3a); it has much in

common with ferrobasalt–granite silicate immiscibility (Fig. 3b). However, experimental data on the silicate–salt element partitioning are sketchy and detailed comparisons would be premature. It should also be noted that experiments in silicate–carbonate systems were mostly performed with mixtures of natural rocks or synthetic compositions containing significant amounts of F, Cl and P_2O_5 ; thus, the data on element partitioning presented in Fig. 4c may reflect combined effects of several components and not the carbonate complexes alone.

Boron in silicate melts forms trigonal (BO_3) and tetrahedral (BO_4) structural units and, generally, is a network former. Metastable immiscibility was reported in the B_2O_3 – SiO_2 binary and there are stable miscibility gaps in many borosilicate systems (Levin et al., 1964). Veksler et al. (2002a,b) studied two-melt partitioning of Na, Mg and Ca in multicomponent borosilicate compositions, and information about partitioning of other element can be derived from the M_xO – B_2O_3 – SiO_2 ternaries (Fig. 5a). The extent of miscibility gaps varies broadly in the ternary borosilicate systems of mono- and divalent network modifiers. Consistent quantification and comparisons can be done in a similar way as in the oxide binaries (Hudon and Baker, 2002a) by measuring the extent of the gap at the monotectic temperature of invariant equilibrium of two immiscible liquids with two crystal phases at 1 atm, one of which is a silica polymorph. This gives an estimate of the maximal extent of the gap at activity $SiO_2 = 1$. In Fig. 5b, the mole fractions of network-modifying oxides in the B-rich invariant melts are plotted against Z/r , and the plot shows, as in Fig. 3b, a strong correlation with the same increasing tendency to immiscibility from alkalis to alkaline earth elements (with a possible exception of Li).

I found no direct data on two-melt element partitioning in chloride–silicate systems, but some hints can be obtained from solubility studies. For example, a recent study of Cl solubility in aluminosilicate melts (Webster and De Vivo, 2002) showed that the association of network-forming cations with Cl^- and their influence on Cl solubility decrease in the order: $Mg > Ca > Fe > Na > K > Li > Rb > Cs$. This sequence is not identical, but very similar to those established for the oxide and silicate–fluoride systems (Figs. 2 and 4a). Immiscible chloride globules were not analysed in run

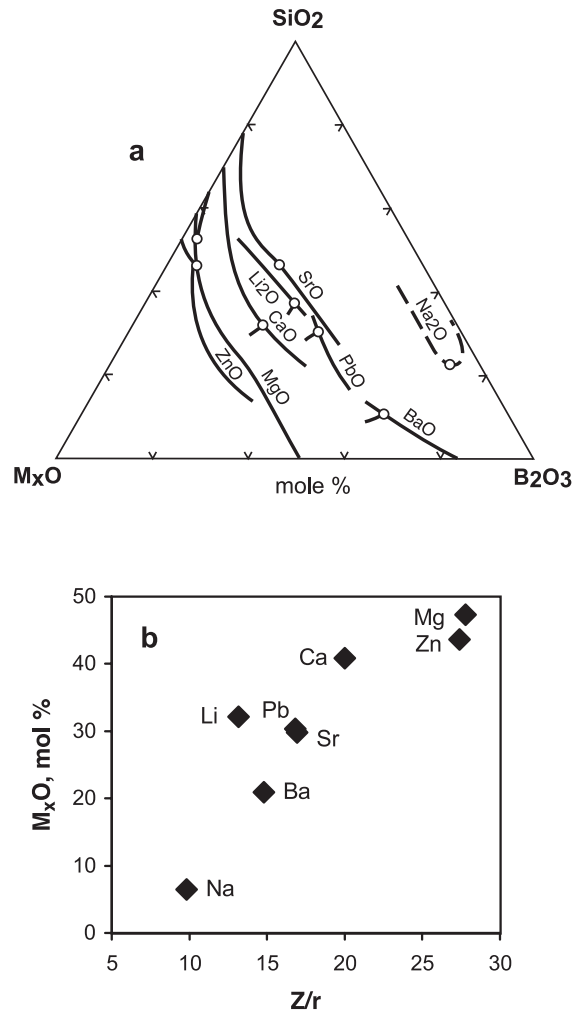


Fig. 5. Partitioning of network modifiers between borate and silicate immiscible liquids. (a) Segments of two-melt fields on different oxide ternaries and invariant points of silica saturation (Levin et al., 1964; see text for details). (b) Concentrations of network-modifying oxides in the invariant ternary points shown in Fig. 4a. Z/r —the same as in Fig. 2b.

products; hence, the two-liquid partition coefficients cannot be calculated.

5. Immiscibility in salt–water systems

5.1. Salt–water binaries

With respect to aqueous solutions, salts fall in two major groups. Those that have low to moderate

solubilities at room conditions usually become even less soluble with growing temperature; hence, at P – T conditions close to the critical point of water, the solubilities approach 0. On the other hand, the solubilities of highly soluble salts tend to increase further with temperature up to 100% at the salt melting point. The solubility threshold between the two groups lies somewhere between 5 and 10 mol% of salt in vapour- and salt-saturated solution at temperatures above 200 °C (Valyashko, 1990 and Fig. 6). The effects of temperature on solubility determine the topological types of salt–water phase diagrams. Topological classification of binary and ternary salt–water systems is an advanced field of physical chemistry, and a great number of theoretical and experimental studies have been dedicated to this subject (e.g., Ravich, 1974; Valyashko, 1990, 2002 and references therein). The key topological elements of the diagrams are the critical curve ($L=V$) and the vapour-saturated melting curve ($L=S+V$, Fig. 7). Depending on whether these curves intersect or not, the systems are divided into two major classes, which are further subdivided into groups according to effects of crystallisation and different types of immiscibility that may occur in the fluid phases (Valyashko, 2002). If the solubility of salt is high and constantly increases with temperature, the salt and water are likely to form a continuous range of liquids from one pure component to another and the curves $L=V$ and $L=S+V$ do not intersect (Fig. 7a). The system NaCl–H₂O is a famil-

iar example of this type. On the other hand, many fluoride–H₂O, sulphate–H₂O and most silicate–H₂O binaries and ternaries, including the simplest SiO₂–H₂O system (Kennedy et al., 1962), belong to the second (so-called p – Q) class, in which the critical and the three-phase melting curves intersect at two critical end-points p and Q (Fig. 7b). Between those critical points, solid phases coexist with a single fluid phase (F), which, depending on P , T and chemical composition, may have physical properties similar to those of a vapour or a liquid.

