

Chapter 4

Experimental and Theoretical Studies of the Viscosity of the Fluid Magmatic Systems in Conjunction with the Structure of Melts at the Thermodynamic Parameters of the Earth's Crust and Upper Mantle



E. S. Persikov and P. G. Bukhtiyarov

Abstract Paper provides a brief overview of the results of the established general regularities of the concentration, temperature, pressures and phase dependency of viscosity of the fluid-magmatic systems in connection with the anniversary of IEM RAS (50 years have passed since the establishment of this unique Institution). The study of the viscosity of such melts was carried out in the full range of compositions of natural magmas (acid-ultrabasic) in a wide range of fluid compositions (Ar, H₂O, H₂O + HCl, H₂O + NaCl, H₂O + HF, CO₂, H₂O + CO₂, H₂), and thermodynamic parameters of the earth's crust and upper mantle ($T = 800^{\circ}$ – 1950° °C, $P = 100$ MPa– 12.0 GPa, $P_{fl} = 10$ – 500 MPa). The study of the viscosity of such melts was carried out in the IEM RAS in conjunction with the study of structural features of melts. The features of the unique equipment and techniques developed in the IEM RAS for such original studies are briefly considered. The possibilities and advantages of the developed structural-chemical model of reliable predictions and calculations of viscosity of fluid-magmatic systems in the full range of magma compositions from acidic to ultramafic at thermodynamic parameters of the earth's crust and upper mantle are discussed. Some examples of successful application of the obtained experimental and theoretical results to natural processes are briefly considered.

Keywords Viscosity · Structure · Acidic-ultramafic melts · High temperatures and pressures · Activation energy · Crust · Mantle · Model · Sphere

4.1 Introduction

The processes of origin of magmatic melts in the earth's crust and upper mantle, kinetics and dynamics of their evolution in a variable range of temperatures and

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pressures, structural and textural features of magmatic rocks, the processes of differentiation, and partial melting are largely control by the viscosity of magma. The great diversity in the composition of main and volatile components, heterogeneity, a wide range of temperatures and pressures are the main features of the existence of magmatic melts in nature. Experimental study of viscosity of such systems at high temperatures and pressures is an important and at the same time complex scientific problem.

Significant results have been obtained of the experimental and theoretical study of the viscosity of model and magmatic melts in the process of intensive development of experimental methods of physical-chemical petrology and geochemistry over the past half a century. It should be noted that progress in this field of petrology and geochemistry has been achieved by many researchers in various laboratories of the world, for example: (USA—Shaw et al. 1968; Shaw 1972; Waff 1975; Mysen et al. 1979; Mysen 1991; Hui and Zhang 2007; Lange 1994; Kono et al. 2014; Wolf and McMillan 1995; Allwardt et al. 2007; and other); (France—Carron 1969; Bottinga and Well 1972; Richet 1984; Neuville and Richet 1991; Champaller et al. 2008; and other); (Germany—Dingwell 2006; Dingwell et al. 2004; Hess and Dingwell 1996; Reid et al. 2003; Liebske et al. 2005; Behrens and Schulze 2003; and other), (Japan—Kushiro 1980; Fujii and Kushiro 1977; Uhira 1980; Ohtani et al. 2005; Suzuki et al. 2005; and other); (Canada—Brealey et al. 1986; Scarfe 1986; Scarfe et al. 1987; Russell et al. 2002, 2012; and other); (Italy—Giordano and Dingwell 2003; Giordano et al. 2004, 2008; Vetere et al. 2010; Poe et al. 2006; and other); (England—Sparks et al. 2009; Dobson et al. 1996; and other); (Russia—Volarovich 1940; Lebedev and Khitarov 1979; Sheludyakov 1980; Ivanov and Stiegelmeier 1982; Chepurov and Pokhilenko 2015; and others), including our long-term research in IEM RAS (Persikov 1984, 1991, 1998; Persikov and Bukhtiyarov 2004, 2009; Persikov et al. 1990, 2018a; and others). This paper provides a brief overview of the results of the established generalized regularities of temperature, pressure, concentration and phase dependences of the viscosity of fluid-magmatic systems in the full range of compositions of natural magmas (acid-ultrabasic) and thermodynamic parameters of the earth's crust and upper mantle ($T = 800\text{--}1950\text{ }^{\circ}\text{C}$, $P = 20\text{ MPa--}12.0\text{ GPa}$, $P_{\text{H}} = 20\text{--}500\text{ MPa}$). The study of the viscosity of such melts is carried out in conjunction with the study of the structural features of the melts. The developed structural-chemical model of reliable predictions and calculations of viscosity of fluid-magmatic systems in the full range of magma compositions from acidic to ultramafic at thermodynamic parameters of the earth's crust and upper mantle are also discussed. Some examples of successful application of experimental and theoretical results to natural processes are briefly considered.

4.2 Experimental and Analytical Methods

Viscosity of model and magmatic melts without and with volatile components was investigated using four types of original equipment. Unique high gas pressures radiation viscometer, discussed in detail earlier (Persikov 1991), was used to study the viscosity of melts of different compositions at fluid pressures up to 500 MPa (developed in IEM RAS). Solid-state high pressures apparatuses were used to study the viscosity of melts at pressures up to 12 GPA: (1) The “anvil with a hole” type apparatus (developed in IEM RAS, e.g., Litvin 1991). (2) The multi-anvil devices of the “BARS” type (developed in IGM SB RAS, e.g., Sokol and Palyanov 2008). (3) “Kawaii” type apparatuses (developed at Tokyo University, Japan, e.g., Persikov et al. 1989). To conduct experiments on the synthesis of fluid-bearing glasses and subsequent experiments on measurements of melt viscosity at high temperatures and fluid pressures of almost any composition, a unique device has been developed, which is located inside the high gas pressure vessel (IHPV) of the radiation viscometer (Persikov and Bukhtiyarov 2002). The scheme of this device with the scheme of the internal heater of the IHPV is shown in Fig. 4.1. The internal volumes of the reactor (5) with a platinum or molybdenum ampoule with a starting sample (6) and a separator equalizer (9) under the piston (10) were filled with a fluid of the required composition at a pressure of 10 MPa using a special system. In experiments with water fluid the mentioned internal volumes of the device were filled with purified water at atmospheric pressure. The device assembled in this way, together with the internal heater (2), was placed inside the IHPV so that the ampoule with the sample (6) was in the gradient-free temperature zone of the heater. Due to the displacement of the piston (10), the gas pressure (Ar) in the IHPV during the experiment was always equal to the fluid pressure in the internal volume of the reactor (5). At the beginning of the experiment on the synthesis of fluid-bearing glasses, the pressure of Ar in the IHPV and, accordingly, the fluid in the reactor (5) was raised within one hour to the required value, for example 100 MPa. Further, the temperature of the experiment was raised to the required value. At these parameters, the samples were kept in automatic mode for the required time of experiments. After that, isobaric quenching was carried out with the internal heater turned off. At the same time, a sufficiently high melt quenching rate (~ 300 °C/min) was achieved, which ensured the production of quenched glasses with a fluid dissolved in them. After isobaric quenching, the device was removed from the IHPV, an ampoule with a sample (6) was extracted from the reactor for subsequent analysis of the glass composition and for experiments on measurements of melt viscosity. In experiments with oxidizing fluid, the inner surface of the reactor (5) was lined with platinum to prevent oxidation of the molybdenum reactor. The falling sphere method was used to measure the melt viscosity in all experiments. Platinum or platinum-rhodium spheres with a diameter of 0.13–0.21 cm, filled with radioactive isotope Co^{60} and manufactured in a special device, were used to measure the viscosity of relatively viscous polymerized melts on a radiation viscometer. At the same time, full safety of work was ensured, since the activity of each sphere was very low ($\leq 10^{-4}$ curie). The time of falling of the

