MECHANICAL SPECTROSCOPY OF NATURAL AND SYNTHETIC SILICATE GLASSES AND MELTS

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ABSTRACT

Mechanical relaxation behaviour of various natural volcanic and synthetic binary, ternary and multicomponent silicate glasses and melts (having NBO/T from 0 to 2, and T_g varying from 468°C to 1148°C) have been studied in the temperature range RT-1000°C using special low frequency flexure (f~0.63Hz) and torsion (f=0.002…20Hz) pendulum experiments. The rheological properties complex Young's modulus $M^*(\omega,\tau)$, complex shear modulus $G^*(\omega,\tau)$ and internal friction $Q^{-1}(\omega,\tau)$ have been investigated from a pure elastic solid at room temperature to pure viscous melt at $\log(\eta[Pas])=8$. Three relaxation processes are assumed to act: one primary α-relaxation (viscoelastic process) above the glass transition temperature T_g and two secondary anelastic β and β'-relaxation processes below T_g. The dynamic glass transition, i.e. the viscoelastic α-transition, can be characterized with hierarchically coupled relaxation processes which lead to an equivalent distribution of relaxation times nearly independent of the fragility for all examined glasses. The observed secondary relaxation processes can be explained with different mechanisms: (β) cooperative movement of alkali ions in the vitreous state. (β') cooperative movement of alkaline earth ions and non bridging oxygen's near the glass transition range. Here the influence of the water must be taken into account as well as the alteration effects due to the structural α-relaxation. The mechanical relaxation behaviour is described with the use of a simple fractional Maxwell model having an asymmetrical relaxation time distribution $H(\tau)$.

INTRODUCTION

It is of great importance today, in material and geoscience, to be able to understand and predict the mechanical response (elasticity, anelasticity and viscoelasticity) of multicomponent silicate glasses and melts[1,2,3,4,5,6,7,8]. Accurate modelling of the most of volcanic or magmatic processes requires data on the rheological properties of magma[9]. In this context the rheological properties of natural and synthetic silicate glasses and melts are of interest. The field of special interest is focused on the influence of chemical composition, water content, bubble and crystal content on complex shear modulus G^*, bulk modulus K^*, Young's modulus M^*, internal friction $Q^{-1}=\tan(\delta)$ (viscoelastic α-relaxation of supercooled melts above T_g) and structural relaxation time τ (or viscosity η) which defines the location of the dynamical glass transition in the $\log(\omega)$-T-plane (time-temperature-plane)[3,4,10,11,12,13,14,15,16,17,18,19,20,21].

In this study the rheological properties complex shear modulus $G^*(\omega,\tau)$, complex Young's modulus $M^*(\omega,\tau)$ and internal friction $Q^{-1}(\omega,\tau)$ of various natural volcanic and synthetic

binary, ternary and multicomponent silicate glasses and melts (Tab. 1) have been investigated in a wide temperature range from a purely elastic solid at room temperature to purely viscous melt at a viscosity $\log(\eta\ [Pas])=8$.

Table 1: Chemical composition of the synthetic (a) and natural (b) glasses (wt.%) [35].

(a)	SiO$_2$	NCS	KCS	CCS	Na$_2$Si$_3$O$_7$	To[§]	Co[*]	Di[*]	JeIIa[#]
SiO$_2$	100	74.12	68.25	46.72	73.61	72.1	51.52	53.44	45.3
Al$_2$O$_3$					0.27	1.3	35.28	0.93	29.6
Fe$_2$O$_{3t}$						0.2			
CaO		6.35	8.61	5.86		7.7		26.42	
MgO						4.1	13.21	19.21	12.01
Na$_2$O		16.53			26.12	13.5			3.5
K$_2$O			23.14			0.7			5.1
Cs$_2$O				47.39					
NBO/T	0	0.7	0.7	0.7	0.67	0.74	0.02	2.07	(0.25)
F$^-$									4.5

