#Temperature and pressure effects on viscosity of model and magmatic melts in the acid - ultrabasic series

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Abstract. Viscosity of melts of the system albite($NaAlSi_3O_8$) - diopside($CaMgSi_2O_6$) - H_2O has been studied at lithostatic pressures up to 50 kbar and H_2O pressures up to 5 kbar in the temperature range 1200° - 1900^oC using a few types high pressure apparatuses. Viscosity of the melts studied decreases with temperature according to the exponential law. It also decreases with increasing melts basicity. New comparable values of activation energies of viscous flow of studied melts have been obtained at high and super-high pressures. An inverse dependence of the viscosity and activation energy of viscous flow of model and magmatic melts as a function of lithostatic and water pressure has been first determined. Minima of the dependencies of melt viscosities and activation energies of viscous flow on lithostatic pressure were shown to shift into the region of lower pressures with increasing basicity of magmatic melts. A basis principles of a new structural - chemical model has been proposed for calculating and predicting the viscosity of magmatic melts at high and super-high pressures within the full range of their basicity.

Introduction.

Data on the viscosity of magmatic melts in the wide P-T range are of prime importance for understanding much of the processes of origin and evolution of magmas as well as their dynamics under the natural conditions of their existence in the Earth's crust and upper mantle and during volcanic processes.

In spite of a rather long history, up to now only the viscosity of silicate and magmatic melts from acidic to basic composition at the atmospheric and relatively low pressures, corresponding to the Earth's crust is well studied [2, etc.]. The highly essential investigations of the water- bearing ultrabasic melts, as well as the study of the viscosity of magmatic melts under the mantle P-T parameters are rather limited. In fact, such investigations have been just initiated. The mechanism of negative anomaly of pressure dependence of magmatic and aluminosilicate melt viscosities experimentally established in a number of works [1-8, etc.] is still under discussion. Besides, the development of a physical-chemical model for calculating and predicting the viscosity of magmatic melts remains a burning problem especially at P-T parameters of the upper mantle. The most appropriate model [2] allows to predict with high accuracy concentration (by petrogenic and volatile components) and temperature dependencies of the magmatic melt viscosities in the acidic to basic compositional series. However, the mentioned model can be only applied to the range of crust depths and pressure dependence of viscosity in this case is just empirical.

The model system albite-diopside-H_2O is a pretty good analogue of natural magmas in a wide range of compositions from rhyolite to lherzolite ones. Viscosity of some melts of this system was earlier studied at atmospheric [9] and high pressure[10]. However the study was carried out with volatiles-free melts and at a pressure not more than 25 kbar.

The present work is concerned with the effect of the major volatile component of magmas (H_2O) on the viscosity of some melts of the above system, the range of lithostatic pressures being widen up to 50 kbar. The results obtained on temperature and pressure dependencies of the melt viscosities are considered in relation to melt structure. Theoretical analysis of the results obtained allowed to suggest the basis principles of a new structural-chemical model for calculating and predicting the viscosity of magmatic melts at the P,T- parameters of the Earth's crust and upper mantle.

Apparatuses and experimental techniques.

Viscosity of some melts in the join Ab-Di-H_2O has been studied using the apparatuses of three types. High gas pressure radiation viscometer was described in detail earlier [1,2,18]. It was used to study melts viscosity at H_2O and Ar pressure up to 5 kbar. High pressure "anvil-with-hole" type [11] and split-sphere anvil type [22] apparatuses have been used for investigations of the viscosity of volatile-free melts in the join Ab-Di at pressure up to 50 kbar.

A falling (floating) sphere method has been used in all the experiments for viscosity measurements. Platinum and platinum-rhodium spheres ranging in diameter from 0.13 to 0.21 cm and filled with ^{60}Co were used for viscosity measurements in comparatively viscous melts using a radiation viscometer. Herewith, the extremely low activity of each sphere (< 10^{-4} Curie) provided safe experiments. We measured the time it took the sphere to cover the known distance between the collimators of the viscometer vessel at given T and P of the run. A "quenching" version of the falling sphere method was applied to measure viscosity of more viscous melts using all the mentioned above apparatuses. In this case very small spheres (0.01-0.05 cm) made of different materials (ruby, diamond, graphite, palladium) were used. The time of sphere falling in a melt was determined from the point of given T and P and to the point of quenching onset. The distance covered by the spheres during the run was determined in polished sections under microscope. The relative error of the viscosity measurement in this case was about twice as high as that of the radiation method (25-30 rel.% against 15 rel.%) [1,2].

The viscosity at given T and P was calculated by the Stokes' equation with the Faxen correction for the wall effect [2].

$$\eta= 2gr^2\Delta\rho[1-2.104r/r_a+2.09(r/r_a)^3 - 0.95(r/r_a)^5] / 9V(1+3.3r_a/h) \qquad (1)$$

where η is the melt viscosity (poise), g is a gravitation constant, r is a sphere radius (cm), $\Delta\rho$ is the difference between the sphere and melt densities (g/cm^3), V is the velocity of sphere falling in a melt (cm/sec), h and r_a are the height and the inner radius of the cylinder containing the melt (cm).

