Kinetics of crystal nucleation in lithium silicate glasses

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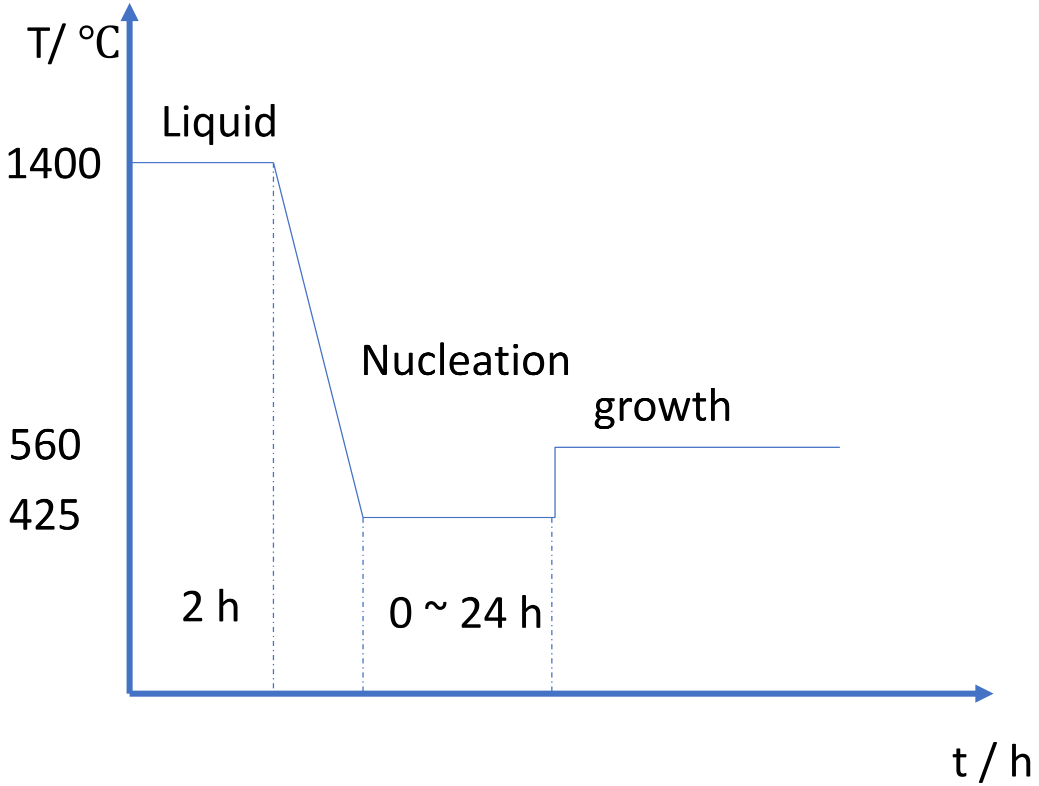
Experimental: preparation of glasses and heat treatment



