SOLUBILITY OF PHOSPHORUS IN THE MELTS OF NA-CA-AL-SI-O-F SYSTEM

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Starting materials were prepared by mixing of nephelinitic glass ($NaAlSiO_4$)+ SiO_2 with calcium metaphosphate ($Ca_2P_2O_7$) in proportion 1:1. Additional amount of NaF (10% wt. of the mixture) was added to decrease melting temperature and viscosity of centrifuging melts.

High-temperature experiments were carried out in welded Pt capsules at 1300-1500^{o}C within 17-20 hours with following fast cooling. We made 2 series of experiments: with- and without NaF. Experiments using the centrifuge were conducted at temperatures lower than 1250^{o}C with NaF-containing mixtures. Cooled samples were studied by EMA and immersion microscopic method. Image of fast-cooling run products changes from clear division into 2 layers to finest emulsion with inhomogeneities less than one micrometer. In the last case it's almost impossible to distinguish two-liquids division from crystallization in the cooling process and liquation limits can be stated by unfocused beam (25x25 μm and more) basing on EMA only.

All preparations received by centrifuging techniques have a very clear two layers structure with clear border between the layers. The upper layer is homogenous aluminasilica glass that usually contains small (grains of millimeters) gas bubbles (or blowholes?). It's fully free of any crystal phases. The lower layer consists of crystal sediment of apatite. The size of independent crystals is 10-100 microns... In the samples of join $E_{Ab\text{-}Q}$-$Ca_2P_2O_7$, some quantity of small (tens of microns) isometric quartz crystals were found. Crystal sediment is fixed with interstitial glass, which a little differs from the upper layer glass according to its composition. There is also a small quantity of glass with completely different composition. Its main components are P, Na and F with minor concentration of aluminum, silicon and calcium. This glass has micro inhomogeneous character, clear fiber structure with fibers thickness of 1 and less than 1 micron. This phase is easily destroyed by beam and its analysis causes certain difficulties/

Two-liquid field occupies a sizeable area of the phase diagram of the investigated system at temperatures over than 1500^{o}C (fig.1). Below this temperature two-liquids surface crosses the solidus surface and crystal phases are in equilibrium with 2 liquid phases simultaneously. Three-calcium phosphate and/or apatite were hard phases in our experiments for majority of our samples.

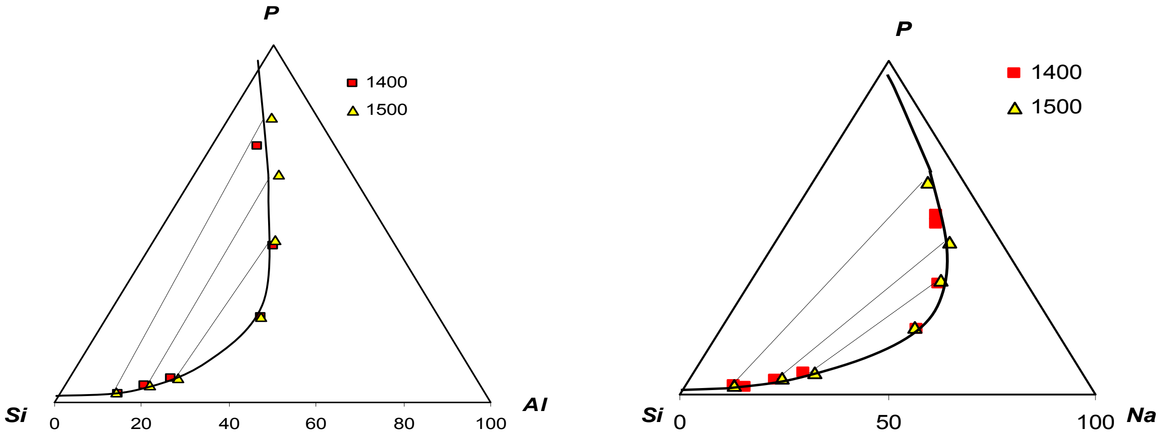

Fig.1. Two Liquids field projected on the ternary diagrams Si-P-Na (-Ca, Al) and Si-P-Al (-Ca, Na). The dashed lines are conodes.

In many cases, we found a secondary two-liquid decay "drop into drop"; however co-existing phases are practically the same as those of initial division. Phosphates crystallize from phosphate melt and conglomerates of crystals take the shape of the area occupied by phosphate melt... Crystallization of phosphates is accompanied by isolation of small drops of aluminasilica melt (fig.2), composition of which differs sufficiently from the main aluminasilica melt by higher content of SiO_2. The aluminasilica drops did not achieve equilibrium during the time of the experiment because they are separated from the bulk aluminasilica melt by the phosphate solid phase.