Table 1. Chemical composition of studied melts, wt.% (explanation in the text)

melt (mol.%)	SiO_2	Al_2O_3	Na_2O	MgO	CaO	H_2O	Σ	K
(Ab_{100}) $NaAlSi_3O_8$	68.73	19.45	11.82	---	---	---	100.0	0.0
$Ab_{93}(H_2O)_7$	67.65	18.90	11.54	---	---	1.9	99.99	14
$Ab_{85}(H_2O)_{15}$	65.86	18.40	11.24	---	---	4.5	100.0	34.2
$Ab_{75}(H_2O)_{25}$	64.21	17.94	10.95	---	---	6.9	100.0	50.1
(Di_{100}) $CaMgSi_2O_6$	55.51	---	---	18.75	25.74	---	100.0	200.0
$Di_{96}(H_2O)_4$	54.95	---	---	18.56	25.49	1.0	100.0	146.3
$Di_{92}(H_2O)_8$	54.68	---	---	18.47	25.34	2.0	100.0	123
$Ab_{80}Di_{20}$	65.75	14.45	8.92	4.65	6.22	---	99.9	33.2
$Ab_{57}Di_{43}$	62.7	10.65	6.5	8.45	11.8	---	100.1	67
$Ab_{30}Di_{70}$	59.30	5.56	3.43	13.25	18.46	---	100.0	120.0

When calculating viscosity by equation (1) corrections for compression and thermal expansion were taken into account. The melt density was determined by two ways:

1.the density of quenched melts (glasses) was measured by the method of hydrostatic weighting and correction for experimental temperature was introduced;

2.two spheres of different density were used simultaneously [1,21], one of which (diamond, $\rho=3.5$ g/cm^3) was falling within a melt and another one (graphite, $\rho=2.4$ g/cm^3 with corrections for T and P) was floating up. After the velocities of spheres falling (floating up) were determined, two Stokes' equations (eq.1) were used. The solving of both equations gave the viscosity and density of the melt. It should be noted that the mathematical analysis of the method errors showed that simultaneous determination of melt viscosity and density using two spheres of different density within an error of <1 rel.% requires the difference in sphere and melt densities be inessential - $\Delta\rho < 1.5$ g/cm^3 which imposes certain restrictions on using this original method [1].

Temperature range (1200-1900°C) was chosen so that liquidus interval of viscosity investigations was provided over the whole range of compositions studied. Platinum-rhodium and tungsten-rhenium thermocouples were used depending on the experimental target. As usual, the correction for pressure effect on the e.m.f. of thermocouples was not taken into account. The error of temperature measurements did not exceed $\pm5^o$C, and relative error of pressure measurements was $\pm1\%$.

The starting materials were homogeneous glasses prepared by melting the natural mineral powders and their stoichiometric gel mixtures. Platinum, molybdenum, or graphite capsules were used depending on the experimental parameters.

The chemical composition of the glasses obtained was determined by X-ray analyser of "Camebax" type. The results are summarised in table 1 which also presents the values of a structural-chemical parameter (the degree of depolimerization) K=100NBO/T. It was used to characterize the bulk chemical composition and structural peculiarities of magmatic melts [1, 2,17]. The bulk compositions of melts in mole amounts obtained by calculation to O_2 molar basis are presented in table1,2 (column1). It should

be noted that the choice of oxygen molar basis for comparing peculiarities of chemical compositions of polycomponent magmatic melts is still under discussion. The above problem is considered in detail in [1,2]. This work confirms that calculation of molecular quantities of melt components allowing for two oxygen molar basis is preferential for the analysis of concentration dependencies of rheological and other physical-chemical properties of magmatic melts.

Results and discussion.
Temperature dependence of melts viscosity.

The some results of the experimental study on melt viscosities in the join Ab-Di-H_2O are given in table 2. For comparison, the table also presents the results obtained by other authors [9,10] on the viscosity of some compositions of the mentioned system. The temperature dependence of viscosity of the melts studied is given in Fig.1. The diagram shows that the temperature dependence of viscosity of all these melts is adequately described by the well-known Arrhenius Frencel-Eyring equation [1].

η = η$_o$exp (E/RT) or
lg η=lg η$_o$ + E/4.576 T　　　　　　　　　**(2)**

where: η_o is a pre-exponential constant characterising viscosity of liquids at T→∞, T is the absolute temperature in K, E is the activation energy of viscous flow (cal/mole), R=1.987 cal/mole·K is the universal gas constant, η is the viscosity of melts in poises.

It should be noted that the pre-exponential constant value in eq. (2) does not depend on melt composition, temperature and pressure. Its numerical value is close to the theoretical one. The earlier theoretical analysis of all experimental data on temperature dependence of the viscosity of silicate, aluminosilicate, and magmatic melts showed that lgη$_o$ = - 3.5 ± 0.1 [1,2]. The results obtained in this work agree well with the above conclusion. On this basis, new comparable values of activation energies of viscous flow were obtained for the melts in the join Ab-Di-H_2O (table 2) as well as for the melts of the Ab-Di system studied earlier at atmospheric and high pressures [9, 10].

Table 2. Viscosity (η) and activation energy (E) of the melts in the join Ab-Di-H$_2$O; (explanation in the text);[*] - are the melts compositions obtained by calculation to O$_8$ molar basis (albite) and to O$_6$ molar basis (diopside), respectively from [9,10]; [**] - new values of E obtained on the base of experimental data from [9,10].