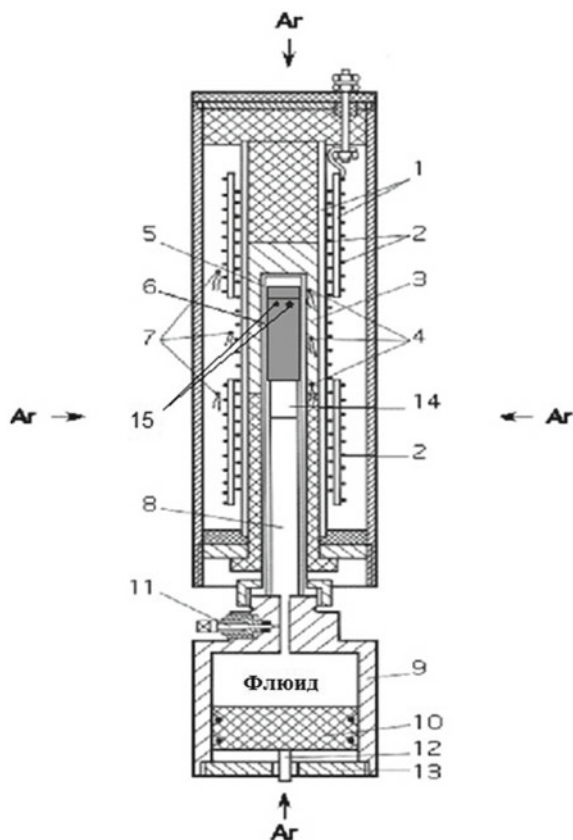


Fig. 4.1 Scheme of the unique internal device and heater of IHPV. 1, 3—insulators; 2—two windings of the heater; 4—three thermocouples to control gradient free zone along the Pt capsule with the sample; 5—molybdenum tube; 6—Pt ampoule with sample (melt) and spheres; 7—two thermocouples to control the temperatures of each windings of the heater; 8—sapphire cylinder; 9—vessel of the separator-equalizer; 10—piston of the separator-equalizer; 11—valves; 12—sensor to control of the piston position; 13—cover; 14—Pt ampoule with oxygen buffer; 15—two Pt60Rh40 spheres of different diameter

sphere in the melt of a certain distance between two collimators of the viscometer (the distance between the maxima of gamma radiation intensity) at the experiment parameters was measured in such kind experiments. To measure the viscosity of low-viscosity depolymerized melts on all types of apparatus, a quenching version of the falling sphere method was used. In this case, two platinum-rhodium spheres of small and different diameter (50–250 μk) were used as a rule. The spheres made by wire fusing with water quenching. The time of falling of the spheres in the melt was determined from the moment of reaching the required values of temperature and pressure of the experiment to the moment of isobaric quenching. The distances covered by the spheres in quenching experiments were determined in sections under

a microscope. Naturally, the viscosity measurement error increased by about half (up to 25–30 rel. %) compared with the radiation method of viscosity measuring (≤ 15 rel. %). The melt viscosity at given T and P was calculated according to the known Stokes law with the Faxen correction for the wall effect (e.g., Persikov 1991):

$$\eta = \frac{2gr^2\Delta\rho}{9V(1 + 3, 3r/h)} \left[1 - 2, 104 \frac{r}{r_a} + 2, 09 \left(\frac{r}{r_a} \right)^3 - 0, 95 \left(\frac{r}{r_a} \right)^5 \right] \quad (4.1)$$

where g is the gravitational constant, r is the radius of the falling sphere, r_a is the internal radius of the ampoule with the melt, $\Delta\rho$ is the density contrast between the sphere and the melt, V is the falling velocity, h is the height of the ampoule. The term in square brackets is the Faxen correction for the wall effect.

Calculation viscosity with Eq. (4.1) requires a knowledge of melt and sphere densities. The melt density was determined by the next way: the density of quenched melts (glasses) from runs at the different pressures was measured by the method of hydrostatic weighting. The correction for experimental temperatures was applied. The spheres density at normal conditions was measured by the same method of hydrostatic weighting and was used to calculate the melts viscosity by Eq. (4.1). The correction on temperature and pressure on spheres density was not used because the temperature and pressure have opposing effects (Persikov 1991; Liebske et al. 2005). In fact, the melt density can vary from 2.46 to 3.09 g/cm³ without changing the calculated viscosity by more than $\pm 3\%$ (Brearley et al. 1986; Persikov et al. 2018a). The relative error of viscosity measurements calculated was ± 15 –30% rel. Temperature range (800–1950 °C) was chosen so that liquidus interval of viscosity measurements was provided over the whole range of pressures and for all studied compositions (in the limit of ~ 200 –250 °C above the corresponding liquidus temperatures). Platinum-rhodium or tungsten-rhenium thermocouples calibrated at the different pressures using melting points of Au, Al and Ag were used. Relative errors of temperature measurement did not exceed ± 5 °C on a radiation viscometer and ± 20 °C on solid-phase high pressure devices. As usual, the correction for pressure effect on e.m.f. of thermocouples was not taken into account for these devices. The relative error of pressure measurement on the radiation viscometer did not exceed $\pm 0.1\%$ using a special pressure sensor. The error of pressure measurement on solid-phase high pressure devices did not exceed ± 0.1 GPa. A characteristic feature of the performed experiments is the wide range of fluid compositions used to study viscosity of the fluid-magmatic systems: Ar, H₂O, H₂O + HCl, H₂O + NaCl, H₂O + HF, CO₂, H₂O + CO₂, H₂. Homogeneous glasses prepared by melting of powders of natural minerals and rocks, as well as synthetic glasses obtained by melting stoichiometric mixtures of natural minerals at a temperature of 1400 °C and ambient pressure were used as starting materials in the experiments. A pressure of CO₂ equal to 100 MPa at a temperature of 1400 °C were used to prepare the starting materials for the experiments with carbonate-bearing model kimberlite and dunite melts.

Chemical composition of the starting glasses and run products were determined by microprobe analysis, on CamScan MV2300 (VEGA TS 5130 MM) digital electron microscope with INCA Energy 450 and Oxford INCA Wave 700 energy dispersive

X-ray spectrometry (EDS). Analyses were conducted at an acceleration voltage of 20 kV with a beam current of 0.3 nA and counting time was 50–100 s. The following standards were used: SiO₂ for Si and O, albite (NaAlSi₃O₈) for Na, microcline for K, wollastonite (CaSiO₃) for Ca, pure titanium for Ti, corundum for Al, pure manganese for Mn, pure iron for Fe, periclase for Mg. Data reduction was performed using the standard INCA Energy 200 and the INCA program of A. Nekrasov (IEM RAS). The concentration of water in the quenching melts (glasses) was determined by Karl-Fischer titration method using KFT AQUA 40.00 device and IR spectroscopy. CHN-1 type gas chromatograph is used to determine the concentration of H₂ in glasses. The concentration of Cl in quenched melts (glasses) were determined by the method of microprobe analysis, the F concentration by the photometric method using analazon of chelating agent (Persikov et al. 1990). The concentrations of the two forms of water (hydroxyl OH⁻ and molecular water H₂O) and carbon dioxide (CO₃²⁻ and CO₂) in quenched melts (glasses) were measured using the methods of Raman and IR spectroscopy. Raman spectroscopy was mainly used to qualitatively illustrate the dissolution of the carbonate form in melts (glasses). Raman spectra of the glasses were obtained using a RENIS/HAW-1000 spectrometer equipped with a Leica microscope. The slit width for spectra was 50 μk, and the spectra were processed using the standard GRAMS program. The results of microprobe analyses of some samples are shown in Table 4.1, which also shows the values of the structural-chemical parameter of the melts—the degree of depolymerization or basicity coefficient ($K = 100\text{NBO}/\text{T}$) used for comparative evaluation of the chemical composition and structure of magmatic melts (see below).

The water content in melts (glasses) for different types of dissolved water (OH⁻ groups and H₂O molecules) was determined by quantitative infrared microspectroscopy using the Bouguer-Beer-Lambert ratio (Stolper 1982; Persikov et al. 2010):

$$C = 100 \cdot 18.015 \cdot A / (\rho \cdot \delta \cdot \varepsilon_{\text{H}_2\text{O}}), \quad (4.2)$$

where C is the concentration of the corresponding forms of water (OH⁻ or H₂O) in the melt (glass) wt%, A is the peak height of the absorption, ρ is the glass density, g/L, δ —thickness of the plate, cm, $\varepsilon_{\text{H}_2\text{O}}$ —molar absorption coefficient of the appropriate type of water, L/mol cm, 18.015 is the molecular weight of water, g/mol.

The thickness of the glass plates was determined by a micrometer with an error of ± 2 μk. IR spectra of hydration samples were obtained using the infrared spectrometer Nicolet Magna-IT 860, equipped with a microscope Nicolet Continuum IR (Caltech, USA). The total concentration of water in the melt (glass) was determined by summing the concentrations of its two forms, determined by the reduced Eq. (4.2).

