





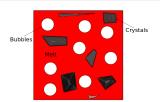
#### Magma density and viscosity

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### Magma density



Bulk density depends on volume fraction of crystals and bubbles

$$\rho = \rho_{\rm m} \left( 1 - \sum_{i} \phi_{i} \right) + \sum_{i} \rho_{i} \phi_{i}$$

 $\rho_{\mathsf{m}} = \mathsf{Melt} \; \mathsf{density}$ 

• Depends on T, P, X

i = quartz, hornblende, plagioclase etc. and  $H_2O$ ,  $CO_2$  bubbles etc.

 $\rho_i = \text{Density of phase } i$ 

- Depends on *T*, *P* for bubbles
- Depends on composition for crystals

 $\phi_i$  = Volume fraction of phase i



#### Melt density

$$\rho_m = \sum_i X_i M_i \left( \sum_i X_i \bar{V}_i(T, P) \right)^{-1}$$

 $M_i = \text{Molar mass of component } i$ 

- Mass of 1 mol of i
- $M_{SiO_2} = 28 \text{ g mol}^{-1} + 2 \times 16 \text{ g mol}^{-1} = 60 \text{ g mol}^{-1}$
- $M_{\text{H}_2\text{O}} = 2 \times 1 \text{ g mol}^{-1} + 16 \text{ g mol}^{-1} = 18 \text{ g mol}^{-1}$

 $\bar{V}_i$  = Partial molar volume of component i

• Change in mixture volume when 1 mol of *i* is added

Need to determine  $\bar{V}_i(T, P)$  empirically



# Melt density - Equation of state (EoS)

Relationship between **pressure**, **volume** (density) and **temperature** Experiments - measure volume of a sample of X at a different P and T. Find **empirical** EoS

$$V_m(T,P,\mathbf{X}) = \sum_i X_i \left[ \left. \bar{V}_i(T=T_{\mathsf{R}},P=P_{\mathsf{R}}) + \left. \frac{\partial \bar{V}_i(T,P=P_{\mathsf{R}})}{\partial T} \right|_{T=T_{\mathsf{R}}} (T-T_{\mathsf{R}}) + \left. \frac{\partial \bar{V}_i(T=T_{\mathsf{R}},P)}{\partial P} \right|_{P=P_{\mathsf{R}}} (P-P_{\mathsf{R}}) \right] \right]$$

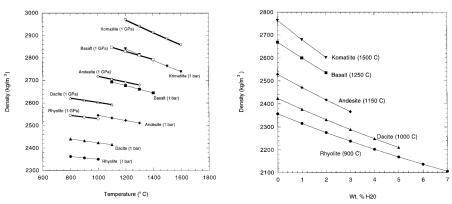
 $T_R$  = Reference temperature = 1673 K  $P_R$  = Reference pressure =  $10^{-4}$  GPa

Lange & Carmichael (1990) Lange (1997)

Ochs & Lange (1997)

	$\bar{V}_i(T=T_{R},P=P_{R})$	$\left. \frac{\partial \bar{V}_i(T, P=P_{R})}{\partial T} \right _{T=T_{R}}$	$\frac{\partial \bar{V}_i(T=T_R,P)}{\partial P}\Big _{P=P_R}$
	$/10^{-6} \text{ m}^3 \text{ mol}^{-1}$	$/10^{-9} \text{ m}^3 \text{ mol}^{-1} \text{ K}$	$/10^{-6} \text{ m}^3 \text{ mol}^{-1} \text{ GPa}$
SiO <sub>2</sub>	26.86	0.0	-1.89
TiO <sub>2</sub>	23.16	7.24	-2.31
Al <sub>2</sub> O <sub>3</sub>	37.42	0.0	-2.31
Fe <sub>2</sub> O <sub>3</sub>	42.13	9.09	-2.53
FeO	13.65	2.92	-0.45
MgO	11.69	3.27	0.27
CaO	16.53	3.74	0.34
Na <sub>2</sub> O	28.88	7.68	-2.40
K <sub>2</sub> O	45.07	12.08	-6.75
Li <sub>2</sub> O	16.85	5.25	-1.02
H <sub>2</sub> O	26.27	9.46	-3.15
$\overline{\text{CO}_2}$	33.0	0.0	0.0

### Melt density - Effect of T and $X_{H_2O}$



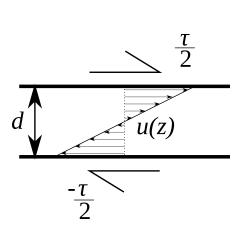
Temperature has small effect on density, particularly for high-silica melts

Water content has much stronger effect



### Magma viscosity - Viscosity definition

**Viscosity** - A measure of a substance's resistance to flow (deformation). It relates an applied shear stress to the velocity gradient.



