Rheology of partially crystallized simulated nuclear glass melts

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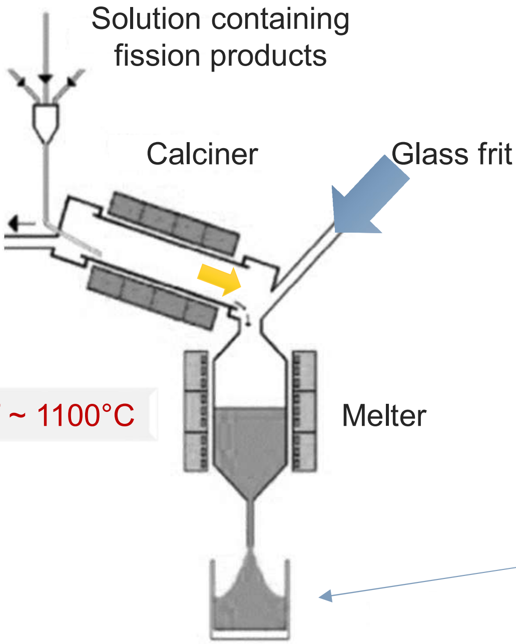
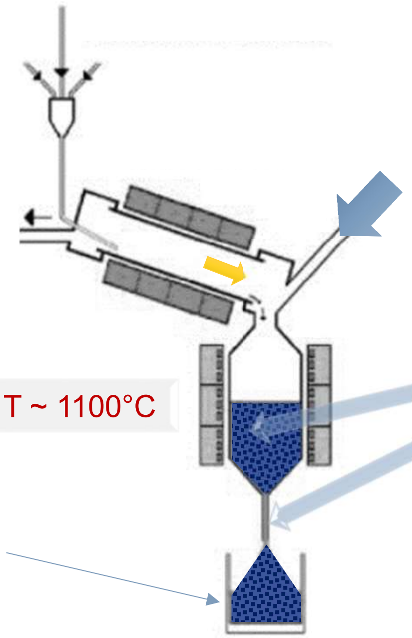
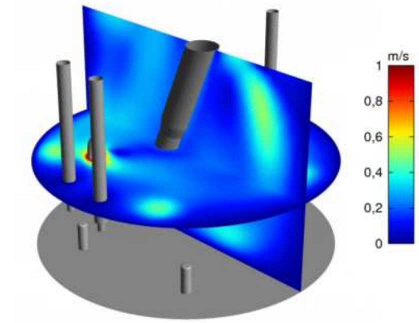
Context of the study:
motivation for studying the impact of crystals on melt rheology

CURRENT SCENARIO:
Melt with no crystals (except Pt^{ides})



PERSPECTIVE:
Melt with crystals





The viscosity of the melt is a key property for the vitrification process (pouring, glass homogeneization…)

How do crystals affect the rheology of the melt?

Solubility limits of elements likely to lead to the precipitation of crystals (Mo, Ce, RE…) are respected
⇒ waste loading < 18,5 wt%

⇒ Increase the waste loading
⇒ Reduce the vitrified waste volume
⇒ Reduce the cost of the storage

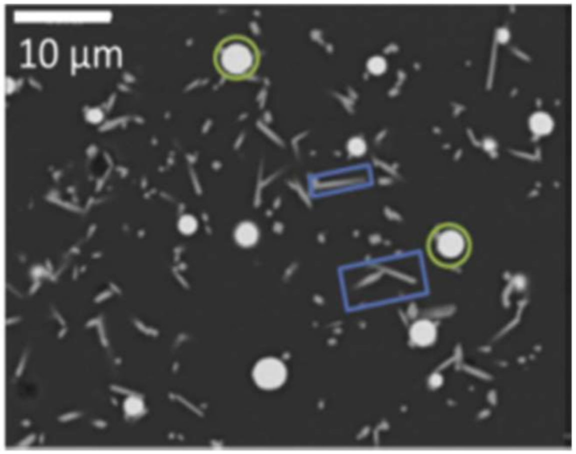
Context of the study:
impact of Pt^{ide} particles on glass melt rheology

French nuclear glass

~ 40 elements in an alumino-borossilicate glass

Platinoids => particles in suspension in the glass melt

Pd(Rh-Te) **beads** (1-10 µm)
$Ru(Rh)O_2$ **needles** (10-50 µm)

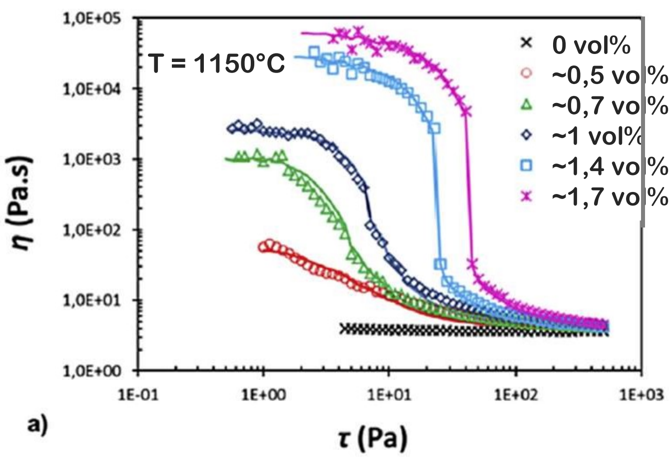


(Hanotin et al., 2016)

Typically ~1 vol% of Pt^{ide} particles (∀T) => strong impact on glass melt rheology

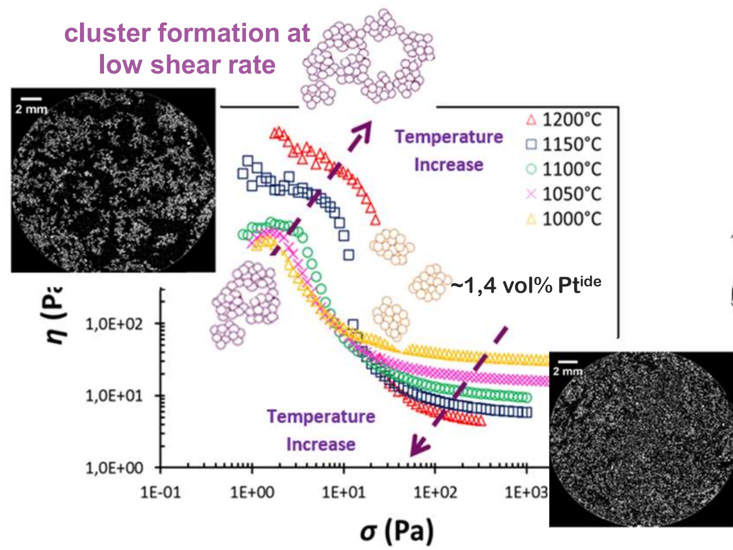
Context of the study:
impact of Pt^{ide} particles on glass melt rheology

