Persikov E.S., Bukhtiyarov P.G. The nature of anomalous dependence of viscosity of silicate and magmatic melts on lithostatic and water pressure.

Institute of Experimental Mineralogy

key words: [rheology of magmas, mechanism of H_2O dissolution, high pressure, melt, structure, anomaly]

Experimental studies of viscosity of silicate melts of various basicity (albite –Ab, diopside – Di, $Ab_{25}Di_{75}$, $Ab_{50}Di_{50}$, $Ab_{75}Di_{25}$, jadeite –Jd) have been carried out at super-high lithostatic pressures (P_{lith} up to 120 kbar) and high water pressures (P_{H2O} up to 5 kbar) within the temperature range 1200-1850°C.

Determined for the first time was the inversion character of the dependence of viscosity (η) and activation energy of viscous flow (E) of model and magmatic melts on water and lithostatic pressure. Fig. 1 presents the dependences of activation energy and viscosity of model and magmatic melts on water pressure for the full composition range from acid (albite) to ultrabasic (diopside). The given data suggest that viscosity and activation energy of albite and basalt melts decrease essentially and those of diopside melt by contrast increase with water pressure, which is obviously related to the mechanism of H_2O dissolution in the melts of various basicity.

As we proposed earlier in [1] an amphoteric nature of H_2O may be shown up at its dissolution in magmatic melts under high pressures. This suggestion was based on the theoretical analysis of the regularities of concentration dependence of rheological parameters of model and magmatic melts in the range acid-basic, in particular, on the analysis of the summarized diagram of activation energy of viscous flow – melt composition. Such a diagram for acid (albite), basic (basalt), and ultrabasic (diopside) melts is given in fig. 2. According to the theory of regular solutions, linear dependences E – composition characterize H_2O dissolution in melts without chemical interaction (physical mechanism of dissolution – molecular H_2O). This is shown in fig.2 in dotted lines. H_2O dissolution accompanied by chemical interaction with the formation of new compounds is shown by different curves including those with minima and maxima. The analysis of the diagram (fig.2) suggests that within the whole range of magmas basicity, there are two mechanisms of water dissolution in them:

Chemical dissolution (OH hydroxyl)

Physical dissolution (molecular H_2O), OH/H_2O ratio depending on melt basicity and bulk concentration of H_2O (PHO) in melts.
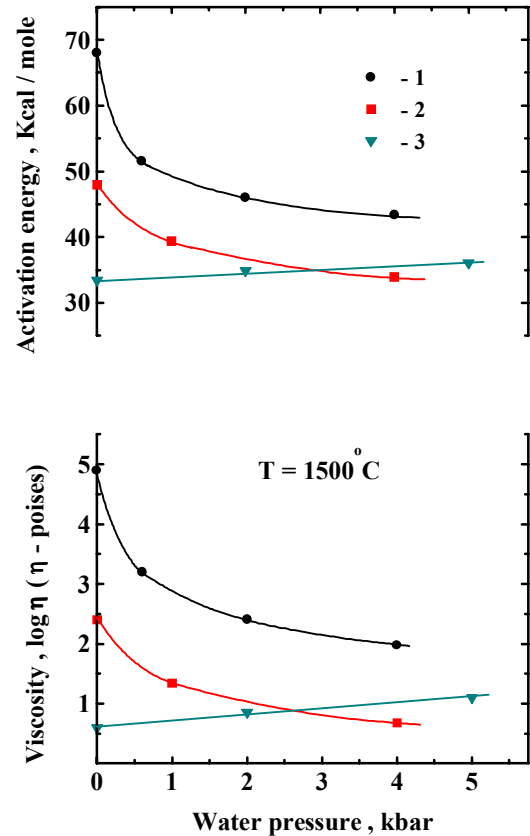

Fig.1. Dependence of viscosity (1500°C) and activation energy of viscous flow on pressure in the series acid-ultrabasic. 1,2,3- albite, basalt, and diopside melts ,respectively (see explanation in the text).

