#### **Calorimetric Glass Transition Temperatures**

&

#### Magmatic Processes

#### Kelly Russell University of British Columbia

Jim Nicholls University of Calgary &

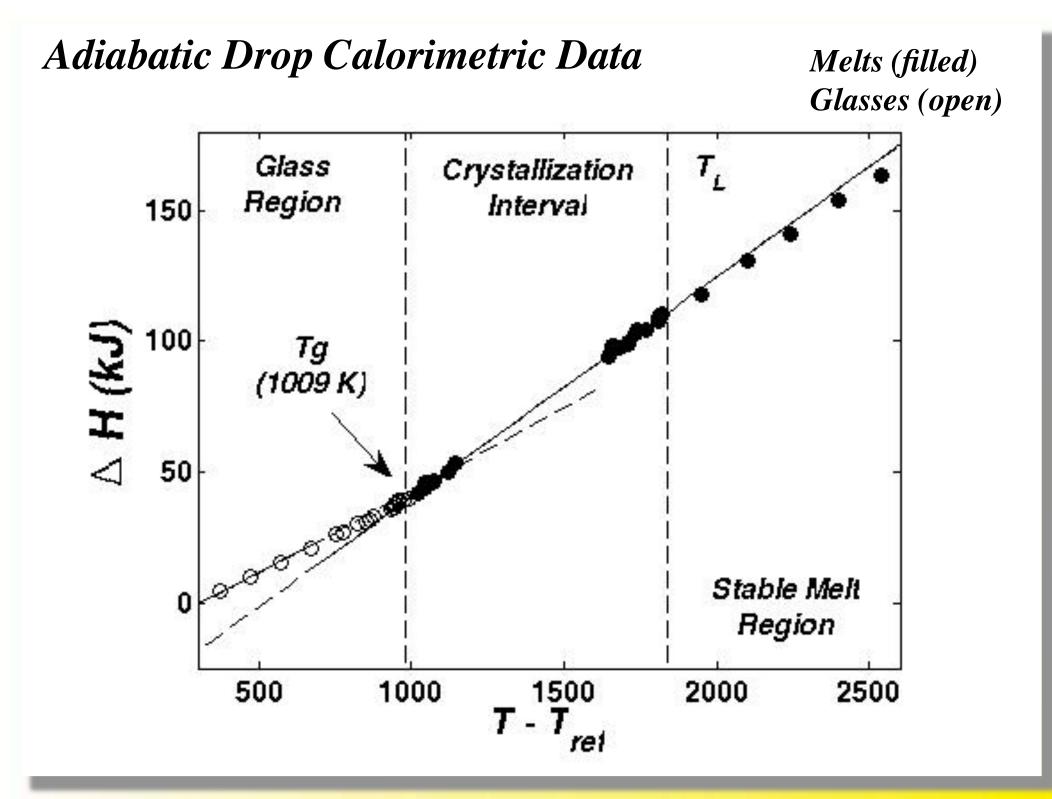
Daniele Giordano CSIC, Barcelona

*EGU General Assembly, April 3 - 8<sup>th</sup> 2011, Vienna* GMPV2/IG20: Magmas, Melts, and Magma Mixing: from lab to nature.