(b)	Yellow-stone USA	Vulcano Italy	Lipari Italy	Milos Greece	Hrafntin-nuhryggur Island	Artenis Armenia	Atis Armenia	Jalisco Mexico	Ikizidere Turkey	Quiron-colo Argentina
	YEL	VUL	LIP	MIL	RAB	DRY	ATS	JAL	IKI	QUI
SiO$_2$	77.01	74.66	74.84	77.03	74.56	78.67	78.57	76.39	74.79	77.11
TiO$_2$	<dtl	<dtl	<dtl	0.22	<dtl	0.26	<dtl	<dtl	0.14	0.13
Al$_2$O$_3$	11.97	12.84	12.92	12.72	13.04	11.60	11.95	10.79	13.78	14.06
Fe$_2$O$_{3t}$	1.53	1.98	1.86	1.34	1.88	0.60	0.57	3.53	0.88	0.64
CaO	0.54	0.81	0.86	1.52	0.89	1.60	1.34	0.18	0.83	0.46
MgO	<dtl	<dtl	<dtl	<dtl	<dtl	<dtl	<dtl	<dtl	0.13	<dtl
MnO	<dtl	<dtl	<dtl	<dtl	<dtl	<dtl	<dtl	<dtl	0.05	<dtl
Na$_2$O	3.11	3.29	3.87	3.05	4.04	0.70	2.31	3.94	3.93	2.55
K$_2$O	5.61	5.92	5.20	3.98	5.17	6.28	5.07	5.05	4.96	4.56
Total	99.77	99.5	99.9	99.86	99.94	99.71	99.81	99.88	99.49	99.51
AI^{-1}	1.07	1.08	1.08	1.36	1.06	1.46	1.29	0.92	1.16	1.55
ASI	0.99	0.96	0.95	1.05	0.94	1.07	1.02	0.88	1.03	1.42
NBO/T	0.010	0.020	0.023	0.0002	0.020	0.004	0.005	0.023	0.031	0.409
H$_2$O [wt.%]	0.096	0.163	0.210	0.113	0.101	0.085	0.106	0.027	0.44	0.222

[§]To - Torgauer Normalglas, [*]Co - cordierite glass and Di - diopside glass, [#]JeIIa - starting glass for a machinable glass ceramic Jenit II (JENA^{er}GLASWERK)[35], aluminium saturation index (mol%) ASI=Al$_2$O$_3$/(K$_2$O+Na$_2$O+CaO). agpaitic index (mol%), AI= (K$_2$O+Na$_2$O)/Al$_2$O$_3$, Fe$_2$O$_{3t}$=total Fe as Fe$_2$O$_3$, <dtl=less than detection limit, NBO/T according to Mysen[15].

NATURAL VOLCANIC GLASS SAMPLES

The ten natural volcanic glasses used were fresh, unaltered, and non-hydrated obsidians free of cracks with low crystal (<1%) and bubble content (<1%). Chemical composition of the

matrix glass was quantified by electron microanalysis (SEM-EDX) and X-Ray Fluorescence Spectrometer (WDX, Philips PW 2400). Volatile-species and thus water content are determined in high-vacuum degassing experiments (DEGAS, controlled heating rate 10K/min from RT-1500°C) coupled with a quadropole mass spectrometer (QMA 125 Balzers)[22].

METHODIC

Torsion Device

The oscillatory torsion deformation device has been already used for measurements of the viscoelastic behaviour of mica-based glass-ceramic aggregate[23], internal friction spectroscopy in Li_2O–$2SiO_2$ partially crystallised glasses[5], internal friction in partially molten rocks[24,25,26,27] and for the complex shear modulus and viscosity measurements in silicate melts at high temperatures[28,29,30]. A detailed description of the oscillatory torsion deformation device, its operational principle and the calibration procedure has been described elsewhere[5,23-29]. Cylindrical samples (diameter 8mm, length 20mm) were placed between two alumina rods (Al_2O_3-Frialit-Degussit, diameter 8mm, length ~190mm) used as holders in the oscillatory torsion deformation apparatus.

The data collected during a slow stepwise heating of the sample allowed to calculate the magnitude of the complex shear modulus $|G*(\omega,\tau)|$, and the phase shift $\varphi(\omega,\tau)$ between the applied torque and the resultant angular strain of the sample, where $\omega = 2\pi f$ is the angular frequency. Before starting the measurement, the sample was kept at each temperature for 2–3 hrs in order to reach a relaxed thermal state of a sample. With decreasing temperature, the relaxation time increases dramatically. When they become longer then the timescale of an experiment, the measurements refer to a material with a fixed configurational state, i.e. a glass. Relaxation times τ scales via the well-known Maxwell-relation with shear viscosity η