According to the principle of acid-basic interaction and maximum polarity of chemical bonds water dissolving in melts in the range acid-basic is a base relative to them because it is a donor of free oxygen and its dissolution leads to their depolymerization i.e. to an increase in their basicity. This statement is experimentally proved by the regular decrease in energy of viscous flow of the above melts with increasing H_2O concentration in them (fig.2).

An analysis of the data presented in fig.1,2 testifies that water dissolving in ultrabasic melts, by contrast, is an acid relative to them and its dissolution leads to the depolymerization (decrease in basicity) of ultrabasic melt and corresponding increase in viscosity and activation energy of viscous flow.
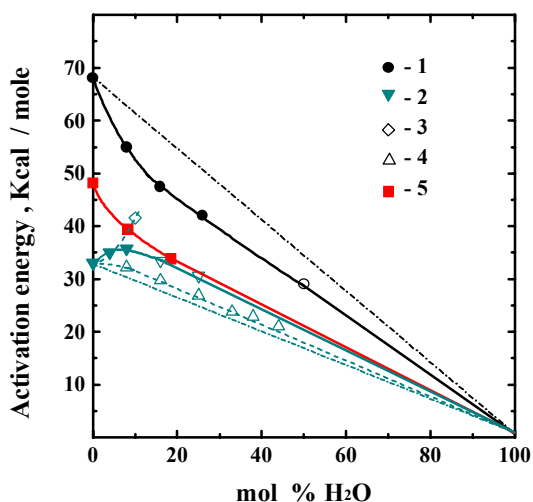
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Fig.2. Diagram of the dependence of activation energy on composition for a pseudobinary system melt-H$_2$O.1,5- albite and basalt melts, respectively (chemically dissolved water is a base relative to the water-free melt); 2- diopside melt (chemically dissolved water is an acid relative to the water free melt); 3- diopside melt (all water dissolved in a melt is an acid relative to the water-free melt); 4-diopside melt (all water dissolved in a melt is a base relative to the water-free melt); filled symbols stand for experiment, open symbols – for calculation.

Whereas for acid and basic melts chemical (base) and physical dissolved water has a cymbate effect on the rheological parameters of the melt (η and E decrease), for the diopside ultrabasic melt the effect of chemical (acid) and physical water on E and η is quite opposite. This explains the appearance of the maximum on the curve E=f(N$_{H2O}$) and hydrated melt at N$_{H2O}$=8.5 mol% (fig.2). So the above idea on the manifestation of

H$_2$O amorphous nature at its dissolution in magmatic melts was first proved.

The results obtained on the investigation of the dependence of viscosity (η) and activation energy of viscous flow (E) of model melts of the system albite-diopside on lithostatic pressure are given in figs. 3 and 4, respectively. These results suggest that viscosity and activation energy decrease essentially with an increase in lithostatic pressure within the whole range of compositions except the diopside melt, for which pressure dependences of viscosity and activation energy are of the reverse character i.e. the values η and E of the diopside melt by contrast increase with lithostatic pressure.