Consider fluid between two sheared parallel plates

 $au = \mbox{Applied shear stress}$   $d = \mbox{Separation between plates}$   $u(z) = \mbox{Fluid velocity in gap}$ 

Viscosity  $\eta$  is defined as:

$$\tau = \eta \frac{\mathrm{d}U}{\mathrm{d}z} = \eta \dot{\epsilon}$$

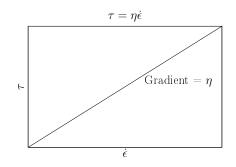
where  $\dot{\epsilon} = dU/dz =$ strain rate

### Magma viscosity - Newtonian fluids

Generally, viscosity is a function of strain rate:  $\eta = \eta(\dot{\epsilon})$ 

Therefore, impossible to assign a single value of  $\eta$  to a material

Newtonian fluids - Special case where  $\eta$  is independent of  $\dot{\epsilon}$ 



Flow curve - Relationship between  $\tau$  and  $\dot{\epsilon}$ 

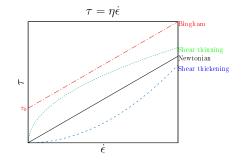
$$\tau = \eta(\dot{\epsilon})\dot{\epsilon}$$

For Newtonian fluid,  $\eta = \text{constant}$ 

⇒ flow curve is straight line

$$\implies$$
 gradient =  $\eta$ 

#### Magma viscosity - Rheological materials



#### Newtonian

- Constant  $\eta$
- e.g. water, magmatic melt

#### **Shear thickening**

- $\eta$  increases with  $\dot{\epsilon}$
- e.g. cornstarch

#### Shear thinning

- $\eta$  decreases with  $\dot{\epsilon}$
- e.g. butter

#### **Bingham**

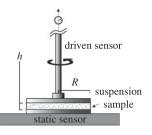
- Fluid has **yield stress**  $\tau_0$
- For  $au < au_0$  fluid does not flow  $(\dot{\epsilon} = 0)$
- e.g. Mayonaise

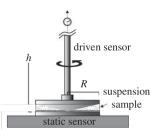
#### Measuring rheological properties

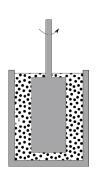
#### Parallel plate

#### Cone and plate

#### Concentric cylinder







Apply torque  $M\Longrightarrow$  stress auMeasure angular velocity  $\Omega\Longrightarrow$  strain rate  $\dot{\gamma}$ Determine flow curve  $au=\eta(\dot{\gamma})\dot{\gamma}$ 

### Magma viscosity - Melt as a Newtonian fluid

Silica melt is almost perfectly Newtonian.

However, at extremely high shear rates, all materials start to undergo shear-thinning

Critical shear rate is given by

$$\dot{\epsilon_c} pprox rac{10^{-3}G}{\eta_m}$$

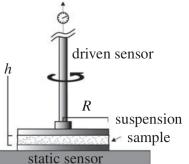
 $G = {\sf Shear \ modulus} \approx 10^{10} {\sf \ Pa}$ 

At even higher shear rates, the melt cannot deform as a fluid and snaps in a brittle manner.

#### Magma viscosity - Melt viscosity

Melt is modelled according to the Vogel-Fulchner-Tammann (VFT) equation (Giordano et al., 2008)

torque,  $M \to \text{stress}$ ,  $\tau$  angular velocity,  $\Omega \to \text{strain rate}$ ,  $\dot{\gamma}$ 



$$\log \eta_{\mathsf{m}} = A + \frac{B(\mathbf{X})}{T - C(\mathbf{X})}$$

$$\eta_{\mathsf{m}} = 10^{A+B(\mathbf{X})/[T-C(\mathbf{X})]}$$

Measurements of the viscosity of samples of different  $\mathbf{X}$  at different T are used to determine  $A, B(\mathbf{X}), C(\mathbf{X})$ 

N.B: This is a fitted, purely empirical equation - it is not dimensionally consistent!

