Mechanical Spectroscopy on Volcanic Glasses

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Abstract

Mechanical relaxation behaviour of various natural volcanic glasses have been investigated in the temperature range $RT - 1000^\circ C$ using special low frequency flexure ($f \approx 0.63\text{Hz}$) pendulum experiments. The rheological properties complex Young’s modulus $M^\star(\omega, \tau)$ and internal friction $Q^{-1}(\omega, \tau)$ have been studied from a pure elastic solid at room temperature to pure viscous melt at $\log(\eta[\text{Pa}\text{s}]) = 8$. The Young’s modulus at room temperature $M_{RT} = (70 \pm 10)\text{GPa}$ is nearly constant. There is a positive correlation with the water content and a weak negative correlation with the cooling rate. Several relaxation processes are assumed to act: the primary $\alpha$-relaxation (viscoelastic process, $E_a = (344...554)\text{kJ/mol}$) above the glass transition temperature $T_g = (935...1105)\text{K}$ and secondary anelastic $\beta', \beta$ and $\gamma$-relaxation processes below $T_g$. The dynamic glass transition, i.e. the viscoelastic $\alpha$-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: $(\gamma, \beta)$ cooperative movement of alkali ions in the vitreous state, $(\beta')$ cooperative movement of alkaline earth ions and non bridging oxygen’s near the glass transition range. Here the influence of water must be taken into account as well as alteration effects due to structural $\alpha$-relaxation. With a simple fractional Maxwell model with asymmetrical relaxation time distribution, $H(\tau)$, phenomenological the mechanical relaxation behaviour, is described. This establish a basis of realistic concepts for modelling of volcanic or magmatic processes.

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1 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((PS92), (Web97), (BZKH97), (Don01), (SSHB03), (DRVdB03), (MBJ03), (Buc03a), (WBH04)). The evolution of terrestrial planets is determined by the rheological properties of silicate melts and their stability under different atmospheric conditions. An important role plays the water content as well as the chemical composition of the natural materials which reflect and cause the evolution processes ((MS99)). By optical microscopy we know already since more than one hundred years textural patterns in vitreous and crystalline volcanic rocks ((Zir73), 1). This observations clearly indicate degassing induced crystallization as well as a high mobility of crystalline phases in the magma and lava during the emplacement process ((Hei89), (SML00)). According to theoretical and experimental investigations of (GH96) formation of such patterns are only possible below viscosities \[ \log(\eta[\text{Pa}s]) = 4 \], i.e. at temperatures far above the glass transformation range. In the case of rhyolitic glasses at approximately 1300°C under atmospheric conditions, i.e. far above field experience of emplacement of dacitic lava at \( \approx 925^\circ C \) (Tab. 1).

In addition in daily life silicate melts products are ubiquitous. Natural handling with glass usually misleads us to believe that the glass transition is one of the ten great outstanding challenges in physics ((GYI01), (Nga00), (ANM00), (Don01), (DS01)).

From a geoscientific point of view, experimental vulcanology and petrology examine the structure, dynamics and properties of natural and synthetic silicate systems ((PK91), (Sax92), (SMD95), (Mys03)). The rheological properties determine emplacement mechanisms generally and the hazard implications especially ((Fin90), (Smi97), (MS99)). Whereby fragmentation of vesicular magma

| Locality            | Rock type                        | Temperature [°C] |
|---------------------|----------------------------------|------------------|
| Taupo, New Zealand  | Rhyolite lava and pumice         | 735-890          |
| Mono Craters, USA   | Rhyolite lava                     | 790-820          |
| Island              | Rhyodacite obsidian              | 900-925          |
| New Britain         | Andesite pumice                  | 940-990          |
| New Britain         | Dacite lava and pumice           | 925              |
| New Britain         | Rhyodacite pumice                | 880              |

Table 1
Estimated extrusion temperatures from field observations as well as calculations from the mineralogy of various high viscose lavas ((Hal96))
Fig. 1. (top) Copperplate engraving by Zirkel 1873 of a “magnetite spider” in an obsidian from Armenia (adapted from (Zir73)). (bottom) Turbulent hairline magnetite (fibres) in vitreous matrix of obsidian from Graber, Armenia together with fluidal adjusted bubbles.

is one of the main processes governing explosive volcanism ((Din96), (Pap99), (GM03)). Besides the material consuming and dangerous direct observation of lava flows it is also in some cases possible to reconstruct the emplacement history from microscopic texture in combination with experimental techniques under laboratory conditions ((Hei89), (Fin90), (MCCL99), (CC99), (ML01), (RM02), (CMC02), (CTCa04), (CTC04)). As products of very viscous melts
volcanic (rhyolitic in particular) glasses (obsidian) are the link to the melt. The characterization of rheological properties of these volcanic glasses are the subject of this work.

The material property, by which glass formation is determined, is the viscosity \( \eta \) or the structural or \( \alpha \)-relaxation time \( \tau_\alpha \). Their dependence on pressure \( P \), temperature \( T \), chemical composition \( X \), bubble content \( c_b \), crystal content \( c_{xx} \) and volatile content \( c_v \) represents the goal of intensive geoscientific investigations ((BW72), (Sha72), (Ric84), (HA85), (Per91), (PS92), (SS92), (BDW94), (SDWB95), (LR95), (SDWS96), (Bak96), (HDW96), (BD97), (MCCL98), (SBDR98), (BLT00), (ML01), (SMCF01), (SBR01), (GD03)).

Since in the glass transition range the relaxation time reaches orders of magnitude, which are no longer accessible under laboratory conditions. Thus, the transition from viscous melt to solid elastic body, i.e. the viscoelastic response, determines the material behavior ((Ver92), (BD93), (BDW93), (BD97), (Bag99), (BMP+01), (Web97), (DGBP97a), (DGBP97b), (DG97), (DGB+97), (Duf98), (MBJ+03), (WBH03), (WJ03)).

In the vitreous state the structure of the melt is frozen in, however, here in addition dynamic processes (mobility of ions in the glassy network) take place, which can be measured by mechanical spectroscopy as internal friction, whereby a small water content cause unresolved phenomena ((Roe41), (Fit51a), (Fit51b), (Roe58a), (Roe58b), (RR61), (Coe61), (DR62a), (DR62b), (DS60), (SD69), (MD70), (SD70), (DS72), (Roe74), (Roe75), (DS74), (Day74a), (Day74b), (VS74), (TR74), (ZRD76), (TB79a), (TB79b), (Bar83), (Ver92), (Ke96), (BL96), (BZKH98a), (RI98a), (RI98b), (Rol01)).

In this study the rheological properties, Young’s modulus \( M^* \) and internal friction \( \tan \delta = Q^{-1} \), of natural volcanic glasses have been investigated in a wide temperature range from a purely elastic solid at room temperature to purely viscous melt at a viscosity \( \log(\eta[\text{Pas}]) \approx 8 \). It will contribute to the understanding of the thermocinetis and dynamics that govern the glass transition, at temperatures well above, below and at the glass transition temperature \( T_g \) ((Don01)). In this context the rheological properties of natural and synthetic silicate glasses and melts are of interest. With a simple generalized fractional Maxwell model, the relaxation behavior is described phenomenologically. This establish a basis of realistic concepts for modelling of volcanic or magmatic processes.
2 Basics

A necessary and sufficient condition to glass formation is a corresponding (critical) cooling rate $q_K$ to avoid crystallization. A coarse approximation for the estimate of $q_K$ gives (Owe85), (Fel83) and (Deb96):

$$q_K = 2 \cdot 10^{-6} \frac{T_m^2 R}{V \eta(T_n)} = \frac{T_m - T_n}{\tau_{K,n}}$$

(1)

with the fusing temperature $T_m$, the gas constant $R$, the molar volume $V$, viscosity $\eta$, the so called nose temperature $T_n$, and corresponding critical time $\tau_{K,n}$. Here, according to (Deb96) or (Ang88) the time $\tau_K$ for formation of a critical volume $V_K$ as well as the structural relaxation time $\tau_\alpha$ and their interplay (time-temperature-transformation) is of great significance (cf. Fig. 2). Above the thermal glass transition temperature $T_{g}^{exp}$ specified by the experimental conditions, which is determined by a characteristic structural or $\alpha$ relaxation time $\tau_\alpha$, the mechanical glass transition occurs at the ‘mechanical’ relaxation time $\tau_\alpha(T_\alpha)\omega \approx 1$. The mechanical glass transition temperature $T_\alpha$ shifts with measurement frequency $\omega = 2\pi f$ in general via the Arrhenian equation

$$\ln \left( \frac{\Omega}{\omega} \right) = \frac{E_a(T)}{k_B T_\alpha}$$

(2)

with jump frequency $\log(\Omega[Hz]) \approx 12 - 14$ as typical frequency of molecular vibration (RGD03), Boltzmann-constant $k_B$ and a temperature dependent activation energy $E_a(T)$ with $\frac{dE_a}{dT} \leq 0$ (GS95), (BL96)). The most common entrances to the modelling of the temperature dependence of the activation energies are:

(1) the empirical VFT-equation ((Vog21), (Ful25), (TH26)) with the adjustable parameters $B_{VFT}$ and $T_0$ ($T_0$ is usually equated with the Kauzmann-temperature (Hod94), (Hod97))

$$E_a(T) = \frac{B_{VFT}}{1 - \frac{T}{T_0}}.$$  

(3)

(2) the Adam-Gibbs-equation (AG65)) with the adjustable parameter $B_{AG}$ and a temperature dependend configurational entropy $S_c(T)$

$$E_a(T) = \frac{k_B B_{AG}}{S_c(T)}.$$  

(4)

(3) the Avramov-equation (AM88)) with a dimensionless activation energy
Fig. 2. Schematic representation to the construction of the TTT-curve (time-temperature-transformation). (a) Isobar dependence of the free enthalpy $G$ on temperature $T$ of a gas, a liquid (stable and supercooled liquid), and a crystal as well as the corresponding glass of a pure substance with the boiling point $T_B$, melting point $T_m$ and the glass transition temperature $T_g$. (b) The hypothetical intersection point between $\tau_K$ and $\tau_\alpha$ is not reached, since (c) $\tau_K$ goes up strongly due to the drastic viscosity increase with $\tau_\alpha$ (after Deb96).