# SYNOPSIS

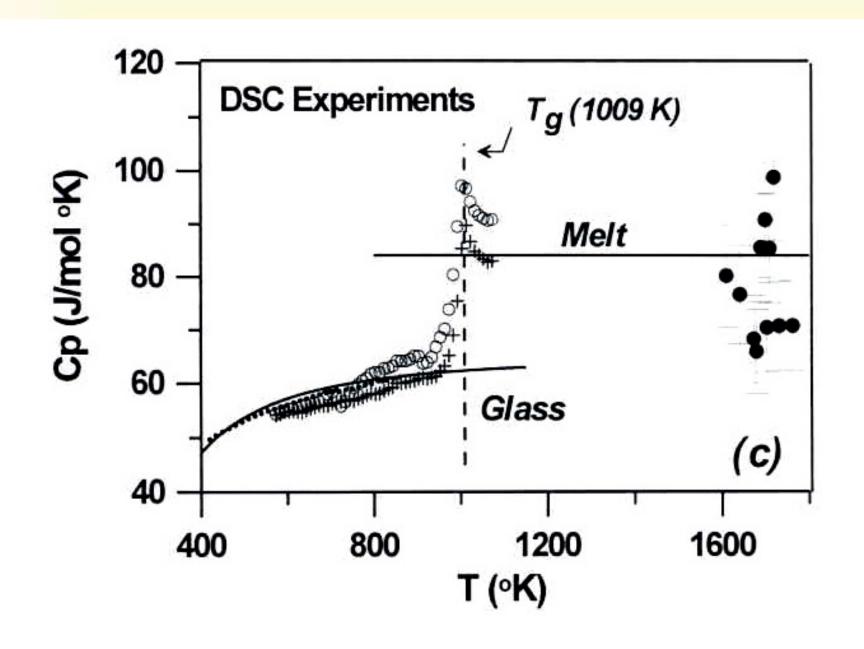
- (1) Natural glasses record melt composition attending magmatic processes.
- (2) Natural glasses form under diverse conditions.[silicic to mafic melts; fast to slow cooling]
- (3) Glass transition temperature (**Tg**) marks the transition from the liquid to the glassy state.
- (4) Glass is the consequence of the liquid line of decent[T-X] intersecting the Tg

## (5) EMPIRICAL MODEL PREDICTS CALORIMETRIC Tg AS A FUNCTION OF MELT COMPOSITION



#### DSC vs. Model Functions:

Data: Stebbins et al. 1983; Knoche et al. 1992; Lange et al., 1991.



**Empirical Model for predicting Tg in Natural Melts** 

Based on ADC datasets including: > 500 experiments on 60 melt compositions > 400 observations on 30 glass compositions

**PLUS** constraints from independent estimates of Tg

Provides T-dependent melt & glass heat contents curves

$$\Delta H_{m} = A \cdot T(K) + B$$

$$\Delta H_g = a \cdot T(K) + \frac{c}{T}(K) + d$$

Intersection of heat content curves defines Tg

# Multicomponent Model for Calorimetric Tg UNCONSTRAINED MODEL

$$X^{2} = \sum_{i=1}^{n} \left\langle \frac{\Delta H_{i}^{obs} - h(T)_{i}}{\sigma_{i}} \right\rangle^{2}$$

$$\mathbf{h}_{i}^{\text{Melt}}(\mathbf{T}) = \boldsymbol{\Sigma}_{k}^{\text{nc}} \langle \mathbf{A}_{k} \mathbf{x}_{k} \cdot \mathbf{T}(\mathbf{K}) + \mathbf{B}_{k} \mathbf{x}_{k} \rangle$$

$$h_i^{Glass}(T) = \Sigma_k^{nc} \langle a_k x_k \cdot T(K) + \frac{c_k x_k}{T(K)} + d_k x_k \rangle$$

## **CONSTRAINED MODEL**

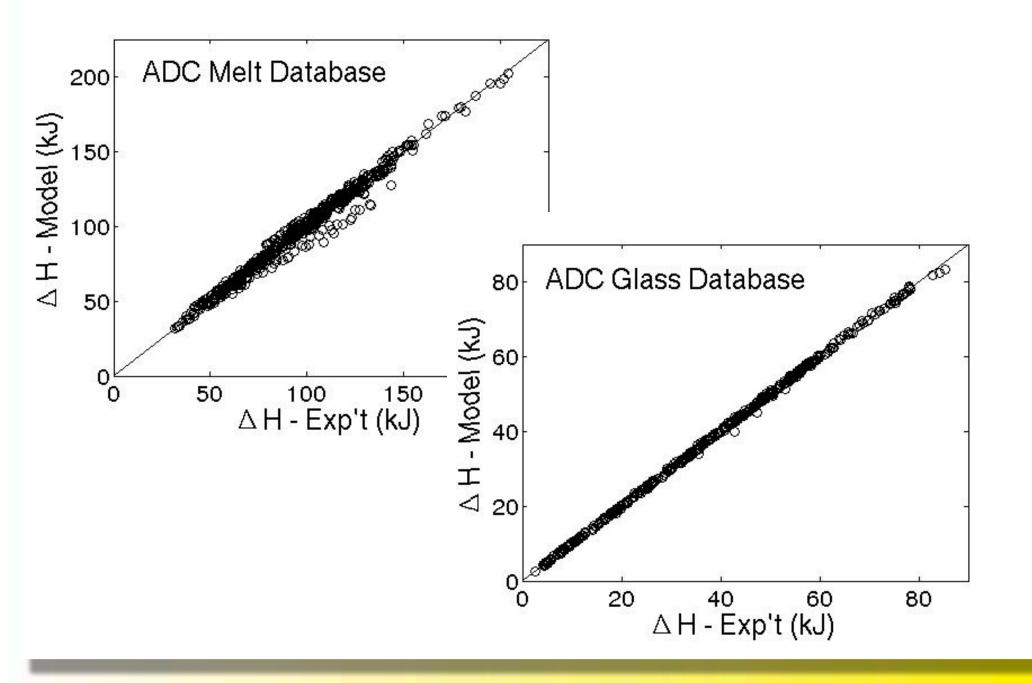
- Model equations for melts and glasses are UNCOUPLED
- Compositional coefficients are linearly independent
- Use Tg values as linear equality constraints
- Couples the coefficients for melts and glasses
- N < = RANK of compositional matrix (RANK =7)