Comp. of melt (mol.%)	P_{lit} kbar	P_{H2O} kbar	T^{o}C	Log η η- pouses	E ,kcal/mole ($log\eta_o=3,5\pm0,1$)
Ab$_{100}$	10^{-3}		1400	5.25	68.0
	4		1400	5.02	65.2
	50.0		1800	1.77	
	50.0		1900	1.53	50.0
Ab$_{93}$(H$_2$O)$_7$	0.5	0.5	1200	4.58	
	0.5	0.5	1400	3.60	54.4
Ab$_{85}$(H$_2$O)$_{15}$	2.0	2.0	1200	3.75	
	2.0	2.0	1400	2.76	48.0
Ab$_{75}$(H$_2$O)$_{25}$	4.0	4.0	1200	3.0	
	4.0	4.0	1400	2.2	44.5
Di$_{100}$	10^{-3}		1600	0.47	33.9
	5.0		1600	0.54	34.6
	10.0		1600	0.7	36.0[**]
	40.0		1850	1.11	45.6
	50.0		1850	1.49	48.5
Di$_{96}$(H$_2$O)$_4$	2.0	2.0	1400	0.96	34.9
Di$_{92}$(H$_2$O)$_8$	5.0	5.0	1400	1.1	36.0
Ab$_{80}$Di$_{20}$ [*]Ab$_{75}$Di$_{25}$	10^{-3}		1500	2.79	49.7
	5.0		1600	2.32	48.2
	10.0		1600	2.17	46.6[**]
	15.0		1600	1.9	45.4[**]
	40.0		1800	0.61	39.0
	50.0		1900	0.12	36.0
Ab$_{57}$Di$_{43}$ [*]Ab$_{50}$Di$_{50}$	10-3		1400	2.3	43.3
	5.0		1600	1.66	41.8
	10.0		1600	1.28	41.2[**]
	15.0		1600	1.28	40.1[**]
	20.0		1850	0.36	37.5[**]
	50.0		1850	0.36	37.5
Ab$_{30}$Di$_{70}$ [*]Ab$_{25}$Di$_{75}$	10^{-3}		1500	1.3	36.8
	5.0		1500	0.94	35.5
	10.0		1600	0.7	35.1[**]
	15.0		1600	0.54	33.8[**]
	20.0		1600	0.78	35.8[**]
	50.0		1850	1.13	45.0

The activation energy of viscous flow is the major rheological and, accordingly, structural parameter of melts (see below). It is determined from the slope of experimental curve of temperature dependence of viscosity (fig. 1), i.e. by the simple equation:
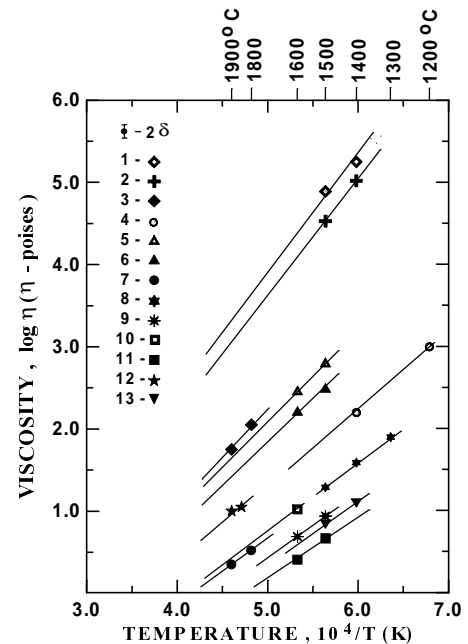
E= 4.576 T (lgη_T + 3.5) (3)

where: η_T is the melt viscosity at a temperature T, E is the activation energy, cal/mole.

Analysis of the diagram plotted in fig.1 and experimental data (table 2) shows that activation energy of viscous flow regularly decreases with increasing melt basicity, lithostatic and water pressure up to the melt of metasilicate composition (diopside). The viscosity and activation energy of such melts under isothermal conditions, on the contrary increase with increasing $P_{lith.}$ and P_{H2O} or H$_2$O content in melts. The change in the activation energy with changing melt basicity, P_{lith} , P_{H2O}, and N_{H2O} is a direct experimental evidence of the corresponding changes in melt structure.

The high lithostatic and water pressure effect on the viscosity of studied melts.

As it was noted, the effect of high pressures on the viscosity of magmatic and model melts needs further investigations, both theoretical and experimental. The effect of high pressure on molecular liquids of simple composition is reduced to the changes in free volume of liquids. As for magmatic melts this effect is manifold. Eutectic and cotectic ratios, phase relations , melt structure and, accordingly, rheological characteristics of magmas may change under high pressures. Besides, magmatic melts may exist in the Earth's crust and mantle under different pressures: lithostatic pressure , fluid pressure produced by the fluid phase, modelled in the present work by H$_2$O pressure.

Fig.1. Temperature dependence of the viscosity of studied melts. 1 -Ab$_{100}$, P = 1atm.; 2 - Ab$_{100}$, $P_{lit.}$= 4 kbar; 3 - Ab$_{100}$, $P_{lit.}$= 40 kbar; 4 - Ab$_{75}$(H$_2$O)$_{25}$, P_{H2O} = 4kbar; 5 - Ab$_{80}$Di$_{20}$, P = 1atm.; 6 - Ab$_{80}$Di$_{20,}$ $P_{lit.}$= 5 kbar; 7 - Ab$_{80}$Di$_{20,}$ $P_{lit.}$= 40 kbar; 8 - Ab$_{30}$Di$_{70,}$ P = 1atm.; 9- Ab$_{30}$Di$_{70,}$ $P_{lit.}$= 5 kbar; 10 - Ab$_{30}$Di$_{70,}$ $P_{lit.}$= 25 kbar; 11 - Di$_{100}$, P = 1atm.; 12 - Di$_{100}$, $P_{lit.}$= 40 kbar; 13 - Di$_{92}$(H$_2$O)$_8$, P_{H2O} = 5 kbar.