$$\eta = G_\infty \tau \tag{1}$$

and the unrelaxed shear modulus $\lim_{\omega\tau\to\infty} G* = G_\infty$. The relaxation times are of the order of 100s when the viscosity is about $10^{12.3}$ Pas at T_g. A few tens of degrees below this temperature, relaxation times have still further increased and the material structure does no longer undergo significant configurational changes, even over long periods of time. For temperatures $T < T_g^{ex}$ the configurational state is fixed and vibrational contributions dominate the elastic properties[6,33]. It is possible to measure thermally activated ion transport processes[31,32,33] as well as small-scale flexural-torsional motions of bridging Si-O-Si bounds[53]. For temperatures higher then T_g^{ex} the configuration changes rapidly with temperature and the response is glass like. At $T_g^{mech}(\omega)$ the viscoelastic mechanical glass transition from "glass-like" to relaxed liquid takes place[34]. From the results of $|G*(\omega,\tau)|$ and $\varphi(\omega,\tau)$ storage $G'(\omega,\tau)$ and loss modulus $G''(\omega,\tau)$ of the complex shear modulus $G*(\omega,\tau)$, internal friction $Q^{-1}(\omega,\tau) = G''(\omega,\tau)/G'(\omega,\tau)$, complex compliance $J*(\omega,\tau)\cdot G*(\omega,\tau) = 1$ and complex shear viscosity $i\omega\cdot\eta*(\omega,\tau) = G*(\omega,\tau)$ can be calculated.

$$G'(\omega,\tau) = |G^*(\omega,\tau)| \cos(\varphi(\omega,\tau)), \quad G''(\omega,\tau) = |G^*(\omega,\tau)| \sin(\varphi(\omega,\tau)) \qquad (2),(3)$$

The temperature dependence of the relaxed shear viscosity and the recoverable compliance is then obtained and the retardation part of the compliance $J'' - (\omega\eta_0)^{-1}$ can be calculated[8]

$$\eta_0(T) = \lim_{\omega\to 0}\eta''(\omega,T), \qquad J_0 = \lim_{\omega\to 0}J' = \lim_{\omega\to 0}\left(\frac{G'}{G'^2 + G''^2}\right) = \frac{1}{G_\infty}. \qquad (5),(6)$$
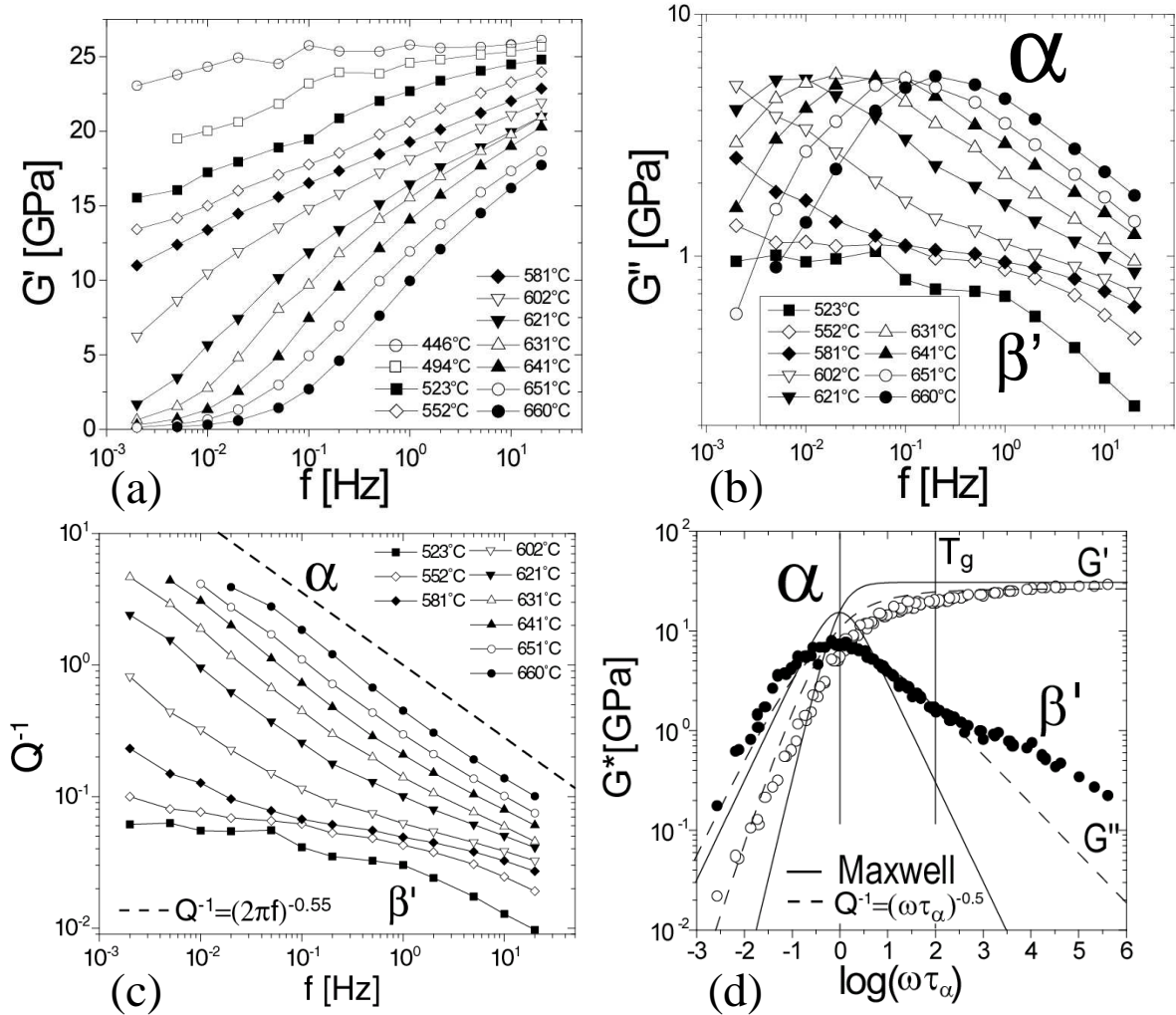
Figure 1: Variations of the (a) real part G' (storage modulus), (b) the imaginary part G'' (loss modulus) of the complex shear modulus $G^* = G' + iG''$ and (c) internal friction $Q^{-1} = G''/G'$ with frequency of the thermo-rheological complex melt JeIIa and a power law $Q^{-1} \sim \omega^{-0,55}$ on the high frequency side for Q^{-1}. (d) Master plot of the complex shear modulus G^* for the thermo-rheological simple natural volcanic melt IKI.