$\varepsilon_A$, the Avramov fragility index $\alpha_A$ and the glass transition temperature $T_g$ at a viscosity of $\log(\eta[\text{Pas}]) = 12.3$

$$E_a(T) = \frac{k_B \varepsilon_A T_g}{T^{\alpha_A - 1}}.$$  (5)

(4) the Williams-Landel-Ferry-equation (WLF, [WLF55]) with the parameters $A_{WLF}, B_{WLF}$ and the fragility index $m = \frac{d \ln(\tau_\alpha)}{d (T_g/T)} |_{T_g}$ at the glass transition temperature $T_g$ ([BA92], [Don01])

$$E_a(T) = mT - \frac{A_{WLF}T(T - T_g)}{B_{WLF} + (T - T_g)}.$$  (6)

$\log(\Omega)$ and the Kauzmann-Temperature $T_0 \approx (48...815)K$ are the asymptotes concerning the frequency or temperature ([Don81], [Don92], [Don01], [Hod94], [ANM+00]).
The mechanical glass transition for small deformations $10^{-4}$ is the linear viscoelastic response of the material. Then the linear response is completely determined by properties of the equilibrium melt if thermal fluctuations are included in the equilibrium concept. The fluctuation-dissipation theorem (FDT) of statistical physics implies the important statement that it is exclusively thermal fluctuations which determine the linear response ((Don01), (Rol01)). Especially for the understanding of processes\(^1\) on a geological time scale these concepts are very useful ((NJ03)). Nonlinearity has to be take into account for large deformations and high strain rates, i.e. under emplacement conditions ((BD93), (DT94), (DT96), (REH00), (BB00), (BM02)).

Above a critical temperature $T_C$ predicted by the idealized mode coupling theory, MCT, the system is retained to ergoic and below non-ergodic (GS92). Non-ergodicity means that the correlation function $\Phi$ does not converge against an expected equilibrium value of $\lim_{t \to \infty} \Phi(t) = \Phi_{\infty} = 0$, but reaches a final value $\Phi_{\infty} > 0$. Since the corresponding coupling parameters are temperature dependent, one finds the critical temperature $T_C$ if the existence of a non-ergodic stage to the first time have been observed. In this sense one speaks of a phase transition at the glass transition but The precise designation is egodicity transition. That is, that density fluctuations froze below $T_C$. Above $T_C$ the structural $\alpha$-relaxation and second $\beta$-relaxation can not be distinguished. Below $T_C$ diffusion processes and the structural $\alpha$-relaxation are to be observed separately. In the internal friction spectrum the characteristic secondary $\beta$ loss maxima occur. Ergodicity can be restored by introduction of hopping-processes in the enlarged MCT also below $T_C$. The temperature dependence of the $\alpha$-time scale for $T > T_C$ is of the form (Sch00a, Don01):

$$\tau_{\alpha} \propto \eta \propto (T - T_C)^\gamma. \quad (7)$$

with a parameter $\gamma$. The following general rule is valid (Buc03b)

$$\tau_{\alpha}(T_c) \approx 10^{-7}s. \quad (8)$$

The distinction of the dynamics of the primary $\alpha$ process and a $\beta_{fast}$ process (in the sense of a microscopically fast movement) above $T_C$ in the field of the undercooled liquid is predicted, however, through the MCT and confirmed by neutron and light scattering experiments onto different glass formers as well as through computer simulations (RS96, SR97, HK02, Buc03b). The main problem with the MCT consists in the analysis of the $\alpha$-process. So (7) can only be observed experimentally in a small temperature range. If one identifies $T_C$ with the Vogel temperature $T_0$ or the glass transition

\(^1\) Within glass science these processes called 'Thermometereffekt' according to internal friction investigations of Roe41.
temperature \( T_g \), then experimental relaxation times and (7) are not to bring into agreement. A comparison with experimental data leads to the reasonable statement \( T_C > T_g > T_0 \) and \( T_C/T_g \approx 1.3...2.6 \propto 1/m \) for silicate melts ((Hes96), (Pfe98)). There according to the mode coupling theory for \( T < T_C \) the \( \alpha \) process no more is supposed to occur but is experimentally even strongly observed at \( T \approx T_g \). For this reason one is today generally of the opinion, that the mode coupling approximation is a good theory for \( T > T_C \) and break down for temperatures below \( T_C \) especially for strong melts. In spite of these difficulties the MCT is today the widest driven forward analytical representation, that understands essential appearances of the glass transition correctly and contains also many possibilities of a generalization ((Sch00)).

**Fig. 3.** Schematic representation of thermokinetic and dynamic \( \alpha \)-transition of an inorganic-glass or melt and related phenomena: \( \gamma_{R^+} \)-alkali ion transport, \( \beta_{H_2O} \)-water peak, \( \beta' \)-superposition of Johari-Goldstein relaxation and the thermal glass transition (c.f. (Dol02)).

During cooling, the mobility of the atoms decrease. At the (nonlinear) thermal glass transition range (the relaxation time is a function of temperature \( T \) and the structural state \( \tau(T, T_f) \)) typical relaxation times are reached by seconds or minutes, in order to take the (metastable) equilibrium position. If the temperature now falls, the structure can not reach their equilibrium and is therefore “trapped” in a definite configurational state at the limit of the fictive temperature \( T_f \) ((Too41), (GN70), (Mar85), (Rit56),
In the vitreous state it is possible to measure $\beta$ or secondary mechanical relaxation processes which are substantially decoupled of the structural alpha relaxation (c.f. Fig. 3). This processes can be explained with different mechanisms: $(\gamma, \beta)$ cooperative movement of alkali ions in the vitreous state. $(\beta')$ cooperative movement of alkaline earth ions and non bridging oxygen’s near the glass transition range. Here the influence of water must be taken into account as well as alteration effects due to structural $\alpha$-relaxation. The temperature dependents of diffusion, electrical conductivity and mechanical relaxation processes can be described in most cases by an Arrhenian-law via equation (2) with an equivalent activation energy (see (Fri75), (Pau98), (Maa99), (Nga00)).

Relaxation processes (ion mobility, viscoelasticity) deviating from the classical exponential (Debye) behavior are often encountered in the dynamics of complex materials such as silicate glasses below and above $T_g$, glass ceramics and partially molten rocks ((Jon77), (Mue83), (KB85), (BD93), (Web97), (RI98b), (ANM00), (Don01), (Nga00)). In many cases experimentally observed relaxation functions exhibit a stretched exponential (Kohlrausch-Williams-Watts) decay (Koh47)

$$\Phi \propto \exp \left( - \frac{t}{\tau}^{\beta_{KW W}} \right)$$

(9)

with $0 < \beta_{KW W} < 1$, or a scaling decay

$$\Phi \propto \left[ \frac{t}{\tau} \right]^a$$

(10)

with $0 < a < 1$ ((BD93), (BDW93), (BD97), (Bag99), (BLT00), (MBJ03)). An appropriate tool to describe phenomenologically this richness of dynamical features is fractional calculus (FC, see below) ((SOB95)).