The importance of critical phenomena and p – Q topology for natural hydrothermal and magmatic systems was recognised early on and for almost a century the diagrams similar to those in Fig. 7a and b have been copied from one geological textbook to another. However, one important detail is missing in Fig. 7b. The plot gives the impression that although the critical and three-phase curves intersect, their stable and metastable (between the points p and Q) segments merge into smooth curves not much different from those in Fig. 7a. However, such continuity is not observed in real inorganic systems and is not supported by experimental data. In fact, all the salt–water binaries of the p – Q type studied so far show that the two segments of the critical curve actually belong to two physically different phase equilibria and do not merge into a single continuous curve (Ravich, 1974; Valyashko, 1990). A more accurate depiction of the systems with critical phenomena is presented in

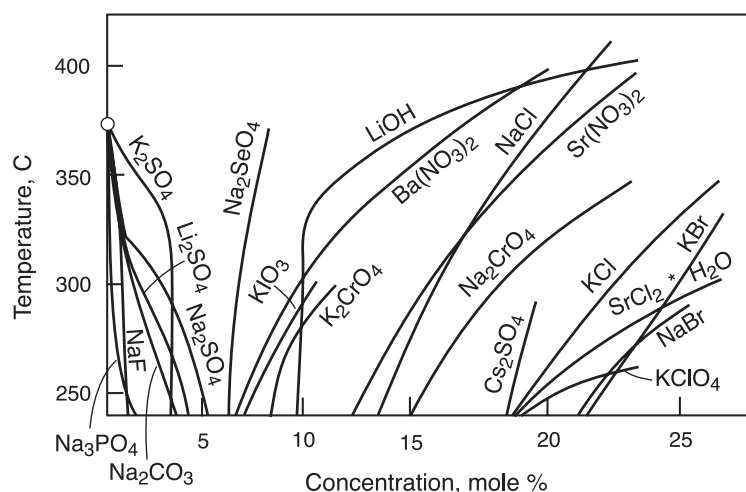


Fig. 6. Effects of temperature on solubilities of salts in aqueous solutions at pressures of vapour saturation (after Valyashko, 1990).

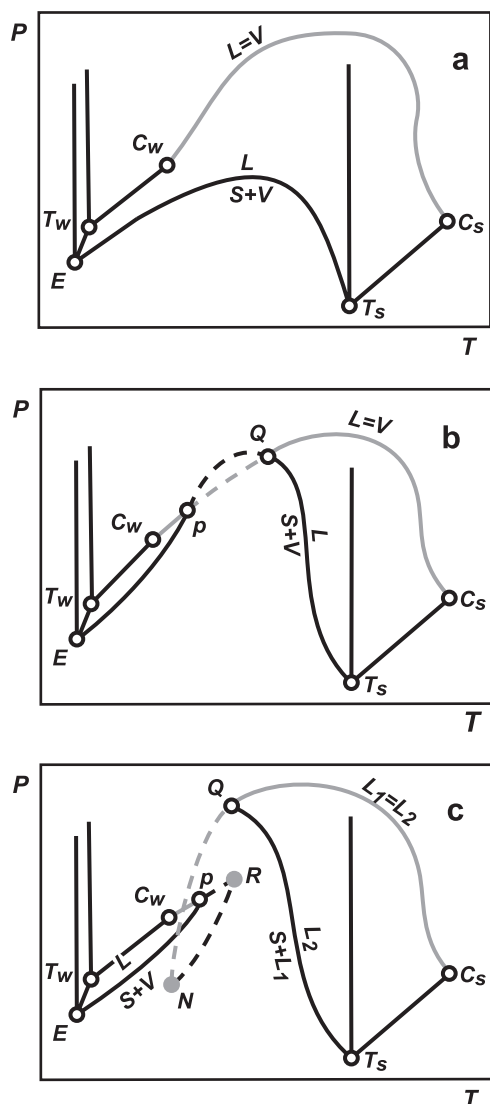


Fig. 7. Topological types of salt–water binaries in schematic P – T projections. (a) no critical phenomena along the melting curves; (b and c) with critical phenomena, so-called p – Q type (see text for discussion). L —liquid, V —vapour, S —solid salt. Open circles— invariant points, solid black curves—monovariant equilibria, grey curves—critical equilibria $L=V$ and $L_1=L_2$. Dashed lines and grey circles are metastable continuations of monovariant curves and metastable invariant points. T_w and T_s —ternary points, C_w and C_s —critical points of the pure components, E —eutectic point, $L=S+V$ —the vapour-saturated melting curve, $L_2=S+L_1$ —melting in equilibrium with two immiscible liquids.

Fig. 7c. The segment between the critical point of water (C_w) and the low-temperature end-point p refers

to the critical phenomena between liquid and vapour ($L=V$), whereas the segment between Q and the critical point of salt (C_s) is better described as the critical curve of two liquid-like immiscible phases ($L_1=L_2$) or dilute and concentrated solutions. Metastable invariant points N and R and the curve connecting them (Fig. 7c) correspond to the three-fluid equilibrium $L_2=L_1+V$.

The first theoretical analysis of the system topology characterised by critical phenomena and metastable liquid immiscibility was presented by Büchner (1918). In the following decades, the number of experimentally studied systems grew and Ravich (1974) came up with new empirical criteria for recognising this type of phase equilibria. His approach was based on the comparison of the positions of upper critical points Q on the P – T projections with supercritical extrapolation of the liquid–vapour (L –

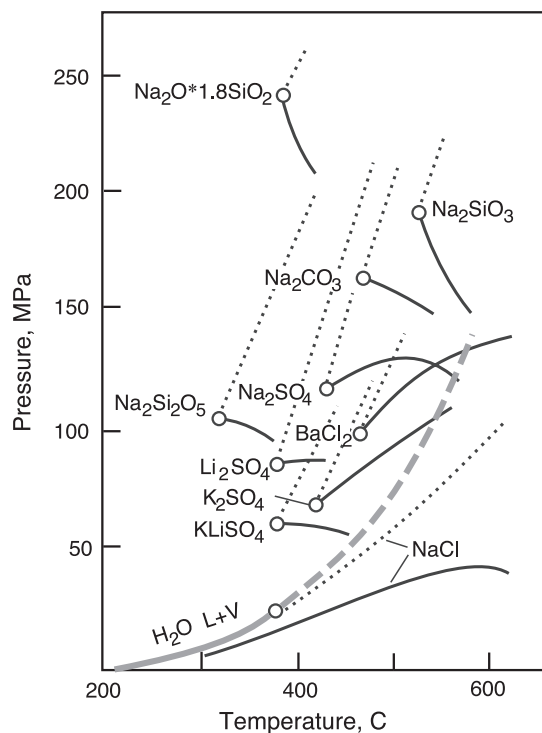


Fig. 8. Segments of three-phase melting curves (solid lines), critical curves (dotted lines) and upper critical end-points (open circles) of different salt–water binaries in a P – T projection. Heavy grey solid and dashed lines show the position of boiling curve of pure water and its metastable extrapolation beyond the critical point. See text for discussion.