## CONSTRAINT EQUATIONS

$$\Sigma_{k}^{nc}\langle (\mathbf{A}_{k}-\mathbf{a}_{k})\cdot\mathbf{x}_{k}\rangle\cdot\mathbf{T}g^{2}+\Sigma_{k}^{nc}\langle (\mathbf{B}-\mathbf{d})\mathbf{x}_{k}\rangle\cdot\mathbf{T}g-\Sigma_{k}^{nc}(\mathbf{c}_{k}\mathbf{x}_{k})=0$$

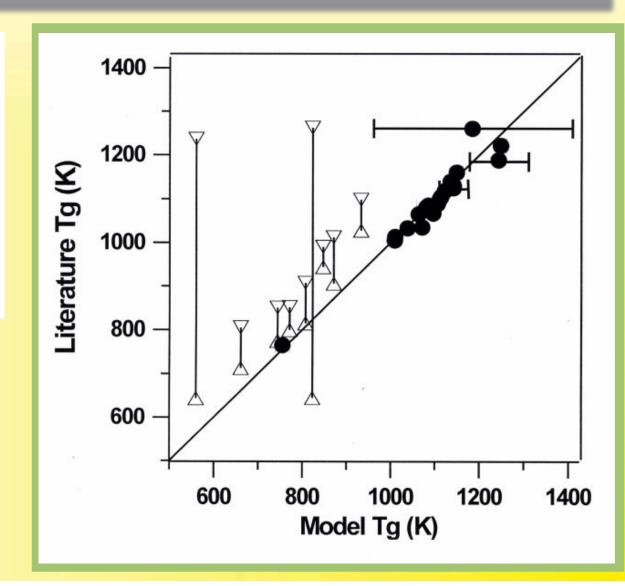
ALLOWS use of 7 independent estimates of Tg Compositions must be LINEARLY INDEPENDENT

#### MODEL vs. DATA



$$Tg(K) = \frac{-\beta(x) \pm \sqrt{\beta(x)^2 - 4 \cdot \alpha(x) \cdot \gamma(x)}}{2 \cdot \alpha(x)}$$

$$\alpha(\mathbf{x}) = \Sigma_{i=1}^{n} (\mathbf{A}_{i} - \mathbf{a}_{i}) \cdot \mathbf{x}_{i}$$
$$\beta(\mathbf{x}) = \Sigma_{i=1}^{n} (\mathbf{B}_{i} - \mathbf{d}_{i}) \cdot \mathbf{x}_{i}$$
$$\gamma(\mathbf{x}) = -\Sigma_{i=1}^{n} (\mathbf{c}_{i} \cdot \mathbf{x}_{i})$$