#### Magma viscosity - Fitted parameters

$$A = {\sf constant} = -4.55$$
  $\log n$   $B = \sum_{i=1}^7 b_i M_i + \sum_{j=1}^3 b_{1j} M_{1j}$   $C = \sum_{i=1}^6 c_i N_i + c_{11} N_{11}$ 

$$\log \eta_{\mathsf{m}} = A + \frac{B(\mathbf{X})}{T - C(\mathbf{X})}$$

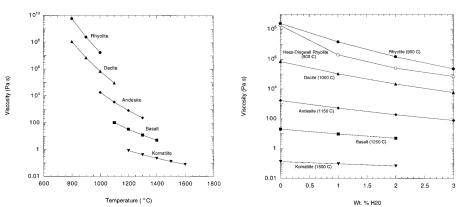
$$\eta_{\mathsf{m}} = 10^{A+B(\mathbf{X})/[T-C(\mathbf{X})]}$$

$b_1 = 159.6$	$M_1 = X_{SiO_2} + X_{TiO_2}$	$c_1 = 2.75$	$N_1 = X_{SiO_2}$
$b_2 = -173.3$	$M_2 = \bar{X}_{Al_2O_3}$	$c_2 = 15.7$	$N_2 = X_{\text{TiO}_2} + \tilde{X}_{\text{Al}_2\text{O}_3}$
$b_3 = -72.1$	$M_3 = X_{\text{FeO}} + X_{\text{MnO}} + X_{\text{P}_2\text{O}_5}$	$c_3 = 8.3$	$N_3 = X_{\text{FeO}} + X_{\text{MnO}} + X_{\text{MgO}}$
$b_4 = -75.7$	$M_4 = X_{\text{MgO}}$	$c_4 = 10.2$	$N_4 = X_{CaO}$
$b_5 = -39.9$	$M_5 = X_{CaO}$	$c_5 = -12.3$	$N_5 = X_{\text{Na}_2\text{O}} + X_{\text{K}_2\text{O}}$
$b_6 = -84.1$	$M_6 = X_{\text{Na}_2\text{O}} + X_{\text{H}_2\text{O}} + X_{\text{F}_2\text{O}}$	$c_6 = -99.1$	$N_6 = \ln(1 + \tilde{X}_{H_2O} + \tilde{X}_{F_2O})$
$b_7 = -141.5$	$M_7 = X_{\text{H}_2\text{O}} + X_{\text{F}_2\text{O}} + \ln(1 + \bar{X}_{\text{H}_2\text{O}})$		
$b_{11} = -2.43$	$M_{11} = M_1 N_3$	$c_{11} = 0.3$	$N_{11} = (M_2 + N_3 + N_4 -$
$b_{12} = -0.91$	$M_{12} = (N_1 + N_2 + X_{P_2O_5})(N_5 + X_{H_2O})$		$X_{P_2O_5}$ )( $N_5 + X_{H_2O} + X_{F_2O_{-1}}$ )
$b_{13} = 17.6$	$M_{13}=M_2N_5$		

For a given melt composition, can evaluate  $\eta$ 



# Melt viscosity - Effect of T and $X_{H_2O}$



Increase in T and  $X_{H_2O}$  can reduce melt viscosity by orders of magnitude

### Magma viscosity - Effect of crystals

Particles suspended in a fluid increase the viscosity of the medium **Suspension** - A mixture of particles and fluid

 $\phi_{\rm c}=$  **Volume fraction** of crystals

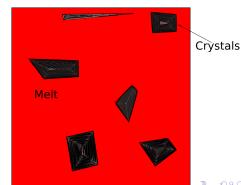
Define **relative viscosity**  $\eta_{\rm r}(\phi_{\rm c})$  to contain effect of  $\phi_{\rm c}$ 

$$\eta = \eta_{\mathsf{m}} \eta_{\mathsf{r}}(\phi_{\mathsf{c}})$$

$$\phi_{\rm c} \lesssim 0.01$$
 - **Dilute**

$$0.01 \lesssim \phi_{\rm c} \lesssim 0.25$$
 - Semi-dilute

$$\phi_{\rm c} \gtrsim 0.25$$
 - Concentrated



### Magma viscosity - Dilute particle suspensions

Dilute suspension:  $\phi_c \lesssim 0.01$ 

Interactions between particles are weak and effect on viscosity is small

Viscosity depends linearly on  $\phi_c$  (Einstein, 1906; 1911)

$$\eta_{
m r}=1+B\phi_{
m c}$$

Experiments suggest that  $B \approx 2.5$ 

Suspension rheology models are only strictly valid for suspensions on spherical particles.