V) boiling curve of pure water (Fig. 8). He pointed out that all the experimentally determined points Q of salt–water systems lie at much higher pressures than the water boiling curve and its metastable continuation, and thus the points and the high-temperature segments of the critical curves must correspond to equilibrium $L_1=L_2$ and not $L=V$. It was also noted that in some systems, the temperature at the point Q may be even lower than that at the point p , while the pressure and concentrations of equilibrium solutions are much higher; thus, there is no way that the two points could be connected by a smooth curve (Valyashko, 1990). In contrast, in salt–water binaries without critical phenomena (e.g., the NaCl–H₂O system), not only the three-phase melting curve $S+V=L$ but even the critical curve $L=V$ lie below the extrapolated boiling curve of pure water (Fig. 8).

Because the stable equilibria in diagrams Fig. 7b and c are virtually the same, the subtle differences in metastable region may seem irrelevant. However, the issue is important because it bears on the exact nature of fluid phases at and above the upper critical end-point Q . If the fluid phases coexisting with a solid salt above point Q are two immiscible liquids of contrasting salinity, this emphasises the fundamental difference between dilute and concentrated hydrothermal solutions. The solutions are different to the point that they do not mix, and this, as argued above and illustrated with experimental examples, requires a fundamental difference in predominant type of chemical bonds.

The notion of fundamental difference between dilute and concentrated hydrothermal solutions is supported by numerous studies of their physical properties (Valyashko, 1990). In short, the dilute solution can be defined as a predominantly molecular liquid with some dissolved electrolyte, while the concentrated solution (or hydrosaline melt) is a predominantly ionic liquid, which is a molten salt with some dissolved water. The distinction is not purely semantic, but fundamental and indeed practical. As demonstrated by salt–water systems of the p – Q type, the liquids not only unmix but also behave differently in response to changes in pressure and temperature. This can be demonstrated in many typical salt–water binaries of the p – Q type, such as the Na₂CO₃–H₂O (Fig. 9). At pressures below 160 MPa, rising temperature has a negative effect on the solubility of Na₂CO₃ and the solubility isobars have characteristic S-shapes, approaching 0 above the

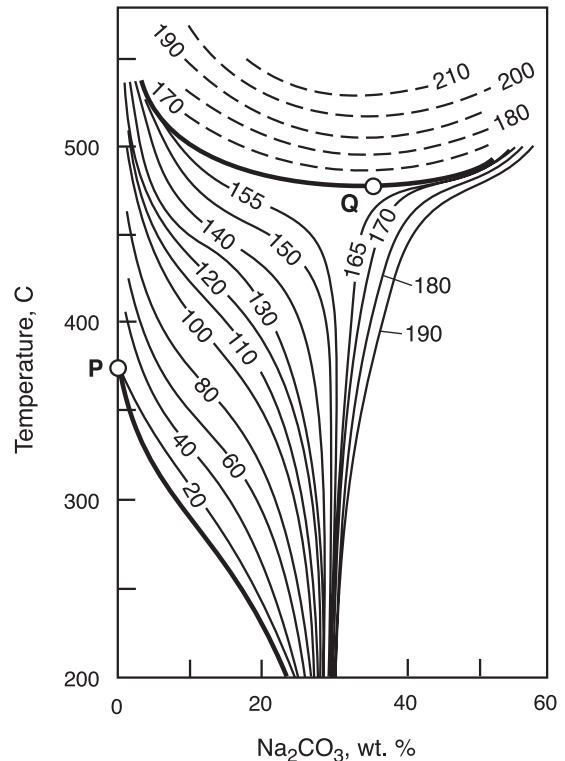


Fig. 9. T - x projection of the Na₂CO₃–H₂O system, according to Ravich (1974). Heavy solid curves—monovariant equilibria $L=S+V$ and $L_2=S+L_1$; p and Q —lower and upper critical end-points (see Fig. 7); light curves—solubility isobars; dashed curves—solvi of two immiscible solutions. Numbers denote pressures in MPa.

lower critical end-point p . The lower critical point itself is close to that of pure water, which is not surprising taking into account the very low salt solubilities in this P – T range. At pressures above 165 MPa, the solubility isobars are quite different, because at those pressures the solubility starts to increase with temperature. The pressure and the concentration (around 6.5 mol% Na₂CO₃) at which the transition takes place correspond to those of the upper critical end-point Q . Above the point Q lies a solvus of two coexisting solutions of contrasting salinity.

Not only the Na₂CO₃–H₂O system but many other salt–water binaries show a rather sharp change in physical and chemical properties of solutions at about 5–12 mol% of salt concentration (Valyashko, 1990). This range of compositions is called the transitional zone and the transition appears to be from a molecular,

dilute solution to a concentrated, ionic melt-like liquid. The salt concentrations of the transitional zone normally increase slightly with temperature and depend strongly on the Coulombic properties of salt ions. The concentrations are highest (20–25 mol%) for the so-called 1–1 electrolytes (composed of single-charged cation and anion, e.g., NaCl) and lowest (2–3 mol%) for the 2–2 electrolytes (e.g., UO₂SO₄). For the latter whose solubilities even at high pressures may not reach the transitional zone, a dramatic increase in solubility and the transition to the positive solubility–temperature relationships can be achieved by the addition of a second, highly soluble salt to the solution. Thus, no matter by which means the compositional threshold is crossed (pressure increase, addition of another salt, etc.), the change in properties of hydrothermal solutions appears to be profound and of a structural nature. The concentrated solutions should be better considered as hydrosaline melts, i.e., molten salts with some amount of dissolved water.