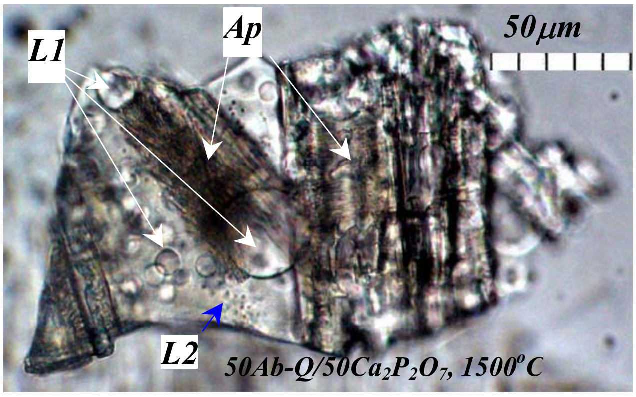

Fig. 2. Immersion image of three phase equilibrium.

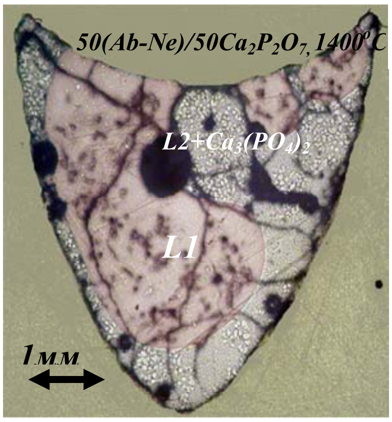

Fig. 3. Separation into two layers

Image of fast-cooling run products changes from clear division into 2 layers (fig.3) to finest emulsion with inhomogeneities less than one micrometer. In the last case it's almost impossible to distinguish two-liquid division from crystallization in the cooling process and liquation can be observed basing on study using unfocused beam (25x25 □m and more) of EMA only.

Our results showed that content of silica in the system are the main factor controlling the size of two- liquid field and compositions of the co-existing liquid phases. Solubility of P in aluminasilica melt increases rapidly with acidity decrease, the most rapid increase is observed for albite-type compositions. In case of albite-type compositions the concentration of P in the melt is 3.5%, in contrast to 17% in the case nepheline-type compositions (at 1200°C). The values reflect the *real solubility* of the components in the melt, because of the high speed of the cooling process preventing phosphates and fluorides phase formation.

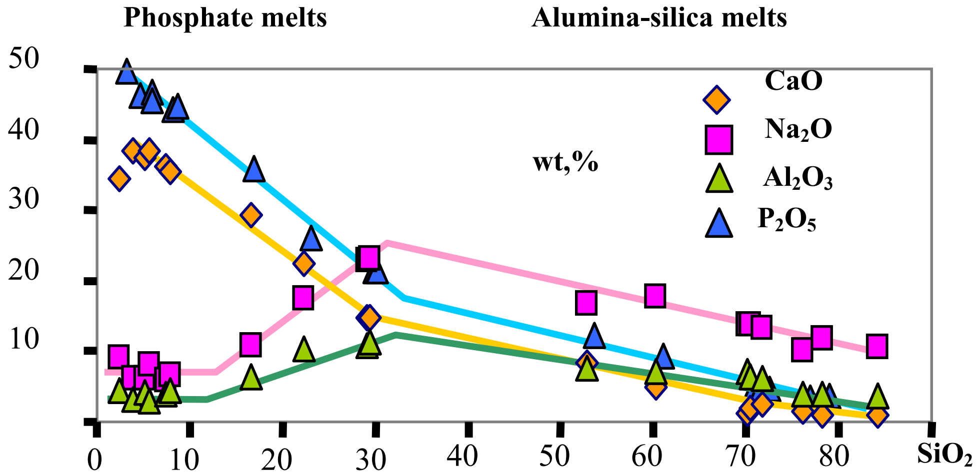

Fig. 4. Composition of coexisting melts at 1300-1500ºC.

The temperature reducing leads to increase of the silica concentration in the melt resulting from crystallization of phosphates.

For appearance of two-liquid separation in acid melts more than 3%P_2O_5 is needed, that sufficiently exceeds the content of the component in any magmas. At the same time eutectic in joins of the “aluminosilicate” (rock)-phosphate type contains much less of phosphorus. It's very important, that the two-liquid field is observed at phosphate concentrations higher than eutectic except case of melts that are more acid than eutectic Ab-Q composition. It means that phosphorus enrichment needed for the two-liquid division cannot be achieved in the process of the crystallization differentiation. This conclusion was made by L.N. Kogarko on the basis of analysis of apatite-nepheline deposit genesis. This study provides proofs for applications of this conclusion to any aluminasilica rocks.

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