MAGMATIC HYDROSALINE MELTS: NEW EXPERIMENTAL DATA

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Unquenchable, unstable aqueous fluids remain a challenge for experimental petrology and experiments often fail to determine not only the exact properties but the number of coexisting fluid phases. Well-studied topologic examples from inorganic chemistry, some recent observations in multicomponent, geologically-relevant systems [1] and studies of natural fluid inclusions [2] suggest that liquid immiscibility is likely to play an important role in natural magmatic systems at final stages of magma evolution, that is, at so-called magmatic-hydrothermal transition. Cases in natural magmatic systems may also include three-fluid immiscibility: coexistence of aluminosilicate melt with two hydrous fluids of contrasting density and salinity. Analysis of simple binary and ternary oxide silicate systems implies that the most important factors controlling liquid immiscibility are the Coulombic properties (electric charges Z and ionic radii r) of the main network-modifying cations. Among the major network-modifying cations of natural magmas the capacity for immiscibility decreases in the following sequence: Mg>Ca>Sr>Ba>Li>Na>K [3]. Immiscible separation of aqueous fluid and silicate melt at elevated P and T as illustrated by the simplest example of the SiO_2-H_2O system [4] may be viewed as another case of immiscibility phenomena similar to those in the other binary oxide systems (although H^+ is a very peculiar cation without any ionic radius *per se*). The simplest experimental model, which allows insights into the role of aqueous phases and liquid immiscibility in natural residual silicate systems (e.g., evolved granites and granitic pegmatites) is the SiO_2-Al_2O_3-Na_2O-K_2O-H_2O system. In the P range corresponding to that of the crustal magma chambers (1-10 kbar) liquids stable at the lowest temperatures are found in the extremely peralkaline and H_2O-rich part of the system. It has been demonstrated [5, 6, 7, Veksler, unpublished] that feldspars and quartz at 1-2 kbar and 350-450 ^oC can be in equilibrium with two aqueous phases: dilute solution of alkali silicates and a concentrated, denser phase with about 70 SiO_2, 10-20 alkali oxides, 15-20 H_2O and only 1-2 Al_2O_3 (in wt%). The latter phase should be viewed as the final composition of granitic silicate melts after extensive fractional crystallisation of ordinary rock-forming minerals. The melt-like phase is likely to play an important role at the final stages of pegmatite formation (e.g., quartz core, miarolitic cavities and replacement zones).

Liquid immiscibility is enhanced by non-silicate ligands (CO_3^{2-}, Cl^-, F^-, BO_3^{3-}, PO_4^{3-} etc.), but their influence is subordinate to that of the cations. Carbonatitic melts are by far the best studied and most voluminous natural hydrosaline liquids. They are probably the only ones that form distinct and unambiguous crystallisation products represented by various types of carbonatite rocks. However, less obvious examples of natural hydrosaline liquids (magmatic brines) may also include chloride-, fluoride-borate- and phosphate-rich melts, which are likely to form in silica-rich magmas. Chloride and fluoride melts appear to be poorly miscible not only with aluminosilicate melts but carbonatitic melts as well [8, 9]. Two-liquid trace element partitioning is well constrained only in the silicate-carbonate [10, 11, 12] and silicate-fluoride systems [13, Veksler, unpublished], although a thorough study of the effects of H_2O is needed for the silicate-carbonate systems and some published data on silicate-fluoride systems also need revision. Despite Coulombic forces appear to be the main factor responsible for the immiscibility phenomena, liquid-liquid partition coefficients of trace elements may be strongly affected by factors other than the simple ionic Z-r relationships, e.g., by subtle changes in stabilities of non-silicate complexes. Separation of aluminosilicate and hydrosaline melts in nature should cause significant fractionation of alkali earths, Na and Li from K, Rb and Cs. Some compositions may effectively decouple geochemically-similar trace elements (e.g., Zr-Hf, Nb-Ta, Y-Ho) and produce unusual geochemical imprints on igneous rocks, e.g., those related to the lanthanide tetrad effect [14]. The network-modifying cations, the non-silicate ligands and H_2O are involved in hydrolysis reactions, which are poorly studied experimentally, but may have significant effects on metasomatism and ore formation. For example, albitites and greisens within a single granitic intrusion may be products of complimentary processes related to hydrolysis combined with immiscibility phenomena.

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