Horizon 2020 - Marie Sklodowska-Curie Actions
Innovative Training Network (ITN)
Complex RhEologies in Earth dynamics and industrial Processes

High pressure dependence of properties and structure relaxation of glass

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Background

- There were several classic models, including Tool(1946), Ritjand(1956), Narayanaswamy(1971) and Scherer(1986), showed the temperature and time dependence of properties as well as structural relaxation of glass in the glass transition region. While those studies were all based on the pressure of 1 bar, the influences of **pressure** are not well described.
- The importance of understanding pressure dependence of density and structure relaxation is as a reason of the fact that they strongly influence the **viscoelasticity** of glass (Cook, et al. 1994).
- The study of rheology of glass under high pressure is also very important for the geological process since rapid cooling of magma produces about a billion cubic of glass each year (Morgan & Spera, 2001), and some of them were melted and solidified in a process that is still ongoing today (Christiansen & Drozdov, 2002).

Experimental

Pressure cells development

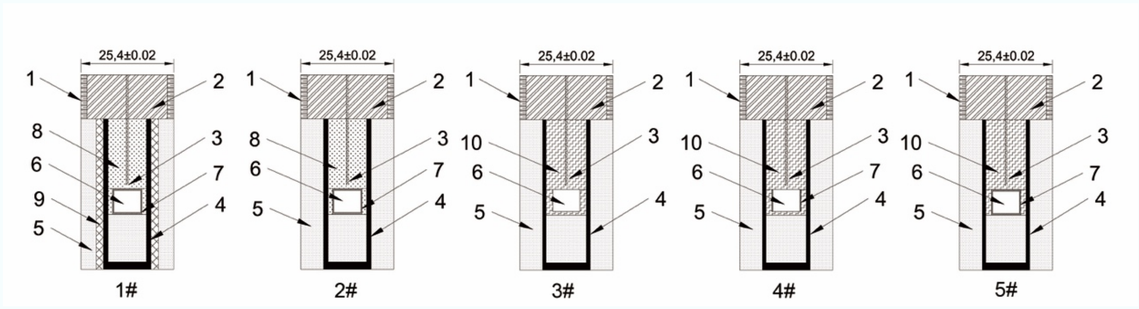

Fig.1 Pressure cells developed for high pressure experiments in piston-cylinder apparatus. 1-Pyrophyllite; 2-Steel plug; 3-Thermocouple; 4-Graphite; 5-NaCl; 6-Sample; 7-Pt; 8-Al_2O_3; 9-Borosilicate glass; 10-h-BN.
1# for 1 GPa, 2# for 0.5 GPa, 0.75 GPa & 1.1 GPa, 3# for 1.5 GPa, 4# for 1.25 GPa.