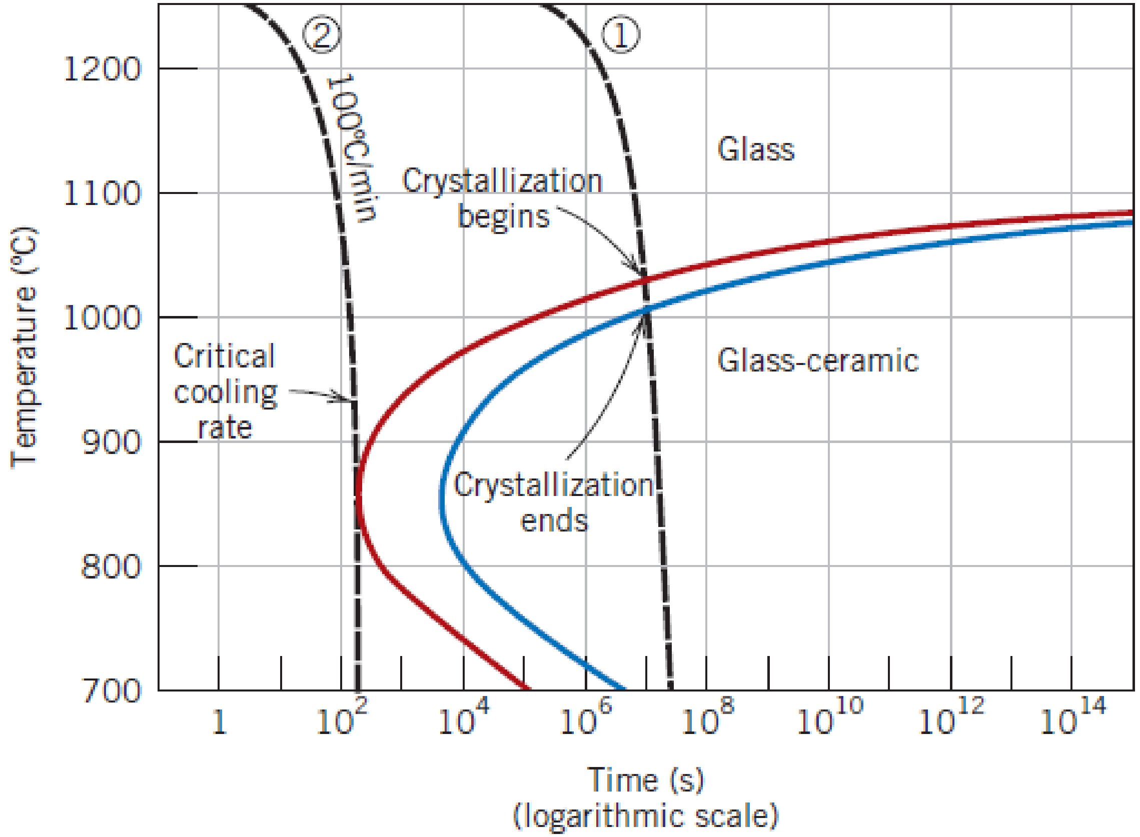
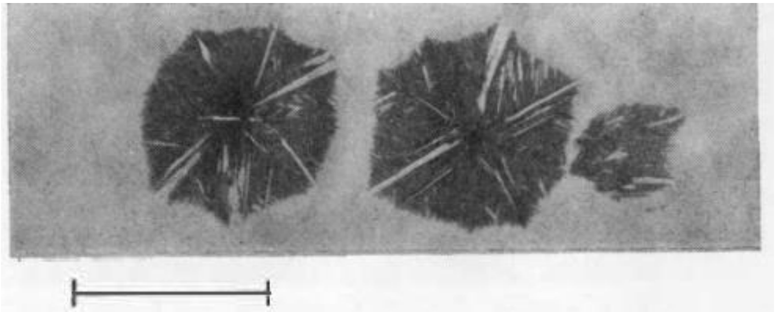