Developing models for suspensions of differently shaped particles is difficult

- particularly for magmas where crystals have many different and irregular shapes

However, for dilute and semi-dilute suspensions, models work well.



#### Magma viscosity - Semi-dilute suspensions

**Semi-dilute suspension**:  $0.01 \lesssim \phi_c \lesssim 0.25$ 

Particles interact with each other, affecting the viscosity

Viscosity depends non-linearly on  $\phi_{\rm c}$  (Guth & Gold, 1938; Vand, 1948; Manley & Mason, 1955)

Can model the viscosity with a polynomial expression

$$\eta_{\rm r} = 1 + B\phi_{\rm c} + B_1\phi_{\rm c}^2 + ...$$

Experiments suggest that  $7.35 \lesssim B_1 \lesssim 14.1$ 

Predictions from polynomial models get worse as  $\phi_c$  increases.

- This is because as particles begin to touch the viscosity rises very fast

# Magma viscosity - Maximum packings

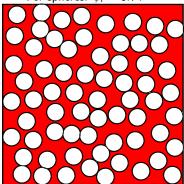
Concentrated suspension:  $\phi_c \gtrsim 0.25$ 

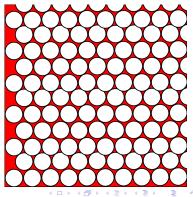
Random close packing - Maximum volume fraction of crystals that can be obtained in a disordered system

For spheres:  $\phi_{\rm m} \approx 0.64$ 

Densest regular packing - Maximum possible packing if crystals are arranged orderly

For spheres:  $\phi_r \approx 0.74$ 





#### Magma viscosity - Concentrated suspensions

Concentrated suspension:  $\phi_c \gtrsim 0.25$ 

Once  $\phi_c = \phi_m$ , then further deformation is impossible

- the material is rheologically locked
- $\eta_{\rm r} o \infty$

For magmas,  $\phi_{\rm m}$  depends on crystal shape and size distribution

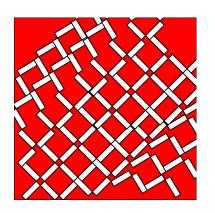
- Very difficult to accurately predict
- Many experiments, find  $\phi_{\rm m} pprox 0.4$

Multiple models describe rheology of concentrated suspensions, but commonly used model is Krieger & Dougherty (1959)

$$\eta_{\mathsf{r}} = \left(1 - rac{\phi_{\mathsf{c}}}{\phi_{\mathsf{m}}}
ight)^{-B\phi_{\mathsf{m}}}$$

#### Magma viscosity - Yield stress

Once a touching network of crystals exists, then the magma has a **yield** stress



Experiments show magmas with  $\phi_{\rm c}$  as small as 0.2 can have a yield stress

 $\phi_{\rm y}=$  Minimum value of  $\phi_{\rm c}$  at which yield stress exists

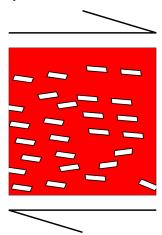
$$au_0 = 6.9 \left(rac{\phi_{ extsf{c}}}{\phi_{ extsf{y}}} - 1
ight) \left(1 - rac{\phi_{ extsf{c}}}{\phi_{ extsf{m}}}
ight)^{-1}$$

(Saar et al., 2001; Andrews & Manga, 2014)

#### Magma viscosity - Non-Newtonian effects

Definition of  $\eta_{\rm r}$  assumes Newtonian or Bingham rheology i.e.  $\eta$  is independent of  $\dot{\epsilon}$ 

In reality:



Elongated particles align with the flow

Longest axis becomes parallel to flow lines

The greater the strain rate the larger the reduction in viscosity  $\implies$  shear thinning

More complicated models exist to describe suspensions of elongate particles e.g.

$$\eta_{
m r} = \left(1 - rac{\phi_{
m c}}{\phi_{
m m}}
ight)^{-2} \dot{\epsilon}^{0.2 r_{
m p} (\phi_{
m c}/\phi_{
m m})^4}$$

 $r_p = Crystal$  aspect ratio

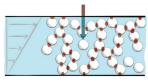
### Magma rheology - Suspension or granular media

Classically, model mixtures of particles and fluid as **suspensions**:

- No relative motion between fluid and particles
- $\bullet$   $\phi$  is control variable
- System described by equations of fluid dynamics with effective viscosity

In reality, particularly for dense suspensions:

- Phase segregation can be important
- $\phi$  can depend on particle pressure  $P_{\rm p}$
- System is described by Granular mechanics with interstitial fluid



Guazzelli and Pouliquen (2018)

How to describe these systems remains highly contentious Extremely difficult to model theoretically, numerically or experimentally

#### Magma viscosity - Effect of bubbles

Rheological behaviour is determined by the capillary number

$$\mathsf{Ca} = rac{\eta_\mathsf{m} \dot{\epsilon} \mathit{r}_\mathsf{b}}{\sigma}$$

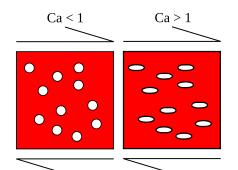
 $\eta_{\rm m} = {\sf Melt viscosity}$  $\dot{\epsilon} = \text{Shear rate}$ 

 $r_{\rm b} = \text{Bubble radius}$ 

 $\sigma = Surface tension$ 

Ca is a balance between:

- Deforming viscous stress  $\eta_{\rm m}\dot{\epsilon}$
- Restoring surface tension stress  $\sigma/r_b$



If  $Ca \leq 1$ , surface tension stress dominates and bubbles remain spherical

Bubbles behave like solid particles ⇒ increase in viscosity

If  $Ca \geq 1$ , deforming stress dominates and bubbles can have irregular shapes Bubbles streamline with shear

⇒ Decrease in viscosity and

shear thinning

### Magma viscosity - Modeling the effect of bubbles

Bubble deformation makes it difficult to model effect of bubbles on rheology

**Relaxation time** - Characteristic time for a deformed bubble to return to equilibrium state

$$\lambda = \frac{\eta_{\mathsf{m}} r_{\mathsf{b}}}{\sigma}$$

Compare with timescale for changing shear conditions  $\dot{\gamma}/\ddot{\gamma}$ 

Define Dynamic capillary number:

$$\mathsf{Cd} = rac{\lambda \ddot{\gamma}}{\dot{\gamma}}$$

 $\begin{array}{cccc} \mathsf{Cd} < 1 \implies \mathsf{Steady} \; \mathsf{flow} & \implies \mathsf{Rheology} \; \mathsf{controlled} \; \mathsf{by} \; \mathsf{Ca} \\ \mathsf{Cd} > 1 \implies \mathsf{Unsteady} \; \mathsf{flow} \implies \mathsf{Bubbles} \; \mathsf{never} \; \mathsf{in} \; \mathsf{equilibrium} \\ & \mathsf{Viscosity} \; \mathsf{is} \; \mathsf{less\_than\_bubble\_free} \; \mathsf{fluid}_{\mathsf{Ca},\mathsf{Ca}} \end{array}$ 

# Magma viscosity - Modeling the effect of bubbles

Whether bubbles increase or decrease viscosity depends on  $\dot{\gamma}$  and  $\ddot{\gamma}$  Semi-empirical model of Mader et al. (2013):

$$\eta_{\mathsf{r}} = \eta_{\mathsf{r},\infty} + \frac{\eta_{\mathsf{r},\mathsf{0}} - \eta_{\mathsf{r},\infty}}{1 + \mathsf{Cx}^{m}}$$

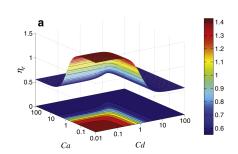
where

$$\eta_{\mathsf{r},\infty} = 1 - rac{5\phi_\mathsf{b}}{3}$$

$$\eta_{\rm r,0} = 1 + \phi_{\rm b}$$

$$Cx = \sqrt{Ca^2 + Cd^2}$$

m depends on size distribution
= 2 for mono-disperse bubbles



Mader et al. (2013)

Experimentally tested for  $\phi_b < 0.46$ 

For  $\phi_{
m b} \geq$  0.74 a foam forms

#### Magma density and viscosity - conclusions

- Empirical and semi-empirical models parameterise magma density and viscosity
- Both depend on volume fraction of solid and gas phases
- Melt density is described by an empirical equation of state and depends strongly on water content
- Melt viscosity is described by an empirical VFT equation and depends on temperature and composition
- Magma viscosity strongly depends on crystal and bubble content