Using of an Arrhenian-ansatz for the temperature dependence of the relaxed shear viscosity, the apparent pre-factor and the apparent activation energy for viscous flow could be calculated. For

thermo-rheological simple systems, the time-temperature superposition principle of viscoelasticity could be used to construct a master curve[5,8,28,30] (Fig. 1 d).

Flexure Pendulum Device

The measurement principle and calibration procedure has been described elsewhere[1, 35]. It operates in air at a frequency of about 0,63 Hz and temperatures up to 1000°C. The sample is a combination of two bars with a rectangular cross section of $(1x1)mm^2$ and a length of 40mm. The free sample length is about 20 mm. One end of the specimen is held rigid and the other end is connected with the movable part of the flexure pendulum. An adjustable weight gives the opportunity to vary the period of pendulum oscillations in a limited way.
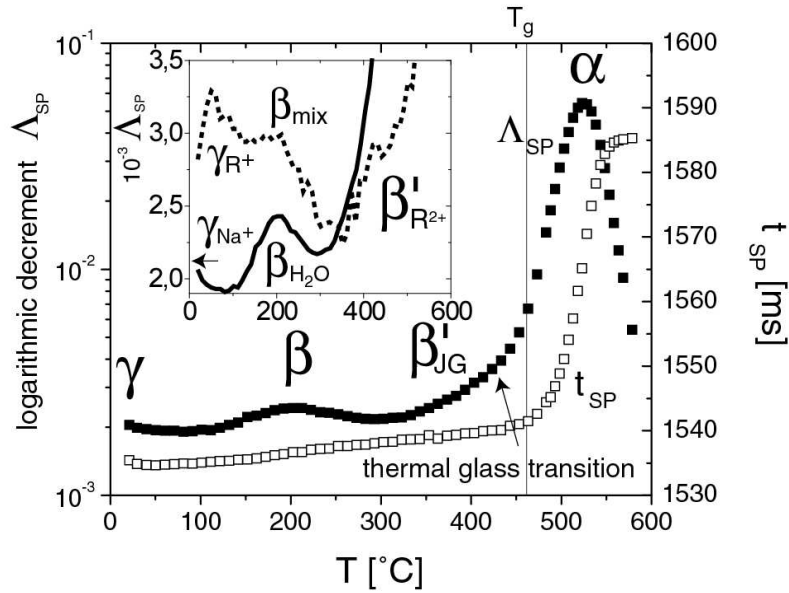

Figure 2: Measurement quantities (see text) for $Na_2Si_3O_7$. (inset) Comparison of the logarithmic decrement Λ_{SP} for $Na_2Si_3O_7$–glass (solid line) and JAL-obsidian (doted line): γ_{R^+} -alkali ion transport, β_{mix} - mixed alkali peak, β_{H_2O} - water peak, β' - superposition of Johari-Goldstein relaxation, alkali earth ion transport processes and the thermal glass transition[31,32,33,35,53,36].