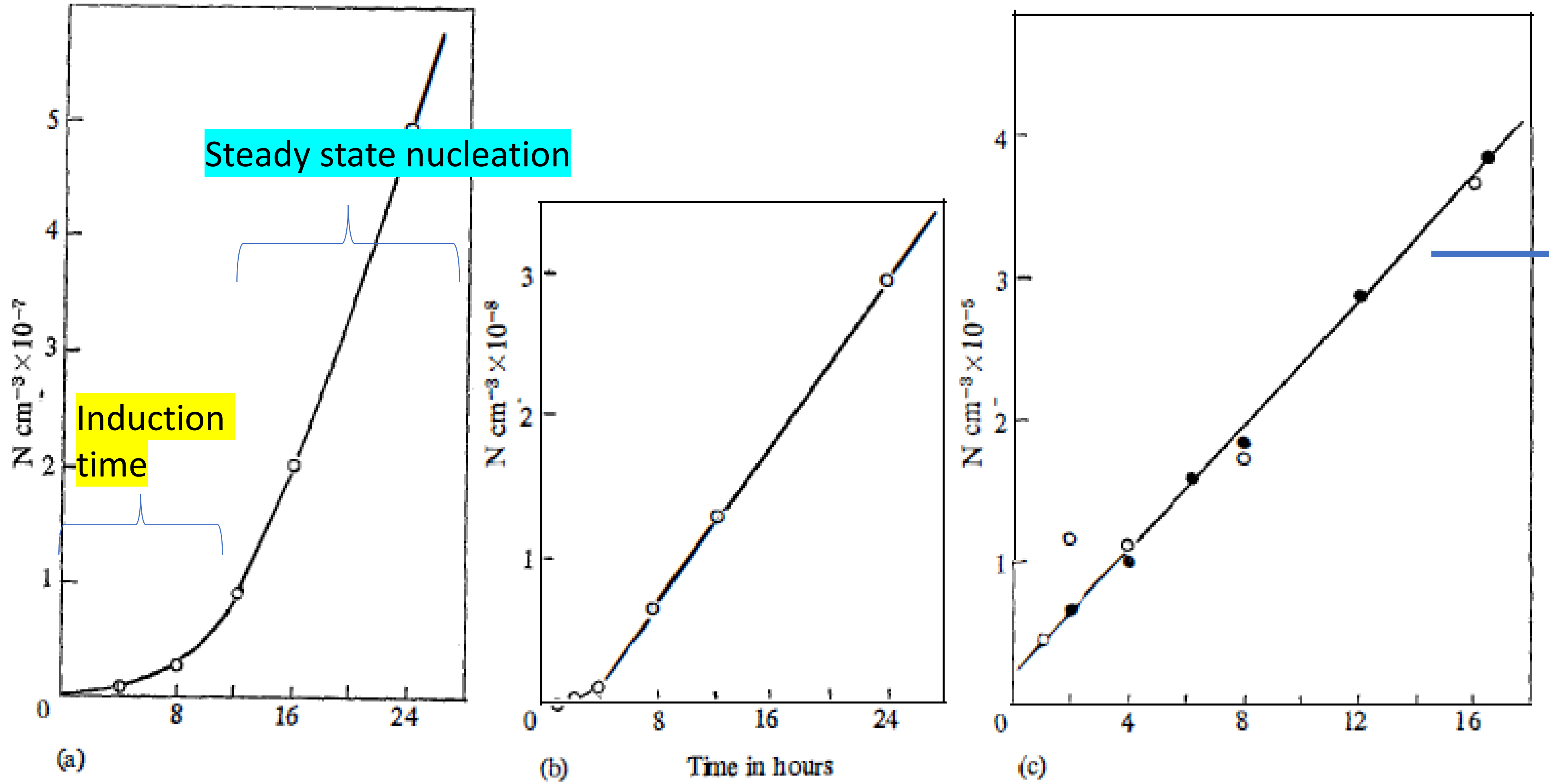