Experimental process

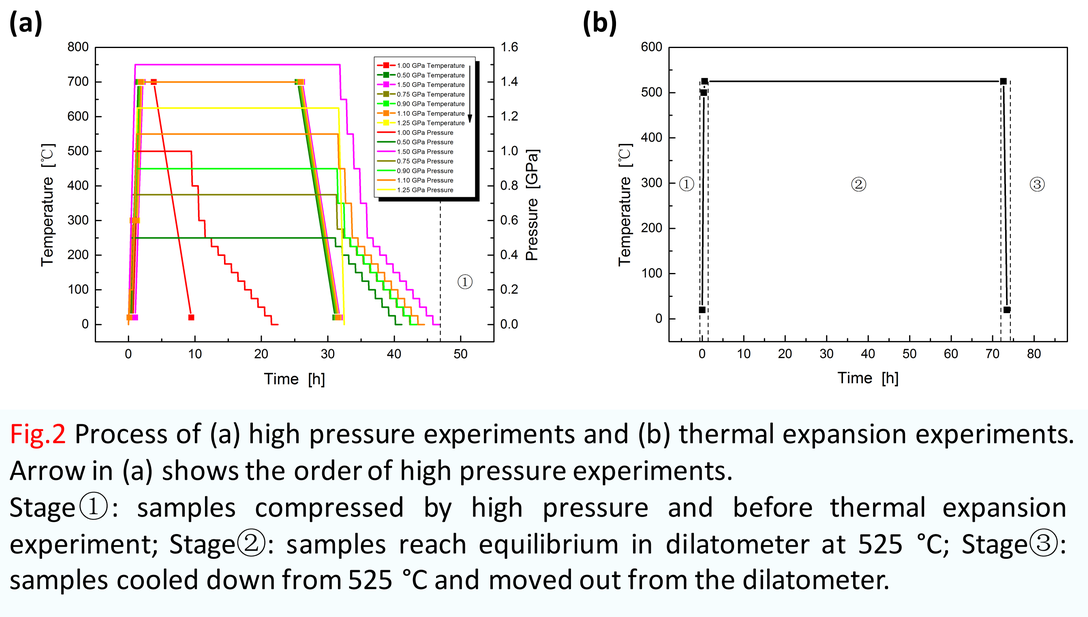

Fig.2 Process of (a) high pressure experiments and (b) thermal expansion experiments. Arrow in (a) shows the order of high pressure experiments.
Stage①: samples compressed by high pressure and before thermal expansion experiment; Stage②: samples reach equilibrium in dilatometer at 525 °C; Stage③: samples cooled down from 525 °C and moved out from the dilatometer.

(a) Process of piston-cylinder apparatus

Compressing to HP (0.25 Kbar/min) → Heating to 700 ℃ (10 K/min) → Thermal insulation for 24 h (2 h for 1 GPa sample) → Cooling down 2 K/min → Depressing (2 Kbar/h to 5 Kbar,0.5 Kbar/h to 1 bar; 15 Kbar/h for 1.25 GPa sample)

(b) Process of dilatometer

Heating to 700 ℃ (20 K/min) → Heating to 525 ℃ (2 K/min) → Thermal insulation for 72 h → Rapid cooling to the room temperature

Results

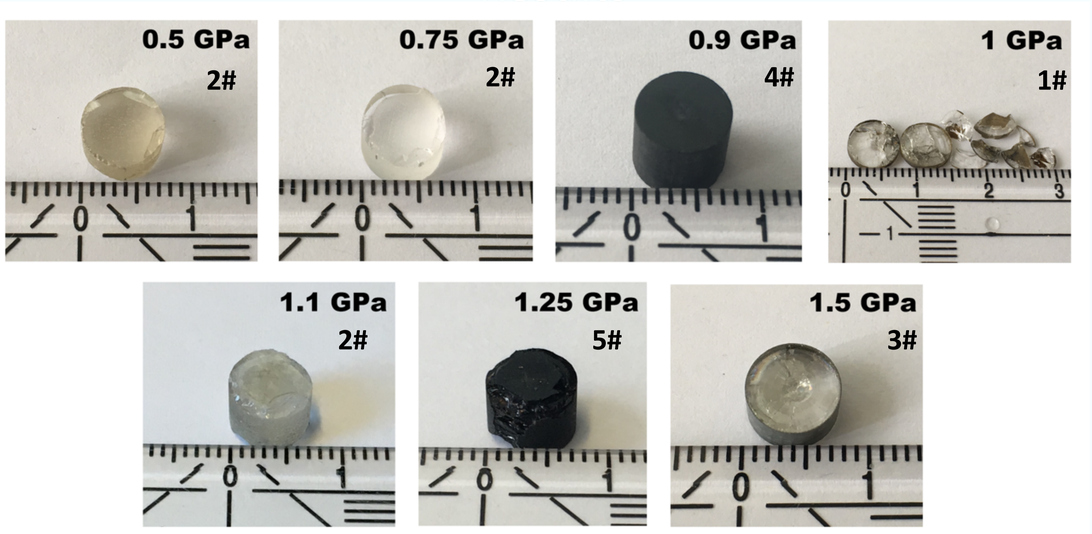

Fig.3 Pictures of glass samples after high pressure compressing.
1 GPa sample with shorter thermal time-**broken**; 0.5 GPa, 0.75 GPa and 1.1 GPa sample-**few cracks** on the surface and **not** black; 0.9 GPa sample-**blackening** with a thicker crystal layer outside; 1.25 GPa sample with fast depressing-**blackening** together with lots of fractures inside.