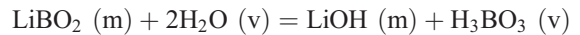
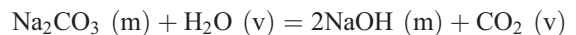
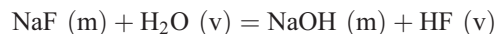
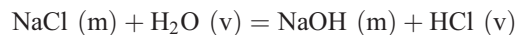
5.2. Multicomponent systems

Recognising correctly system topology, including metastable relationships, is also important because in complex, multicomponent systems, the metastable region and nonvariant points *N* and *R* (Fig. 7c) may become stable. Valyashko (2002) presented a detailed theoretical analysis of ternaries with one volatile and two nonvolatile components and examined different scenarios in which liquid immiscibility is brought to stability. Put simply, stable immiscibility is enhanced when nonvolatile components have eutectic relations with each other and thus crystallisation in ternary mixtures is suppressed to lower temperatures. Suppressed crystallisation and related increase in solution concentrations are factors that favour the transformation of metastable immiscibility, hidden in boundary salt–water binaries of the type shown in Fig. 7c, to stable ternary miscibility gaps. Some types of ternary system topology allow the stable coexistence of a solid salt with two immiscible liquids (solutions) and vapour. Experimentally, the transition from metastable to stable immiscibility in ternary mixtures between two salt–water boundaries of the *p*–*Q* type was demonstrated in the K₂SO₄–KLiSO₄–H₂O system (Valyashko, 1990). However, much more relevant to geology is another example of such a transition, with

stable three-fluid coexistence observed in the system Na₂O–SiO₂–H₂O. That and other similar silicate–water systems are discussed in more detail in Section 6.

5.3. High-temperature hydrolysis

Hydrolysis does not require heterogeneous phase equilibria, but the coexistence of two or three aqueous fluids (e.g., volatile-saturated melt and conjugate vapour) enables physical separation of the products of hydrolysis reactions and thus may dramatically enhance their chemical effects. In the most schematic way, examples of hydrolysis reactions relevant for magmatic systems may be expressed as follows (where *m* = melt, *v* = vapour):



The equations demonstrate that fluoride, chloride, carbonate, borate and similar nonsilicate components of aluminosilicate or hydrosaline melts can react with water of the coexisting vapour phase in such a way that the resulting hydroxide species remain preferentially in the melts, while acid components partition remain to the vapour. Because of hydrolysis, even the simplest systems, such as NaCl–H₂O, cannot strictly be considered as binary. Another consequence is that in vapour-saturated experimental charges, phase equilibria may depend on the exact amount of excess H₂O in the vapour phase. Such effects, apparently related to the hydrolysis reactions, were observed by Veksler and Keppeler (2000) in a study of element partitioning between carbonatitic melt and aqueous fluid.

Abundant experimental data exist on high-temperature hydrolysis in chloride–H₂O systems (e.g., Bischoff et al., 1996; Shmulovich et al., 1995), but other reactions are poorly studied. From what is known so far, it is reasonable to suggest that the controls of hydrolysis at elevated *P* and *T* are not much different from the well-established regularities in aqueous solutions at low temperatures and atmospheric pressure. Thus, species of weaker bases and acids (e.g., borates and carbonates in the equations above) should be more prone to

hydrolysis, and in some cases, only the right-side assemblages may be stable. Experimental data suggest that, in general, hydrolysis is enhanced at higher T and suppressed at higher P . However, I am not aware of quantitative information on equilibrium constants of the hydrolysis reactions at magmatic pressures and temperatures for salts other than chlorides.

6. Immiscibility between silicate melts and aqueous fluids

At pressures below 1 GPa and temperatures lower than 800 °C, natural aluminosilicate melts are extremely low in divalent cations (with the possible exception of Fe^{2+}), so that Na and K remain the only major network-modifying elements. Some rare compositions become enriched in Li, B, F, P_2O_5 , CO_2 and other components, but most of the common magmas do not and can be closely modelled by three- to five-component synthetic systems. Crystallisation drives residual melts towards two main eutectics: silica-saturated (granitic) and silica-undersaturated (phonolitic). In this section, I am dealing only with silica-saturated phase equilibria because granitic melts are much more abundant and they are better studied experimentally.

Since the classical work of Tuttle and Bowen (1958), experimental studies of granites logically have been focused mostly on the $\text{NaAlSi}_3\text{O}_8$ – KAlSi_3O_8 – SiO_2 haplogranitic join. The join is a part of the broader SiO_2 – Al_2O_3 – Na_2O – K_2O system and with the addition of H_2O , the five components enable to cover the most essential phase equilibria at the magmatic–hydrothermal transition. The amount of experimental data on the haplogranitic join is enormous, but it is of limited importance for this review, simply because the evolution of silicic melts in general does not stop on the haplogranitic join. Melt is exhausted at the haplogranitic minimum only if the molar ratio $(\text{Na}_2\text{O} + \text{K}_2\text{O})/\text{Al}_2\text{O}_3$ is kept strictly at 1. Obviously, natural compositions do not necessarily comply with this condition and with a slight excess of alkalis over alumina, small fractions of melts pass through the haplogranitic minimum and proceed to the lowest melting peralkaline eutectics. In the dry SiO_2 – Al_2O_3 – K_2O and SiO_2 – Al_2O_3 – Na_2O systems, the terminal quartz-saturated eutectics lie far in the peralkaline region, at about 74 wt.% SiO_2 and only 3–4 wt.% Al_2O_3 and the eutectic temperatures are 710 and

740 °C (Levin et al., 1964). Evaluating the effects of H_2O on these eutectics has proved, however, to be a very difficult task for experimental studies. Solubility of water in haplogranitic melt is relatively low (2.9 wt.% at 100 MPa, Dingwell et al., 1984), but it increases dramatically in peralkaline compositions, and with falling temperature, the increasing amounts of dissolved H_2O gradually transform melts into unusual, poorly quenchable liquids. Until now, there is no consensus on some key features of phase equilibria in seemingly simple three- to five-component hydrous peralkaline systems, and in my view, they deserve a thorough revision with employment of modern experimental and analytical methods. Below is a brief summary of the previous results.