All the theories concerning liquid viscosity despite different conceptions they are based on, state that the viscosity of liquids should increase with pressure and obeys the exponential law [1,2]:

$$\eta^P = \eta_o \exp (P/P_o + E/RT), \qquad\qquad (4)$$

where P_o is the pressure producing an increase in viscosity by a factor of $e = 2.7$, η^P is the viscosity at given pressure - P, other symbols are borrowed from eq. (2).
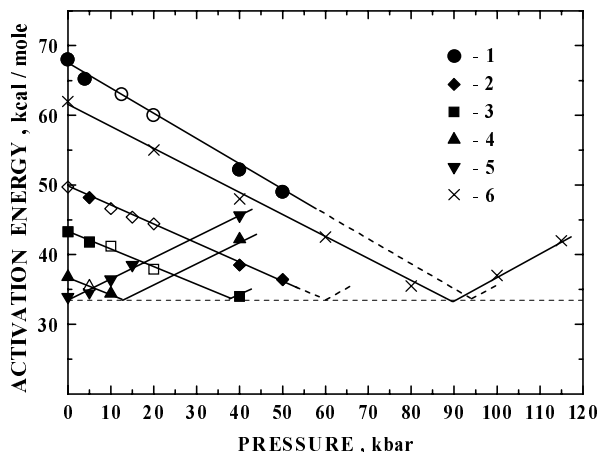

Fig.2. Pressure dependence of the activation energy of viscous flow of studied melts. 1 - Ab_{100}; 2 - $Ab_{80}Di_{20}$; 3 - $Ab_{57}Di_{43}$; 4 - $Ab_{30}Di_{70}$; 5 - Di_{100}; 6- Jd_{100} (the data for jadeite melts have been obtained in [3]; the dark symbols are experimental data of the present work, the open ones are a new calculated values which obtained using experimental data from [9 ,10].
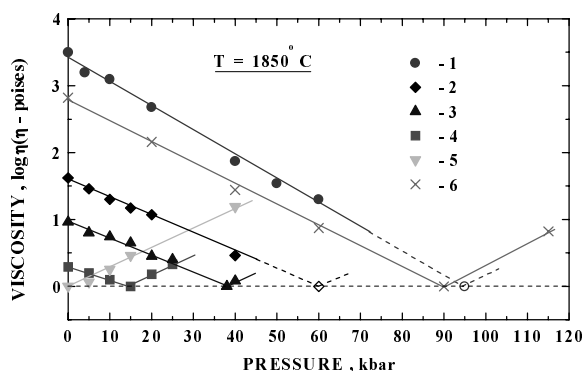

Fig.3. Pressure dependence of the viscosity of studied melts in the isothermal condition. (the calculated data at T=1850°C have been obtained using a new values of activation energy of viscous flow of studied melts). 1 - Ab_{100}; 2 - $Ab_{80}Di_{20}$; 3 - $Ab_{57}Di_{43}$; 4 - $Ab_{30}Di_{70}$; 5 - Di_{100}; 6- Jd_{100} (the viscosity of jadeite melts have been studied in [3]; the dark symbols are based on the experimental data, the open ones are extrapolated values).

Water is known to stand out against the total regularity for the molecular liquids of simple composition [12].

Shown in fig. 2 and 3 are the results obtained on the dependencies of viscosity (η) and activation energy of viscous flow (E) of model melts in the system albite-diopside on the lithostatic pressure. The results obtained indicate that viscosity and activation energy notably decrease with lithostatic pressure all over the compositional range, except the diopside melt. For the latter pressure dependencies of viscosity and activation energy are of the reverse character, i.e. η and E values for diopside melt increase with pressure. Absolute values of the derivatives $(d\eta/dP)_T$ and dE/dP systematically decrease with increasing melts basicity which is in full accord with the data obtained of the viscosity on pressure dependence in the system SiO_2-$CaAl_2O_4$ [13] and for the granite, andesite and basalt melts [1,2,18], (see below). It should be emphasised that the inverse pressure dependence of melts viscosity in the system Ab-Di was first experimentally obtained in [10] for $Ab_{25}Di_{75}$ melt composition. In the present work the such dependence was determined for the $Ab_{50}Di_{50}$. The same dependence was predicted in [3] and then experimentally determined for a jadeite melt at pressures up to 120 kbar in Tokyo University by the authors of work [3]. It should be emphasized that in the present work the inverse character of pressure dependence was proved for the activation energy of viscous flow which is a radically new result (see fig.2).

Analysis of the diagrams (fig.2,3) shows an extreme character of the dependencies obtained. Herewith, pressure in the minimum viscosity and activation energy points is strongly dependent on melt composition. It decreases with increasing melt basicity whereas the value of activation energies in the minimum points are independent on melt composition

and in the first approximation are equal to activation energy for viscous flow for metasilicate melt at atmospheric pressure.