Impact of Pt^{ide}-content on glass melt rheology



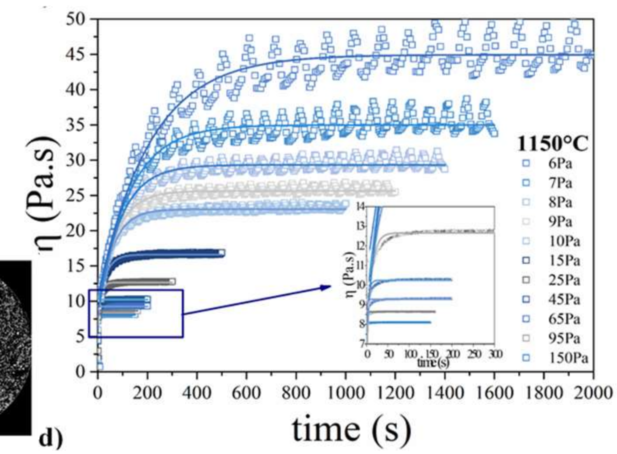
[Puig et al, 2016]

Impact of Temperature on the rheology of a Pt^{ide}-bearing melt



[Hanotin et al, 2016]
[Machado et al, 2022]

Impact of time on the rheology of a Pt^{ide}-bearing melt

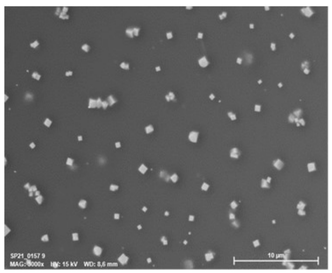


[Machado et al, 2022]

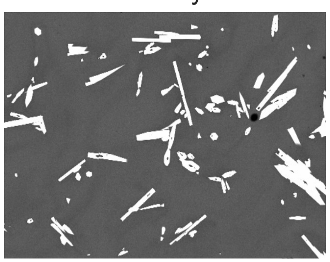
Knowing and integrating these effects in our magneto-thermo-hydraulics models is important to drive the vitrification furnaces (cf E. Sauvage presentation).

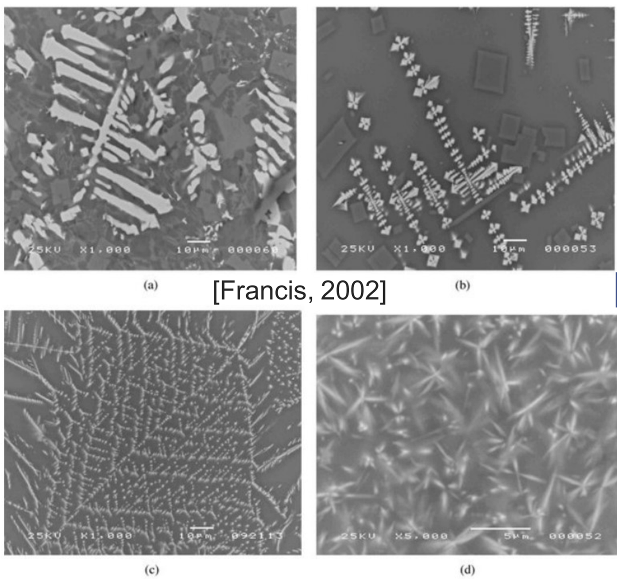
Challenge of the study

Do crystals affect the rheology of the melt as Pt^{ide} particles do?



This study





[Francis, 2002]

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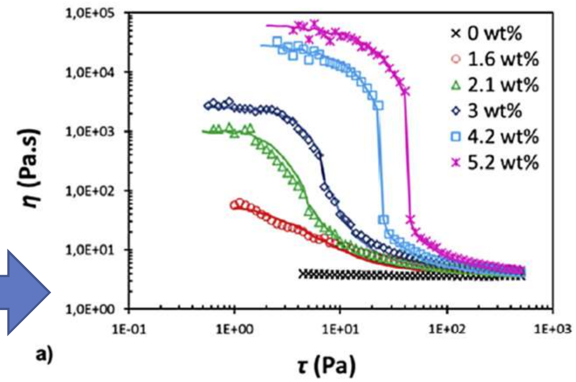
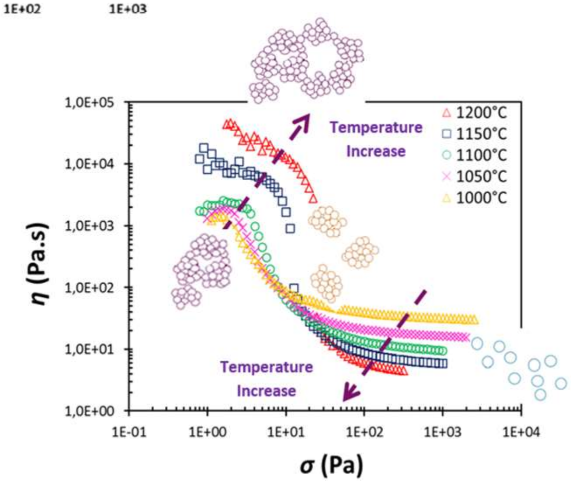


?

?



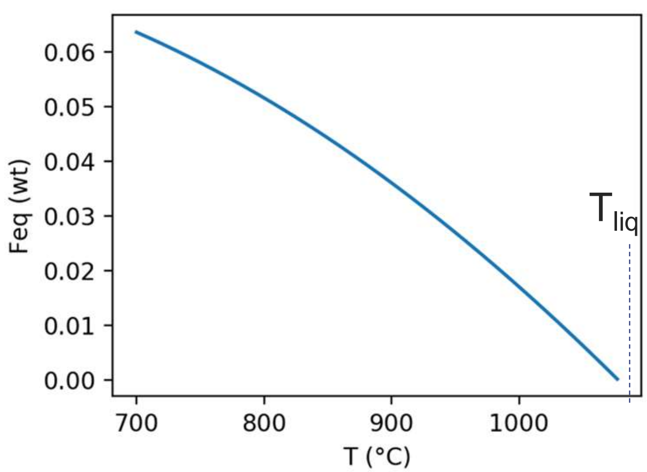
NB: the morphology of crystals can be very different from a system to another, and even within a given system (cf thermal history) + …