Table 4.1 The chemical composition of some melts (glasses, wt%) and their structural-chemical parameter ($K = 100NBO/T$)

Acidic-mafic melts and melts of some minerals															
Samples	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	H ₂ O	OH ⁻	Σ	K
Granite	73.23	0.19	13.6	2.56	0.48	0.20	0.17	1.69	3.78	4.11	0.13	-	-	99.94	0.3
Granite + H ₂ O	69.22	0.18	12.84	2.46	0.56	0.18	0.17	1.59	3.66	3.98	0.13	-	5.20	99.99	41.0
Andesite	58.56	0.64	18.98	3.95	3.90	0.15	3.48	6.17	3.24	0.92	-	-	-	99.84	17
Andesite + H ₂ O	55.92	0.62	18.14	1.72	6.00	0.14	3.3	5.86	3.08	0.9	0.10	-	4.60	100.1	63
Basalt	53.54	1.05	17.29	7.46	1.11	0.12	5.46	8.32	3.59	1.64	0.21	-	-	99.95	47
Basalt + H ₂ O	50.2	0.98	16.2	2.91	5.31	0.1	5.12	7.8	3.37	1.54	0.19	2.36	4.0	99.98	103
Albite	68.73	-	19.45	-	-	-	-	-	11.82	-	-	-	-	100	0
Albite + H ₂ O	64.21	-	17.94	-	-	-	-	-	10.95	-	-	0.5	6.4	100	50
Jadete	59.45	-	25.22	-	-	-	-	-	15.33	-	-	-	-	100	0
Diopside	55.51	-	-	-	-	-	18.75	25.74	-	-	-	-	-	100	200
Diopside + H ₂ O	54.68	-	-	-	-	-	18.47	25.34	-	-	-	-	2.0	100	123
Model ultramafic melts															
Samples	SiO ₂	TiO ₂	Al ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	H ₂ O	OH ⁻	P ₂ O ₅	CO ₂	CO ₃ ²⁻	Σ	K
Kimberlite ^a	34.4	-	10.3	-	39.8	4.9	-	-	-	0.05	-	0.15	10.4	100	313
Kimberlite ^a + H ₂ O	33.06	-	9.91	-	38.24	4.85	-	-	2.04	1.86	-	0.32	10.0	100	247
Dunite ^b	39.85	-	2.98	34.11	21.68	1.38	-	-	-	-	-	-	0.2	100	340

Notes

Dash—no data

^aModel kimberlite melt after melting the initial mixture (Ab₃₈Cal₆₂, wt%) at $T = 1300$ °C and at a CO₂ pressure of 100 MPa (Persikov et al. 2017, 2018a)^bModel dunite melt after melting the initial mixture (Ab₅Di₃₀Mg₇₀Cal₅₀, mol%) at $T = 1400$ °C and at a CO₂ pressure of 100 MPa (Persikov et al. 2018b)

4.3 Results and Discussion

The generalized regularities of temperature, pressure, concentration and phase dependences of viscosity of fluid-magmatic systems in the full range of compositions of natural magmas (acid-ultrabasic) and thermodynamic parameters of the earth's crust and upper mantle were established during of long-term experimental and theoretical studies of viscosity of such melts.

4.3.1 *Temperature Dependence of Viscosity of Magmatic Melts*

The temperature dependence of viscosity is the key parameter of melts. The knowledge of this dependence allows estimating quantitatively the ascent rates of magmatic melts and their heat and mass transfer in different geodynamic setting. Some equations for temperature dependence of the viscosity in model silicate and natural magmatic melts have been suggested earlier (Adam and Gibbs 1965; Shaw 1972; Richet 1984; Whittington et al. 2000; Giordano and Dingwell 2003; Giordano et al. 2008; Russell et al. 2002; etc.). We have proved that the temperature dependence of the viscosity of near-liquidus magmatic melts at ambient, moderate and high pressures, in a large range of viscosity $0.1\text{--}10^8$ Pa s (last one for anhydrous near-liquidus granitic melts) fits quite well the fundamental Arrhenian-Frenkel-Eyring equation (e.g., Persikov 1998; Persikov et al. 2018a):

$$\eta = \eta_0 \exp(E/RT), \quad (4.3)$$

where η_0 is the pre-exponential factor for the viscosity of melts at $T \rightarrow \infty$, ($\eta_0 = 10^{-4.5} \pm 10^{-0.1}$ Pa s); T is the absolute temperature in K; $R = 8.3192$ (J/mol K) is the gas constant; E is the activation energy of viscous flow (J/mol), which is a function of the pressure and melt compositions; and η is the melt viscosity at the given temperature, in Pa s.

Figure 4.2 shows the temperature dependence of viscosity for melts of the albite-diopside-water system and jadeite melts at atmospheric and high pressures. Figure 4.3 shows the temperature dependences of the viscosity of model ultrabasic kimberlite melts at a moderate CO_2 pressure of 100 MPa and high lithostatic pressures (5.5 and 7.5 GPa), in comparison with the temperature dependence of the viscosity of the basalt melts. According to Eq. (4.3), the temperature dependence of viscosity for all studied melts (e.g., Fig. 4.2), is exponential, i.e. the viscosity of these melts decreases exponentially with increasing temperature, and conversely, increases exponentially with decreasing temperature, both at moderate and high pressures. It is necessary to emphasize the following important result. The constancy of the pre-exponential factor (η_0) of Eq. (4.3) and its independence from the melt composition and pressure are experimentally established (e.g., see the equations given in Fig. 4.3a–c). It is

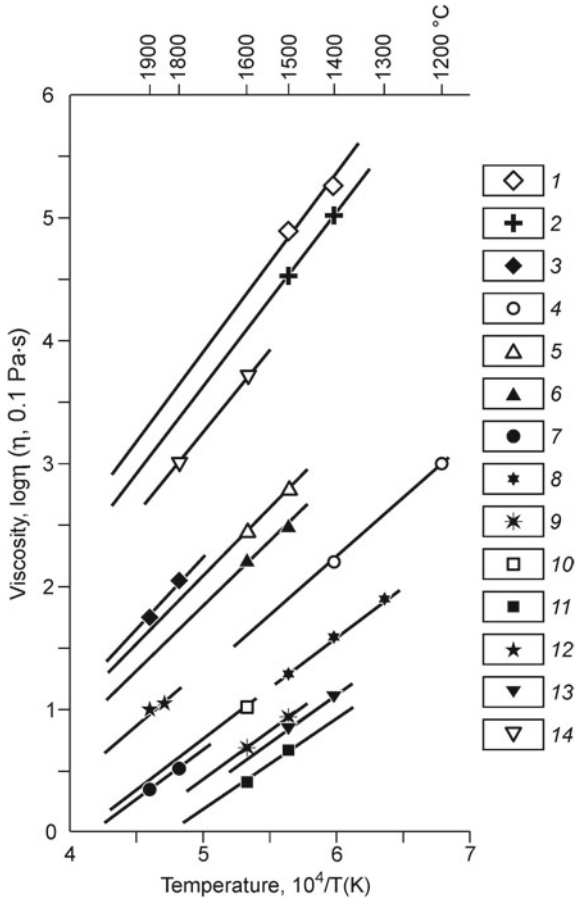


Fig. 4.2 Temperature dependence of the viscosity of some melts of the system albite–diopside–H₂O and jadeite melts at atmospheric and high pressures (Persikov et al. 1989; Persikov and Bukhtiyarov 2004, 2009). 1—Ab₁₀₀ (model granite), P = 1 atm.; 2—Ab₁₀₀, P_{tot.} = 400 MPa; 3—Ab₁₀₀, P_{tot.} = 4 GPa; 4—Ab₇₅(H₂O)₂₅, P(H₂O) = 400 MPa; 5—Ab₈₀Di₂₀, P = 1 atm; 6—Ab₈₀Di₂₀, P_{tot.} = 500 MPa; 7—Ab₈₀Di₂₀, P_{tot.} = 4 GPa; 8—Ab₃₀Di₇₀, P = 1 atm; 9—Ab₃₀Di₇₀, P_{tot.} = 500 MPa; 10—Ab₃₀Di₇₀, P_{tot.} = 2.5 GPa; 11—Di₁₀₀, P = 1 atm. and Jd₁₀₀, P_{tot.} = 9 GPa; 12—Di₁₀₀, P_{tot.} = 4 GPa; 13—Di₉₂(H₂O)₈, P(H₂O) = 500 MPa; 14—Jd₁₀₀, P = 1 atm. (melts compositions in mol%)

fully consistent with the theoretical findings (Frenkel 1975) and previously obtained data at moderate and high pressures (Persikov 1991; Russell et al. 2002; Persikov et al. 2018a). On this basis temperature-independent values of activation energies of the viscous flow of all studied fluid-magmatic melts were obtained for the first time with high accuracy ($\pm 1\%$ rel.). Note that the activation energy of viscous flow is a very important energy and structural-chemical parameter of the melt, which has a strict physical meaning as a potential barrier or a change in free energy of the system