Measurements were done under isothermal conditions in the range below the glass transition temperature T_g in 10K-steps and above T_g in 5K-steps. Experimentally determined quantities are the logarithmic decrement without specimen Λ_P and of the coupled system specimen-pendulum Λ_{SP}, oscillation period of pendulum $t_P = f_P^{-1} = 2\pi\omega_P^{-1}$ and of the coupled system specimen-pendulum t_{SP} (Fig. 2). With the direction moment D_P of pendulum and geometrical quantities of the specimen: free length l, moment of inertia I and experimentally determined quantities rheological parameters complex Young's modulus $M^* = M'(\omega_P, T) + iM''(\omega_P, T)$ and internal friction Q^{-1} were calculated

$$M'(T, \omega_P) = \frac{3}{2}\frac{D_P l}{I}\left(\frac{t_P^2}{t_{SP}^2} - 1\right), \quad M''(T, \omega_P) = \frac{3D_P l}{2\pi I}(\Lambda_{SP} - \Lambda_P) \qquad (7),(8)$$

$$Q^{-1}(T, \omega_P) = \frac{M''(T, \omega_P)}{M'(T, \omega_P)} = \frac{t_{SP}^2 (\Lambda_{SP} - \Lambda_P)}{\pi (t_P^2 - t_{SP}^2)}. \tag{9}$$

For the special ansatz of Maxwellian material behaviour[1] the rheological parameters of the glass sample: stress relaxation time τ, Young's modulus E and shear viscosity η can be calculated:

$$\tau = \left(\frac{t_P}{t_{SP}} - 1 \right) \left(\frac{\Lambda_{SP}}{t_{SP}} - \frac{\Lambda_P}{t_P} \right)^{-1}, \quad E = \frac{3}{2} \frac{D_P l}{I} \left(\frac{t_P^2}{t_{SP}^2} - 1 \right) \left(1 + \frac{t_P^2}{4\pi^2 \tau_S^2} \right), \quad \eta = \frac{E\tau}{3} \tag{10)-(12}$$

BASIC RELATIONS

Relaxation processes (ion mobility, anelasticity and viscoelasticity) deviating from the classical exponential (Debye) behaviour are often encountered in the dynamics of complex materials such as silicate glasses, glass ceramics and partially molten rocks[1,5,8,23-33,35,37,38,39]. In many cases experimentally observed relaxation functions exhibit a stretched exponential (Kohlrausch-Williams-Watts) decay

$$\Phi(t) \propto \exp\left(-[t/\tau]^{\beta_{KWW}} \right) \tag{13}$$

with $0 < \beta_{KWW} < 1$, or a scaling decay $\Phi(t) \propto (t/\tau)^{-\alpha}$ with $0 < \alpha < 1$. An appropriate tool to describe phenomenological this richness of dynamical features is fractional calculus (FC)[40].

Rheological Models

Usually phenomenological viscoelastic models are described by using a combination of springs and dampers. A spring is purely elastic element and describes the instantaneously acting Hookeian law with the instantaneous dynamic response (complex shear $G*$, adiabatic bulk $K*$ or Young's $M* = 9K* \cdot G*/(3K* + G*)$ modulus) $M* = M' + iM''$ being constant and real ($Q^{-1} = 0$). A damper is a purely viscous element and describes the instantaneously acting Newtonian law with purely imaginary dynamic responses ($Q^{-1} = \infty$). The mechanical relaxation behaviour of standard viscoelastic bodies, such as Maxwell's or Zener's, is described through combinations of springs and dashpots. These standard bodies involve a fairly small number of single elements. The problem here is that the corresponding ordinary differential equations have a relatively restricted class of solutions, which is, in general, too limited to provide an adequate description for the complex systems discussed in the introduction. To overcome this shortcoming one can relate stress and strain through fractional equations (FEs)[40]:

$$\sigma(t) = M_0 \tau^b \frac{d^b \varepsilon(t)}{dt^b}, \tag{14}$$

with $0 \le b \le 1$ and the relaxation time τ. In this way one readily obtains scaling decays. In general, FC allows the interpolation between the purely elastic behaviour, obtained for b = 0 and

the purely viscous pattern, obtained for $b = 1$ in equation (14). Heymans[41] have demonstrated that the fractional relation, equation (14), can be realised physically through hierarchical arrangements of springs and dampers, such as ladders, trees or fractal structures.