2.1 Rheological models

Usually phenomenologic viscoelastic models are based on springs and dampers. A spring is purely elastic and describes the instantaneously acting Hook’s law with the dynamic responses (complex modulus $M^* = M' + iM''$ with storage modulus $M'$ and loss modulus $M''$ or complex creep compliance $M^* \cdot D^* = 1$) being constant and real ($M''/M' = Q^{-1} = 0$). The constitutive equation of stress $\sigma$ and strain $\varepsilon$ is of the form

$$\sigma(t) = M_0 \varepsilon(t), \quad M^* = M' = M_0 = D_0^{-1}$$

(11)
with an idealized Young’s modulus $M_0$. A damper is purely viscous and describes the instantaneously acting Newton law with purely imaginary dynamic responses ($Q^{-1} = \infty$) (Don92):

$$\sigma(t) = \eta \frac{d\varepsilon(t)}{dt}, \quad M^* = iM'' = i\omega\eta$$

(12)

Through combinations of springs and dashpots one arrives at standard viscoelastic models, such as the Maxwell or the Zener, these models 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 (SOB95):

$$\sigma(t) = M_0 \tau^\beta \frac{d^\beta \varepsilon(t)}{dt^\beta}$$

(13)

with $0 \leq \beta \leq 1$ and the relaxation time $\tau$. In this way one readily obtains scaling decays. In general, $FC$ allows the interpolation between the purely elastic behaviour of equation (11), obtained for $\beta = 0$ in equation (13), and the purely viscous pattern of equation (12), obtained for $\beta = 1$ in equation (13). (SB93, SOB95, SB95, SMBN95, HB94) and (Hey96) have demonstrated that the fractional relation, equation (13), can be realized physically through hierarchical arrangements of springs and dampers, such as ladders, trees or fractal structures. We now introduce the term fractional element (FE) to denote such a hierarchical structure and specify it by the trible $(\beta, M_0, \tau)$.

### 2.2 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 the damper by a $FE$. The dynamic responses for this model is:

$$\frac{M^*(\omega, \tau)}{M_0} = \frac{(i\omega\tau)^\gamma}{1 + (i\omega\tau)^\gamma}, \quad \frac{D^*(\omega, \tau)}{D_0} = 1 + (i\omega\tau)^{-\gamma}$$

(14)

which is the so called Caputo-Model (BLT00), (Bag99) or Cole-Cole-Model (CC41). In the high temperature and low frequency limit (14) leads to constant-$Q^{-1}$. For $\gamma = 1$ (14) is transformed to the classical Maxwell model. When both elements are replaced by $FE$’s the dynamic responses is of the
Jonscher-type \((\text{Jon77})\):
\[
\frac{M^*(\omega, \tau)}{M_0} = \frac{(i\omega\tau)^\alpha}{1 + (i\omega\tau)^{\alpha-\beta}}, \quad \frac{D^*(\omega, \tau)}{D_0} = (i\omega\tau)^{-\alpha} + (i\omega\tau)^{-\beta}
\]
(15)

with \(\beta < \alpha\) and the constitutive equation is of the form:
\[
\sigma(t) + \tau^{\alpha-\beta}d^{\alpha-\beta}\sigma(t) = M_0\tau^{\alpha}d^{\alpha}\varepsilon(t)
\]
(16)

Since \(0 \leq \beta < \alpha \leq 1\) the condition for thermodynamic compatibility is fulfilled \((\text{HB94}, \text{Hey96})\). 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 \(Q^{-1}\) then become:
\[
\frac{M^*(\omega, \tau)}{M_0} = \frac{M_1(i\omega\tau)^\alpha}{M_1(1 + (i\omega\tau)^{\alpha-\beta}) + M_0(i\omega\tau)^\alpha}, \quad \frac{D^*(\omega, \tau) - D_1}{D_0} = (i\omega\tau)^{-\alpha} + (i\omega\tau)^{-\beta}
\]
(17)

\[
Q^{-1}(\omega, \tau) = \frac{(\omega\tau)^{-\alpha} \sin\left(\frac{\alpha\pi}{2}\right) + (\omega\tau)^{-\beta} \sin\left(\frac{\beta\pi}{2}\right)}{(\omega\tau)^{-\alpha} \cos\left(\frac{\alpha\pi}{2}\right) + (\omega\tau)^{-\beta} \cos\left(\frac{\beta\pi}{2}\right) + \frac{M_0}{M_1}}
\]
(18)

It is also possible to give an analytical expression for the relaxation time distribution \(h(\tau)\) with the relation \(M^*(\omega, \tau) = \hat{M}(p, \tau)|_{p=i\omega}\) \((\text{Glo93})\):
\[
h(\tau) = \pm \lim_{\varepsilon \to 0} \Im[\hat{M}(p)]|_{p=-1/\tau \pm \varepsilon}
\]
(19)

and one gets:
\[
h(\tau) = \frac{\Omega^S_{\alpha,\beta} + \frac{M_0}{M_1}}{\tilde{\tau}^{-2\alpha} + \tilde{\tau}^{-2\beta} + 2\tilde{\tau}^{-\alpha-\beta} \cos([\alpha - \beta]\pi) + \frac{2M_0}{M_1} \Omega^C_{\alpha,\beta} + \frac{M_0}{M_1}}
\]
(20)

with \(\tilde{\tau} = \tau/\tau_{\text{max}}, \quad \Omega^C_{i,j} = \tilde{\tau}^{-i} \cos(i\pi) + \tilde{\tau}^{-j} \cos(j\pi), \quad \Omega^S_{i,j} = \tilde{\tau}^{-i} \sin(i\pi) + \tilde{\tau}^{-j} \sin(j\pi)\).
Table 2
The summary of various spectral functions and their power-law behaviour. Abbreviation: $p = i\omega\tau$, $A'$, $A$ - constants.

|                | $\omega\tau \rightarrow 0$                                                                 | $\omega\tau \rightarrow \infty$                                                                 |
|----------------|-------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------|
|                | $M^*/M_0$                                                                                  | $M'/M_0$                                                                                           |
| (Deb41)        | $(1 + p^{-1})^{-1}$                                                                        | $(\omega\tau)^2$                                                                                   |
| (CC41)         | $(1 + p^{-\alpha})^{-1}$                                                                    | $(\omega\tau)^{1+\alpha}$                                                                            |
| (Jon77)        | $(p^{-\alpha} + p^{-\beta})^{-1}$                                                          | $A'$                                                                                              |
| KWW (Koh47)    | $\exp(-(t/\tau)^\beta)$                                                                   | $A'$                                                                                              |
| (HN67)         | $1 - (1 + p^\alpha)^{-\beta}$                                                               | $1$                                                                                                |
| (DC51)         | $1 - (1 + p)^{-\beta}$                                                                      | $(\omega\tau)^{-\beta}$                                                                              |
| (Mue83)        | $Q = (\omega\tau)^\gamma$                                                                   | $1$                                                                                                |
| FC1            | $(p^{-1} + p^{-\beta} + \frac{M_0}{M_1})^{-1}$                                              | $1$                                                                                                |
| FC2            | $(p^{-\alpha} + p^{-\beta} + \frac{M_0}{M_1})^{-1}$                                        | $1$                                                                                                |
3 Sample selection

The nine natural volcanic glasses used were fresh, unweathered, unaltered, and nonhydrated 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, DSM 940 CARL ZEISS, eXL 10 Spektrometer, Oxford Instruments). Volatile species and thus water content are determined in high-vacuum degassing experiments (controlled heating rate 10K/min from RT-1500C) coupled with a quadropole mass spectrometer (QMA 125 Balzers, (SH00), (LBW+03), (HS03)).

YEL is a grey crystal-poor obsidian from Yellowstone (USA). VUL from Vulcano, LIP from Lipari (Italy) and JAL from Jalisco (Mexico) are grey crystal-free glasses. The sample MIL from Milos (Greek) is grey-black crystal-poor. RAB from Hrafntinnuhryggur (Island) and DYR from Artenis (Armenia) are black crystal-poor glasses. The obsidian ATS from Artis (Armenia) is grey crystal-poor with crystal bands. QUI from Quironcolo (Argentinia) and IKI from Ikizidre (Turkey) are transparent homogeneous obsidians with very few large crystals.

4 Experiments

The flexure pendulum is shown in Fig. 4. It operates in air at a frequency of about 0.63Hz (small deformations ≈ 10^{-5}...10^{-3}) and temperatures up to T ≈ 1000°C (cf. (BZ94), (BZHK97), (BZHK98), (BZKH98a), (BZKH98b), (WHBZ01)). The sample is a combination of two bars with a
Table 3
Chemical composition and water-content (wt.%) of the volcanic glasses. <dtl: less then detection limit, aqpaitic index (mol%) $AI = \frac{K_2O+N_2O}{Al_2O_3}$, aluninium satturation index $ASI = \frac{Al_2O_3}{K_2O+N_2O+CaO}$, structur modifier (mol%) $SM$ from (GD03), exess oxides (mol%) $EO = SM - 0.5Fe_2O_3 - Al_2O_3$ from (GGD02).