Figure 13.2 Continuous cooling transformation diagram for the crystallization of a lunar glass (35.5 wt% SiO_2, 14.3 wt% TiO_2, 3.7 wt% Al_2O_3, 23.5 wt% FeO, 11.6 wt% MgO, 11.1 wt% CaO, and 0.2 wt% Na_2O). Also superimposed on this plot are two cooling curves, labeled "1" and "2." (Reprinted

The nucleation rate was negligible at growth temperature.



Results



The slope

Nucleation rate: I_0 (cm^{-3} s^{-1})

Figure 8. *Increase in the number of crystal particles per unit volume with time in glass 1 after nucleation at (a) 440° C, (b) 454° C, and (c) 527° C*

○ growth temperature 560°C
● growth temperature 620°C

Results

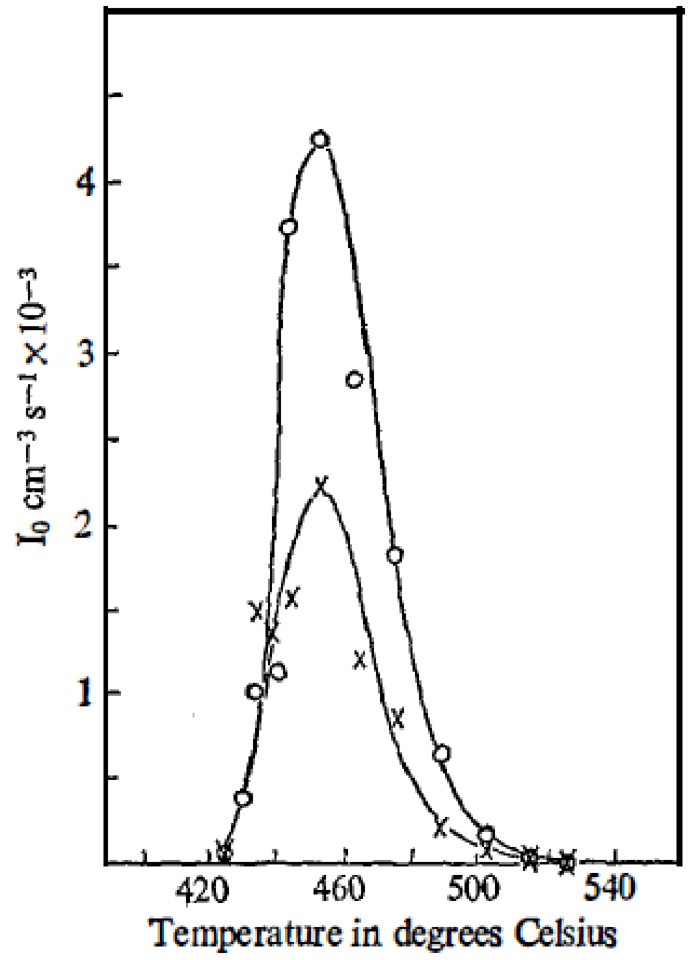


Figure 10. *Steady state nucleation rate as a function of temperature*
○ glass 1
× glass 2

Table 3. *Values of τ and I_0 at different nucleating temperatures*

	Glass 1		Glass 2	
Temperature (°C)	τ (min)	I_0 ($cm^{-3}\ s^{-1}$)	τ (min)	I_0 ($cm^{-3}\ s^{-1}$)
425	3046 (approximately)	45 (approximately)	1532	43·3
430	2170	368	—	—
435	1040	1041	948	1488
440	480	1147	378	1366
445	288	3761	292	1581
454	136·8	4253	177·6	2249
465	36·5	2863	21·9	1202
476	12·8 (approximately)	1868	11	868
489	7 (approximately)	639	—	212
502	—	149	—	86·2
516	—	24·5	—	18·8
527	—	6·00	—	5·94

Nucleation kinetics. Comparison with theory of non-steady state homogeneous nucleation

1. Time dependence of nucleation density

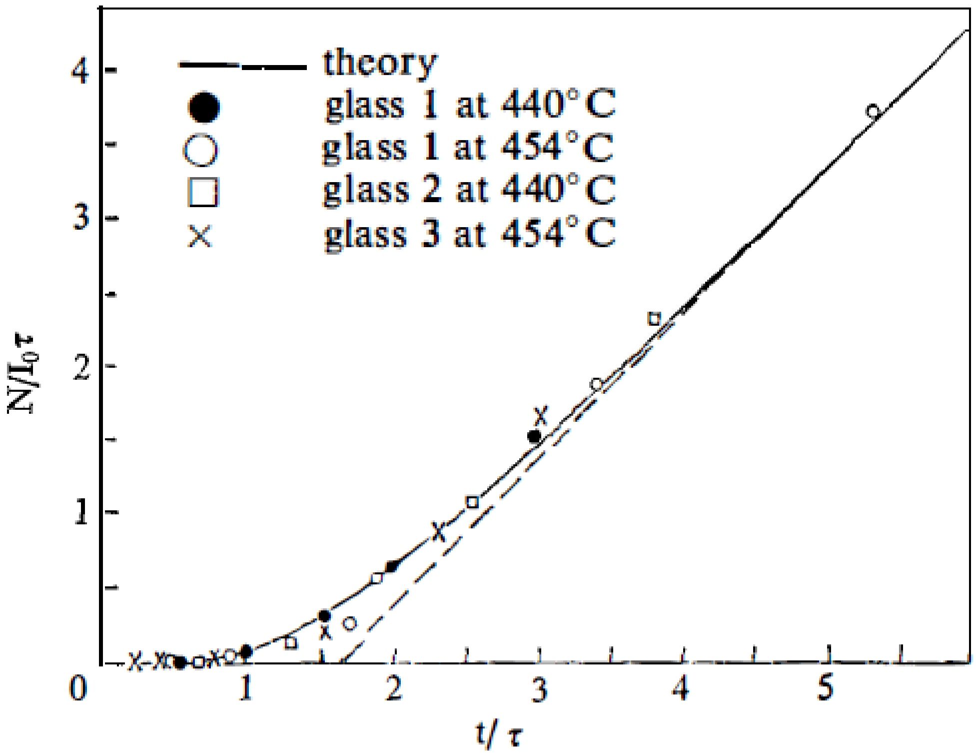


Figure 13. *Comparison of experimental data with theory of nonsteady state nucleation*

$$I = I_0\left[1+2\sum_{n=1}^{\infty}(-1)^n \exp(-n^2 t/\tau)\right] \qquad (4)$$