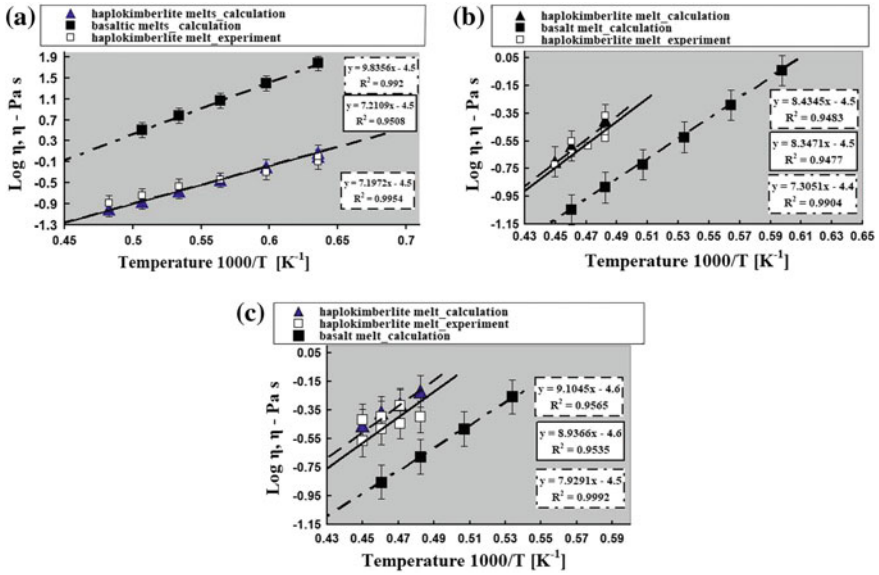


Fig. 4.3 Temperature dependence of the viscosity of haplokimberlite and basaltic melts. (uncertainties of experimental and calculating data are $\pm 30\%$ rel.; the calculated data on the temperature dependence of the viscosity of melts is obtained by our model, see text). **a** Pressure is 100 MPa, **b** pressure is 5.5 GPa, **c** pressure is 7.5 GPa

during shearing motion. Activation energy reflects intermolecular interaction, and consequently, a molecular structure and melt composition, and its value is close to the heat of compound formation (Adam and Gibbs 1965; Frenkel 1975; Richet 1984; Persikov 1998). The simple equations were suggested (Persikov 1998; Persikov and Bukhtiyarov 2009) to calculate the values of the activation energy for magmatic melts using the constant pre-exponential factor value ($\log \eta_0 = -4.5 \pm 0.14$).

$$E = 19.284 T (\log \eta_T^P + 4.5), \quad (4.4)$$

where: η_T^P is the melt viscosity at the given temperature and pressure, in Pa s; E is the activation energy of viscous flow, in J/mol; factor $19.284 = R/0.4314$; $R = 8.3192 \text{ J/mol K}$ is the gas constant. For example, the following values of the activation energy of viscous flow were obtained for some melts: model dunite melts, $E = 137 \pm 1.37 \text{ kJ/mol}$ ($P = 100 \text{ MPa}$) and $E = 171 \pm 1.7 \text{ kJ/mol}$ ($P = 7.5 \text{ GPa}$); basalt melts, $E = 186 \pm 1.86 \text{ kJ/mol}$ ($P = 100 \text{ MPa}$), and $E = 153 \pm 1.53 \text{ kJ/mol}$ ($P = 7.5 \text{ GPa}$). It is obvious that such high accuracy of determination of the activation energies of viscous flow ($\pm 1.0\%$ rel.) is unattainable for many studies of the viscosity of magmatic melts in which (η_0) in Eq. (4.3) was assumed to be non-constant. For example, the viscosity of a model peridotite melt was measured at a wide pressure range of 2.8–13.0 GPa using a multi-anvil device combined with a synchrotron X-ray source (Liebske et al. 2005). The constant of the activation energy of the viscous flow

of peridotite melts in a wide range of pressures (0.1–8 GPa) has been suggested in this work. It is obvious that the constancy of activation energy of the viscous flow (E) for peridotite melts in such a wide range of pressures contradicts our data (e.g. Persikov et al. 2018a), and the theoretical premises mentioned above.

4.3.2 *The Concentration Dependence of Viscosity of Magmatic Melts*

The viscosity of magmatic melts complex depends on composition of the melt and its structure, which causes serious difficulties of development of models for calculation and prediction the concentration dependence of viscosity. Viscosity is highly sensitive to the change of composition of magmatic melts, which is proved by the following data: the viscosity of near-liquidus melts in the granite-dunite series decreases very much, approximately by a factor of 10^7 times. There is certain progress in solving the problem of concentration dependence of the viscosity of such melts in an empirical way (Carron 1969; Bottinga and Weill 1972; Shaw 1972; Sheludyakov 1980; Hess and Dingwell 1996; Giordano and Dingwell 2003; Hui and Zhang 2007; Giordano et al. 2008; Russell et al. 2002). We propose quite a different approach (Persikov 1998; Persikov and Bukhtiyarov 2009). We have used an adequate criterion, which reflects the structure and composition of magmatic melts correctly and with proper sensitivity. It is a structural chemical parameter of the melt $K = 100(\text{NBO}/\text{T})$, depolymerization degree or coefficient of relative basicity (Mysen et al. 1979; Mysen 1991; Persikov 1991). The calculation of this parameter is made from chemical composition of the melt in wt% of oxides, according to a simple technique (Persikov 1998) with the use of the following equation:

$$K = 200 (\text{O} - 2\text{T})/\text{T} = 100 (\text{NBO}/\text{T}), \quad (4.5)$$

where T is total amount of gram-ions of the network-forming cations (Si^{4+} , Al^{3+} , Fe^{3+} , Ti^{4+} , P^{5+} , B^{3+}), which are in tetrahedral coordination over oxygen and enter the anionic part of the melt structure; O is a total amount of gram-ions of oxygen in the melt; NBO/T is the total amount of gram-ions of non-bridging oxygen in the melt; Note that B. Mysen sometimes used a $100\text{NBO}/\text{T}$ parameter too (Mysen 1991, Figs. 26–28).

Note that the isothermal comparison of viscosity in the full range of magma compositions has often no physical—chemical meaning that because of essential differences in liquidus temperatures of magmatic rocks as, for example, the viscosity of granite-dunite melts. It is more correctly to consider the activation energies of the viscous flow as temperature-independent structural—chemical and rheological parameters. The new comparable values of activation energies of viscous flow of the melts for all the published experimental data on the viscosity of near-liquidus silicate, aluminosilicate and magmatic melts have been obtained, based of the proven

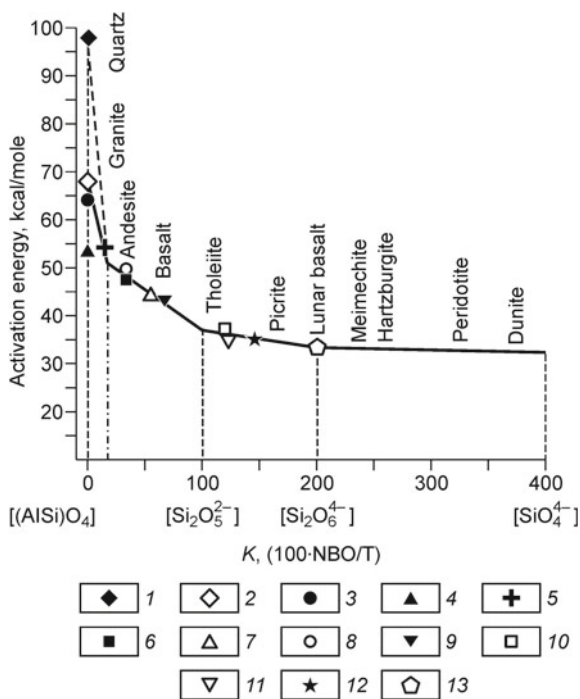


Fig. 4.4 Generalized structural-chemical dependence of activation energies of a viscous flow of model magmatic melts [bracketed are the basic terms of the melt anion structure (Persikov 1991, 1998; Persikov and Bukhtiyarov 2004)]. 1, Q_{100} ; 2, Ab_{100} (model granite); 3, Jd_{100} ; 4, $Nepf_{100}$; 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, $Di_{96}(H_2O)_4$; 13, Di_{100} (melts composition in mole %)