6.1. The system SiO_2 – Na_2O – H_2O

A large number of experimental studies dealt with the silica-rich portion of this system, partly in connection to commercial hydrothermal growth of quartz crystals, so that the Na_2SiO_3 – SiO_2 – H_2O ternary is one of the best studied among the silicate– H_2O systems. However, on a number of important issues authors arrive at different conclusions and the results are hard to reconcile.

Tuttle and Friedman (1948), Morey and Hesselgesser (1952), Kennedy et al. (1962), Rowe et al. (1967), Mustart (1972), Valyashko and Kravchuk (1978), Kravchuk and Valyashko (1979) studied key joins within the Na_2SiO_3 – SiO_2 – H_2O ternary. It appears that the Na_2SiO_3 – H_2O , SiO_2 – H_2O , $\text{Na}_2\text{Si}_2\text{O}_5$ – H_2O joins all belong to the p – Q topological type (see Section 5.1) with either stable or metastable immiscibility between dilute and concentrated solutions (see also Figs. 7c and 8). The dry SiO_2 – Na_2O join (Fig. 2) also has a metastable immiscibility solvus below the liquidus of SiO_2 polymorphs. According to Tuttle and Friedman (1948) and Morey and Hesselgesser (1952), the join $\text{Na}_2\text{Si}_2\text{O}_5$ – H_2O is pseudo-binary and immiscible solutions of contrasting concentrations were reported at 250 °C on the join. Mustart (1972) doubted the pseudo-binary nature of the join, but concluded that only direct sampling of coexisting fluids, which was not possible in his studies, could resolve the issue. Rowe et al. (1967) gave quite different interpretation of the concentrated hydrous phase. They proposed that the phase was amor-

phous, unquenchable crystal hydrate of composition $\text{Na}_2\text{Si}_3\text{O}_7 \cdot n\text{H}_2\text{O}$. This interpretation was based on visual observations of phase separation at 200–350 °C in sealed glass tubes, but no other researches seem to accept the “amorphous” crystal hydrates.

The latest and probably the most comprehensive studies of the Na_2SiO_3 – SiO_2 – H_2O ternary are those by Valyashko and Kravchuk (1978) and Kravchuk and Valyashko (1979). The authors presented general analysis of system topology based on previous results, their own quench runs and detailed experimental study of the 350 and 400 °C isotherms with direct sampling of the fluid phases. They concluded that at these temperatures and pressures of vapour saturation stable liquid immiscibility was absent on the Na_2SiO_3 – $\text{Na}_2\text{Si}_2\text{O}_5$ – H_2O join, but did take place within the $\text{Na}_2\text{Si}_2\text{O}_5$ – SiO_2 – H_2O ternary (Fig. 10). It appears that at pressures up to 200–250 MPa, each of the solids (sodium disilicate or quartz) can coexist with aqueous vapour and two liquids of contrasting composition: dilute aqueous solution with only 0.8 wt.% of solute and a much more concentrated phase with about 20% H_2O , 60% SiO_2 and 20% Na_2O (by weight). The authors argued against the crystal hydrates suggestion of Rowe et al. (1967) and pointed out that the experimentally determined variations in the amount of H_2O in the concentrated, colloidal phase with P and T were more consistent with the formation of concentrated immiscible liquid. The

lowest P – T limit of the stability of the concentrated hydrosilicate liquid saturated with quartz was estimated to be 200 °C and 80 MPa. The authors concluded that the SiO_2 – $\text{Na}_2\text{Si}_2\text{O}_5$ – H_2O ternary belonged to the type with critical phenomena and stable liquid immiscibility in saturated solutions.

6.2. The system SiO_2 – Al_2O_3 – Na_2O – H_2O

Friedman (1950) studied 300 and 450 °C isotherms in the alumina-poor (1.2–6 wt.% Al_2O_3) part of the SiO_2 – Al_2O_3 – Na_2O – H_2O system. The polybaric SiO_2 – Na_2O – H_2O projections that he presented were similar to that of the SiO_2 – Na_2O – H_2O ternary in Fig. 10 with the addition of crystallisation fields of aluminosilicate phases at the H_2O corner. Pressure was not controlled in the runs, but it was known that the experiments at 300 °C were carried out in the presence of vapour. Probably the most important result of the study was that it demonstrated stable coexistence of two immiscible hydrosilicate liquids with vapour, albite and quartz on both isotherms. The concentrated hydrosilicate liquid saturated with albite and quartz at 300 °C apparently contained about 70% SiO_2 , 20% Na_2O and only 1.2–1.7% Al_2O_3 (by weight). In addition to albite, analcite and two other unidentified hydrous aluminosilicates were found in some of the run products.

Mustart (1972) studied several isothermal and isobaric sections in the $\text{NaAlSi}_3\text{O}_8$ – $\text{Na}_2\text{Si}_2\text{O}_5$ – H_2O

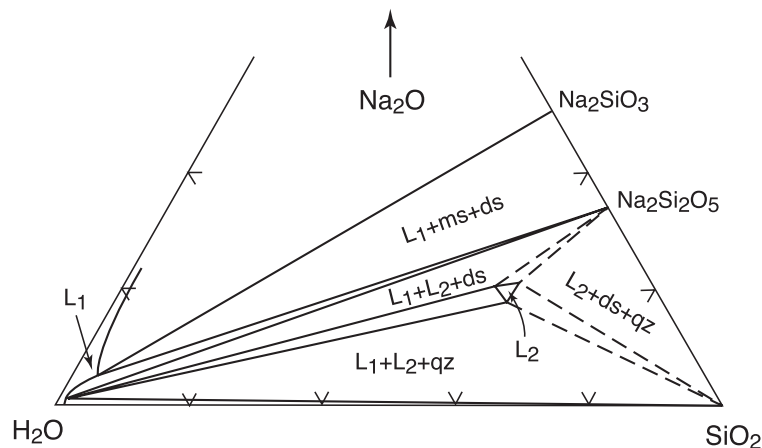


Fig. 10. Isothermal projection of the SiO_2 – Na_2O – H_2O system at 350 °C and pressures of vapour saturation (after Kravchuk and Valyashko, 1979, with modifications). Equilibrium phases are connected by heavy tie lines. L_1 and L_2 —dilute and concentrated immiscible liquids; ms—sodium metasilicate; ds—sodium disilicate; qz—quartz.

ternary at temperatures between 400 and 800 °C and pressures of 100–500 MPa. The study confirmed the crystallisation of albite from very peralkaline melts (or solutions) with about 60–75 wt.% of normative $\text{Na}_2\text{Si}_2\text{O}_5$ and 30 wt.% H_2O . He reported the existence of concentrated hydrosilicate liquids even below 400 °C, but claimed a single hydrous fluid phase at 300–320 °C and 120 MPa. Kravchuk and Valyashko (1979) argued against such an interpretation of the low-temperature phase relations and believed that the miscibility gap between the dilute and concentrated hydrous phases extended to low temperatures until the concentrated liquid totally crystallised.