Challenge of the study

Particularity of crystals compared to Pt^{ides}

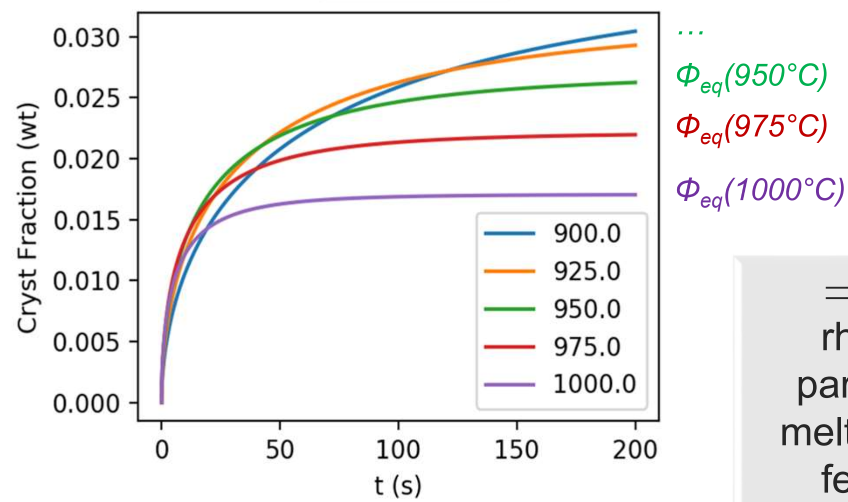
Unlike Pt^{ide} particles, crystals are soluble in the melt at HT → their fraction depends on t and T. Depending on T, they can grow or dissolve. This (T, t)-dependency can be described by JMAK equations:

Φ_{eq} = f(T)



$$\Phi_{eq}(T) = \Phi_{max}\left\{1 - \left[-B_L\left(\frac{1}{T} - \frac{1}{T_L}\right)\right]\right\}$$

Φ = f(t)



$$\Phi(t) = \Phi_{eq}\{1 - \exp[k(t)^n]\}$$

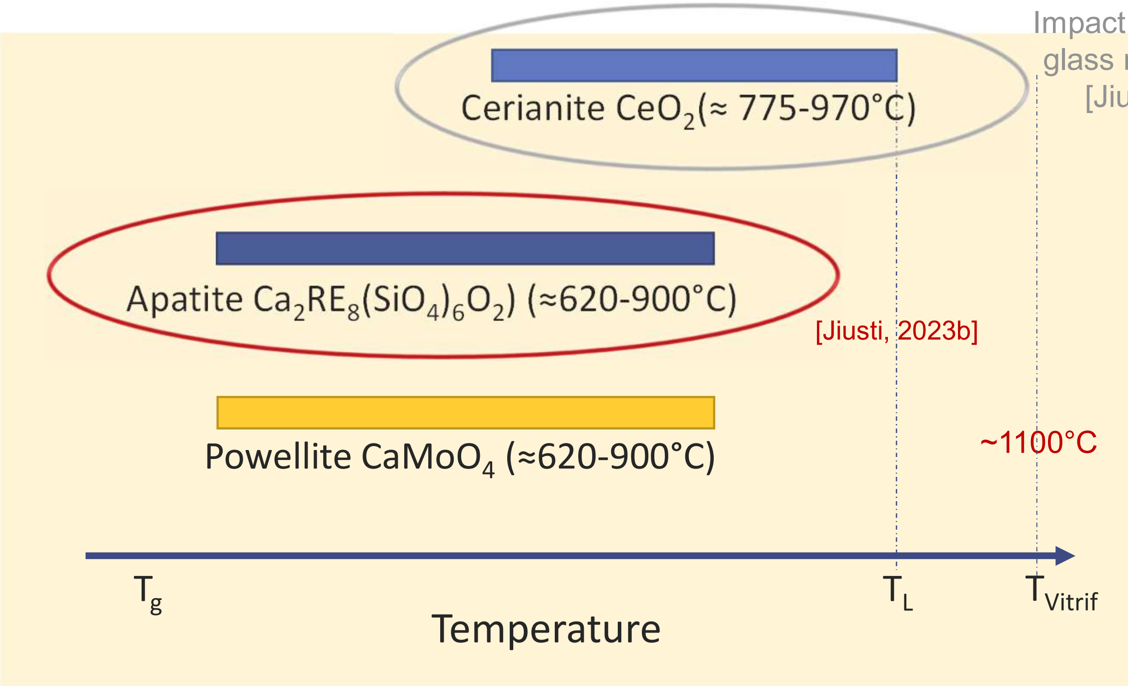
⇒ Before studying the rheological behavior of partially crystallized glass melts, we need to know the features of the crystals (morphology, content = f(t, T))

1. Why studying the impact of crystals on glass melt rheology ?

2. Experimental method

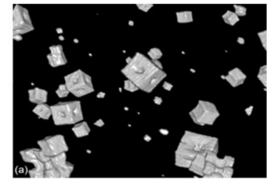
3. Results

Experimental method: choice of studied system



Temperature domains of crystalline phases reported for French simulated nuclear glasses [Delattre, 2014]

Impact of cerianite on glass melt rheology: [Jiusti, 2023a]



If the waste loading is increased, these 3 crystals may be present at higher temperature.

Our aim:

Impact of apatites ~**1100°C** (vitrification temperature) on melt rheology?

Experimental method: studied system

SYSTEM: melt + apatite

Initial glass composition

Oxydes	% mass.	% mol.
SiO_2	36,9	51,5
B_2O_3	13,8	16,6
Na_2O	12,3	16,6
CaO	4,9	7,4
Nd_2O_3	32,1	8,0

Renaud, 2017

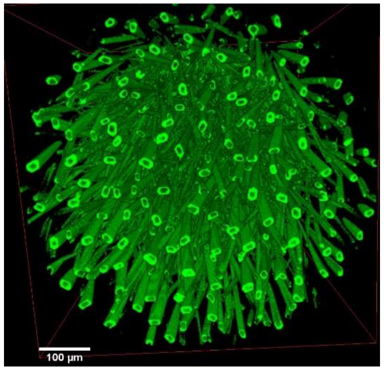
Thermal treatment

Apatite (**$Ca_2Nd_8(SiO_4)_6O_2$**) T_{liq} = 1178°C

Full / hollow hexagonal needles

1000°C – 24h

SEM images of apatites [Renaud, 2017]



Microtomography of apatites [Delattre, 2014] ESRF, ID19.

Experimental method: studied system

SYSTEM: melt + apatite

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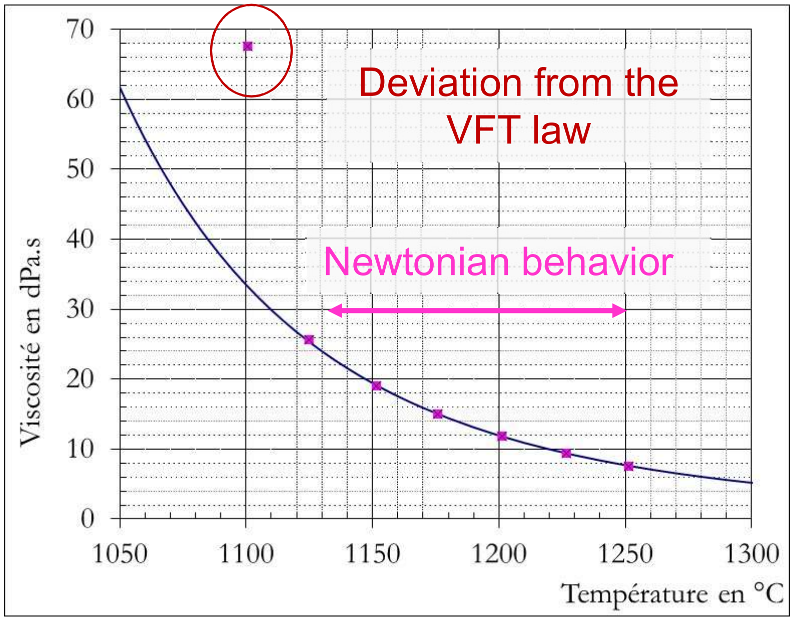
Renaud, 2017