constancy value of η_0 in Eq. (4.3). Moreover, a generalized structural—chemical dependence of activation energies of viscous flow on melts compositions have been suggested (Fig. 4.4). The diagram was analyzed in detail earlier (e.g., Persikov 1998), therefore, we would like to only emphasize some important features. The represented diagram has been corrected compared to the previously published one. Recently obtained experimental data have been taken into account (Dingwell 2006; Dingwell et al. 2004; Giordano and Dingwell 2003; Giordano et al. 2004, 2008; Hess and Dingwell 1996; Whittington et al. 2000, 2001; Vetere et al. 2010; and references therein). The inflection points in the dependence $E = f(K)$ characterize the changes in the melt structure and are interpreted in terms of the silicate melt theory. For a three—dimensional framework structure the break down is completed at $K = 17$, and at $K = 100, 200$, and 400 formation of di-, meta-, and ortho-silicate structures of melts respectively is brought to an end (see Fig. 4.4). A wide field of natural magmas is limited by vertical lines in Fig. 4.4, which was defined as follows: at an average water concentration in acidic magmas (0.67 wt% in granites, and 1.1 wt% in the rhyolites) their degree of depolymerization is $K \leq 5$, depolymerized ultramafic

magmas are characterized by the value $K = 200\text{--}400$, for example, for dunite melts $K = 380$.

4.3.3 Pressure Dependence of Viscosity of Magmatic Melts

Pressure is the most important thermodynamic parameter of magmatic systems. Most of magmatic melts exist of a great depth, under high pressures, except volcanic melts. The influence of high pressure on viscosity of natural magmatic and model silicate melts has been largely studied (Waff 1975; Kushiro 1980; Fujii and Kushiro 1977; Brearley et al. 1986; Scarfe et al. 1987; Persikov et al. 1989, 2017, 2018a; Mysen 1991; Persikov 1991; Wolf and McMillan 1995; Reid et al. 2003; Liebske et al. 2005; Suzuki et al. 2005; Allwardt et al. 2007; Karki and Stixrude 2010; etc.). Note that all theories of liquids presume that viscosity increases exponentially with increasing pressure (Brush 1962; Scarfe 1986; Persikov 1998; Wolf and McMillan 1995; Reid et al. 2003; Liebske et al. 2005; Persikov et al. 2018b):

$$\eta^P = \eta_0 \exp(E + PV)/RT, \tag{4.6}$$

where η^P is the viscosity at given pressure P ; V is the activation volume; the rest designations are the same as in Eq. (4.4).

An increase of melts viscosity with increasing pressures of pyroxene, peridotite, dunite, and kimberlite melts ($200 < 100NBO/T < 400$), as well as more polymerized ($0 < 100NBO/T < 200$) melts, observed after the minimum values (Fig. 4.5, for basaltic melts), is in full agreement with the theoretical predictions (Eq. 4.6).

These results are consistent with free volume theory (e.g. Frenkel 1975; Persikov 1998; Liebsky et al. 2005). According to these theories, an increase in the viscosity of a liquid with increasing pressure is associated with an increase in the potential

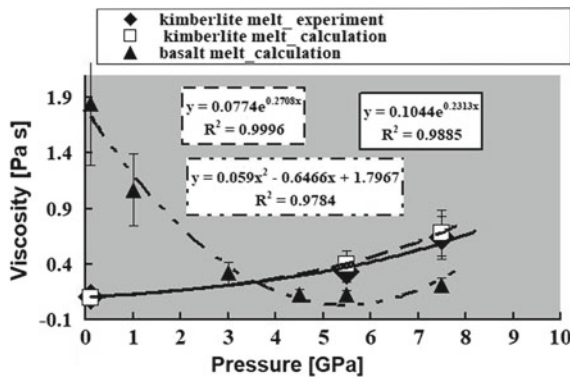


Fig. 4.5 Isothermal (1800 °C) dependence of the viscosity of haplokimberlite and basaltic melts on pressure (uncertainties of experimental and calculating data are $\pm 30\%$ rel., see text)

Table 4.2 Parameters and uncertainties^a obtained from the calculation of Eq. 4.6 for data on the viscosity of haplokimberite and basaltic melts at moderate and high pressures

	Haplokimberite melts			Basaltic melts		
	0.1	5.5	7.5	0.1	4.0	7.5
Pressures (GPa)	0.1	5.5	7.5	0.1	4.0	7.5
Activation energy E (kJ/mol)	138 (1.4)	163 (1.6)	172 (1.7)	177 (1.8)	144 (1.4)	153 (1.4)
Activation volume V (cm ³ /mol)	2.0 (5)	2.0 (5)	2.0 (5)	-2.0 (5)	-2.0 (5)	1.5 (4)
Log η_0 (η_0 – Pa s)	-4.5 (14)	-4.5 (14)	-4.5 (14)	-4.5 (14)	-4.5 (14)	-4.5 (14)

^aUncertainties at the 1 σ level are given in parenthesis in terms of the last units cited

barrier, i.e. respectively, the activation energy of the viscous flow (E in Eq. 4.6) with increasing pressure. A change in the activation volume of the liquid (V in Eq. 4.6) is in the first approximation a positive and constant value in the measured pressure range for a positive viscosity dependence (kimberlite and dunite melts, basaltic and more polymerized melts after a minimum). Accordingly, for a negative dependence of the viscosity of liquids (basaltic and more polymerized melts up to a minimum of this dependence), the activation energy (E in Eq. 4.6) decreases with increasing pressure. A change in the activation volume of the liquid (V in Eq. 4.6) will be, in the first approximation, a negative and constant value in the measured pressure range. Table 4.2 presents the results of calculations of these parameters for the melts studied, which were obtained from Eq. (4.6) using new experimental data on the viscosity and activation energies of the viscous flow of anhydrous kimberlite and basaltic melts over a wide range of temperatures and pressures. The results obtained fully correspond to the above theoretical presumes. Note that this result does not agree with the result of Liebsky et al. (2005), who reported that the calculated activation energy of the viscous flow for peridotite melts (198 ± 23 kJ/mol) does not depend on the pressure in a wide range of pressures ($P = 0\text{--}8$ GPa, Table 5, Liebsky et al. 2005). The constancy of activation energy of the viscous flow (E) for peridotite melts in such a wide range of pressures also contradicts the theoretical premises mentioned above.

An anomalous pressure dependence of the viscosity of polymerized (up to basalt) magmatic melts, which decreases with increasing pressure has been reported in several works (Kushiro 1980; Brearley et al. 1986; Scarfe et al. 1987; Persikov 1998; Mysen 1991; Wolf and McMillan 1995; McMillan and Wilding 2009; and references therein). It was experimentally proven that pressure dependence of viscosity and activation energies of the model silicate and natural magmatic melts are inverse and has extremes (Persikov 1998; Reid et al. 2003; Liebske et al. 2005; Persikov et al. 2018a). As an example, Fig. 4.6 shows a diagram of dependence of melts viscosity on lithostatic pressure for the melts of the system albite-diopside as well as for jadeite melt. The results obtained indicate that viscosity and activation energy of viscous flow markedly decrease with lithostatic pressure all over the range of compositions (up to basalts) and the pressure at the minimum of melts viscosity and activation

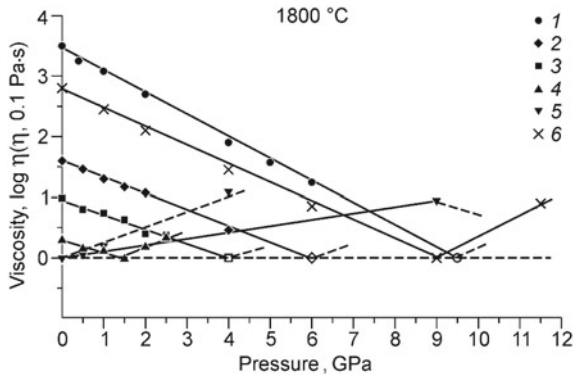


Fig. 4.6 Isothermal dependence of the viscosity of melts in the albite (Ab)–diopside (Di) join (Brearley et al. 1986; Kushiro 1980; Persikov and Bukhtiyarov 2004; Reid et al. 2003) and jadeite (Jd) melt on pressure (Persikov et al. 1989). 1, Ab₁₀₀ (model granite); 2, Ab₈₀Di₂₀; 3, Ab₅₇Di₄₃ (model basaltic melt); 4, Ab₃₀Di₇₀; 5, Di₁₀₀; [dashed line shows extrapolation from the model (Persikov 1998), and solid line shows extrapolation in this paper from the improved model (Persikov et al. 2015 and this study)]; 6, Jd₁₀₀. The composition of melts is in mole %, and open symbols show calculated values

energies strongly depends on melt composition (Liebske et al. 2005; Persikov and Bukhtiyarov 2009).