6.3. Immiscibility in multicomponent peralkaline granitic compositions and the nature of the concentrated alkali hydrosilicate liquid

Regardless of the discrepancies and disagreements on details, most of the studies in the alkali-rich hydrosilicate systems mentioned above report low-temperature concentrated liquids composed of approximately 70 wt.% of alkali silicates and 30 wt.% H_2O . The liquids can precipitate quartz and aluminosilicate phases, including albite and analcite, and they appear to be distinct from dilute hydrothermal solutions and vapour with which they are not miscible. The low-temperature limit of concentrated sodium disilicate liquid in equilibrium with quartz is about 200 °C at 80 MPa (Kravchuk and Valyashko, 1979). Let us now examine what happens to the alkali-rich hydrosilicate liquids at higher, magmatic temperatures, and what relationships they have to conventional aluminosilicate melts such as haplogranite.

Experiments demonstrate that high-temperature aluminosilicate granitic melts and the low-temperature alkali hydrosilicate liquids can be in equilibrium with the same mineral assemblages of quartz and feldspars. Thus, it appears that the hydrosilicate liquids may result from continuous fractional crystallisation of the solids from slightly peralkaline granitic melt because crystallisation will increase both peralkalinity and water content of the residual liquids. Tuttle and Bowen (1958) experimentally demonstrated such aluminosilicate–hydrosilicate evolution in the system $\text{SiO}_2\text{–Al}_2\text{O}_3\text{–K}_2\text{O–H}_2\text{O}$. However, those experiments did not explore the possibility of direct, immiscible separation of the granitic aluminosilicate and alkali hydrosilicate

liquids. The question remained whether the liquids could coexist at some elevated, presumably superliquidus, temperatures in the same manner as aluminosilicate and hydrosaline melts do, provided enough excess alkalis and water are added to haplogranite.

Trufanova and Glyuk (1986) reported such immiscibility in the systems granite–LiOH– H_2O and granite–NaOH– H_2O . The schematic solvus on the granite– $\text{Na}_2\text{O–H}_2\text{O}$ join as they drew it is presented in Fig. 11a, but details of experimental procedures were

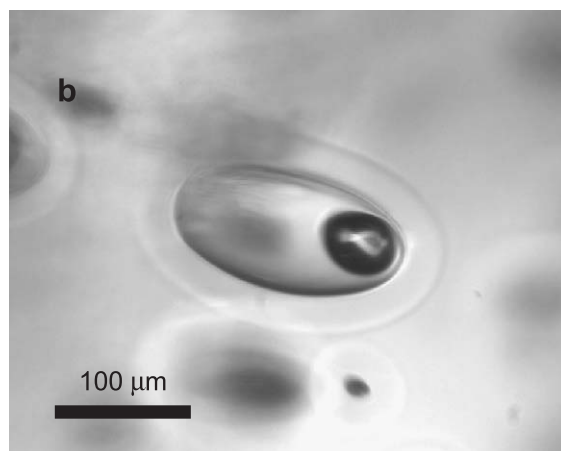
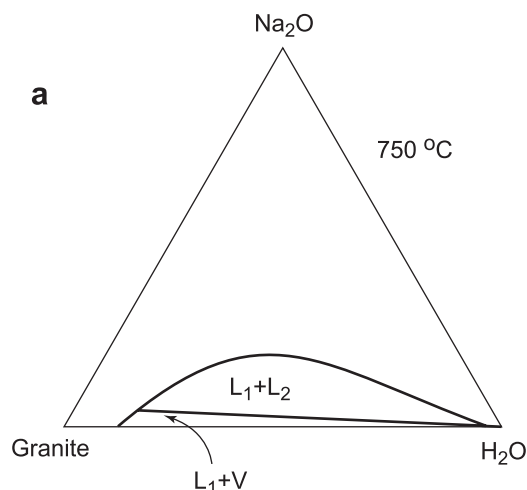


Fig. 11. Immiscibility between granitic and hydrous alkali silicate melts. (a) Schematic projection of the miscibility gap in the granite–NaOH– H_2O system at 750 °C and 100 MPa (Trufanova and Glyuk, 1986). (b) Microphotograph of a globule of alkali hydrosilicate liquid in granitic aluminosilicate glass in the products of rapid-quench experiments (Veksler, unpublished data). See text for details.

not clear in the original reference. I tried to reproduce such liquid immiscibility in cold-seal rapid-quench pressure vessels using mixtures of strongly peralkaline synthetic glass (SiO_2 76.3%, Al_2O_3 8.9% Na_2O 7.1% K_2O 7.7%, by weight) and 30–35 wt.% H_2O . At 770 °C and 100 MPa, I obtained numerous globules of a second, H_2O -rich liquid in aluminosilicate glass (Fig. 11b). No solid phases were present at these conditions. The alkali hydrosilicate liquid quenched to viscous, transparent material with characteristic distorted shrinkage bubbles. These preliminary results, a full description of which will be published elsewhere, are important because they confirm that the alkali hydrosilicate liquid is stable in a broad range of P – T conditions and represents a type of concentrated ionic liquid that has only limited miscibility with both aluminosilicate melts and with dilute hydrothermal solutions. Importantly, the experiments demonstrate that nonsilicate anions, such as F^- , Cl^- , CO_3^{2-} , etc., are not required for aluminosilicate–hydrosaline liquid immiscibility and that network-modifying oxides alone (Na_2O , Li_2O and H_2O) can cause immiscibility that results in formation of melt-like alkali hydrosilicate liquids.