|       | YEL | VUL | LIP | MIL | RAB | DYT | ATS | JAL | QUI |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| $SiO_2$ | 77.01 | 74.66 | 74.84 | 77.03 | 74.56 | 78.67 | 78.67 | 76.39 | 77.11 |
| $TiO_2$ | <dtl | <dtl | <dtl | 0.22 | 0.26 | <dtl | <dtl | 0.13 |
| $Al_2O_3$ | 11.97 | 12.84 | 12.92 | 12.72 | 13.04 | 11.6 | 11.95 | 10.79 | 14.06 |
| $Fe_2O_3$ | 1.53 | 1.98 | 1.86 | 1.34 | 1.88 | 0.6 | 0.57 | 3.53 | 0.64 |
| $CaO$ | 0.54 | 0.81 | 0.86 | 1.52 | 0.89 | 1.6 | 1.34 | 0.18 | 0.46 |
| $MgO$ | <dtl | <dtl | <dtl | <dtl | <dtl | <dtl | <dtl | <dtl | <dtl |
| $MnO$ | <dtl | <dtl | <dtl | <dtl | <dtl | <dtl | <dtl | <dtl | <dtl |
| $Na_2O$ | 3.11 | 3.29 | 3.87 | 3.05 | 4.04 | 0.7 | 2.31 | 3.94 | 2.55 |
| $K_2O$ | 5.61 | 5.92 | 5.2 | 3.98 | 5.17 | 6.28 | 5.07 | 5.05 | 4.56 |
| Total | 99.77 | 99.5 | 99.88 | 99.86 | 99.94 | 99.71 | 99.81 | 99.88 | 99.51 |

AI$^{-1}$ 1.07 | 1.08 | 1.08 | 1.36 | 1.06 | 1.46 | 1.29 | 0.92 | 1.55 |
ASI 0.99 | 0.96 | 0.95 | 1.05 | 0.94 | 1.07 | 1.02 | 0.88 | 1.42 |
$\frac{NBO}{T}$ 0.0103 | 0.0197 | 0.0257 | 2E-4 | 0.0199 | 0.0037 | 0.005 | 0.023 | 0.409 |
EO 0.47 | 0.89 | 1.16 | -0.17 | 0.9 | -0.38 | 0.23 | 1.05 | -1.97 |
H$_2$O 0.096 | 0.163 | 0.21 | 0.113 | 0.101 | 0.085 | 0.106 | 0.027 | 0.222 |

rectangular cross section of (1x1)mm$^2$ and a length $l$ of 40mm. One end of the specimen is held rigid and the other end is connected with the movable part of the flexure pendulum. 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 $\Lambda_P$ and of the coupled system specimen-pendulum $\Lambda_{SP}$, oscillation period of pendulum $t_P = f_P = 2\pi \omega_P$ and of the coupled system specimen-pendulum $t_{SP}$. With the direction moment $D_P = (5.35 \pm 0.36)Nm$ of the pendulum and geometrical quantities of the specimen: free length $l$, moment of inertia $I$ and experimentally determined quantities rheological parameters complex Young’s modulus $M^*(\omega_P, T)$:

$$M'(\omega_P, T) = \frac{3D_P}{2I} \left( \frac{t_P^2}{t_{SP}^2} - 1 \right),$$

$$M''(\omega_P, T) = \frac{3D_P}{2\pi I} (\Lambda_{SP} - \Lambda_P)$$
and internal friction $Q^{-1}(\omega_p, T)$ were calculated

$$Q^{-1}(\omega_p, T) = \frac{M''(\omega_p, T)}{M'(\omega_p, T)} = \frac{t_{SP}^2(\Lambda_{SP} - \Lambda_p)}{\pi(t_p^2 - t_{SP}^2)}.$$ \hspace{1cm} (23)$$

The mechanical spectra are characterized by the complex Young’s modulus $M^*(T)$, complex shear modulus $G^*(T)$, internal friction $Q^{-1}(T)$, complex creep compliance $D^*(T)M^*(T) = 1$, shear compliance $J^*(T)G^*(T) = 1$ and/or the complex shear viscosity $\eta^*(t)$. The complex quantities can be separated into real (storage modulus $M'$) and imaginary parts (loss modulus $M''$). The Kramers-Kronig (dispersion) relations \((Kra26), (Kro26)\) couple the real and imaginary parts of the complex quantities $A^* = A' + iA''$ of a material by

$$A'(\omega) = -H[A''(\xi)], \quad A''(\omega) = H[A'(\xi)] \hspace{1cm} (24)$$

with the Hilbert-transform by principal value integral \((Don01)\)

$$H[f(\xi)](\omega) = \frac{1}{\pi} \int \frac{f(\xi)d\xi}{\xi - \omega}, \quad H^{-1} = -H.$$ \hspace{1cm} (25)$$

These are purely mathematical implications of the linear and causal material equations. The discussion of the mechanical spectra can take place thereby on the individual modulus.

5 Results

Fig.5 represents the storage modulus $M'$ and the loss modulus $M''$ for the investigated natural glasses. All obsidians show a relatively similar behaviour. A deviation from the general trend shows the LIP sample due to strong vesiculation. Here, a particularly long-drawn-out thermal and mechanical glass transition can be observed in the storage modulus.

The storage modulus at room temperature $M_{RT}$ is a material constant, i.e. the Young’s-modulus \(^2\) of the glass $E = M_{RT}$, which ranges for silicate glasses between 60GPa and 100GPa \((Wag04)\). The obsidians exhibit a relatively constant value of $(70 \pm 10)GPa$. In principle, $E$ is a function of the chemical composition, water-, bubble-, crystal content and temperature prehistory, however, the sensitivity on these influences is much less than those on the relaxation times \((Wag04)\). There is a positive correlation with the water content and a weak negative correlation with the cooling rate (Fig. 7).

\(^2\) If measurements of $M'(T)$ are carried out below $RT$, one observes a further rise
Fig. 5. Temperature dependence of the real part (storage modulus) $M'$ and imaginary part (loss modulus) $M''$ of the complex Young's modulus $M^* = M' + iM''$ for the natural volcanic glasses. (inset) Asymptotic behaviour of storage modulus at high temperature.
In the examined temperature range $M'(T)$ decreases continuously for most silicate glasses (Fig. 8). An exception is silica glass with an anomalous increase of Young’s modulus with temperature between 100 K and $T_g$ ([Bru70], [Bru71]). Fig. 8 and Tab. 4 clearly indicate that the examined natural glasses have to be assigned to the silica glass with the exception of the LIP-obsidian.

The total temperature dependence of Young’s modulus is given by the differential ([Bru71], [AMR93], [RC87], [VPR96], [SSHB03]):

$$\frac{dM'(T)}{dT} = \alpha_T V \left( \frac{\partial M'}{\partial V} \right)_T + \left( \frac{\partial M'}{\partial T} \right)_V$$

with volume $V$ and thermal coefficient of expansion $\alpha_T = \frac{1}{V} \frac{\partial V}{\partial T}$. The sign of $dM'/dT$ will be governed by the sign of $\left( \frac{\partial M'}{\partial T} \right)_V$, if $\alpha_T$ is negligibly small. In the case of a Born-von-Kármán solid, as in the case of a Debye and Gruneisen solid, it was shown that $dM/dT$ is negative at low temperatures and large $\alpha_T$, and positive at high temperature and small $\alpha_T$ ([Bru70]). However, steps occur in the storage modulus curve at the secondary relaxation transitions $\gamma, \beta, \beta'$ (Fig. 9). Especially for the natural rhyolitic glasses $dM'(T)/dT$ below $T_g$ is very small and it is possible to observe the relaxation steps. A constant value of $dM'/dT$ follows at a superposition of several processes or with a high thermal coefficient of expansion $\alpha_T$ (c.f. and Tab. 4). If relaxation processes are strong and in different temperature ranges, then minima occur in $dM'/dT$. 

with falling temperature or rising frequency due to relaxation processes ([Jag60]).
Fig. 7. Dependence of the Young’s modulus $M_{RT}$ on the chemical composition (according to NBO/T as well as EO and Al$^{-1}$ to Tab. 3) as well as the water content for the examined obsidians. Lines are guides to the eye.