The nature of this anomaly is still under discussion. The more probable mechanism of this anomaly can involve the change of melts structure under isochemical conditions, i.e. the transformation of Al and Si cations in the melts from four- to six-fold oxygen coordination with increasing pressure. It means that Al and Si transformation from network-forming to modifier cations is followed by an increase in depolymerization degree of melts (100NBO/T). This idea was first proposed by (Waff 1975) and has been supported by a wealth of experimental and spectroscopic data (Kushiro 1980; Wolf and McMillan 1995; Persikov 1998; Reid et al. 2003; Allwardt et al. 2007; Persikov et al. 2018a; and references therein). Note that the assumption on structural changes of Al and Si at high pressures in melts with pressure perfectly fits the phase correspondence principle, according to which the temperature increase expands the stability fields of polymerized phases and on the contrary, pressure increase expands the stability fields of depolymerized phases (Persikov 1998; Liebske et al. 2005; Karki and Stixrude 2010).

4.3.4 Viscosity of Heterogeneous Magmas

Experimental study of viscosity of subliquidus heterogeneous magmatic melts (liquid + crystals + bubbles) is the most urgent problem of magmatic rheology, because such state is natural for them in the Earth's crust depth and, probably, in the mantle.

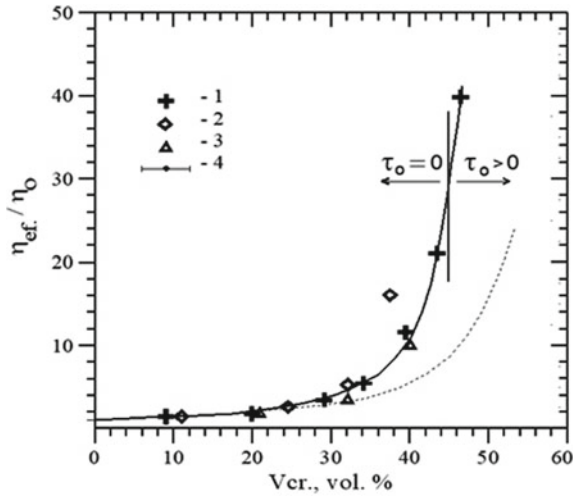


Fig. 4.7 Dependence of effective viscosity of model system (liquid + crystal) on volume content of crystals. 1, $\eta_0 = 3.8$ Pa s, crystal size 0.2–0.4 mm; 2, $\eta_0 = 0.68$ Pa s, crystal size 0.2–0.4 mm; 3, $\eta_0 = 0.68$ Pa s, crystal size 0.16–0.2 mm; 4, experimental errors; dash curve is consist to equation of Rosco (Persikov 1991, 1998; Persikov and Bukhtiyarov 2009)

Weak knowledge of this problem is caused not only by technical and methodological difficulties of experimental study of viscosity of such systems, especially at high pressures. To these are added the complexity of theoretical calculations, as such melts can exhibit the entire range of melt flows, referred to in rheology abnormally viscous (non-Newtonian, viscoplastic or Bingham, pseudoplastic). The separate account of the influence of crystalline phase and bubbles on viscosity of subliquidus magma can be estimated as the first approximation. As an example, Fig. 4.7 shows our results of viscosity measurements of the model (silicone) liquid + corundum crystals. Analysis of these results showed that the effective viscosity of the mixture increases significantly with increasing volume content of crystalline phase ($V_{cr.}$). At $V_{cr.} < 0.1$ dependence character $\eta = f(V_{cr.})$ is well approximated by the theoretical Einstein equation, and in the interval $0.1 < V_{cr.} < 0.30$ by the Roscoe empirical equation. However, with $V_{cr.} > 0.30$ the effect of the crystalline phase on the effective viscosity of the mixture is much greater (Fig. 4.7), which corresponds to the following empirical equation (Persikov 1998):

$$\eta_{ef.} = \eta_0(1 - V_{cr.})^{-3.35}, \quad 0 < V_{cr.} < 0.45 \quad (4.7)$$

where η_0 is the viscosity of the liquid phase.

The Newtonian flow behavior of melts was observed at $V_{cr.} \leq 0.45$. At a further growth of crystal content, the Newtonian behavior of melts changed to the Bingham one with the limit of fluidity equal to 2900 din/cm².

As for a separate effect of bubbles on the effective viscosity of the mixture, then the data obtained by us agree well with the results from (Uhira 1980; Pal 2003) and at $V_b \leq 0.45$ are described by the following empiric equation:

$$\eta_{ef.} = \eta_o(1 - 1.5V_b)^{-0.55}, \quad 0 < V_b \leq 0.45 \quad (4.8)$$

where V_b —volume fraction of bubbles in the liquid.

In this connection it is useful to note that the maximum content of crystal and fluid phases in magmas, reliably taken into account in our model was 45 vol%, because according to experimental data, exceeding of this limit leads to a fundamental change in the rheology of magmas—Newtonian flow regime, observed for almost all natural magmas, transforms into non-typical Bingham flow regime with yield stress increasing with increasing the content of these phases (Shaw et al. 1968; Pal 2003; Persikov and Bukhtiyarov 2009; and others). According to (Sparks et al. 2009; Russell et al. 2012; McMillan and Wilding 2009), the content of mantle and crustal xenoliths in basaltic and kimberlite magmas (including diamonds) during their evolution is not more than ~45 vol%, which is close to the threshold value of 50–60 vol%, when magma eruption becomes impossible (Kavanagh and Sparks 2009; Russell et al. 2012).

4.3.5 Structural-Chemical Model of Calculations and Prediction of Magmatic Melts Viscosity at High and Super High Pressures

A few models to predict and calculate temperature and concentration dependences of viscosity of magmatic melts at ambient pressure have been published (Giordano and Dingwell 2003; Hui and Zhang 2007; Giordano et al. 2008) after the pioneer works of (Bottinga and Weill 1972; Shaw 1972). The positive feature of these models is a very large temperature range to predict viscosity of silicate and magmatic melts: (700–1600 °C, Giordano et al. 2008); 300–1700 °C, (Hui and Zhang 2007). However, the essential disadvantages typical for all of them restrict the possibility to use these models for realistic prediction of magma viscosity. The main drawbacks of those models are as follows (see Table 4.3): (1) empiric approach with numerous fitting parameters: 285 (Bottinga and Weill 1972), 10 (Giordano and Dingwell 2003; Giordano et al. 2008), 37 (Hui and Zhang 2007); (2) low accuracy; (3) the effect of pressure, crystal and bubble content is ignored; (4) the effect of Al and Si ratio in melts (5) and the influence of oxygen fugacity are not considered either; (6) the effect of volatile content in melts is not considered in (Bottinga and Weill 1972; Giordano and Dingwell 2003); (7) only the effect of total water content on viscosity of silicate and magmatic melts is included into a few models (Shaw 1972; Hui and Zhang 2007; Giordano et al. 2008); (8) the amphoteric nature of dissolved water, and its polymerized effect in kimberlite and ultrabasic melts (see Table 4.1) is not

Table 4.3 Comparison of models suggested for calculating and predicting the viscosity of magmatic melts