An increase in η and E of both ultrabasic ($200 \leq K \leq 400$) and more polymerised melts ($0 \leq K < 200$) after minima points with pressure is in full agreement with the theoretical predictions (see eq. 4). However, an essential decrease in η and E of aluminosilicate and magmatic melts with pressure at the first stage is anomalous. The nature of this anomaly is still under discussion because none of modern theories of the viscosity of liquids is able to give a plausible explanation for this phenomenon. The more likely mechanism of this anomaly can involve the change of melt structure, i.e. the transformation of Al and Si cations in the melts from four- to six-fold oxygen coordination with pressure, i. e. Al and Si transformation from network-forming to modifier cations followed by an increase in depolymerization degree of melts. This idea was first proposed in [14] and it has been now supported by a great deal of experimental and theoretical data:

1. The study on the structure of glasses of albite and jadeite composition obtained by quenching the melts at pressures up to 100 kbar (10GPa) using the NMR-spectroscopy allowed to determine five- and six-fold coordinated Al cations in them [15, 16, Persikov et al., unpublished data].

2. Calculated E values for jadeite melts at pressures up to 90 kbar derived from the model [1, 2] taking account of an only assumption on the $Al^{IV} \rightarrow Al^{VI}$ transformation agree well with the later experimental data [3] (see Fig. 2).

3. The assumption on the structural transformation of Al and Si (at super-high pressures) in melts with pressure is in complete agreement with the principle of phase-relation. According to this principle an increase in temperature expands the stability fields of highly polymerised phases (albite, quartz, etc.) and vice versa an increase in pressure widens the stability fields of depolymerised phases (jadeite, stishovite, etc.).

However, we may agree with the opponents of this idea [7] who suggest that structural transformation $Al^{IV} \rightarrow Al^{VI}$ and $Si^{IV} \rightarrow Si^{VI}$ are not all-embracing explanation of the anomalous nature of the η and E dependence on pressure for all the aluminosilicate and magmatic melts with the depolymerization degree $0 \leq K < 200$. The theoretical analysis of the present work results showed that structural transformation $Al^{IV} \rightarrow Al^{VI}$ properly explains viscosity anomaly for the melts with the mole ratio of Al and Si, $\varepsilon = Al^{IV}/(Al^{IV}+Si^{VI}) \geq 0.33$, for the jadeite melts in particular. At $\varepsilon < 0.33$ together with the $Al^{IV} \rightarrow Al^{VI}$ transformation the weakening of O-Al-O, O-Si-O bonds is likely to have place due to the decrease of their angles and ordering of melt structures with pressure[7]. The calculations proved that the role of the second mechanism should decrease with increasing melt basicity. For instance, for the albite melt at P= 95 kbar which corresponds to the minimum η and E values the complete $Al^{IV} \rightarrow Al^{VI}$ transformation provides about 70 % of the observed decrease in η and E whereas for the melt of $Ab_{30}Di_{70}$ composition the complete transformation $Al^{IV} \rightarrow Al^{VI}$ at $P_{min}= 15$ kbar provides about 90% of the experimentally determined decrease in η and E. But as it is rightly noted in [16] only the direct "in situ" investigations of the structure of aluminosilicate and magmatic melts at high T and P by spectroscopy methods could cast light to the mechanism of anomalous η and E dependence of such melts on pressure.
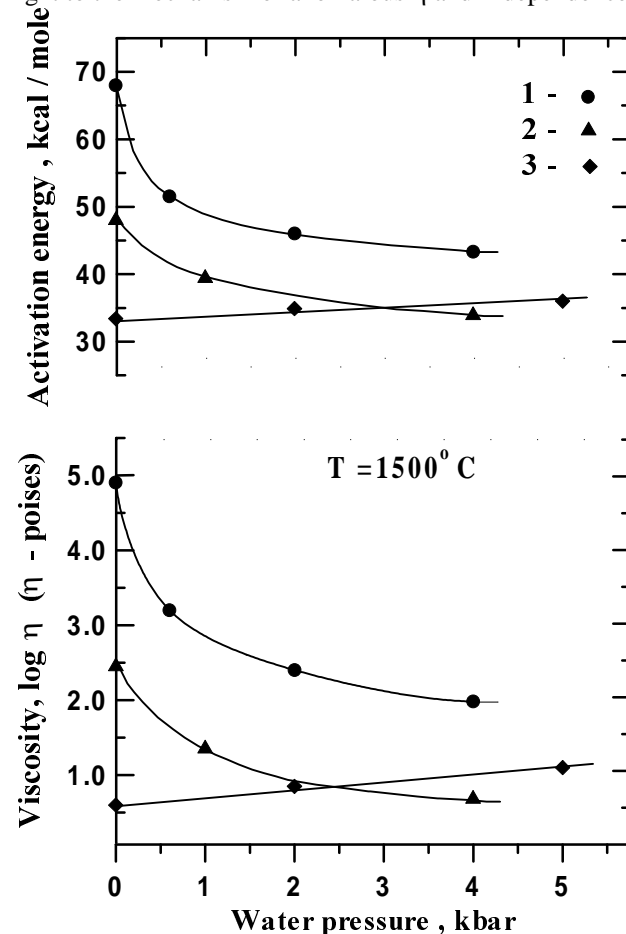
Fig.4. The high water pressures effect on viscosity and activation energy of viscous flow of studied melts. 1 - Ab_{100} ; 2 - basalt; 3 - Di_{100}.

The dependencies of rheological parameters (η, E) of model and magmatic melts on H_2O pressure are also of inverse character which is illustrated in fig. 4 by the example of albite, basalt and diopside melts. The above data show that viscosity and activation energy of albite and basalt melts decrease essentially whereas those of diopside melts, on the contrary, increase with increasing H_2O pressure which is obviously related to the peculiarities of H_2O dissolution in the melts of various basicity. This is experimental verification of the amphoteric nature of H_2O shown up at its dissolution in model and magmatic melts [1, 17, 18].