7. Discussion and petrologic implications

Although fractional crystallisation is surely the main mechanism by which natural magmas evolve, liquid immiscibility and multiple coexisting fluids become increasingly important at near-solidus temperatures, so that in some volatile-rich systems, the solidus itself is hard to define. Metasomatism is a notion frequently invoked whenever crystal fractionation models fail to explain natural rock compositions and textural evidence of mineral replacements is observed. But since Bowen's pioneering studies until the present day, fluids still remain, in the words of Bowen (1928), "a Maxwell demon", doing whatever one wishes them to do. There seems to be a need for better experimental characterisation of aqueous fluids, especially the highly concentrated, ionic hydrosaline melts and hydrosilicate liquids, because their capacity for element transport and chemical fractionation is much greater than those of the dilute, molecular solutions. Unfortunately, many experiments performed in the past did not distinguish between the

dilute and concentrated aqueous fluids; hence, it is often not clear which of the phases (or both) existed before the quench. Thus, experimental studies of immiscibility in volatile-rich systems have a long way to go, but they already have numerous petrologic implications, some of which are outlined below.

The examples presented here deal mostly with granitic rocks. Several factors make the occurrences of liquid immiscibility and nonsilicate hydrosaline melts more likely in granitic systems than in many other types of natural magmas. Firstly, parental granitic magmas often have high initial concentrations of volatile and fluxing components (F, Cl, B, Li, etc.). Secondly, saturation in immiscible fluid phases is likely to be achieved earlier, at lower concentration levels in highly polymerised silicic melts than in mafic, basaltic compositions. Thirdly, the low pressure of crustal magmatism seems to favour liquid immiscibility and coexistence of multiple fluid phases, and thus granitic magmas in shallow-level magma chambers have a good chance to encounter these phenomena.

7.1. Geochemical fingerprints of immiscibility

Signs of liquid immiscibility are notoriously elusive (Bowen, 1928; Roedder, 1979), especially in slowly cooled plutonic rocks and where one of the conjugate fluids is unstable and leaves so little crystallisation products, as, for example, hydrosaline melts would do. Thus, geochemical indicators are likely to be more reliable than textures. Those systems which produced hydrosaline melts, and where liquid immiscibility was a significant factor of magma evolution, should demonstrate unusual geochemical characteristics, not explainable by fractional crystallisation alone. One of the geochemical fingerprints of the silicate–hydrosaline liquid immiscibility should be a strong fractionation of alkalis and alkaline earth elements resulting from the dependence of two-liquid partition coefficients (D) on Z/r that was stressed in Section 3 (Fig. 4). It appears that any chemical type of hydrosaline melt is likely to be enriched in Na, Li and alkaline earths and depleted in K and heavier rare alkalis. Thus, the separation of hydrosaline melt from silicate phases provides an effective means to fractionate Na and Li from K. The consequences of such process seem to show in granitic pegmatites (Veksler

and Thomas, 2002) and mineralised Li–F granites (Badanina et al., 2002). For instance, it may explain the extensive zoning often observed in pegmatitic bodies and separate crystallisation of Na and K feldspars.

In addition to the fractionation related to the Z/r systematics, immiscibility appears to be capable of effective decoupling of elements with very similar, almost identical ionic charges and radii. Theoretical explanations for this may be not yet available, but experimental, empirical evidence is strong. For example, in silicate–carbonate system large differences in two-liquid partition coefficients were reported for geochemical “twins”, such as Nb–Ta and Zr–Hf (Veksler et al., 1998b), and similar effects were revealed in the silicate–fluoride and silicate–phosphate systems (Suk, 1998; Gramenitskiy and Shekina, 2001). The experimentally determined D are such that Ta and Hf appear to be much less compatible with hydrosaline melts than Nb and Zr and thus such types of liquid immiscibility are expected to decrease the Zr/Hf and Nb/Ta values in the residual silicate melts. The lanthanide tetrad effect is another geochemical feature of evolved granitic systems, which is likely to be related to immiscibility between granitic melt and fluoride-rich liquid (Irber, 1999). Many volatile-rich granitic systems show significant deviations of Zr/Hf, Nb/Ta, Y/Ho and other similar elemental ratios from chondritic values (Bau, 1996) and fractionation of concentrated hydrosaline liquids is one of the processes that may be responsible for these variations.

7.2. Parallel evolution of coexisting silicate and hydrosaline liquids

It is possible that the first separation of immiscible hydrosaline melts may take place early in the evolution of granitic magmas and that the chemical compositions of the conjugate aluminosilicate and hydrosaline melts may undergo parallel chemical changes in response to magma cooling, fractional crystallisation and vapour separation. Because of relatively low solubility of Cl in aluminosilicate melts and its high abundance in the crust the early hydrosaline liquids are likely to be enriched in chlorides, mostly NaCl (Webster and De Vivo, 2002 and references therein). At the final stages of crystallisation, e.g., in pegmatites, melts may become

strongly enriched in other incompatible elements, such as F, B, P, Be and Li, and after removal of NaCl by dilute hydrothermal fluids, hydrosaline melts may form as predominantly fluoride, borate, carbonate, or phosphate liquids. The presence of such liquids in pegmatites and evolved granites is indicated by melt inclusion studies (e.g., Webster et al., 1997; Thomas et al., 2000; Kamenetsky, 2003, 2004; Badanina et al., 2004). Low viscosities of hydrosaline melts combined with significant density differences between them, aluminosilicate melt and the low-salinity vapour should result in effective gravitational separation of these phases (Veksler and Thomas, 2002). Thus, in view of their mobility and the high concentrations of incompatible and rare elements, hydrosaline melts will be very effective agents of chemical transport and may account for extensive mineral reactions, metasomatism, replacement zones and ore formation. The physical and chemical properties of such melts may be similar to those of technological fluxes and thus hydrosaline melts may account for enhanced crystal growth and formation of gigantic euhedral crystals, for which pegmatites are famous. This transport media meets the criteria imposed by Roedder (1992) for the source of gem-quality crystals in miarolitic zones because the residual hydrosaline melt will eventually form water-soluble solids that can be removed by hydrothermal or groundwater leaching.