Fractional Maxwell Model

The classical viscoelastic Maxwell model (composed of a linear elastic element and a linear viscous element in series) may be modified by replacing both elements by FEs and the constitutive equation and the dynamic responses is of the form:

$$\sigma(t) + \tau^{a-b} \frac{d^{a-b}\sigma(t)}{dt^{a-b}} = \tau^a M_0 \frac{d^a \varepsilon(t)}{dt^a} , \quad M^* = M_0 \frac{(i\omega\tau)^a}{1 + (i\omega\tau)^{a-b}} . \qquad (15), (16)$$

Since $0 \le b < a \le 1$ the condition for thermodynamic compatibility is fulfilled[41]. For $a = 1$ one gets the Cole-Cole or Caputo-Model[25,42] which leads in the high temperature or low frequency limit to constant-Q^{-1}. For $a = 1$ and $b = 0$ (16) is transformed to the classical Maxwell model. Transformation into a standard model is carried out by adding an elastic element of modulus M_1 in series. The dynamic response $M^*(\omega, \tau)$ and internal friction $Q^{-1}(\omega, \tau)$ then become:

$$M^*(\omega, \tau) = \frac{M_0}{X + (i\omega\tau)^{-a} + (i\omega\tau)^{-b}} , \quad Q^{-1}(\omega, \tau) = \frac{\Omega_b^{\sin} + X}{\Omega_a^{\cos} + \Omega_a^{\cos} + X} \qquad (17)$$

with $\Omega_j^k = (\omega\tau)^{-j} k(j\pi/2)$, X=$M_0/M_1$. It is also possible to give an analytical expression for the relaxation time distribution[43] $H(\tau)$ with the relation $M^*(\omega, \tau) = \hat{M}(p, \tau)|_{p=i\omega}$ and $H(\tau) = \pm \lim_{\varepsilon \to 0} \Im[\hat{M}(p)]|_{p=-1/\tau \pm i\varepsilon}$.

In Fig. 2 different relaxation processes are observed: one above the glass transition temperature T_g α-relaxation (viscoelastic process) and two below T_g β and β'-relaxation (anelastic processes). For this reason a generalised fractional Maxwell model (GMM) is used to calculate anelastic and viscoelastic behaviour in the restricted temperature range. This GMM consists of three fractional Maxwell elements with a complex modulus $M_i^*(\omega, \tau_i)$ according to equation (17) in parallel:

$$M^*(\omega, \tau) = \sum_{i=1}^{3} \frac{M_{1,i}(i\omega_P \tau_i)^{a_i}}{(1 + (i\omega_P \tau_i)^{a_i - b_i}) + X_i(i\omega_P \tau_i)^{a_i}} \qquad (19)$$

For $a_i = 1$, $b_i = 0$ and $X_i = \lim_{M_{0,i} \to 0} M_{0,i}/M_{1,i}$ the single fractional Maxwell elements are transformed to Maxwell elements with one relaxation time τ_i. For all relaxation processes the stress relaxation time τ_i are expressed in an Arrhenian form:

$$\tau_i = \tau_{0,i} \exp\left\{ \frac{E_{a,i}}{RT} \right\}, \qquad (20)$$

where $\tau_{0,i}$ is the pre-exponential factor, $E_{a,i}$ the activation energy, R the gas constant and T the absolute temperature. A Levenberg-Marquardt algorithm[44] is used to find the GMM-parameters that give the best fit[35] (Fig. 3). The individual GMM parameters are sensitive for different influences. Comparisons with other measurements (viscosity, diffusion, electrical conductivity) can be made for the activation energies $E_{a,i}$ of the single relaxation processes.
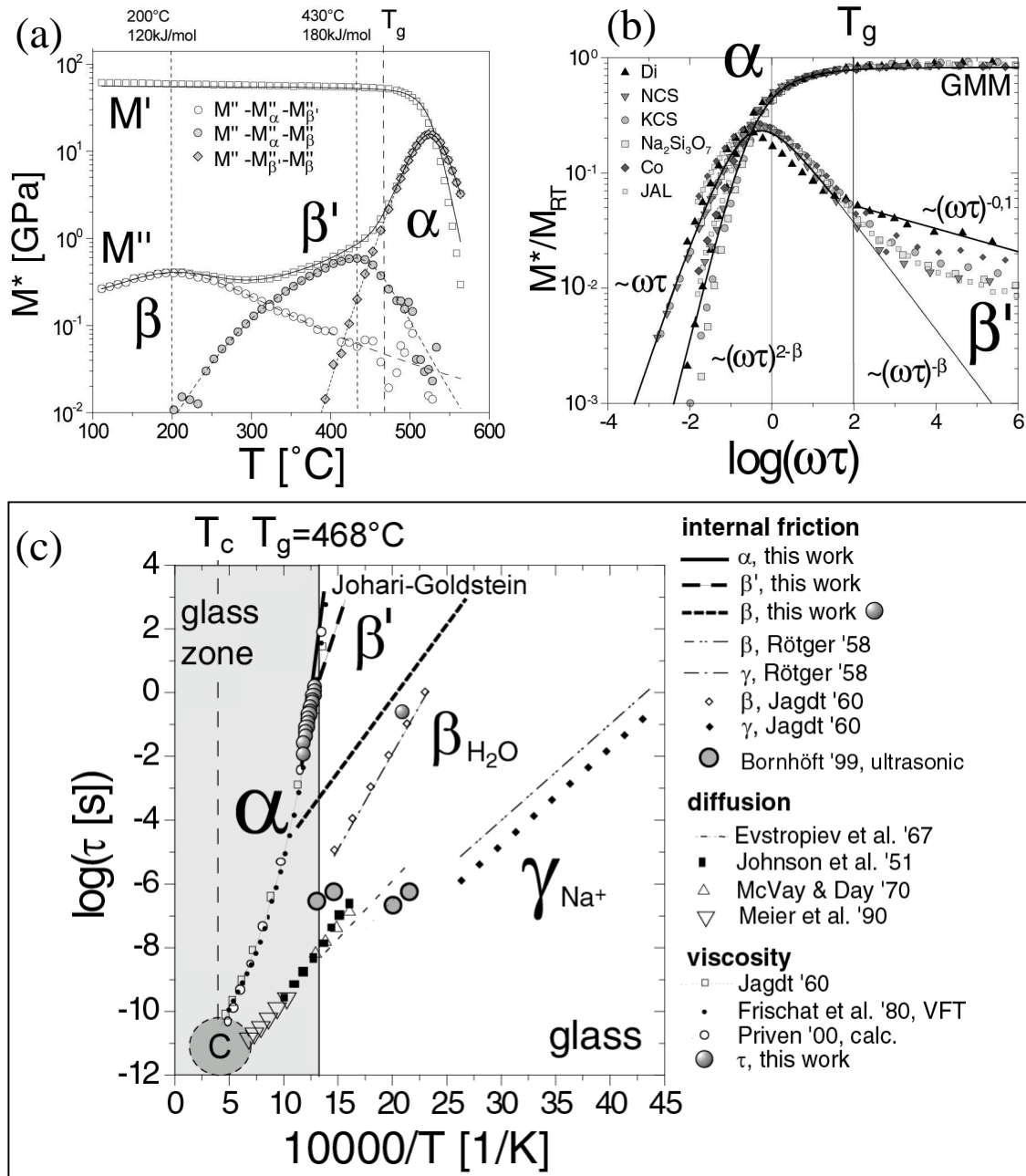

Figure 3: (a) Complex Young's modulus M* for $Na_2Si_3O_7$-glass with GMM-fit. (b) Masterplot of complex Young's modulus M* normalised with the unrelaxed Young's modulus M_{RT} at RT for the investigated synthetic systems and one volcanic glass as well as fractional Maxwell model (17) with $b_\alpha=0,5$, $a_\alpha=1$. (c) Relaxation map[45,46,47,48,49,50,51,52] of the $Na_2Si_3O_7$-glass.

Below we are restricted to the α-process. Calculation of the apparent activation energy E'_α for the α-process at T_g according to the quotient $\delta' = \delta_{Debye} / \delta_\alpha^{1/T}$ of measured full width at half maximum $\delta_\alpha^{1/T}$ in a Arrhenius-plot and the Debye-type function $\delta_{Debye} = 1.144$

$$E'_{a,\alpha} = 2{,}303 R \delta' = \delta'' E_{a,\alpha} \qquad (21)$$

clearly confirms the deviation from Maxwell-behaviour with the distribution parameter $\delta'' = \delta_{Debye}^{1/T} / \delta_\alpha^{1/T} \approx b_\alpha \approx \beta_{KWW}$ (Tab. 2).

Table 2: Selected rheological data (flexure pendulum device $2\pi f = 4Hz$) of the examined glasses[35].