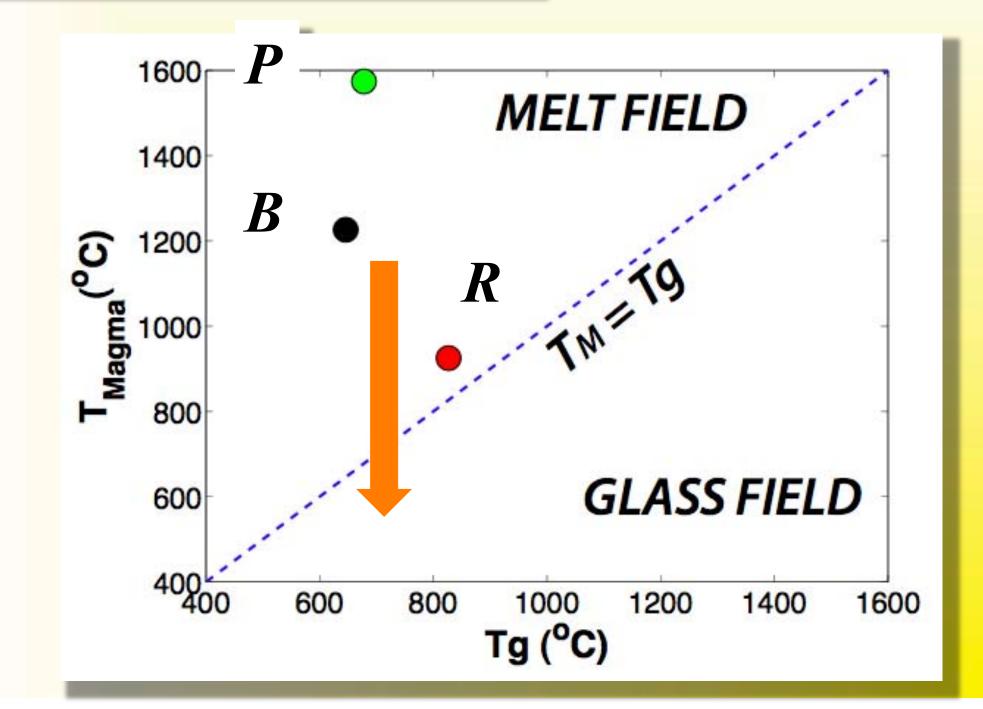
# **APPLICATIONS & TAKE AWAYS**

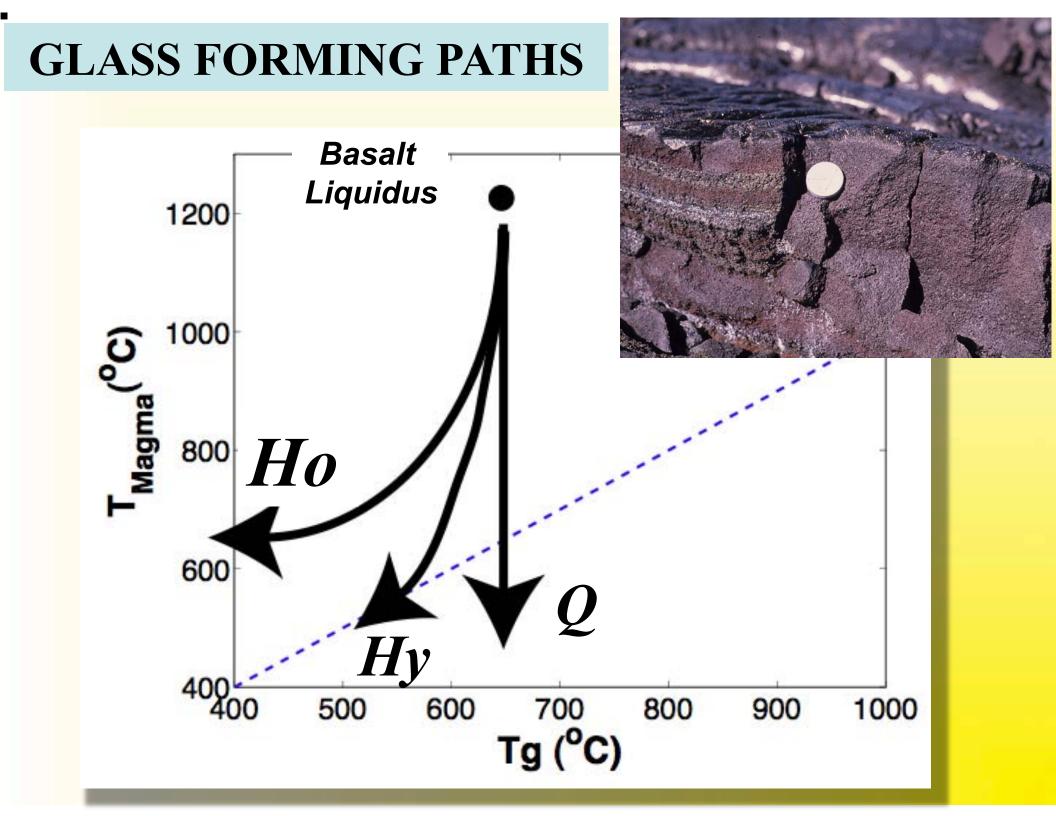
- A) **TRACK**  $T_{magma}$  **vs.** Tg during magmatic processes such as fractional crystallization, vesiculation, melting.
- B) **TERMINATION OF LIQUID LINE OF DESCENT** Where liquid line of descent (e.g., T-X path) intersects Tg of the melt, glass forms and terminates many processes.