7.3. Colloids and “silicothermal fluids”

New interesting reports appeared recently on synthetic and natural alkali hydrosilicate liquids and hopefully the studies will draw more attention of geoscientist to the potentially important geological role of such fluids. Wilkinson et al. (1996) presented experimental study in the system $\text{SiO}_2\text{--K}_2\text{O--CO}_2\text{--H}_2\text{O}$ by the method of synthetic fluid inclusions. They reported formation of K–Si-rich (~ 90 wt.% SiO_2) colloidal inclusions, which coexisted immiscible $\text{K}_2\text{CO}_3\text{--CO}_2\text{--H}_2\text{O}$ fluids at temperatures 300–750 °C and pressures below 200 MPa. Williamson et al. (2002) described natural occurrences of similar inclusions of colloidal silica in greisen topaz. These findings and experimental results appear to corroborate earlier experimental results in synthetic systems (see Section 6) and “silicothermal fluids” (Wilkinson et

al., 1996) may prove to be important agents of element transport in a broad range of geologic environments. The exact nature of such liquids should be better clarified by future experiments. At the moment, however, I would not put too much emphasis on the colloidal appearance of the run products. The fact that the run products are metastable and colloidal (see also Fig. 11b) does not necessarily mean that before quench the silica-rich hydrothermal liquids were metastable and colloidal either. The relationships between quenched colloidal products and their parental liquids may be similar to those between silicate glasses and the corresponding silicate melts. Concentrated alkali silicate aqueous solutions are likely to have a strong tendency to metastable behaviour at low temperatures; however, at higher temperatures, they may still prove to be stable, true solutions and not colloidal gels. Direct in situ observations and spectroscopic studies may help to resolve these issues in the future.

7.4. *The role of hydrolysis*

The idea that hydrolysis may be important as a petrological process is not new (Khitrov, 1954), but surprisingly little has been done in terms of experimental studies of the hydrolysis reactions in geologically relevant systems and their implications to metasomatism and ore formation. It is only in the last few years that high-temperature hydrolysis attracted new attention from experimental petrologists. Recently the effects of hydrolysis have been discussed, for example, in connection to REE partitioning in chloride–H₂O systems (Shmulovich et al., 2002) and in late-stage magmatic fluids related to peralkaline nepheline syenites (Markl and Baumgartner, 2002).

In the case of heterogeneous melt–vapour equilibria, hydrolysis reactions (see Section 5.3) imply the coexistence of acid vapour enriched in HF, HCl, H₃BO₃ and similar components, and basic melt, containing alkali hydroxide species. Spatial separation of the vapour and melt phases (e.g., gravitational, differential flow) provides an effective means for fractionation of the acid and basic components, and two contrasting metasomatic processes, albitisation and greisenisation, associated with them, which can commonly take place in different parts of a magmatic body (e.g., Badanina et al., 2003), can be seen as combined result of the single mechanism of hydroly-

sis. One may expect the vapour and the melt to partition contrasting groups of trace elements and this may result in formation of different types of ores. Acid–base equilibria should be especially important for amphoteric elements such as HFSE (e.g., Nb, Ta, Zr, Hf), Sn, etc. For example, it is likely that solubility of HFSE will increase in basic, hydroxide-bearing melts; this could explain the common observation of Sn and Ta concentration in albite-rich replacement bodies in mineralised pegmatites and granites. The effects of hydrolysis in the presence of H₂O may also help to resolve some apparent discrepancies between experimental data on element partitioning in dry salt–silicate compositions and observations in natural magmatic systems. For instance, experimental studies of element partitioning between dry silicate and carbonate immiscible melts (Jones et al., 1995; Veksler et al., 1998a,b) showed that Nb and Zr strongly concentrate in the silicate melt. This seems to contradict the fact that the world's largest deposits of Nb and Zr ores are associated with carbonatites. However, these and other amphoteric elements may become much more soluble in carbonate melts in the presence of H₂O, when silicate and carbonate melts coexist with the H₂O–CO₂ vapour phase and carbonate species are partly transformed by hydrolysis into hydroxides. Future experiments should clarify this issue, and, of course, the effects of hydrolysis are only one possible explanation, because the relationships between element solubilities and ore deposition are complex and involve many other factors.

7.5. *Immiscibility in hydrosaline melts*

It appears that miscibility gaps exist not only in silicate melts or between dilute (molecular) and concentrated (ionic) hydrothermal solutions but in the predominantly ionic hydrosaline liquids as well. Immiscibility between halogen components (chlorides and fluorides) and molten carbonates is an example with possible significant petrologic bearing. Mitchell (1997) described signs of liquid immiscibility between carbonatitic melt and halogen-rich melt in the groundmass of the unique natrocarbonatitic lavas of the Oldoinyo Lengai volcano (Tanzania) and a similar type of immiscibility has been observed by Fulignati et al. (2001) in chloride–carbonate fluid inclusions from skarn. The importance of chloride–carbonate

liquids in nature may extend far beyond the rare occurrences of skarns and natrocarbonatite lava and include kimberlite magma and processes of mantle metasomatism, as some recent melt inclusion studies indicate (Izraeli et al., 2001; Kamenetsky et al., 2002). This type of liquid immiscibility has not been studied experimentally and phase equilibria in chloride–carbonate systems need quantitative experimental characterisation in the future.

8. Conclusions

Well-studied topologic examples from inorganic chemistry and some recent observations in multicomponent, geologically relevant systems suggest that three-fluid immiscibility, or in other words, coexistence of aluminosilicate melt with two hydrous fluids of contrasting density and salinity, is common in natural magmatic systems. The slow realisation of the role of liquid immiscibility in magmatic systems is partly because its products, in nature and in the lab, are difficult to observe. Unquenchable, unstable fluid phases remain a challenge for experimental petrology and experiments often fail to determine the exact phase properties or even the number of coexisting fluid phases. Immiscibility phenomena are more likely in peralkaline silicic systems, characterised by molar excess of network-modifying cations over Al, and the capacity of the network-modifying cations to produce immiscibility depends on their charges and ionic radii and decreases in the following sequence: Mg>Ca>Sr>Ba>Li>Na>K. Immiscibility is enhanced by non-silicate anions (CO_3^{2-} , Cl^- , F^- , BO_3^{3-} , etc.), but their influence is subordinate to that of the cations. Separation of aluminosilicate and hydrosaline melts is expected to cause fractionation of alkaline earths, Na and Li from K, Rb and Cs, and this is one of geochemical “fingerprints” that can be used to identify immiscibility. Hydrosaline liquids may effectively decouple geochemically similar trace elements, strongly concentrate some components and produce unusual element abundances and ratios in igneous rocks. The network-modifying cations, the nonsilicate anions and H_2O are also involved in hydrolysis reactions, which are poorly studied experimentally but are likely to have significant effects on metasomatism and ore formation.

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