Model	Shaw (1972)	Bottinga and Weill (1972)	Giordano et al. (2008)	Hui and Zhang (2007)	Persikov and Bukhtiyarov (2009; this study)
Basic principle	Empirical	Empirical	Empirical	Empirical	Structural-chemical, theoretical
Composition range of melts	Rhyolite-basalt	Rhyolite-basalt	Rhyolite-peridotite	Rhyolite-peridotite	Rhyolite-peridotite
Temperature range, °C	800–1200	1000–1400	700–1600	300 (?)–1600	Near-liquidus melts ($T = T_m \pm 0.2 T_m$)
Volatiles effect	H ₂ O, up to 5 wt%	No	No	H ₂ O, up to 5 wt%	OH ⁻ , H ₂ O, F ⁻ , Cl ⁻ , CO ₂ , CO ₃ ²⁻ , up to any real contents
Pressure effect	No	No	No	No	Up to 12 GPa
Ration of Al ³⁺ /(Al ³⁺ + Si ⁴⁺)	No	No	No	No	Yes
Ration of Fe ²⁺ /(Fe ²⁺ + Fe ³⁺)	No	No	No	No	Yes
Ration of Al ³⁺ /(Na ⁺ + K ⁺ + Ca ⁺ + Mg ⁺ + Fe ²⁺)	No	No	No	No	Yes
Volume content of crystals and bubbles	No	No	No	No	Up to 45 vol%
Error, ±rel. %	50–100	50–100	250	200	30

Note Experimental uncertainty of the viscosity measurements is 15–30% rel. at ambient and high pressures

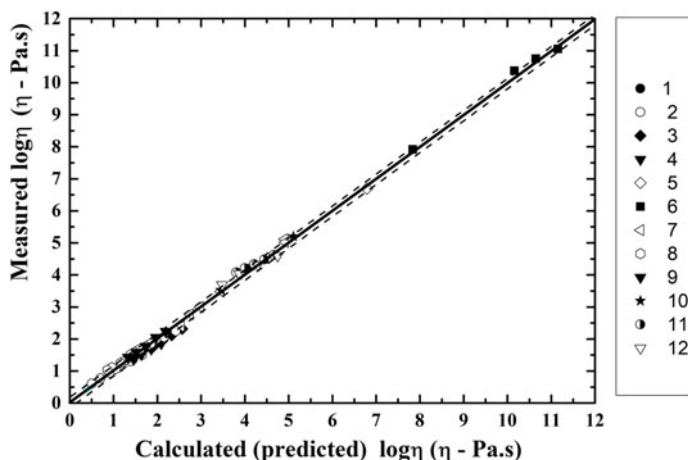


Fig. 4.8 Comparison of experimental viscosity values with calculated (predicted) values using a new model (T is the temperature in K). **1**—basanite (NIQ), $T = 1573$, (Whittington et al. 2000); **2**—tephrite, $T = 1720 \div 1464$, (Whittington et al. 2000); **3**—phonolite, $T = 1816\text{--}1618$, (Whittington et al. 2001); **4**—trachyte, $T = 1929\text{--}1777$, (Whittington et al. 2001); **5**—model rhyolite (HPG8), $T = 1453$, (Dingwell et al. 1996); **6**—model rhyolite (HPG8Na, HPG8K), $T = 1073\text{--}927$, (Hess et al. 1995); **7**—model rhyolite (AOQ), $T = 1673\text{--}1423$, $C_{H_2O} = 0, 03\text{--}5, 0$ mac. %, (Schulze et al. 1996); **8**—andesite, $T = 1978\text{--}1650$, (Richtel et al. 1996); **9**—andesite, $T = 1867\text{--}1670$, (Neuville et al. 1993); **10**—rhyolite, $T = 1173\text{--}973$, $C_{H_2O} = 8, 8$ mac. %, (Burnham 1964); **11**—dacite, $T = 1473\text{--}1375$, (Giordano et al. 2008) **12**—phonolite, $T = 1473\text{--}1326$, (Romano et al. 2003)

considered either. Our new model is an advanced version of the previously published models (Persikov and Bukhtiyarov 2009) which has no the mentioned above disadvantages (see Table 4.3). Figure 4.8 shows the comparison of all the recently published experimental data on viscosity of magmatic melts and calculated values obtained using our model. The field of uncertainty for predicting data on magma viscosity using the new model ($2\sigma = 0.228$ in log scale or $\pm 30\%$ rel.) is presented in Fig. 4.6. It is necessary to emphasize high accuracy of calculations and prediction of viscosity of silicate and magmatic melts by the suggested model as compared to those suggested earlier (see Table 4.3). Moreover, the developed structural-chemical model allows to predict and calculate viscosity of near liquidus silicate and magmatic melts as a function of the following parameters: P ; Pfl ; T ; melt composition, including H_2O , OH^- , CO_2 , CO_3^{2-} , F^- , Cl^- ; the cation ratios: $Al^{3+}/(Si^{4+} + Al^{3+})$, $Al^{3+}/(Na^+ + K^+ + Ca^{2+} + Mg^{2+} + Fe^{2+})$, $Fe^{2+}/(Fe^{2+} + Fe^{3+})$, and a volume content of crystals and bubbles (up to 0.45).

Thus the characteristic features of that model are as follows: (1) structural chemical approach; (2) ultimate simplicity of analytical dependences; (3) high accuracy of prediction (± 30 rel. % for viscosity, and ± 1.0 rel. % for activation energy), which is consistent with the uncertainties of experimental data on viscosity, especially at high pressures.

4.3.6 Example of Successful Application of the Obtained Experimental and Theoretical Results to Natural Processes

A new version of our model allows to predict characteristic features of viscosity of basaltic and kimberlite magmas in the course of their origin in the mantle, evolution during ascent to the crust, and volcanic eruptions. The T and P values are taken from (Wyllie 1980; Yoder 1976; Dalton and Presnall 1998; Dasgupta and Hirschmann 2006; Kavanagh and Sparks 2009; Mitchell 2008; Russell et al. 2012; Sparks et al. 2009). Figure 4.9 shows the dynamics of change in the viscosity of kimberlite and basaltic magmas with different water contents under the T , P -conditions of their origin in the upper mantle and the subsequent evolution during the ascent of such magmas from mantle to crust. The data obtained with a high degree of correlation (Fig. 4.9) show that the viscosity of kimberlite magma in the course of its origin, evolution, and ascent decreases by a factor of ~ 4 despite the considerable decrease in the temperature of kimberlite magma (by ~ 150 °C) (Kavanagh and Sparks 2009; Sparks et al. 2009) during its ascent to the surface and partial crystallization and

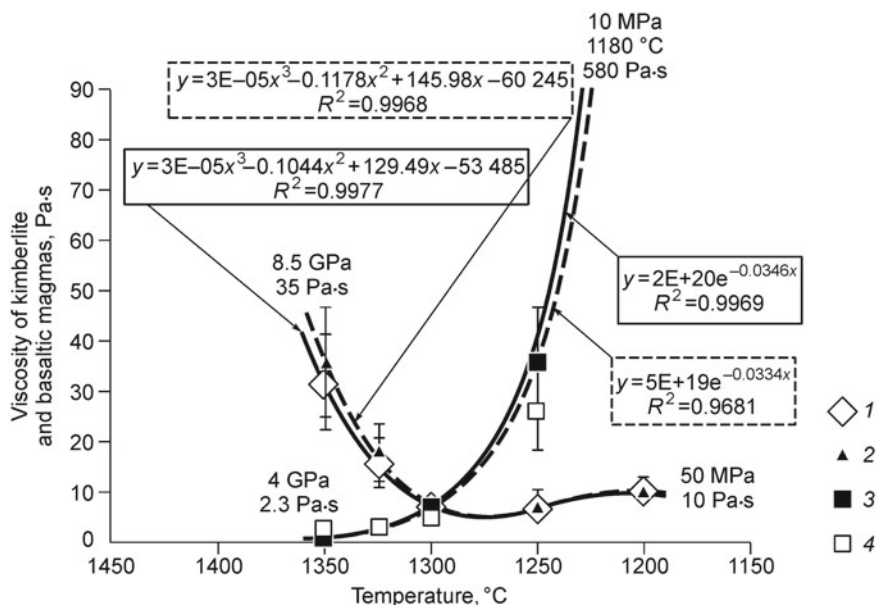


Fig. 4.9 Dynamics of change in the viscosity of kimberlite and basaltic magmas during their origin and ascent to the crust as well as volcanic eruptions. 1, 2, kimberlite magma: 1, water content in magma $X(\text{H}_2\text{O}) = 0.5$ wt% (solid curve); 2, $X(\text{H}_2\text{O}) = 8.0$ wt% (dashed curve); 3, 4, basaltic magma: 3, water content in magma $X(\text{H}_2\text{O}) = 0.5$ wt% (solid curve); 4, $X(\text{H}_2\text{O}) = 8.0$ wt% (dashed curve) (Pressures used in the diagram: 8.5 GPa–50 MPa for kimberlite magma and 4 GPa–10 MPa for basaltic magma; the error of the calculations based on the model ± 30 rel. % is shown on the diagram)

degassing. The viscosity of the formed kimberlite melt is equal to ~ 40 Pa s at $P = 8.5$ GPa and $T = 1350$ °C, during the partial melting of mantle carbonated peridotite (degree of melting < 1 wt%) at the depth of 150–300 km (Wyllie 1980; Brey et al. 2009; Dalton and Presnall 1998; Dasgupta and Hirschmann 2006; Mitchell 2008; Sparks et al. 2009). The volume fractions of the crystal and bubbles in the melts are $V_{cr.} = 20$ and $V_{b.} = 5$ vol%, respectively and water content in the melt is ~ 8 wt%, ($X(OH^-) \sim 2.0$ wt%, and molecular water $X(H_2O) \sim 6.0$ wt%). However, during the formation of kimberlite pipes, dikes, and sills, the viscosity of kimberlite melt near the surface is considerably lower. It is equal to ~ 10 Pa s at $P = 50$ MPa and $T = 1180$ °C, the volume fractions of the crystal and bubbles in the melts are $V_{cr.} = 35$ vol% and $V_{b.} = 5$ vol%, respectively, and water content in magma is $X(OH^-) \sim 0.5$ wt% (Fig. 4.9).