Fig. 8. Fragility index $m$ versus the temperature derivative of the storage modulus $\partial M'(T)/\partial T|_{T<T_g}$ in the temperature range below $T_g$ for the obsidians in comparison with synthetic silicate glasses.
Table 4
Rheological properties of the examined volcanic glasses. NaSi-Na$_2$Si$_3$O$_7$; ♣ (Hei04), Homosil, $T = 1199^\circ$C; ◊ (BL96); ♦ (Bru71); ♣ (EMMB75); ♤ (PVTR02); ♦ (TR00); § (MTS80), $T = RT-350^\circ$C

|   | $M_{RT}$ [GPa] | $T_\alpha$ [°C] | $M_\alpha$ [GPa] | $-\frac{dM'}{dT}$ ($\frac{MPa}{K}$) | $-\frac{\partial \log M'}{\partial (1000/T)} = -\frac{T}{1000} \frac{\partial \log M'}{\partial T}$ | $10^{-7} \alpha T$ |
|---|---|---|---|---|---|---|
| YEL | 75 | 861 | 53 | 5.8 | 0.010 | 0.90 |
| VUL | 77 | 817 | 72 | 4.9 | 0.017 | 1.22 |
| LIP | 61 | 789 | 45 | 20.4 | 0.028 | 0.96 |
| MIL | 67 | 891 | 58 | 4.8 | 0.009 | 0.74 |
| RAB | 73 | 819 | 55 | 8.5 | 0.025 | 0.9 |
| DYR | 72 | 830 | 71 | 0.2 | 0.001 | 3.16 |
| ART | 76 | 864 | 74 | 1.6 | 0.004 | 1.34 |
| JAL | 70 | 782 | 64 | 4.4 | 0.022 | – |
| QUI | 81 | 824 | 81 | -0.2 | -0.001 | 1.47 |
| $SiO_2$ | 79 | 1239° | 75♣ | -5.6 | -0.005 | -0.46§ |
| $Di$ | 92 | 769 | 79 | 18.5 | 0.02 | 4.6 |
| $NaSi$ | 61 | 523 | 55 | 20 | 0.026 | 2.5 |

In the temperature range above $T_g$, $M'$ can be characterized in the Arrhenius-diagram. It can be differentiated into two ranges: $T_g \leq T \leq T_\alpha$ and above $T_\alpha$. Here, $T_\alpha$ is the mechanical glass transition temperature at the loss modulus maximum (Tab. 4). By means of an Arrhenian-ansatz for temperatures $T > T_\alpha$ it is possible to determine the apparent activation energy of viscous flow $E'_{a,\alpha}$ ((Wag04)):

$$\frac{\partial \log M'}{\partial (1/T)} \approx \frac{2E'_{a,\alpha}}{2,303R}.$$   \hspace{1cm} (27)

Above $T_g$ all obsidians show a clear temperature dependence of the storage modulus $M'$ which is caused by the strong change of the structure (configurational states). In principle, it is possible to determine the glass transition temperature $T_g$ at a relaxation time $\tau \approx 300$s from the change of $\partial M'(T)/\partial T$ if a linear decay of $M'$ in the temperature range below and above $T_g$ is observed. Attention must be paid to distinguish between $T_g$ at $q\tau \approx 1$ (Frenkel-Reiner-Kobeko Gleichung, (GS95)), the onset of the mechanical glass transition $T_{ve}$ at $\omega \tau \approx 100$, and the mechanical glass transition temperature $T_\alpha$ at $\omega \tau \approx 1$.
Fig. 9. (top) Relaxation steps $\Delta M$ for two relaxation processes: cooperative motion of alkali-ions $\gamma_{R^+}$ and mixed alkali-peak $\beta_{\text{mix}}$ and (bottom) internal friction $Q^{-1}$ in the case of the RAB obsidian. (see Fig. 10).

Below $T_{VE}$ no relaxation contributions (viscoelastic relaxation of the structure within the observation window) can be observed, and it is only possible to examine the mechanical characteristics of the appropriate “current” configurational state as well as anelastic relaxation processes such as the Johari-Goldstein relaxation or the loss due to the mobility of divalent cations. The temperature dependence is substantially smaller than above $T_{\alpha}$, whereby mechanical glass transition is essentially steered by the Maxwell-$\alpha$-relaxation time $\tau_{\alpha}(T)$.

At relaxed melt viscosity two orders of magnitude above the Maxwell-relaxation time at $T_\alpha([WD90], [Web91], [Web92], [Web97])$ above the temperature $T_{\mu} \approx 930 \pm 60^\circ C$, should hold the relation $\lim_{\eta'\rightarrow\eta_{rel}} M'(T) = 0$ or $\lim_{\eta'\rightarrow\eta_{rel}} G'(T) = 0$.

Since, however, as a function of chemical composition of the glasses phase separation and crystallization features can arise, and a temperature range of a plateau in Young’s and shear modulus, a relaxed modulus $M'_{rel}, G'_{rel} \neq 0$ can occur (vgl. Abb 11, [DGBP97a], [DGBP97b], [DG97], [DGBP+97], [Duf98], [Wag04]). The plateau is typical for Polymers ([Don92]) in addition, for
Fig. 10. Definition of the temperatures used in this article. (a) Complex Young’s modulus $M^\star$ (b) internal friction $Q^{-1}$ of the JAL-obsidian in the Arrhenius diagram. (c) internal friction $Q^{-1}$ as a function of the normalized relaxation time $\log(\omega P \tau_\alpha)$
Fig. 11. Asymptotic behavior for high temperatures and low frequencies in the representation of the complex modulus $M^*$ in the Gaussian-plane (top) for the investigated volcanic glasses and (bottom) for starting glass (1: Jenit I, 3: JenitII) and ceramic (2: Jenit I, 4: JenitII) of machinable glass ceramic ([WHBZ01]), 5: $16\text{Na}_2\text{O} - 10\text{CaO} - 74\text{SiO}_2$, 6: $16\text{K}_2\text{O} - 10\text{CaO} - 74\text{SiO}_2$, 7: cordierite-glass which shows surface crystallization effects ([Wag04]) in comparison to the 8: JAL-obsidian.

partially crystalline rocks or glass ceramics ([BDW94], [BD97], [Sm97], [LJ98], [Bag99], [BLT00], [REH00]). Here, among other things, it was stated
that shear stress induced phase separation can occur ([QZY98], [ZZY+01], [AT01]). In the case of obsidians no plateaus can be observed (Fig. 5 and 11).

The loss modulus $M''$ of the volcanic glasses is represented in Fig. 5. The mechanical spectrum can be essentially divided into three ranges, characterized by typical relaxation processes$^3$: $(\beta)$ low-temperature range (RT-300°C), $(\beta')$ range in the vicinity of $T_g$ and $(\alpha)$ viscoelastic, mechanical glass transition.

![Fig. 12. Loss modulus $M''$ as a function of (top) temperature and (bottom) reduced temperature $T - T_m$ in the temperature range $T < T_g$.](image)

Fig. 12 shows the spectra below $T_g$. By scaling the spectra with $T_\alpha$ it becomes clear that the temperature run of the curve for obsidian of different sources is very similar. It can be distinguished in two types: (A) a nearly temperature independence of the $\beta$-range$^4$ of $M''$ with a average amplitude of 0,7GPa ($QUI$, $MIL$, $VUL$) and (B) a minimum in $M''(T)$ with $T - T_\alpha = -450^\circ$ ($LIP$, $DYR$, $YEL$, $RAB$, $JAL$, $ATS$). The $\beta'$ transition deviates only for

$^3$ The relaxation behaviour in multi-component glasses is rather complex due to the superposition of several relaxation processes.

$^4$ Here it is to be counted for a superposition of several processes, i.e. a broad $\beta$ transition superimposed by a $\beta'$ process.
MIL-obsidian from the general trend. The temperatures of the minima and maxima, $T_{\beta,max,min}$, and the values of internal friction are summarized in Tab. 5. Since the intensity of the effects and signal-to-noise ratio are small, all processes below $T_g$ are understood for the GMM as two processes $\beta$ and $\beta'$. However, it is in the case of RAB, JAL, LIP, YEL and ATS possible to separate the $\beta$-process into two overlapping relaxation transitions: cooperative motion of alkali cations in the glassy network $\gamma_{R^+}$ and a mixed alkali peak $\beta_{mix}$. This overlay was fitted by means of a double power law function of the form ([RI98a]):

$$Q^{-1}(T) = Q_b^{-1} + \sum_{j=1}^{n} \frac{Q_{0,j}^{-1}(\omega \tau_j)^{n_j}}{1 + (\omega \tau_j)^{m_j+n_j}}$$

(28)

with the background $Q_b^{-1}$, a constant $Q_{0,j}^{-1}$ and the relaxation times

$$\tau_j = \tau_{0,j} \exp \left( \frac{E_{a,j}}{RT} \right).$$

(29)

Table 5
Temperature and magnitude of the internal friction maxima for temperature $T < T_g$ without background subtraction.

|   | AI  | $T_{m,\gamma_{R^+}}$ | $Q_{m,\gamma_{R^+}}^{-1}$ | $T_{m,\beta_{mix}}$ | $Q_{m,\beta_{mix}}^{-1}$ | $T_{\min}$ | $Q_{\min}^{-1}$ | $Q_{\text{Plateau}}^{-1}$ |
|---|-----|------------------|------------------|------------------|------------------|-----------|----------------|------------------|
| RAB  | 1,06 | 54 | 0,010 | 182 | 0,0070 | 342 | 0,005 | – |
| JAL  | 0,90 | 63 | 0,009 | 179 | 0,0090 | 342 | 0,006 | – |
| LIP  | 1,08 | 91 | 0,009 | 182 | 0,0070 | 293 | 0,004 | – |
| YEL  | 1,07 | 106 | 0,011 | 264 | 0,0100 | 395 | 0,005 | – |
| ATS  | 1,29 | 152 | 0,007 | 314 | 0,0070 | 389 | 0,005 | – |
| MIL  | 1,36 | 72 | 0,012 | 142 | 0,0110 | (317) | – | 0,009 |
| VUL  | 1,09 | 121 | 0,009 | 280 | 0,0097 | (355) | – | 0,0098 |
| QUI  | 1,55 | 195 | 0,010 | 431 | 0,0080 | (500) | – | 0,0076 |
| DYR  | 1,46 | – | – | 105 | 0,0094 | (431) | – | 0,004 |