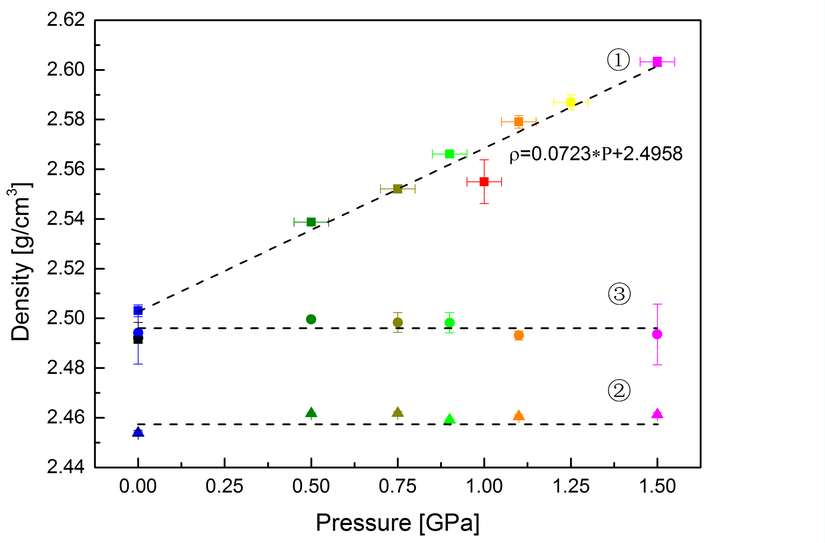

Fig.4 Pressure dependence of density of glass samples in different periods.
Stage①, ②, ③ are the same as the experimental process mentioned before.
Glass samples in stage ① showed a linear increase on density when pressure increasing from 0.5 GPa to 1.5 GPa, specifically, with density increase of 4.49% at 1.5 GPa. Both of the fast cooled and slow cooled samples reached to similar equilibrium densities in stage ②, and then samples achieved higher density with very high uncertainties in stage ③ .

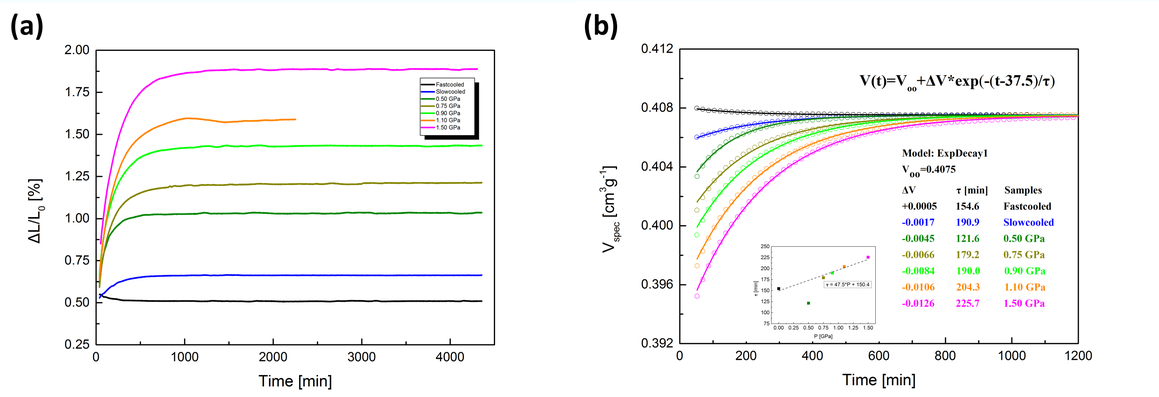

Fig.5 (a) Relative length changes of samples versus time at 525 °C (stage ②); The compressed samples with fast cooling showed large elongation of 1.03 % at 0.5 GPa and 1.89 % at 1.5 GPa. (b) Specific volume change versus time at 525 °C fitted to a simple exponential mode. However, the model obtained different relaxation time for glass at the same condition.