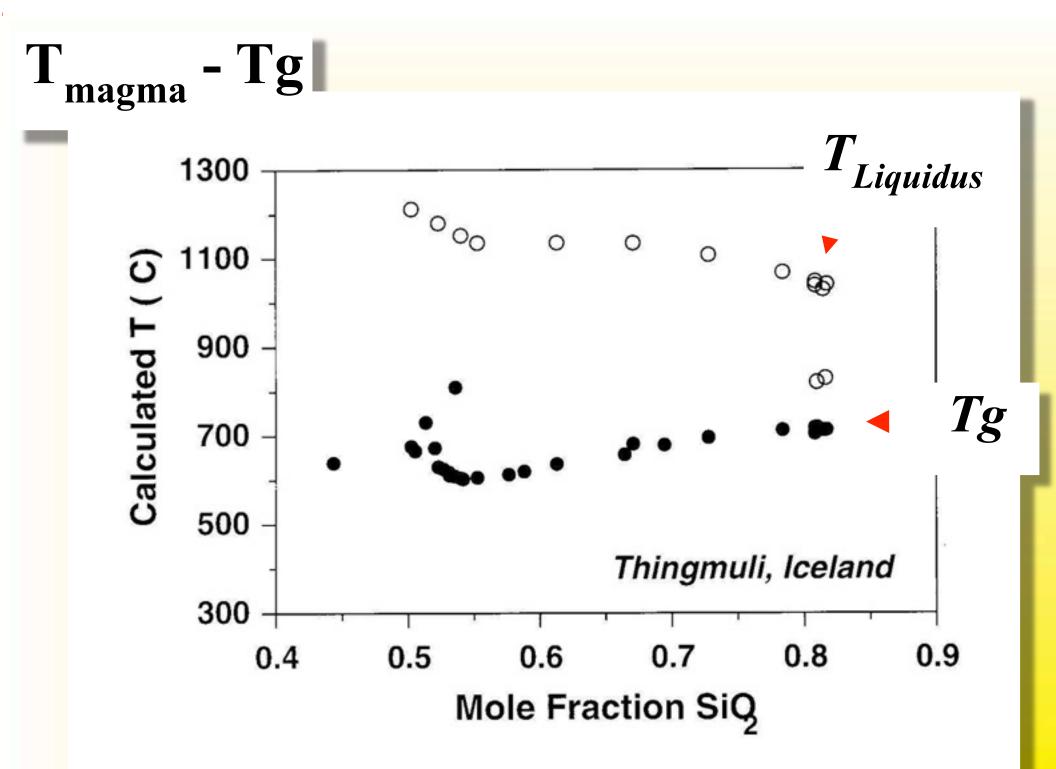
### C) GEOTHERMOMETRY

Glass compositions converted to pre-eruption T<sub>min</sub>.