The volcanic glasses can be likewise divided according to the $\alpha$ process into different groups (Fig. 13). By scaling the temperature axes with the temperature of maxima $T_\alpha$, a master curve for the large group of melts (MIL, VUL, YEL, JAL and ATS) can be constructed, which is an indication for similar rheologic characteristics of these obsidians. Deviations from the general trend show the samples DYR and LIP. The DYR-obsidian has with $\delta_\alpha = 84^\circ C$ a
Fig. 13. (Top) storage modulus $M'$ normalized with the Young’s modulus at the glass transition temperature $M_{VE}$ and (bottom) loss modulus $M''$ as a function of $T - T_m$ in the temperature range $T > T_g$. In the figures (b)-(d) the deviations from the curve are represented, which the obsidians $MIL, VUL, (YEL), JAL, (QUI)$ and $ATS$ follow and which is clarified with the grey line.
substantially smaller half width and steeper slopes of the loss modulus flanks of the $\alpha$-maximum:

$$m_i = \frac{d \log M''}{d(10000/T)} = \begin{cases} 
 1 & \text{for } \log(\omega \tau) < 1 \\
 2 & \text{for } \log(\omega \tau) > 1
\end{cases}$$

(30)

with $m_1 = 2.04$, $m_2 = -1.56$ than the other glasses (general trend $\delta_\alpha \approx 140^\circ C$ and $1.1 < m_1 < 1.5$, $-1 < m_2 < -0.6$). LIP on the other hand exhibits clearly larger $\delta_\alpha = 154^\circ C$ values and a smaller slopes $m_1 = 1.04$, $m_2 = -0.66$. This obsidian has the smallest relaxation strength $s_\alpha = 12GPa$ and $s_D = 27GPa$ ($s_\alpha^{\text{average}} = 20.4GPa$ and $s_D^{\text{average}} = 35.5GPa$). The RAB-obsidian is featured by a pronounced shoulder\(^5\), which suggests a strong $\beta_{R2+}$ relaxation process. In the $\alpha$ process of the QUI-glass an anomaly arises within the glass transition range. Here, it concerns an physical ageing effect during the measurement. Particularly, this obsidian exhibits few large ($d \approx 0.5mm$) crystals (per sample approx. 3-4) causing the sample to crack under the experimental strain of $10^{-4}$.

The mechanical spectra could be parameterized with $GMM$ (17) with the assumption of three relaxation processes ($j = \alpha, \beta, \beta'$):

$$M^*(\omega, \tau) = \sum_{j=1}^{3} \frac{M_{0,j}M_{1,j}(i\omega \tau_j)_{j}^\alpha}{M_{1,j}(1 + (i\omega \tau_j)^{\alpha - \beta_j}) + M_0(i\omega \tau_j)^\alpha}$$

(31)

6 Discussion

Internal friction spectra are shown in Fig. 5. Different relaxation processes can contribute to the relaxation behaviour (3): the dynamical glass transition above the glass transition temperature $T_g$ the so called primary $\alpha$-relaxation (viscoelastic process) and several secondary relaxation processes below $T_g$: cooperative motion of alkali ions in the glassy network $\gamma_{R^+}$, mixed alkali peak $\beta_{mix}$, so-called water peak $\beta_{H_2O}$\(^6\), cooperative motion of alkali earth ions in the vicinity of the thermal glass transition range $\beta_{R2^+}$ ((RI98b), (Rol01), (Mar01)) and a so-called Johari-Goldstein relaxation $\beta_{JG}$

\(^5\) The shoulder-effect always showed up with all internal friction measurements accomplished at the obsidian in the same temperature range.

\(^6\) This peak would be present according to (PJZ80) and (Ste85) only in the systems where non-bridging oxygens, $OH^-$ groups and hydrogen bonds are present at the same time.
Table 6
Parameters of the relaxation processes from GMM-fitting (from top to bottom : $\alpha$, $\beta'$ und $\beta$).

| Obsidian | $-\log(\tau[s])$ | $E_a$ [kJ/mol] | $\beta$ | $M_0$ [GPa] | $X$ | $M_{VE}$ [GPa] |
|----------|-------------------|----------------|---------|-------------|-----|----------------|
| YEL      | 17,02             | 409            | 0,60    | 26          | 0,45| 59             |
| VUL      | 17,87             | 384            | 0,53    | 33          | 0,48| 68             |
| MIL      | 19,68             | 450            | 0,56    | 60          | 1,00| 61             |
| LIP      | 16,13             | 344            | 0,56    | 17          | 0,44| 39             |
| DYR      | 24,74             | 554            | 0,65    | 2           | 0,04| 68             |
| ATS      | 17,80             | 399            | 0,53    | 49          | 0,66| 74             |
| QUI      | 15,74             | 350            | 0,54    | 22          | 0,29| 77             |
| ISL      | 19,49             | 442            | 0,70    | 37          | 0,69| 53             |
| JAL      | 18,60             | 382            | 0,56    | 45          | 0,78| 58             |
| $\beta'$ |                   |                |         |             |     |                |
| YEL      | 9,17              | 171            | 0,36    | 1,26        | 0,30| 4,14           |
| VUL      | 9,28              | 150            | 0,29    | 1,45        | 0,45| 3,23           |
| MIL      | 8,61              | 154            | 0,36    | 2,50        | 1,00| 2,51           |
| LIP      | 12,39             | 197            | 0,18    | 3,40        | 0,34| 9,96           |
| DYR      | 13,92             | 245            | 0,23    | 5,11        | 0,64| 7,95           |
| ATS      | 10,48             | 173            | 0,38    | 1,07        | 0,48| 2,22           |
| QUI      | 10,80             | 186            | 0,31    | 0,66        | 0,20| 3,29           |
| RAB      | 16,82             | 306            | 0,37    | 40,00       | 2,08| 19,27          |
| JAL      | 11,60             | 190            | 0,31    | 1,40        | 0,39| 3,58           |
| $\beta$  |                   |                |         |             |     |                |
| YEL      | 4,67              | 46             | 0,27    | 1,17        | 0,16| 7,35           |
| VUL      | 3,49              | 41             | 0,31    | 0,84        | 0,15| 5,48           |
| MIL      | 4,26              | 46             | 0,26    | 0,96        | 0,14| 6,95           |
| LIP      | 5,30              | 54             | 0,31    | 1,38        | 0,12| 11,11          |
| DYR      | 4,02              | 35             | 0,30    | 0,88        | 0,14| 6,13           |
| ATS      | 4,80              | 49             | 0,26    | 1,02        | 0,20| 4,99           |
| QUI      | 4,70              | 54             | 0,31    | 0,88        | 0,16| 5,37           |
| RAB      | 4,59              | 65             | 0,17    | 0,86        | 0,08| 11,46          |
| JAL      | 2,89              | 23             | 0,31    | 1,05        | 0,24| 4,34           |
Fig. 14. (Top) storage $M'$ and loss modulus $M''$ as a function of temperature of the MIL obsidian with GMM-fit according to equatio (31). (bottom) Residuum of the fit.

(\textit{ANM}^+01), (Don01), (NJ03)). It is impossible to distinguish the specific relaxation processes in every case because of the restricted frequency and temperature range. For this reason three relaxation processes are assumed: $\beta$ - superposition of the $\gamma_{R^+}$, $\beta_{\text{mix}}$ and $\beta_{H_2O}$ process, $\beta'$ - superposition of the $\beta_{R^2+}$, $\beta_{JG}$ and the thermal glass transition as well as the viscoelastic $\alpha$-transition.

Further it is assumed, that the unrelaxed modulus $M_\infty$ is a very weak function of temperature. This is true in the case of volcanic glasses (Fig. 8 and Tab. 4).

Since volcanic glasses are natural materials, these are heterogeneous up to certain degrees. The natural glasses have a smaller signal-to-noise ratio cause by these heterogeneities opposite to synthetic glasses. Thus, sensitivity is limited. Relaxation processes can only seriously be observed in relaxation behaviour if they are strongly enough. The different assumed influences and their effect on different relaxation processes are summarized in Tab. 7. On one hand it is shown, that there are processes, which are sensitive for different influences, c.f. $\beta'$. On the other hand, the $\alpha$ process is caused by the chemical composition and water content. In addition, effects arise due to degassing and vesiculation. Here, however, it showed up clearly that even during very strong vesiculation of the $LIP$-sample, dynamics of the glass transition is detectable. In this specific case, temperature dependence of $\alpha$-relaxation time can only be modelled...
Fig. 15. (a) and (b) storage - $M'$ and loss modulus $M''$ as a function of temperature with GMM-fit. (c) Complex Young’s-modulus $M^*$ with GMM-fit represented in the Gaussian-plane (selection of three obsidians MIL, ATS, JAL).
in first approximation by an Arrhenian-equation due to water release.