The viscosity of basaltic magma during its ascent from mantle to crust increases by more than two orders of magnitude (the high degree of correlation is shown in Fig. 4.9). During the origin of basaltic magmas in the asthenosphere, at depths of ~ 100 km (Yoder 1976), the formed basaltic melt has minimum viscosity (~ 2.3 Pa s) at $P = 4.0$ GPa and $T = 1350$ °C, water content in the melt is $X(OH^-) = 3.0$ wt% and $X(H_2O) = 5.0$ wt%. But at the final stage of evolution (e.g., during the eruption of basaltic volcanoes), the viscosity of basaltic melt is much higher (~ 600 Pa s) at $P = 10$ MPa, $T = 1180$ °C, $V_{cr.} = 30$ vol%, $V_{b.} = 15$ vol%, $X(OH^-) = 0.5$ wt% (Fig. 4.9). The lower viscosity of basaltic magma (at 3.0–4.0 GPa), as compared to ultramafic (kimberlite) magma (at 4.0–8.5 GPa), at the temperatures 1325–1350 °C can be mainly explained by the reverse effect of pressure and chemically dissolved water (OH^-) on the viscosity of melts: the viscosity of basaltic melts decreases, whereas that of kimberlite melts viscosity increases with pressure and (OH^-) content. Such a seemingly anomalous effect is also amplified by the difference between the content of the crystal and bubbles in the magmas under the given T , P -conditions: $V_{cr.} = 10$ –15 vol% and $V_{b.} = 1.0$ vol% in the forming basaltic magma and $V_{cr.} = 20$ vol% and $V_{b.} = 5$ vol% in parental kimberlite magma (Fig. 4.9). The analysis of the results on the dynamics of change in the viscosity of kimberlite and basaltic magmas (Fig. 4.9) in the course of their origin in the mantle and the subsequent evolution during their ascent to the crust leads to an important conclusion on the possible role of dissolved water. According to the data obtained, the dissolution of water (up to ~ 8 wt%) in kimberlite and basaltic magmas cannot have a significant influence on the dynamics of change in the viscosity of those magmas within the error (~ 30 rel.%) of prediction calculations (Fig. 4.9) whereas pressure and the volume content of crystals and bubbles have a considerably greater effect on the viscosity of those magmas as compared to the effect of dissolved water.

The influence of the second important fluid component of kimberlite and basaltic magmas (CO_2) on their viscosity was also taken into account. According to scarce experimental data, summarized, e.g., in (Lange 1994), the dissolution of CO_2 has almost no influence on the viscosity of magmatic melts at ~ 2.5 GPa. That conclusion is true for basaltic magmas, which are characterized by the low solubility of CO_2 . However, a considerable amount of CO_2 can be dissolved in kimberlite magma at 2.5–8.5 GPa due to: (1) the reaction between carbonatite melts and mantle peridotite,

with the dissolution of mainly orthopyroxene (Brey et al. 2009; Chepurov et al. 2013; Kavanagh and Sparks 2009; Russell et al. 2012; Sparks et al. 2009); (2) the possible reaction of decarbonatization at ~ 2.5 GPa carbon dioxide, which forms during those reactions, may partly dissolve in kimberlite melt in carbonate form, but, predominantly, it forms abundant fluid (CO_2) micro-bubbles in the melt. The volume of this fluid phase increases with the subsequent decrease in pressure and temperature. However, the viscosity of subliquidus kimberlite magma (liquid + crystals + CO_2 bubbles) rather decreases under the decisive influence of pressure (Fig. 4.9) than increases.

4.4 Conclusions

1. The generalized regularities of temperature, pressure, concentration and phase dependences of viscosity of fluid-magmatic systems in the full range of compositions of natural magmas (acidic-ultramafic) and thermodynamic parameters of the earth's crust and upper mantle were established in conjunction with the structural features of the melts. The range of viscosity values for the studied melts is extremely large: from $10^{6.3}$ Pa s (water bearing granitic melt (0.5 wt%) at atmospheric pressure, temperature 1100 °C and 100NBO/T = 4.9) to 10^{-1} Pa s (water free dunite melts at $P = 100$ MPa, temperature 1800 °C and 100NBO/T = 340).
2. It is now reliably established that from a wide range of fluid composition of the magma (H_2O , CO_2 , HCl, NaCl, HF, NaF, H_2S), water and CO_2 dissolved in magmas in two forms, has a decisive influence on the viscosity of such magmas. Chemical dissolved water (OH^-) and carbon dioxide (CO_3^{2-}) strongly reduces the viscosity, significantly increases the degree of depolymerization of the melt. Physical ones in the forms of molecular H_2O and CO_2 weakly reduces the viscosity of the magma, without changing its degree of depolymerization, and pseudo-binary system magma- H_2O - CO_2 with a good degree of approximation simulates the rheological behavior of such magmas in the entire range of depths of the earth's crust and upper mantle. Temperature dependence of viscosity for all studied melts is exponential at ambient pressure, moderate and high fluid and lithostatic pressures. The new reliable values of the activation energies of the viscous flow for all studied fluid-magmatic melts at ambient, moderate and high pressures were obtained for the first time with high accuracy ($\pm 1\%$ rel.). The range of values of the activation energies of the viscous flow for the studied melts ranged from 284 ± 2.8 kJ/mol (water bearing granitic melts (0.5 wt%) at ambient pressure) to 137 ± 1.4 kJ/mol (water free dunite melts at $P = 100$ MPa).
3. Pressure dependence of viscosity and activation energies of viscous flow for all studied melts are inverse and has extremes. Viscosity and activation energy markedly decrease with lithostatic and water pressure all over the range of compositions of polymerized melts (from acidic to mafic), except for depolymerized melts, such as diopside, kimberlite and dunite melts for which viscosity and

activation energy increase with lithostatic and water pressure. Pressures at the minimum viscosity and activation energy strongly depends on melt composition decreasing with increasing the degree of depolymerization.

4. An improved structural-chemical model is proposed to predict and calculate the viscosity of silicate and magmatic melts as functions of the following parameters: P_{total} ; Pfl ; T ; melt composition, including volatiles (H_2O , OH^- , CO_2 , CO_3^{2-} , F^- , Cl^-); cation ratios: $Al^{3+}/(Si^{4+} + Al^{3+})$, $Al^{3+}/(Na^+ + K^+ + Ca^{2+} + Mg^{2+} + Fe^{2+})$, $Fe^{2+}/(Fe^{2+} + Fe^{3+})$, and a volume content of crystals and bubbles (up to 0.45, as applied to magma viscosity). The new model is specified by: (1) structural chemical approach; (2) ultimate simplicity of analytical dependences; (3) high accuracy of the prediction ($\pm 30\%$ rel. for viscosity, and $\pm 1.0\%$ rel. for activation energy), which is consistent with the uncertainties of the experimental data on viscosity, especially at high pressures.
5. Prediction results on the ascent of diamonds carrier kimberlite magmas from mantle to the crust with the appreciable acceleration is an unique in that the viscosity of kimberlite magmas will decrease by more than 4 times during this process despite of the decreasing magmas temperature by more than ~ 150 °C. On the contrary, the viscosity of basaltic magmas will increase by more than 2.5 orders of magnitude during their origin, evolution and the ascent from mantle to the crust up to volcanic eruption.

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