An analysis of the diagrams (figs. 3,4) shows that the obtained dependences are of an extreme character. Herewith, the pressure in the maxima and minima points of viscosity and activation energy strongly depends on melt composition, decreasing with its basicity whereas the values of activation energy in the minima points do not depend on melt composition and in the first approximation are equal to the activation energy of viscous flow for metasilicate melts at atmospheric pressure. η and E of ultrabasic and more polymerized melts after minima increase with pressure, which is in complete agreement with theoretical prerequisites. But an essential decrease in η and E of aluminosilicate and magmatic melts with pressure is anomalous at the first stage. The most probable mechanism to explain this anomaly is the structural transition in melts of Al and at super-high pressures of Si from the position of network forming cations to the position of cations-modificators, which is naturally accompanied by an increase in depolymerization degree of melts. This idea was proposed in [2] and nowadays is supported by an increasing number of experimental and theoretical data [3].
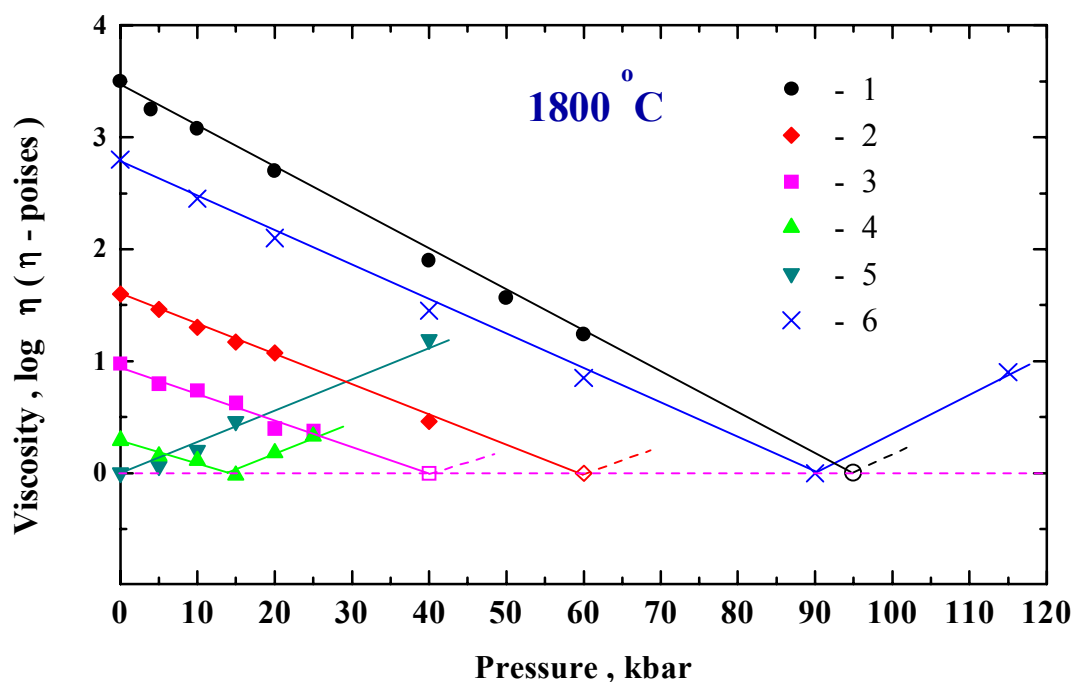