Table 7
Assumed influences on the mechanical relaxation behaviour of the volcanic glasses:
X - significant, (X) - weak, (-) - uncertain

| influence                          | β-process | β′-process | α-process | M<sub>RT</sub> |
|-----------------------------------|-----------|------------|-----------|---------------|
| chemical composition              | X         | (-)        | X         | (X)           |
| water content                     | (X)       | (-)        | X         | (X)           |
| bubble content (degassing)        | (X)       | (X)        | (X)       | (X)           |
| crystals                          | (X)       | (X)        | (-)       | (-)           |
| temperature history               | X         | (X)        | (-)       | (-)           |

6.1 Relaxation behaviour below T<sub>g</sub>

The influences of the chemical composition and the water content on the relaxation processes below T<sub>g</sub> were examined in detail in several mechanical relaxation studies (Q<sup>-1</sup>-spectroscopy) of synthetic glasses. It was shown that different mixing cation effects exist, which in addition depend on the water content and polymerization degree of glasses (c.t. [Day74], [PJZ80] and [Ste85], [Mar01]). The examined volcanic glasses exhibit the following ions: Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Fe<sup>2+</sup> and water in different speciation ([Gab99], [Dor00], [Beh01], [Dor02]), which can contribute to the mechanical relaxation behaviour. Since the place-exchange processes can be observed both in the internal friction spectrum Q<sup>-1</sup>(T) or in equivalence in the loss modulus M′′(T) as maxima and in the storage modulus M′(T) as a step. The following views are accomplished on the basis of internal friction.

The JAL-obsidian is peralkalin, i.e. it exist on NBO bounded alkali ions R<sup>+</sup> (≈ 1mol%), which are mobile in the glass network. The peak of γ<sub>Na</sub> at a measuring frequency of 1Hz is to be expected below RT. Investigations of internal friction of binary R<sub>2</sub>O-SiO<sub>2</sub>-glasses with R<sup>+</sup> = Rb<sup>+</sup>, K<sup>+</sup>, Na<sup>+</sup>, Li<sup>+</sup> show ([ZRD76]) that the intensity Q<sup>-1</sup><sub>m,γ</sub> and the temperature T<sub>m,R</sub> of this maximum depends on the field strength F = 2<sup>z</sup> of appropriate cations with the valence z and the Van der Waals radius a. It becomes clear that the γ<sub>R</sub> process is coupled with the β<sub>H</sub> process, which exhibits a maximum at approximately 200°C.

If one further regards ternary glasses with two different kinds of alkali ions, then one observes the occurrence of a further maximum: the mixed alkali peak β<sub>mix</sub> within the range of the water maximum. At a temperature of ≈ 320°C additional relaxation processes arise: a β<sub>R2+</sub>-process in direct connection to
the mobility of alkaline-earth ions, the mobility of oxygen-ions with an activation energy of $\approx 200 \text{kJ/mol}$ and the Johari-Goldstein relaxation ([Ro01], [NJ03], [Wag04]). A substantial conclusion from the investigations of [Ma01] on ternary alkali and alkaline-earth silicate glasses is the fact that in systems with two kinds of cation, while one is substantially faster than the other one, the cation radius relationship affects the activation energy of the slower ions. The more similar the ion radii are, the smaller is the activation energy.

By the component $\text{Al}_2\text{O}_3$ the location and intensity of the maxima change drastically. For the ternary sodium alumosilicate glass examined by [DR62a] as well as [DR62b] the $\gamma_{Na^+}$ as well as $\beta_{H_2O}$ peak decreases with rising $\text{Al}_2\text{O}_3$-content, whereby at the ratio $\text{Al}_2\text{O}_3/\text{Na}_2\text{O} = 1$ the $\gamma_{Na^+}$ process is maximal and the $\beta_{H_2O}$ process cannot be observed anymore.

Measurements of mixed alkali alumosilicate glasses with $\text{Al}_2\text{O}_3/R_2\text{O} = 1$ of [SY85] as well as [SY89] point out, that as in the case of the ternary mix alkali glasses, these systems exhibit a mixed alkali maximum $\beta_{\text{mix}}$ at $\approx 100^\circ \text{C}$. At a ratio $\text{Na}_2\text{O}/K_2\text{O} = 1$ arise a very strong maximum, which is formed by the superposition of the $\gamma_{R^+}$ and $\beta_{\text{mix}}$ processes.

[SY85] perform additional measurements of glasses, in which the $\text{Al}_2\text{O}_3$-content is varied at the expense of the $\text{SiO}_2$-content, at constant $\text{Na}_2\text{O}/K_2\text{O} = 19$. By the presence of $Na^+$ and $K^+$-cations is formed again apart from the $\gamma_{R^+}$ a mix alkali maximum $\beta_{\text{mix}}$. With rising $\text{Al}_2\text{O}_3$ the intensity of the $\gamma_{R^+}$ peak increases, while those of the $\beta_{\text{mix}}$ decreases. As in the case of ternary sodium alumosilicate glasses from the investigation of [DR62a] as well as [DR62b] acquiring the intensity of the $\gamma_{R^+}$ maximum and of $\beta_{\text{mix}}$ minimum at $\text{Al}_2\text{O}_3/\text{Alk} = 1$.

From the reasons specified above, the following consequences resulted in the mechanical relaxation behaviour below $T_g$ of the examined natural glasses:

- The water maximum is suppressed strongly by the $\text{Al}_2\text{O}_3$-content.
- The ratio $\text{Al}_2\text{O}_3/\text{Alk} \approx 1$ leads to the formation of an intensive $\gamma_{R^+}$ peak.
- The presence of two different alkali ions $K^+$ and $Na^+$ leads to the formation of a mixed alkali peak $\beta_{\text{mix}}$ with $T_{\beta_{\text{mix}}} \approx 140^\circ \text{C}$.
- The $\gamma_{R^+}$ process is superimposed by the $\beta_{\text{mix}}$ process with the result of a relatively high internal friction $Q^{-1} \approx 0.7$ within the temperature range $RT - 300^\circ \text{C}$.
- By the presence of divalent cations a further relaxation process $\beta_{R^+}$ arises in the vicinity of the glass transition range.

The compilation of data to the internal friction of volcanic glasses confirms the above assumptions (Fig. 12). In the case of the samples $\text{LIP, RAB, YEL}$ and $\text{JAL}$ it is suggested that it concerns a superposition of two processes. $\text{ATS, MIL, QUI}$ and $\text{VUL}$ exhibit a pronounced plateau. An exception is the
Fig. 16. Comparison of the Young’s modulus at RT $M_{RT}$ or $T_g$ $M_{VE}$ and loss modulus at the $\alpha$ peak $M''_{\alpha,m}$ of the obsidians and several synthetic glasses (Wag04).

$DYR$ sample. Here it seems that the $\gamma_{R^+}$ peak is below $RT$. It is suggested a further peak occurs at $\approx 100^\circ C$. In Tab. 5 the results are summarized. As mentioned, the decay of the storage modulus with temperature below $T_g$ is likewise dependent on the chemical composition. In the special case of the obsidians it can be assumed that $M_{RT}$ depends secondarily on the chemical composition, due to ion mobility in the glassy network, but is determined essentially by water content. However, practically no investigations of the influence of water content on elastic properties of synthetic and natural glasses exist in contrast to internal friction measurements. The occurrence of the $LIP$ sample is interesting in this context with the smallest Young’s modulus of $M_{RT} = 61 GPa$. It is possible to calculate $M_{RT}$ with the model of (Pri01) (SciGlass information system) in accordance with the measured data.

6.2 Primary $\alpha$-Process

a) Chemical composition and water content

The comparison of the Young’s modulus at RT ($M_{RT}$) or $T_g$ ($M_{VE}$) and loss modulus at the $\alpha$ peak ($M''_{\alpha,m}$) is represented in Fig. 16. The drawn in lines refer to the deviation from simple Maxwell behavior ($x = 1$): $M''_{m} = xM'_{VE,RT}/2$. The linear regression results are $x_{RT} = 0,55 \pm 0,02$ and $x_{VE} = 0,58 \pm 0,02$. 

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The flat curve of the LIP sample is to be explained by strong vesiculation. A change of the sample caused by degassing and formation of bubbles leads to a change in the mechanical behavior, whereby the viscoelastic response is dominated by the mechanical glass transition. The parameter $x$ is a measure relatively independent of the chemical composition, with which deviations can be interpreted as physically induced processes in contrast to the influence of the chemical composition or the water content, which causes a change of the properties of the glass. The GMM-fitting supplies the unrelaxed modulus at $T_{g}$.

Fig. 17. Temperature of the $\alpha$-peak $T_{m,\alpha}$ as a function of the chemical composition and water content of the investigated volcanic glasses. The (HDW96) calculation scheme defined by the solid curve for viscosities ($10^8...10^{11}$ Pas) closely fits the experimental data for the calc- and per-alkaline compositions. The dashed lines are an aid to the eye, and do not conform to any specific mathematical expression.