Viscosity



[Renaud, 2017]

Experimental method: investigation of the studied system

Glass elaboration

Crystallization in static conditions

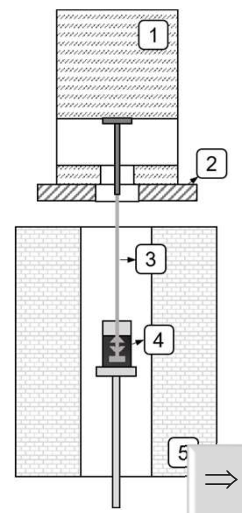
1. **Thermal treatments**

(T < 1178°C; 0,25h < t < 8h)

2. **Post-mortem SEM analysis**

⇒ Morphology of crystals, surf% = f(t, T)

Rheological study (T < 1178°C)



Rheometer-furnace setup

1,2 – Rheometer

3 – Rotor

4 – Crucible + glass

5- Furnace

⇒ Rheology:
- *during crystal growth*
- *after having reached Φ_{eq}*

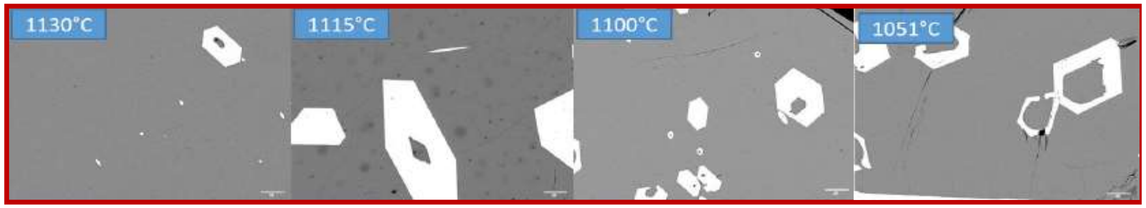
for ≠ shear stresses / rates and ≠ T

1. Why studying the impact of crystals on glass melt rheology ?

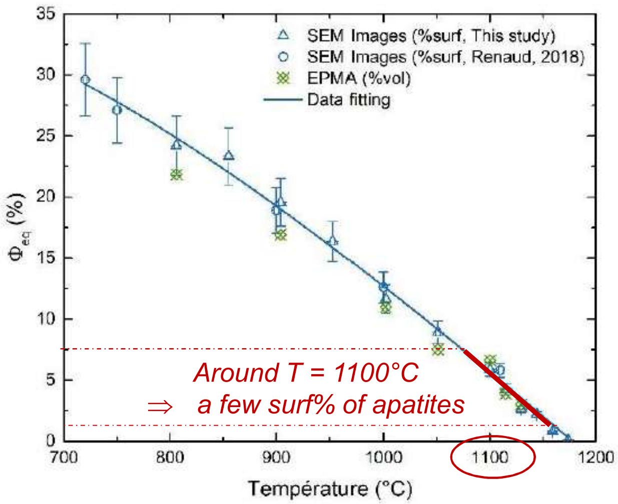
2. Experimental method

3. Results: impact of apatites on melt rheology

Results: apatite crystallization in static conditions

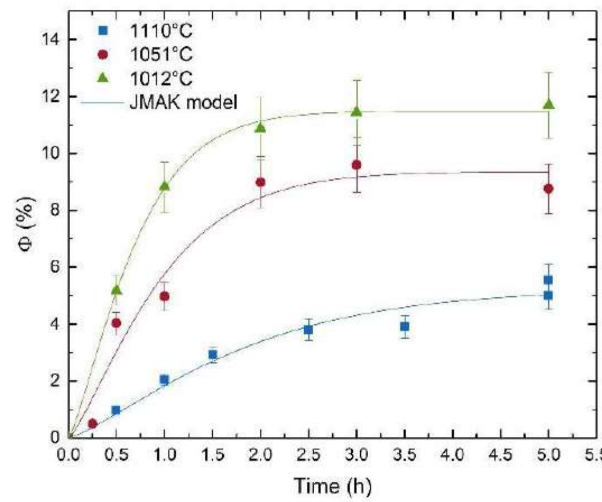


Around T = 1100°C
⇒ hexagonal needles



$$\Phi_{eq}(T) = 37{,}51\left\{1 - \exp\left[-2795\left(\frac{1}{T} - \frac{1}{1178}\right)\right]\right\}$$

rem: surf% = vol% in our case (isotrope crystallization + image analysis performed on large surfaces comp. to crystal dimensions)



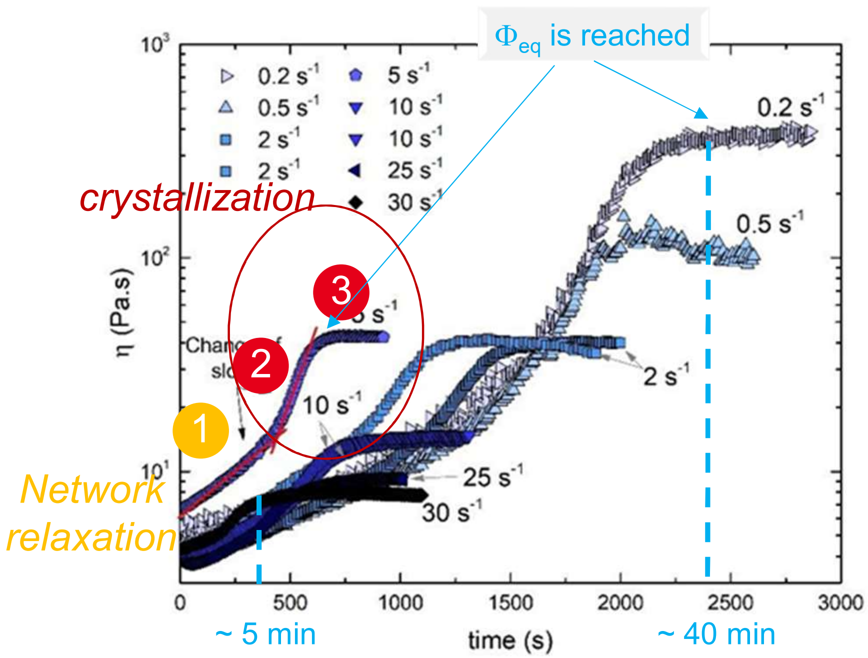
$$\Phi(t) = \Phi_{eq}\{1 - \exp[k(t)^n]\}$$