Fig.3. Isothermal (T=1850°C) dependence of melt viscosity on pressure in the system Ab-Di and Jd. 1-Ab100; 2- Ab80Di20; 3-Ab57Di43; 4- Ab30Di70; 5- Di100; 6- Jd100 (open symbols stand for extrapolation values, see explanation in the text).
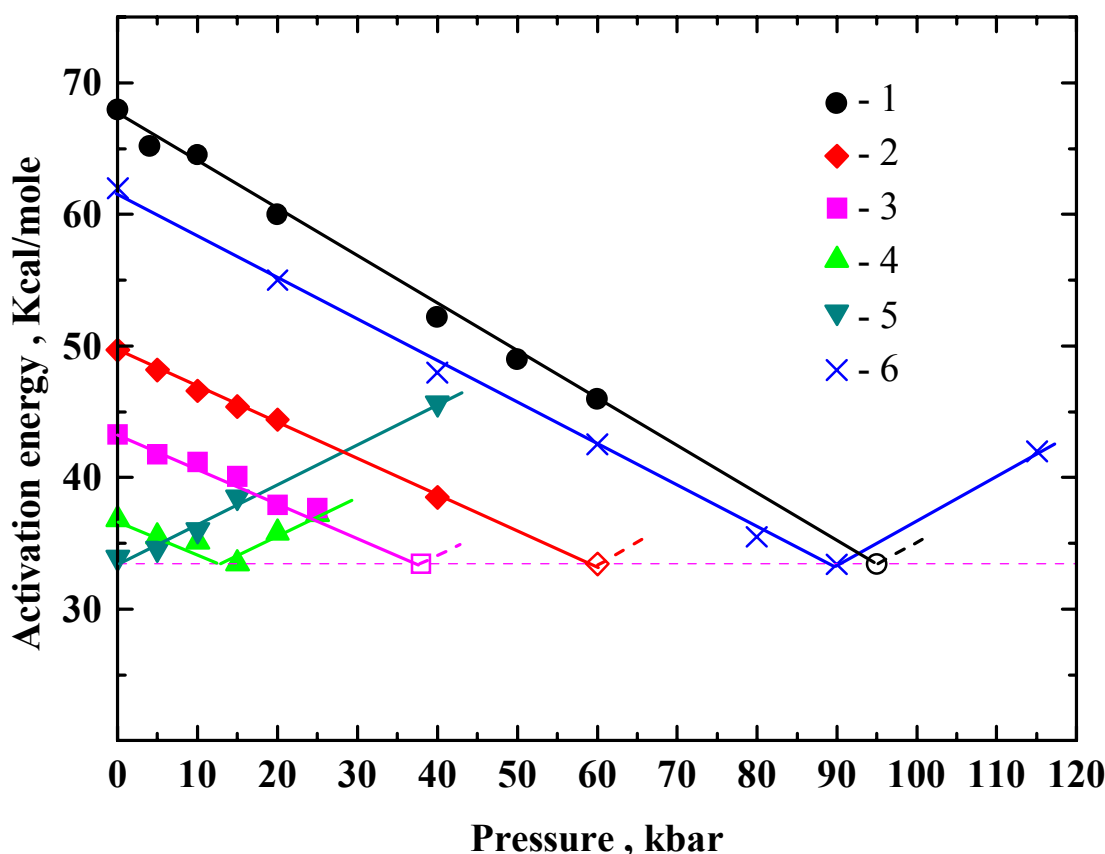
Fig.4. Dependence of the activation energy of viscous flow of the melts on pressure in the system Ab-Di and Jd. 1- Ab100; 2- Ab80Di20; 3- Ab57Di43; 4- Ab30Di70; 5- Di100; 6- Jd100 (open symbols stand for extrapolation values).

The conjecture on structural transitions of Al and Si in melts with pressure is in a full accord with the principle of phase relationships which means that an increase in temperature widens stability fields of highly polymerized phases (albite, quartz, etc.) and an increase in pressure, on the contrary, widens stability fields of depolymerized phases (jadeite, stishovite, etc.).

However, one may go along with the opponents of this theory [4] who argue that structural transitions $Al^{IV} \to Al^{VI}$ and $Si^{IV} \to Si^{VI}$ give no comprehensive explanation to anomalous nature of the η and E dependence on pressure for all the aluminosilicate and magmatic melts with the depolymerization degree $0 <= K < 200$. The theoretical analysis of the results of the present work showed that the structural transition $Al^{IV} \to Al^{VI}$ provides complete explanation to the anomaly of viscosity for the melts with the mole ratio of aluminum and silicon $\varepsilon = Al^{IV}/(Al^{IV}+Si^{VI}) >= 0.33$, for the jadeite melts in particular. At $\varepsilon < 0.33$ alongside with the transition $Al^{IV} \to Al^{VI}$ the weakening of the O-Al-O, O-

Si-O bonds due to reduction of their angles and ordering of the melt structure with pressure proposed in [5] will probably take place. The calculations showed that relative role of the second mechanism must decrease with increasing basicity of melts. For example, for the albite melt at P=95 kbar which corresponds to the minimal values of η and E, a full $Al^{IV} \to Al^{VI}$ transition is responsible for the about 70% of the observed decrease in η and E whereas for the melt of $Ab_{30}Di_{70}$ composition a full transition $Al^{IV} \to Al^{VI}$ at $P_{min}=15$ kbar provides about 90% of experimentally established decrease in η and E.

By and large as it is justly mentioned in [5] the direct investigations of the structure of aluminosilicate and magmatic melts at high T and P are needed in experiments "in situ" to uniquely understand the mechanism of the anomalous dependence of η and E of such melts on pressure.

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