*where **n** is an integer*

$$\frac{N(t)}{I_0\tau} = \frac{t}{\tau} - \frac{\pi^2}{6} - 2\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp(-n^2 t/\tau).$$

If $t > 5\tau$ this reduces to the simple equation

$$N(t) = I_0(t - \pi^2\tau/6).$$

Nucleation kinetics. Comparison with theory of non-steady state homogeneous nucleation

2. Temperature dependence of induction time

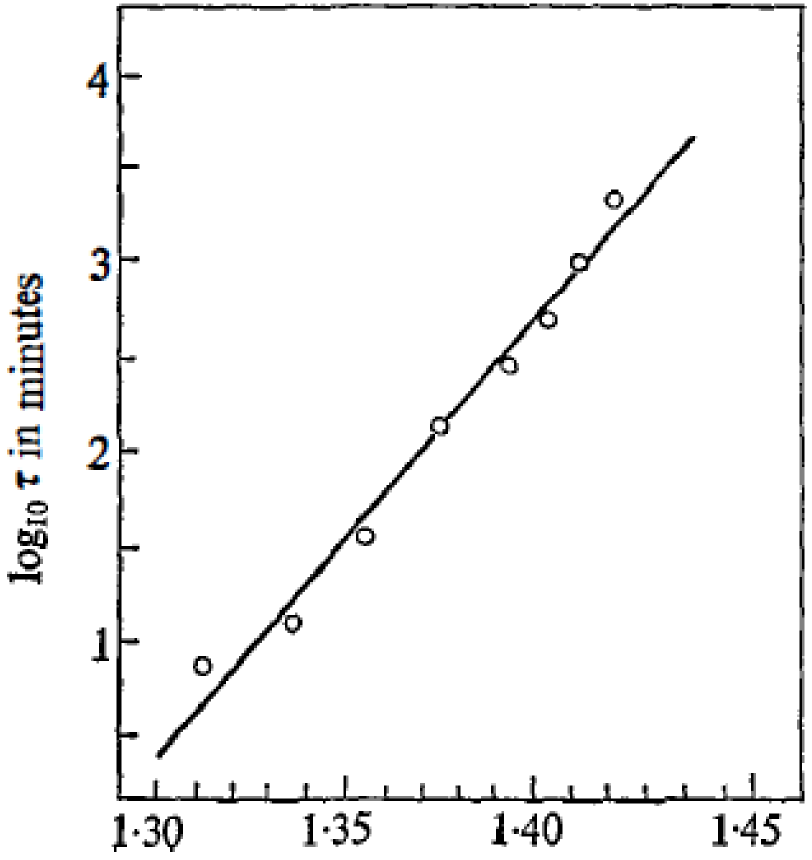


Figure 15. *Relation between induction times and temperature for glass 1*

$$\tau = \frac{16}{\pi^2} \cdot \frac{h\lambda^2\sigma}{V^2\,\Delta G_V{}^2} \exp\left(\Delta G_D/kT\right)$$

h is Planck's constant
λ is a quantity of the order of the atomic dimensions (jump distance),
k is Boltzmann's constant

ΔGv is the difference in free energy between the liquid and crystal phases per unit volume,

V *is the volume occupied per formula unit.*

ΔG_D should be identified with the activation energy involved in transport across the interface between liquid and crystal.

σ is the interfacial free energy per unit area,

Conclusions

The time dependence of the number of nuclei per unit volume at constant temperature was in good agreement with the theory.

The theory also accounts for the temperature dependence of the experimental induction times.

References

James, P. F. "Kinetics of crystal nucleation in lithium silicate-glasses." *Physics and chemistry of glasses* 15.4 (1974): 95-105.

Vesselinov, Markov Ivan. *Crystal growth for beginners: fundamentals of nucleation, crystal growth and epitaxy*. World scientific, 2003, page 122.

Thanks for your attention!