On the principle of acid-base interaction [19] and maximum polarity of chemical bonds [20], water dissolving in acid-basic melts and being a donor of free oxygen is a base relative to melt because its dissolution sets up depolymerization of melts, i.e. an increase of their basicity. The regular decrease in the activation energy of viscous flow in acidic-basic melts with increasing P_{H2O} or H_2O concentration in them is a direct experimental evidence of the above suggestion (see fig.4).

Water dissolving in ultrabasic melts by contrast is an acid relative to them and its dissolution leads to the polymerization (decrease in basicity) of ultrabasic melts and subsequent increase in the activation energy of viscous flow (see fig.4). The detailed analysis of the dissolution mechanism of H_2O in model and magmatic melts within the full range of their basicity is to be discussed in a special paper.

The basis principles of a new structural-chemical model for calculating and predicting the viscosity of magmatic melts at high and super-high pressures.

A new model is advanced version of the previous one developed on the same principles [1,2,18] : 1) structural-chemical approach; 2) maximally simple analytical dependencies; 3) high accuracy in predicting comparable with the uncertainties of experimental data on viscosity of aluminosilicate and magmatic melts especially at high pressures.
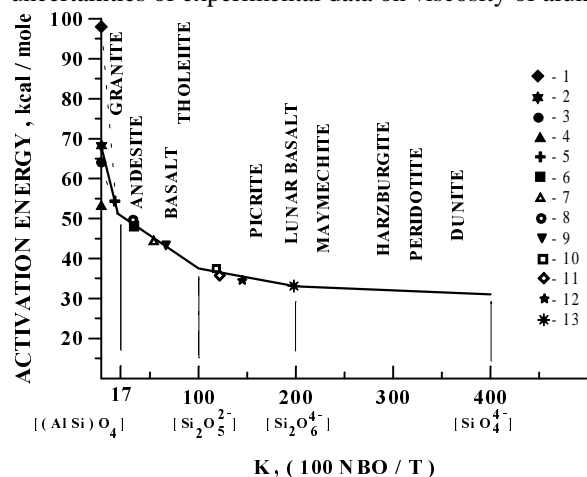

Fig. 5. Generalized structural-chemical dependence of the activation energy of viscous flow for silicate, aluminosilicate and magmatic melts (explanation in the text). 1 - SiO_2; 2 - Ab_{100}; 3 - Jd_{100} ; 4 - Nef_{100}; 5 - $Ab_{93}(H_2O)_7$; 6 - $Ab_{85}(H_2O)_{15}$; 7 - $Ab_{75}(H_2O)_{25}$; 8 - $Ab_{80}Di_{20}$; 9 - $Ab_{57}Di_{43}$; 10 - $Ab_{30}Di_{70}$; 11 - $Di_{92}(H_2O)_8$; 12 - $Di_{96}(H_2O)$; 13 - Di_{100} (in square brackets are the basic terms of the melt anion structure).

Fig.5 presents the generalized diagram of concentration dependence of activation energies of viscous flow for silicate, aluminosilicate, and magmatic melts throughout the basicity range from acidic (quartz, albite, granite melts) to ultrabasic (orthosilicate, peridotite, dunite melts) ones. It is somewhat corrected as compared to that considered in [1,2,18] to take account of the experimental data for the last decade including those of the present work.

The chemical composition and structural peculiarities of melts are described using mentioned above the structural-chemical parameter K= 100NBO/T, i.e. the ratio of non-bridging oxygen (NBO=O^{2-} +O^-) of a melt to the sum of the network-forming cations T=Σ (Si^{4+} +Al^{3+}+ Fe^{3+}). As the similar diagram (fig.5) has been considered in [1, 2,18] we shall dwell just on some details.

The inflections in the dependence E= f(K) characterize the qualitative changes in the melt structure and are interpreted in terms of the silicate melts theory [1,2]: at K=17 the break down of a three dimensional framework structure is completed, and at K= 100, 200, and 400 formation of di-, meta-, and orthosilicate structures of melts, respectively, is brought to end.

A fan of functional dependencies E=f(K) characteristic for the first range (acidic melts) is governed by the different ratio of network-forming cations Al^{IV} and Si^{IV} being in four-fold oxygen coordination, i.e. by the ratio ε = $Al^{IV}/(Al^{IV}+Si^{IV})$. The quartz ($\varepsilon$=0), albite or granite ($\varepsilon$=0.25), jadeite ($\varepsilon$= 0.33) and nepheline ($\varepsilon$=0.5) branches are given as an example in fig. 5. The dependence E= f(ε) for silicate (K=0) and sodium aluminosilicate melts is shown in fig.5. Such an essential decrease in the activation energy of viscous flow at the transition from silicate (ε=0) to sodium-

aluminosilicate melts is dictated by a remarkable difference in bond energies Si-O (about 109 kcal/mole) and Al-O (about 80 kcal/mole) [1, 2,18]. The results presented in fig.6 are approximated by the following dependence:

$$E_\varepsilon = 98 - 158\varepsilon + 152\varepsilon^2 \text{ kcal/mole} \qquad (5)$$
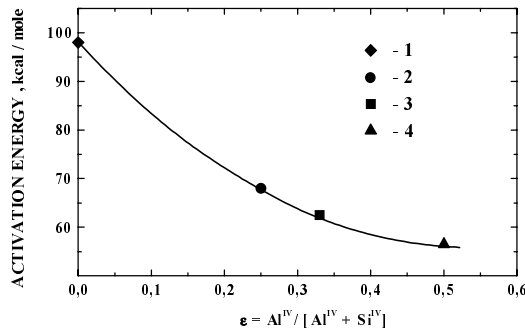

Fig.6. The dependence of activation energy of viscous flow of model melts on relation of Si^{IV} and Al^{IV} (ε) in them (explanation in the text).). 1 - SiO_2; 2 - Ab_{100}; 3 - Jd_{100} ; 4 - Nef_{100} .