The mechanical glass transition $M_{VE}|_{TV_E}$ which is $\approx 2GPa$ lower than the elastic modulus at $T_g$. In the used model the $\beta'$ process represents an overlay of a secondary process and the thermal glass transition caused on experimental conditions. This secondary effect is observed likewise in organic glasses with dielectric spectroscopy, and gave reason to controversial discussions of the existence of the Johari-Goldstein-process (NJ03), (Sch00a), (ANM+00)).

The occurrence of the $\alpha$-process is defined by the chemical composition and $7$ In the case of the obsidians the mobility of divalent cations and the Johari-Goldstein relaxation.
the water content ([Din93], [HD96], [SBDR98], [GD03]). In Fig. 17 one can notice different trends. The temperature $T_\alpha$ decreases with increasing $NBO/T$ and the amount of the absolute excess oxide value ($|EO|$), i.e. with increasing depolymerization. Likewise the glass transition temperature as well as the temperature of water release follow this trend. The mechanical glass transition of the $MIL$ obsidian with the smallest $NBO/T = 2^{-4}$ and a $|EO|$ close to zero $\approx 0,17$ occurs at the highest temperature. The smallest maximum temperature $T_{\alpha,\alpha}$ has the peralkaline $JAl$ obsidian with $NBO/T = 0,023$ and $|EO| = 1,05$. Even the $LIP$ obsidian follows this trend. The occurrence of the mechanical glass transition (thus) is dominated by the chemical composition (see also the investigations of partially crystalline glasses by [MBJ+03]). This conclusion confirm measurements of Cordierite-glass ([WHBZ01], [Wag04]). Impurities (crystals, bubbles, cracks) influence the width of the maxima and relaxation strength. The activation energy and prefactor of the Arrhenius-

![Fig. 18. Activation energy of viscous flow $E_{a,\alpha}$ at the glass transition temperature $T_g$ as a function of water content for the natural volcanic glasses of this work and the natural and remelted obsidians of [SBDR98].](image)

equation for the temperature dependence of the relaxation time $\tau_\alpha(T)$ can be determined from the $GMM$-fit and compared with the results of the measurements of other authors (viscosity measurements, torsion pendulum measurements) (Fig. ??). The activation energy of the $\alpha$ relaxation time or viscosity at $T_g$ is essentially a function of chemical composition and water content. A model that considers both influences sufficient for synthetic or natural silicate melts does not exist. The model of [Pri01] represents the most progressive
at present, in the connection between structure and properties (volatile excluded). For the description of volcanic glass, the empirical model of (Hes96) is most effective. This model was developed for water bearing leucogranitic melts but was also used to calculate the viscosity of metaluminous and peraluminous obsidian (SBDR98).

Fig. 19. Distribution parameter $\beta_\alpha$ ($\alpha_\alpha = 1$) as a function of the apparent activation energy for viscous flow $E_{a,\alpha}$ at $T_g$ of the synthetic and volcanic melts of this work in comparison to literature data. The $\beta_\alpha$ parameter was calculated from $\beta_{KWW}$ with an empirical expression.

Fig. 19 show the range of variation of the distribution of relaxation times on the basis of the $\beta_\alpha$ parameter and activation energy $E_a$ at the mechanical glass transition temperature for structurally different silicate melts. The $\beta_\alpha$-parameter for the obsidians range between 0.5 and 0.6 with two exceptions DYR and RAB. The RAB glass has a very strong $\beta'$ relaxation process so that the GMM-fitting leads to a narrower $\alpha$-process. In comparison, the DYR glass shows anomalous behaviour in all examined parameters.

The average value of all supercooled melts is $\overline{\beta_\alpha} = 0.52$. Deviations can be observed for two volcanic glasses as well as the HPG8-melts from the work of (BDW93).

Under the condition that the distribution of relaxation times is nearly constant it should be possible to predict the occurrence and the width of the mechanical glass transition from viscosity data (see WBH04).

The variation of the distribution parameter is primarily caused by phase separation and crystallization processes as well as degassing and vesiculation. The temperature prehistory has little influence. The DSC investigation of
Fig. 20. Distribution parameter $\beta_a$ ($\alpha_a = 1$) as a function of the apparent activation energy for viscous flow $E_{\alpha,\alpha}$ at $T_g$ of the volcanic melts. (inset) Distribution parameter $\beta_a$ ($\alpha_a = 1$) as a function of the cooling rate $|q|$ of a LIP-obsidian (GD01a).

(GD01a) shows a negative correlation of the distribution parameter and the cooling rate. The variation of the $\beta$ parameter is within the standard deviation of the 45 samples.

**In summary** the following points result:

- The mechanical $\alpha$ relaxation (mechanical or viscoelastic glass transition) overlays a secondary $\beta$ relaxation process.
- The occurrence of the transition is defined by the temperature dependence of viscosity.
- The width $\delta$ of the transition depends on the fragility and the distribution of relaxation times.
- The distribution of relaxation times in the investigated temperature and frequency range is almost constant in comparison to the fragility index for inorganic glasses (see (Wag04)).
- The presence of crystals (in particular due to surface crystallisation) and bubbles $> 1\text{-}2\text{Vol.}\%$ changes the dynamics of the transition and therefore the relaxation time distribution.
• Fragility is defined by the chemical composition and the presence of volatiles.
• Phase separation and degassing processes change strongly the dynamics and thermics of the transition and lead to the rheologic complex behavior.

7 Conclusion

Obsian can considered as a thermorheological simple melt with a low fragility index \( m \approx 20 \). Variations in the ratio \( NBO/T \) determine the polymerization degree of the melts and thus the rheologic properties. A crucial factor which determines the mechanical relaxation behaviour in the thermal and dynamic glass transition range above \( T_g \), is the relatively high water content. In the vitreous state the influence of water on the dynamical processes plays a minor role, since the volcanic glasses are almost completely polymerized \( (NBO/T \leq 0.4) \). For clarifying this fact it requires more exact methods.

Three section can be distinguish in the mechanical spectra (a) \( T < T_g \), (b) \( T \approx T_g \), and (c) \( T > T_g \), with the following characteristics:

(i) The Young’s modulus \( M_{RT} = (70 \pm 10) \text{GPa} \) is nearly constant. There is a positive correlation with the water content and a weak negative correlation with the cooling rate \( ([\text{Wag04}]) \).

(ii) Below \( T_g \) the mechanical relaxation behaviour is characterized by the cooperative motion of univalent cations (alkali-peak \( \gamma_{R^+} \), mixed alkali-peak \( \beta_{\text{mix}} \)) and the polymerisation degree. Impurities (bubbles, crystals, cracks, trace elements) in the natural glasses decrease the signal to noise ratio.

(iii) All glasses exhibit a very weak, and in one case, an anomalous negative decay of the Young’s modulus with temperature like silica glasses. In addition, it is possible to observe steps in the curve of Young’s modulus \( (\Delta M' < 5 \text{GPa}) \) which correspond with the \( \gamma_{R^+} \) or \( \beta_{\text{mix}} \) peak in internal friction.

(iv) In the vicinity of the glass transition temperature there is a superposition of the \( \alpha \) and a \( \beta' \) process (cooperative motion of divalent cations: alkali earth peak \( \beta_{R^{2+}} \), and the Johari-Goldstein relaxation \( \beta_{\text{JG}} \)) as well as the thermal glass transition defined by the experimental conditions. The thermal glass transition is reflected clearly in the loss modulus and in the storage modulus at least less than 1%.

(v) The occurrence of the mechanical or dynamic glass transition at a constant frequency as function of the temperature is specified by the temperature dependence of the structural \( \alpha \) relaxation time \( \tau_\alpha \).

\( ^8 \) Due to the nomenclature of ([Don81] and [Don01]).
(vi) The temperature dependence of the structural α relaxations time is determined by the polymerization degree with water as a quasi controlling parameter and can be computed by means of an empirical equation according to (Hes96) or (HD96) for the per- and metaluminous rhyolitic melts. The model of (Pri98) as well as (Gio02) for the computation of the temperature dependence of the viscosity of multicomponent melts cannot be used for the computation of the α relaxation time. For strong melts and melts with high water content the glass transformation temperature and the activation energy of viscous flow are overestimated.

(vii) Degassing processes in connection with bubble growth as well as other impurities (crystals) lead to macroscopic (cracks) and structural (polymerization degrees) changes, which cause instabilities of the samples.

(viii) The dynamics of the mechanical glass transition is a universal process with very week variation of the relaxation time distribution almost independent of chemical composition and water content (0.027... 0.44)Masse% of the examined natural melts.

The obsidians represents an interesting material class, which has many useful properties (concerning the methods of the mechanical spectroscopy)\(^9\), like thermalrheologically simple behavior, small fragility index and a high glass formation tendency, small variation of the Young’s modulus in a wide temperature range, high polymerization degree, long-term resistance.

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\(^9\) “Impurities” have to keep in mind, which are able to effect the actual glass characteristics, like in the case of the LIP-sample
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