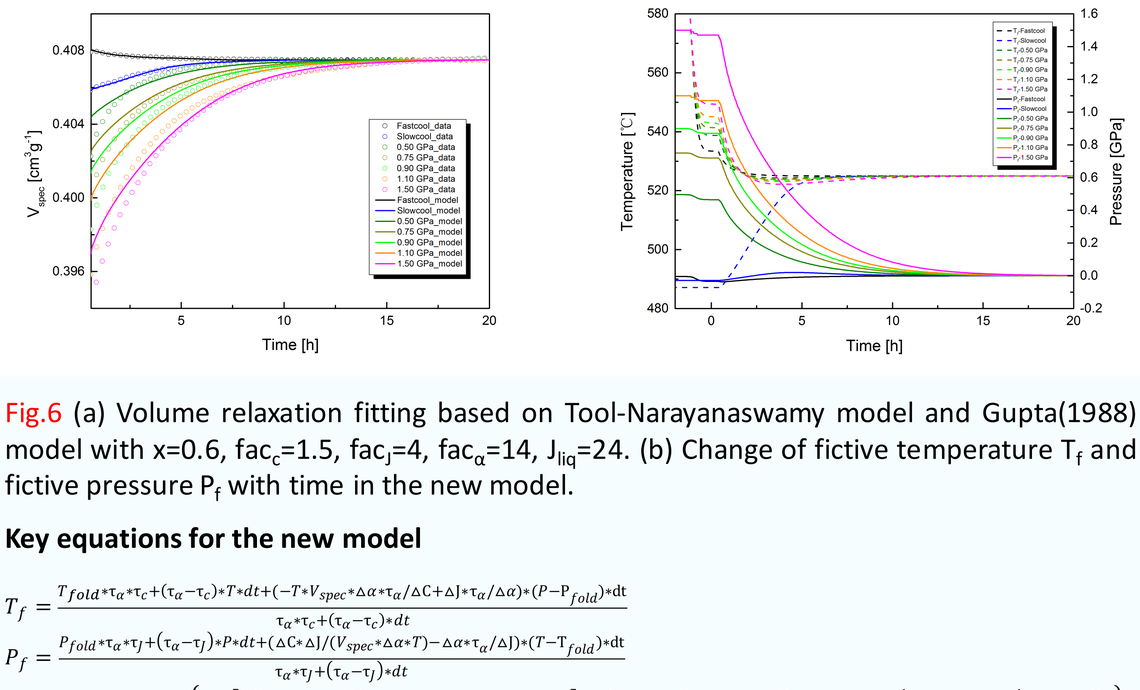

Fig.6 (a) Volume relaxation fitting based on Tool-Narayanaswamy model and Gupta(1988) model with x=0.6, fac_c=1.5, fac_J=4, fac_α=14, J_{liq}=24. (b) Change of fictive temperature T_f and fictive pressure P_f with time in the new model.

Key equations for the new model

$$T_f = \frac{T_{fold}*\tau_\alpha*\tau_c+(\tau_\alpha-\tau_c)*T*dt+(-T*V_{spec}*\Delta\alpha*\tau_\alpha/\Delta C+\Delta]*\tau_\alpha/\Delta\alpha)*(P-P_{fold})*dt}{\tau_\alpha*\tau_c+(\tau_\alpha-\tau_c)*dt}$$

$$P_f = \frac{P_{fold}*\tau_\alpha*\tau_J+(\tau_\alpha-\tau_J)*P*dt+(\Delta C*\Delta]/(V_{spec}*\Delta\alpha*T)-\Delta\alpha*\tau_\alpha/\Delta])*(T-T_{fold})*dt}{\tau_\alpha*\tau_J+(\tau_\alpha-\tau_J)*dt}$$

$$\tau = fac*\tau_{ref}*\exp\left\{\frac{x}{T}*\left[\frac{\Delta H}{R}+fac_p*\frac{M_{mol}}{R}*V_{ref}*(P-P_{ref})\right]+\frac{1-x}{T_f}*\left[\frac{\Delta H}{R}+fac_p*\frac{M_{mol}}{R}*V_{ref}*(P_{f_{old}}-P_{ref})\right]-\frac{\Delta H}{R*T_{ref}}\right\}$$

Conclusions

- A simplified and effective pressure cell (2#) together with a good experimental process is developed for high pressure research of glass in transition region using piston-cylinder apparatus.
- Glass samples can be effectively densified in piston cylinder apparatus with a density increasing of 4.49 % at 1.5 GPa, and it will be a linear change with function of $\rho = 0.0723 * P + 2.4958$.
- A new model was developed with an overall fit to the experimental data.

Acknowledgement

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