It is clear that the energy of the bonds between cations- modifiers (K, Na, Ca, Mg) and oxygen are non equivalent in the .first basicity range. So at K=0 and ε=0.5 a complete substitution of potassium cations (calcilite) by calcium cations (anorthite) causes an essential decrease in the activation energy for viscous flow from 59 kcal/mole for the calcilite melt ($KaAlSiO_4$) to 42.5 kcal/mole for the anorthite melt ($CaAl_2Si_2O_8$). This problem is partially discussed in [1, 10, etc.] and will be considered in detail as concerned silicate and alumosilicate melts in a special paper.

With this we should note that for polycomponent magmatic melts of normal series (ε=0.25) the effect of an individual cation-modifier is levelled and when the framework structure breaks down (K>17), i.e. in the other three compositional ranges the structure of silicate and aluminosilicate melts becomes indistinguishable in energy because at the same K their activation energies become equal.

The fourth compositional range (ultrabasic melts) given in fig.5 is characterized by a very small change of the activation energies of viscous flow (from 33.4 to 32.4 kcal/mole) at the transition from metasilicate (diopside) to orthosilicate (forsterite) melts despite an essential (by a factor of two) change in the depolymerization degree. It means that metasilicate and orthosilicate liquids offer comparable resistance to viscous flow. Probably, the metasilicate structure of magmatic melts is limiting and makes the inverse character of pressure dependence to show up. This assumption is supported by experimental data on diopside (fig.2, 3) and sodium metasilicate melts [5].

Linear approximation of the dependencies E=f(K) given in fig.5 has produced the simple equations for calculating E of magmatic melts in each of the four compositional ranges:

The first range (acidic melts)

O≤K≤17, for model aluminosilicate melts:

$$E_1^{ch} = K/17 (51.6 - E_\varepsilon) + E_\varepsilon \text{ kcal/mole} \qquad (6)$$

where E_ε was calculated by equation (5).

For magmatic melts of normal series (ε=0.25) the equation for calculating E in the first range looks like:

$$E_1^{ch} = 68 - 0.965K, \text{ kcal/mole} \qquad (7)$$

The second range (intermediate, basic melts)

17 ≤ K≤100

$$E_2^{ch} = 54.4 - 0.165K, \text{ kcal/mole} \qquad (8)$$

The third range (basic, ultrabasic, and picrite melts)

100≤K≤200

$$E_3^{ch} = 42.4 - 0.045K, \text{ kcal/mole} \qquad (9)$$

The fourth range (ultrabasic melts)

200≤K≤400

$$E_4^{ch} = 34.4 - 0.005K, \text{ kcal/mole} \qquad (10)$$

The correlation coefficients of the dependencies proposed (equations 6-10), obtained by the method of linear regression were 0.96, 0.97, 0.98, 0.98, 0.95, respectively.

It should be emphasised that either diagram (fig.5) or equations (6) – (10) account only for the effect of chemical interaction of melt components on viscous flow including the effect of volatile components such as H_2O, CO_2, F, Cl etc. By this it meant that data presented on the diagram refer to melts at the atmospheric pressure or under the conditions when $P_{tot.}=P_{fl}$. If the fluid component dissolves into melts by the two-stage mechanism (chemical and physical dissolution), the contribution of the dissolved component is considered in its own right, for example for H_2O by the following simple equation:

$$E = E^{ch} - (E^{ch} - E_{H2O}) X_{H2O}, \text{ kcal/mole} \qquad (11)$$

where X_{H2O} is the amount of physically dissolved H_2O, mole% ; $E_{H2O} = 2$ kcal/mole is the activation energy of pure water [1,2,18]; E is the activation energy, which accounts for the both forms of water dissolution in melts.

The diagram $P_{min.} = f(K)$ (fig.7) was proposed to consider the effect of lithostatic pressure on rheological parameters (η, E) of magmatic melts. When plotting the diagram, all the structural-chemical criteria of the diagram E= f(K) (see fig.5) were used. As shown above, the pressure corresponding to the minimum viscosity (η) and activation energy (E) regularly decreases with basicity of magmatic melts (see fig. 2, 3) up to 0 (atmospheric pressure in real experiments) for metasilicate melts of diopside whose structural-chemical parameter is equal to 200. The analysis of the diagram $P_{min}= f(K)$ (fig.7) showed that linear approximation fairly well describes experimental data at $100 \leq K \leq 200$, i.e. in the third compositional range (basic- ultrabasic, picrite). Therefore, by linear approximation we obtained analytical dependencies $P_{min}=f(K)$ for the first and second compositional ranges in which the inversion points of pressure dependencies of rheological properties of magmatic melts (η, E) have not been determined experimentally and only extrapolated values of minima points have been obtained (fig.2, 3). The dependencies obtained by the method of multiple regression analysis are as follows:

1.the first range $0 \leq K \leq 17$

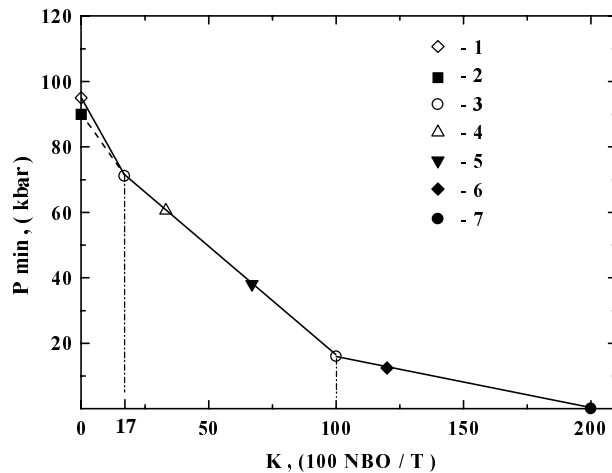$$P_{min}=95 – 1.394K \text{ , kbar} \qquad (12)$$

Fig.7. The structural-chemical dependence of minimum pressures (Pmin). 1 - Ab_{100}; 2 - Jd_{100} ; 3 - the inflection points for the melts at K = 17 and K = 100; 4 - $Ab_{80}Di_{20}$; 5 - $Ab_{57}Di_{43}$; 6 - $Ab_{30} Di_{70}$ (explanation in the text, closed symbols are the experimental data, open symbols are the extrapolated values).

Note that in the above compositional range the minimum pressure value is dependent on the ratio of network-forming cations (Si, Al etc.) and cations – modifiers (K, Na, Ca, Mg etc.). However, deep seated magmatic melts do not belong to the first compositional range of melt basicity and for the simpler model systems the pressure effect on viscosity is inessential (from the technological point of view);

2. the second range $17 \leq K \leq 100$

$$P_{min}= 82.6 –0.666K, \quad \text{kbar} \qquad (13)$$

3. the third range $100 \leq K < 200$

$$P_{min}=32 – 0.16K, \text{kbar} \qquad (14)$$

The correlation coefficients of the dependencies proposed (equations 12-14) were 0.96, 0.97, and 0.97, respectively.

The generalised equation for calculating and predicting concentration, temperature, and pressure dependencies of the viscosity of magmatic melts takes the following form:

$$\eta_T^P = \eta_0 exp(E^P/RT) \qquad (15)$$

where E^P is the activation energy for viscous flow at given P in cal/mole; other symbols are the same as in eq. (2).

$$\text{or} \quad lg\eta_T^P = E^P/ 4.576T - 3.5 \qquad (16)$$

For negative slope curves of the dependence $\eta = f(P)$ the equation for calculating E^P is suggested:

$$E^P = E^{ch} – AP, \text{ kcal/mole} \qquad (17)$$

where $E^{ch} = f(K)$ is the activation energy of viscous flow for the melts at atmospheric pressure or at $P= P_{H2O} = P_{fl}$ which well reflects the chemical interaction of melt components and is calculated by eqs. (6) – (10); P is the pressure, kbar;

$$A = (E^{ch}-Emin) / Pmin \qquad (18)$$

where A is the tangent of the curves slope angle in fig 2 (up to E_{min}); $E_{min} =33$ kcal/mole is the minimum value of activation energy; $P_{min} = f(K)$, kbar, is calculated by eqs. (12) – (14).

The positive sections of the dependencies $E^P=f(P)$ and $\eta^P=f(P)$ are well described by theoretical equation (4), which can be represented as follows:

$$E^P = E_{min} + B\,P, \quad \text{kcal/mole} \qquad (19)$$

where B=0.33 is a slope tangent of the curves E= f(P) (fig.2) which in the first approximation does not depend on melt composition.

The generalized dependence of the viscosity and activation energy for viscous flow of aluminosilicate and magmatic melts should have two minima and one maximum. The minima would correspond to complete transformation of Al and Si from four to six-fold oxygen coordination, respectively. The maximum may correspond to the beginning of .transformation of the Si^{IV} to the six-fold oxygen coordination [3, 6].

Consequently, rheological properties of melts were calculated by the proposed structural-chemical model using the following scheme:

1. K is calculated from the chemical composition of a melt [1,2];

2. E^{ch} is calculated as dictated by the obtained K value from equations (6) – (10), and P_{min} from eqs. (12)-(14), respectively.

If the obtained K values fall in the range $0 \leq K < 200$, the activation energy for viscous flow is calculated from eqs. (17, 18) at given P and then melt viscosity is calculated from eq. (16) at required temperatures.

In case $200 \leq K \leq 400$, E^P at given P is calculated from eq. (19) and then melt viscosity is calculated from eq. (16) at required temperatures.

In conclusion it should be emphasised that within the uncertainty limits of the proposed model ($\Delta\eta = \pm 30$ rel.%, $\Delta E = \pm 1$ rel.%) the calculated values (straight lines in figs. 1, 2, 3) agree well with the experimental data on the system Al-Di-H_2O (marks in figs. 1, 2, 3).

Doubtlessly, the viscosity of magmatic and model aluminosilicate melts needs further experimental investigations at high and superhigh pressures so that E^P and P_{min} will be obtained for other melt compositions at the intermediate K values.

Conclusions.

The viscosity and activation energy for viscous flow of some melts of the system Ab-Di-H_2O have been first determined at high and super-high pressures. The inverse character of the dependence of activation energy for viscous flow and viscosity on lithostatic and water pressures has been established.

The basis principles of a new structural-chemical model for calculating and predicting the viscosity of model alumosilicate and magmatic melts at high and super high pressures have been proposed.

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