		JMAK Fitting		
T (°C)	Φ_{eq} (Eq (10))	Φ_{eq}	k	n
1110	5.0	5.2 ± 0.5	0.4 ± 0.1	
1051	9.2	9.4 ± 0.4	0.9 ± 0.2	1.3 ± 0.2
1012	11.9	11.5 ± 0.4	1.4 ± 0.2	

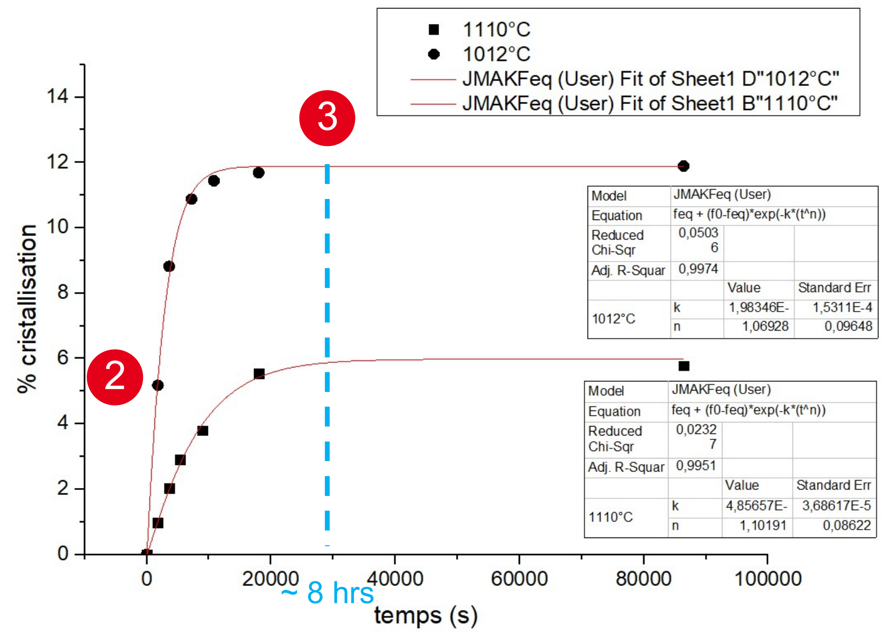
⇒ Reaching the equilibrium crystal fraction takes a few hours

Results: impact of dynamic conditions on apatite crystallization

Viscosity during the crystal growth at T=1100°C



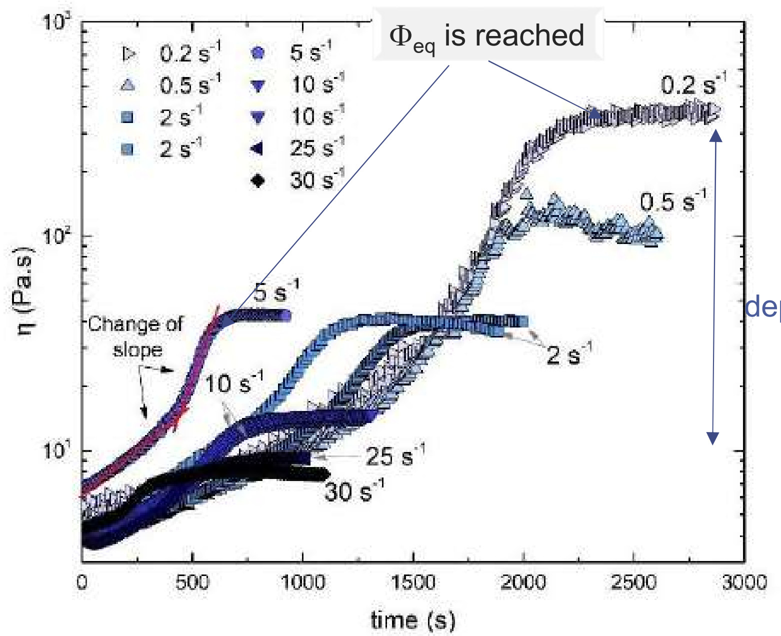
Crystallisation in static conditions



⇒ Crystallization is faster in dynamic conditions

Results: impact of apatite crystallization on melt rheology

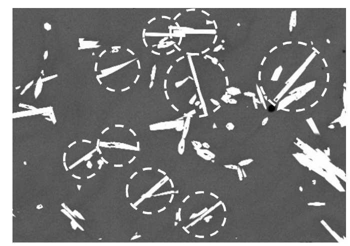
Viscosity during the crystal growth



The plateau level depends on shear rate

Crystallisation in dynamic conditions

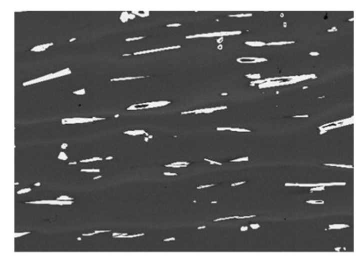
LOW SHEAR



Φ_{eff} (low shear rate)

>

HIGH SHEAR

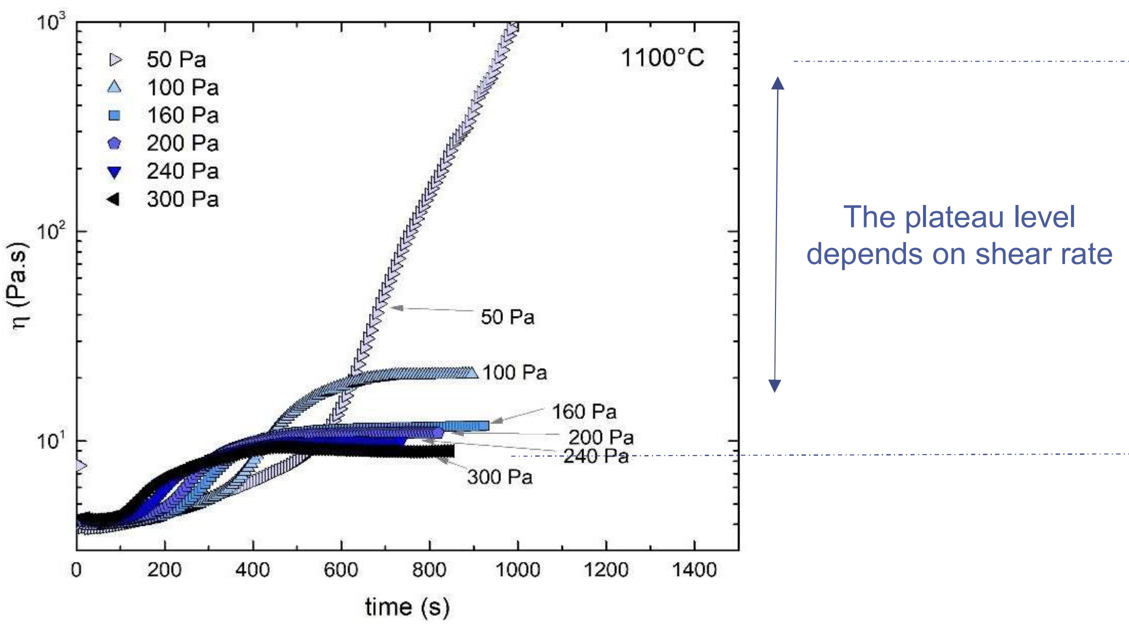


Φ_{eff} (high shear rate)

⇒ The equilibrium viscosity depends on shear rate (Φ_{eff}).