		SiO$_2$	NCS	KCS	CCS	Na$_2$Si$_3$O$_7$	To	Di	Co	JeIIa	Obsidian (mean)
T_g	[°C]	1148	552	597	692	468	564	713	827	620	750
$T_{Max,\alpha}$	[°C]	1239[53]	601	678		523	619	769	878	678	830
$E'_{a,\alpha}$	[kJ/mol]	354	343	362		277	259	551	586	295	221
$E_{a,\alpha}^{GMM}$	[kJ/mol]		663	635		605	581	1150	1190	713	407
$b_\alpha\big|_{Tg}$		0.61§	0.55	0.49		0.48	0.56	0.45	0.55	0.36	0.58
G	[GPa]	31	29	25	21	25	30	39	43	25*	29$^\#$
M_{RT}	[GPa]	79	77	64	53	61	72	92	99	95	74
M'_{Tg}	[GPa]	85	63	52	52	56	51	60	83	65	62
$-dM'/dT$ $_{(T<T_g)}$	$\left[\frac{MPa}{K}\right]$	-5.6	20.8	4.4	0.9	20	19	18.5	19.8	22	3.8
$m = \frac{d\log\tau}{d(T_g/T)}\big|_{T_g}$		21	45	46	47	43	32	69	52	44	18

§calculated[35] from β_{KWW}[37], *shear modulus G at 446°C and 20Hz, $^\#$651°C and 20Hz

DISCUSSION AND CONCLUSION

Obsidian can be characterised as a thermo-rheological simple melt with small fragility m~18. A crucial factor is the relatively high water content, which causes the mechanical relaxation behaviour above T_g. In the vitreous state the influence of water on the dynamic processes is negligible, since the volcanic glasses are almost completely polymerised (NBO/T<0.4). The examined synthetic glasses are fragile in comparison with the obsidians (c.f. Tab. 2). Below T_g the examined glasses exhibit a complex relaxation behaviour due to the superposition of different processes, which can identified only by the use of an appropriate high resolution broadband mechanical, dielectric and ion trace-diffusion measurements to a specific microscopic relaxation process. Within the temperature range above T_g the dynamical or mechanical glass transition can be characterised via a practically constant asymmetrical distribution of relaxation times, almost independent of the fragility index. It can be distinguished into thermo-rheological simple and complex (in this study JeIIa, Di) glasses. The latter group exhibits a broader relaxation time distribution due to the phase separation processes (Fig. 4).
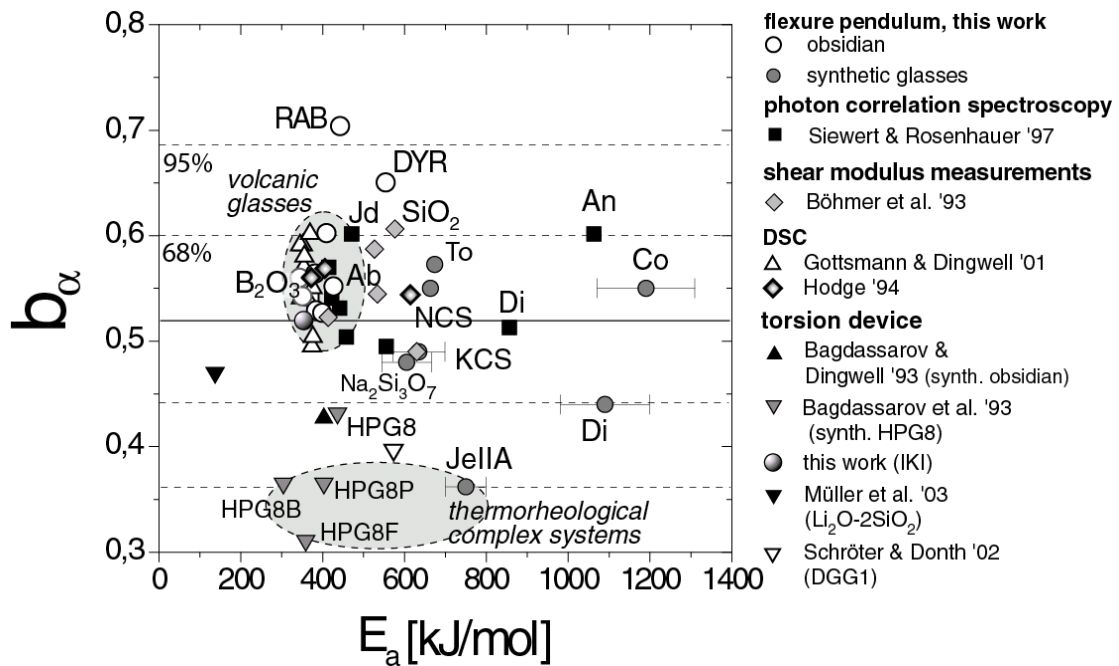
Figure 4: Relaxation time distribution parameter b_α ($a_\alpha = 1$) from GMM-fit as a function of the apparent activation energy for viscous flow E_a at T_g of the synthetic and volcanic melts of this work in comparison to literature data[21,54,55,28,30,5,56,37] (b_α was calculated[35] from β_{KWW}).

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