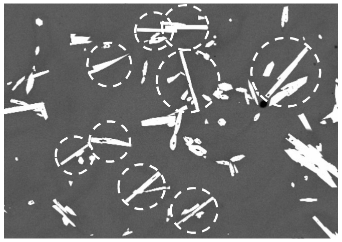
Results: impact of apatite crystallization on melt rheology

Viscosity during the crystal growth



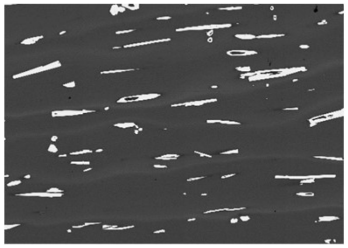
Crystallisation in dynamic conditions

LOW SHEAR



Φ_{eff} (low shear rate) >

HIGH SHEAR

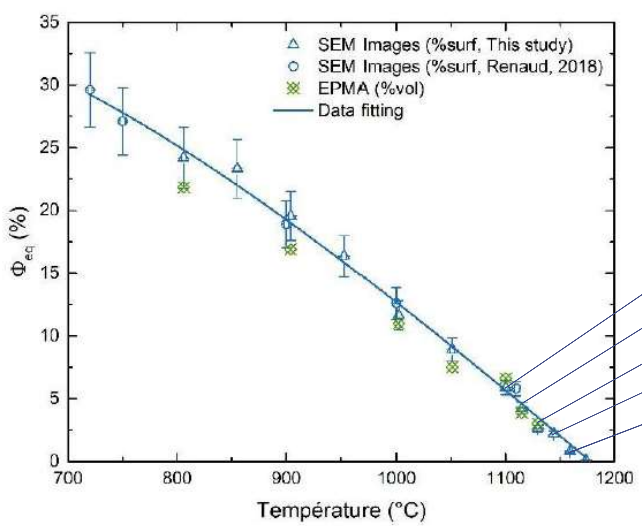


Φ_{eff} (high shear rate)

⇒ The equilibrium viscosity depends on shear stress (Φ_{eff}).

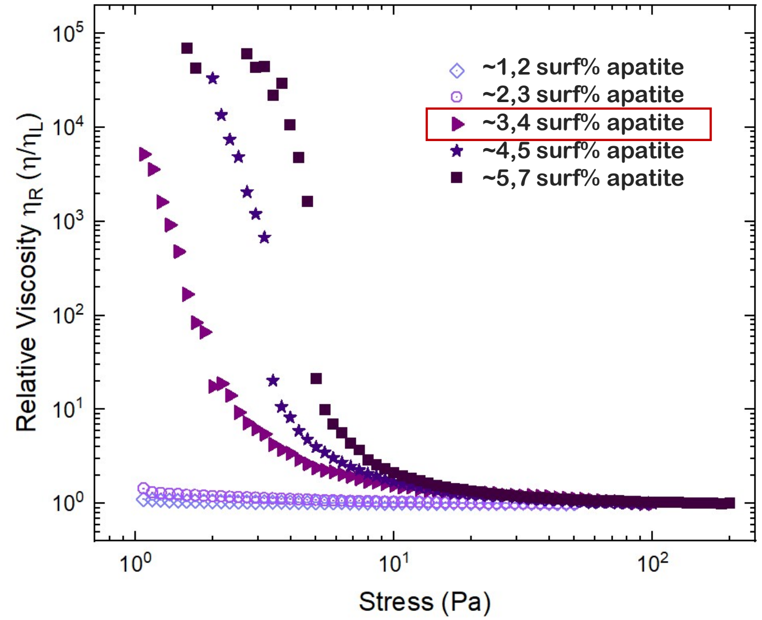
Results: impact of apatite crystallization on melt rheology

Viscosity once Φ_{eq} has been reached



Impact of apatites at several temperatures = several Φ

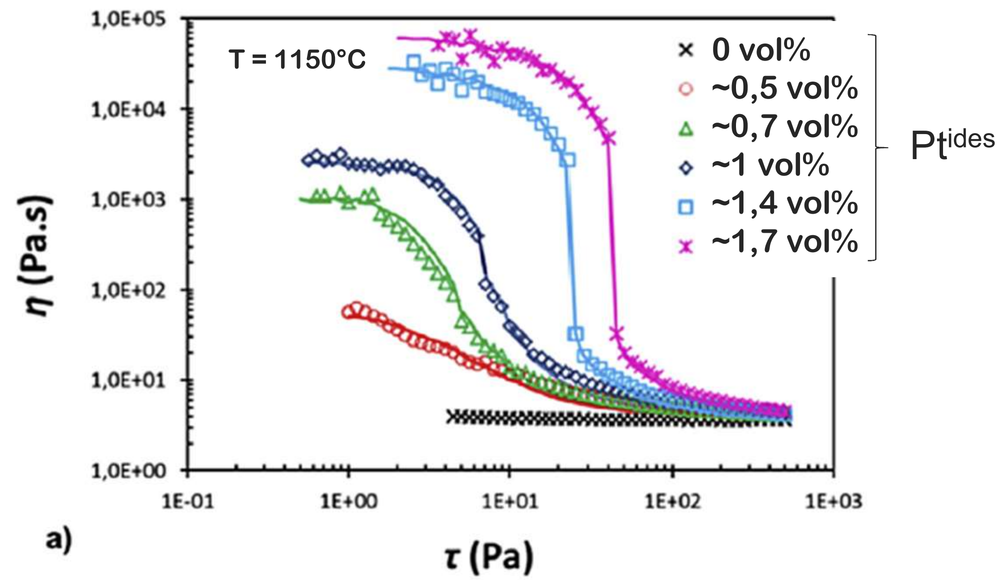
- 1100°C ~ 5,7 vol%
- 1116°C ~ 4,5 vol%
- 1132°C ~ 3,4 vol%
- 1147°C ~ 2,3 vol%
- 1162°C ~ 1,2 vol%

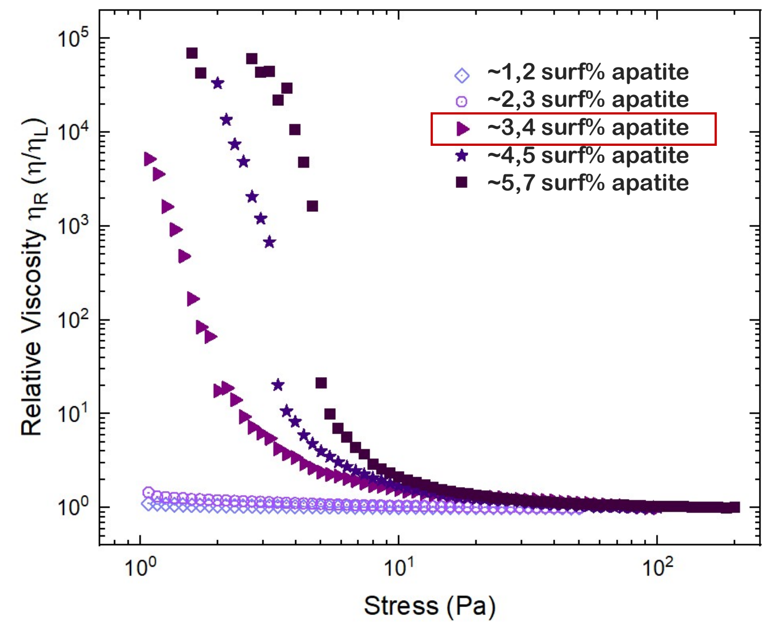


The studied apatite-bearing melt becomes non-newtonian from 3 vol%.

Results: impact of apatite crystallization on melt rheology

Viscosity once Φ_{eq} has been reached





The studied apatite-bearing melt becomes non-newtonian from ~3 vol% (*vs* 0,5 vol% for Pt[ides]).

Results: impact of crystallization on melt rheology

Impact of apatites

The system becomes non-Newtonian from ~3 vol% crystals.

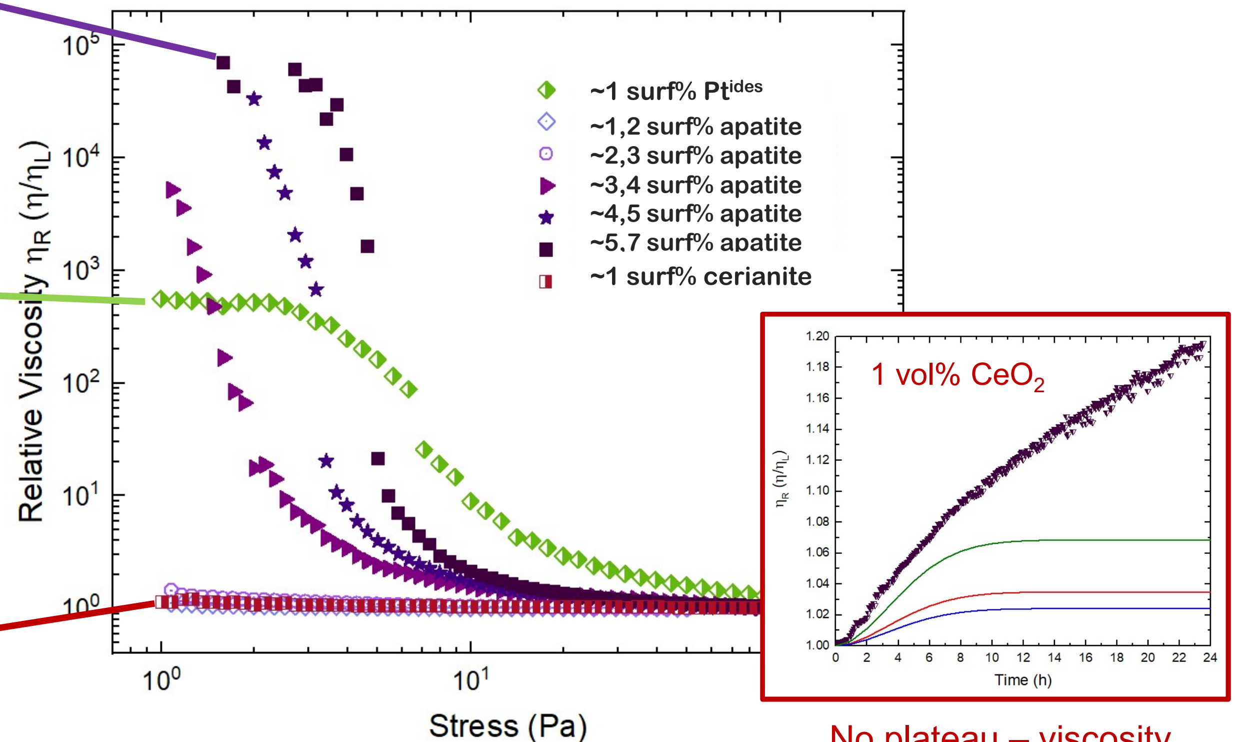
Impact of Pt^ides

The system becomes non-Newtonian from ~0,5 vol% particles.

Impact of cerianite (Jiusti, 2023a)

The system remains Newtonian for 1 vol% of **cerianite**.
It had no sens to test larger cerianite contents.

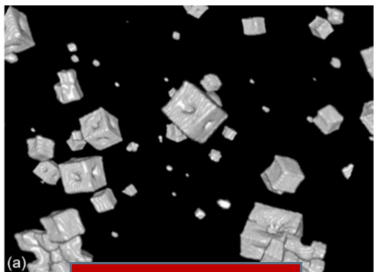
Evolution of relative viscosity with shear stress for crystal-glass melt systems.



No plateau – viscosity increase due to volatility

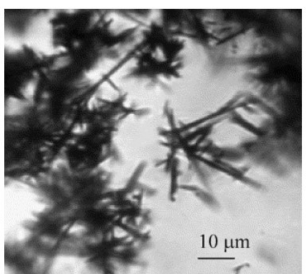
Results: impact of crystallization on melt rheology

The theoretical value of Φ_c seems to be in agreement with our experimental results.



Cerianite

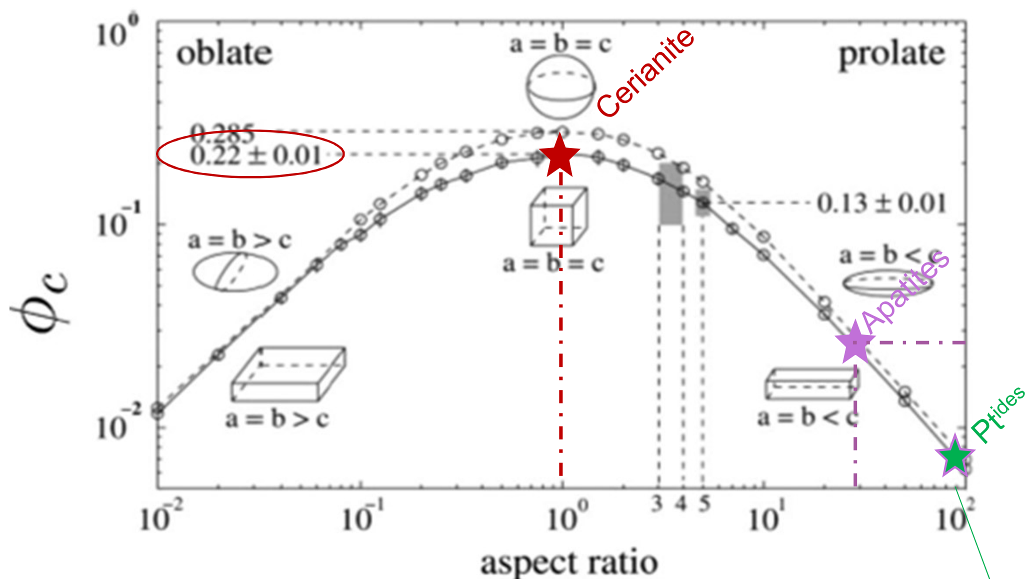
[Jiusti, 2023a]

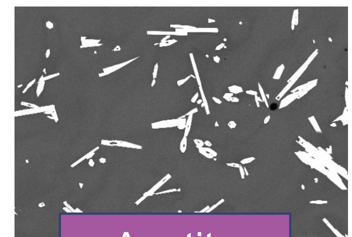


Pt^{ide} part.

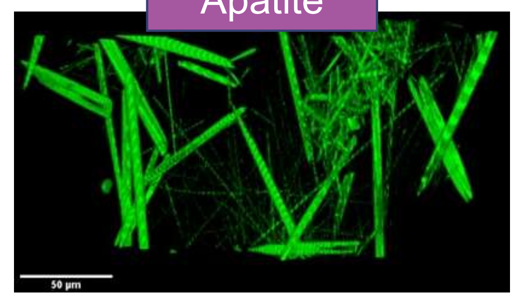
[Simonnet, 2004]

Dependence of the critical particle fraction for a system to present a yield strength as a function of the aspect ratio of the particles (Simulated for shear stress = 0) [Saar, 2007].





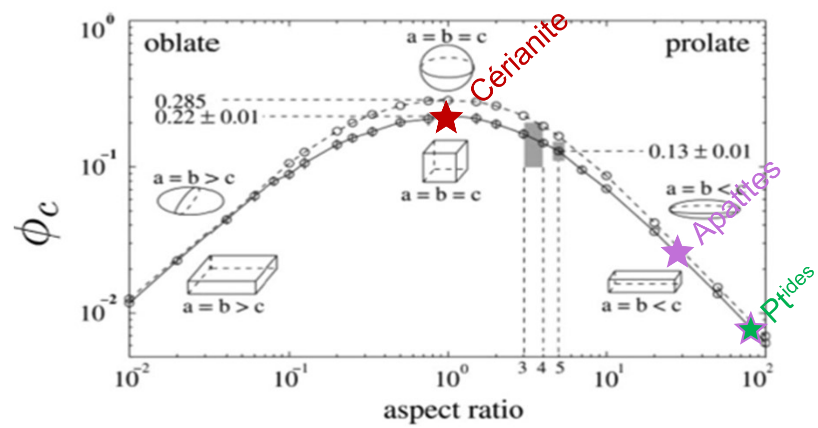
Apatite



In the case of Pt^{ide} particles, particle interaction between the liquid PdRhTe alliage and the $Ru(Rh)O_2$ needles may also play a role

Conclusion: impact of crystallization on melt rheology

- The rheology of a partially crystallized glass melt depends mostly on:
  1) <u>Crystal morphology</u>
  2) The crystallized fraction

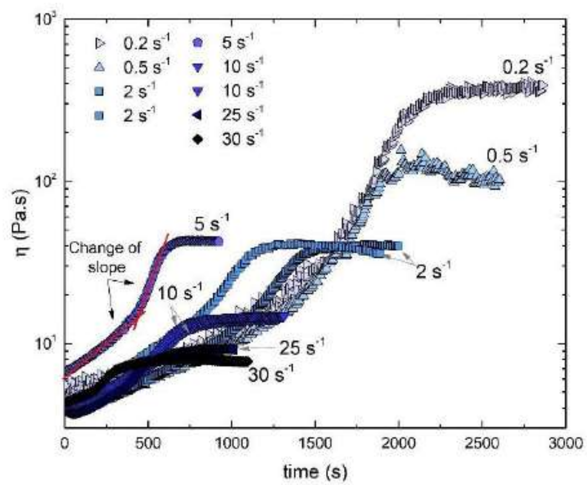


In both cerianite and apatite cases, the melt can tolerate a higher fraction of crystals before becoming non-Newtonian when compared to Pt[ide] particles.

- For a few vol% of cerianite => VFT models can be used
- For a few vol% of apatites => the loss of the Newtonian behavior has to be taken into account in models

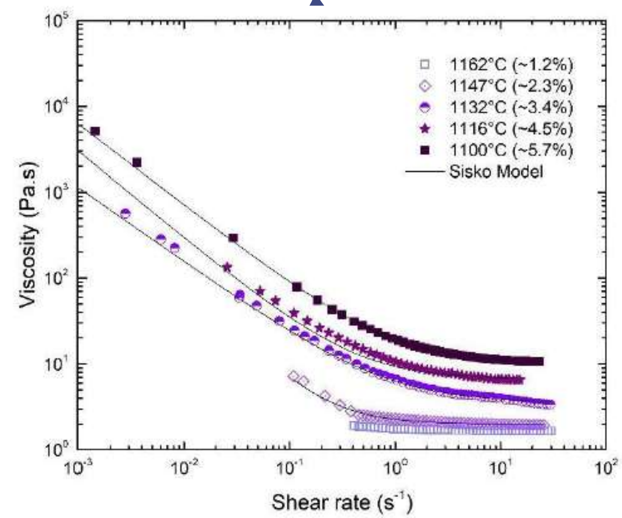
Conclusion: impact of crystallization on melt rheology

Modelization during crystal growth / at crystallization equilibrium



Need to:

- Take into account the relaxation phase (empirical model)
- Developpe a model based on JMAK equation for phases 2 and 3, taking into account the value of the plateau with the applied shear rate (empirical model or model based on Φ_{eff}).



Sisko parameters for the different apatite fractions studied

	Φ = 1.2% (1162 °C)	Φ = 2.3% (1147 °C)	Φ = 3.4% (1132 °C)	Φ = 4.5% (1116 °C)	Φ = 5.7% (1100 °C)
η_∞ (Pa.s)		1.99 ± 23	3.52 ± 0.06	6.01 ± 0.04	10.20 ± 0.03
k	Newtonian	0.27 ± 37	2.8 ± 0.1	4.71 ± 0.06	9.24 ± 0.07
N		-0.27 ± 112	0.13 ± 0.06	0.15 ± 0.02	0.06 ± 0.01

+ crystal sedimentation has to be studied.

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Thanks for your attention!