## **TG - Melt Composition**





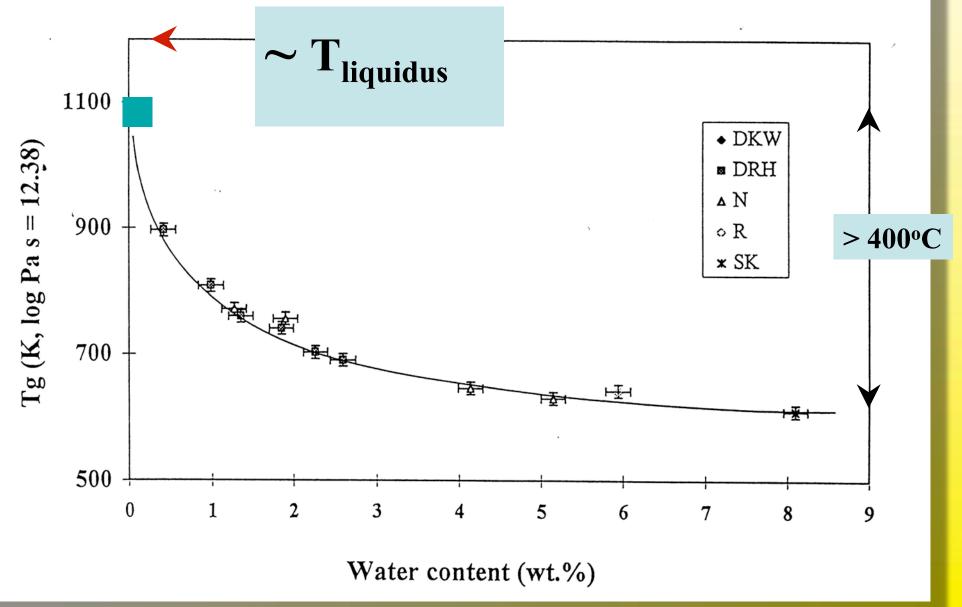


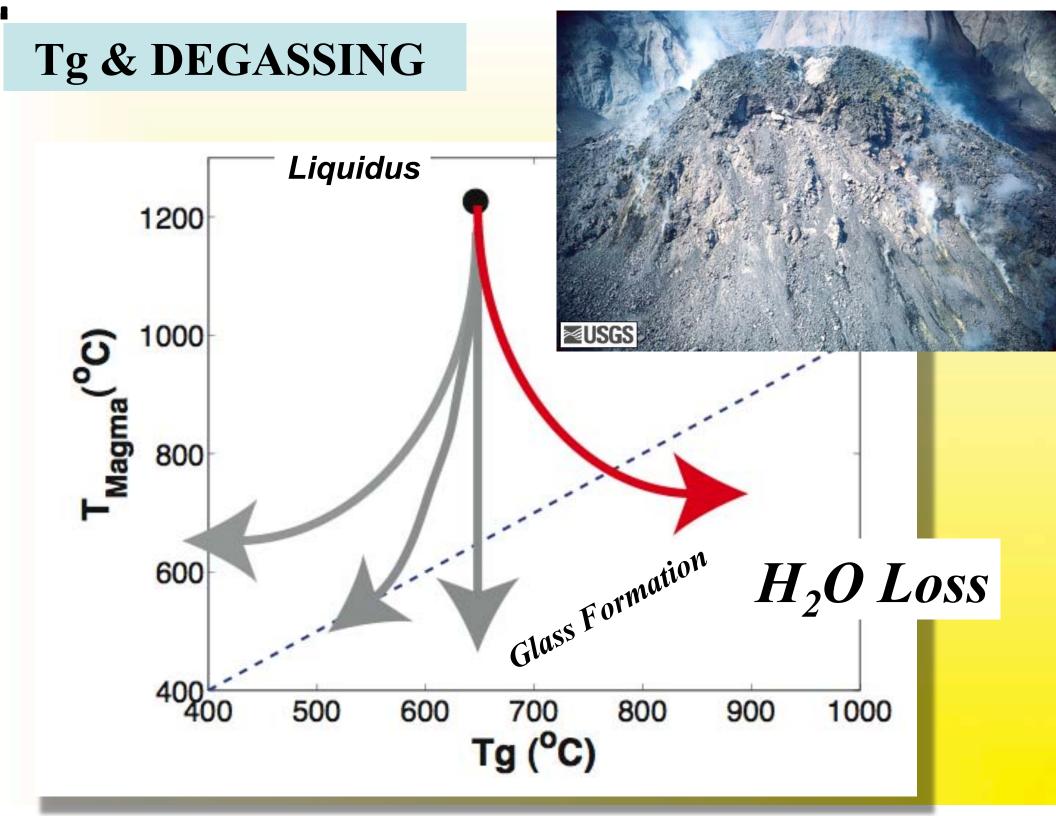
## **Caveat Emptor** (**Construction Zone**)

## Tg Depression by H<sub>2</sub>O

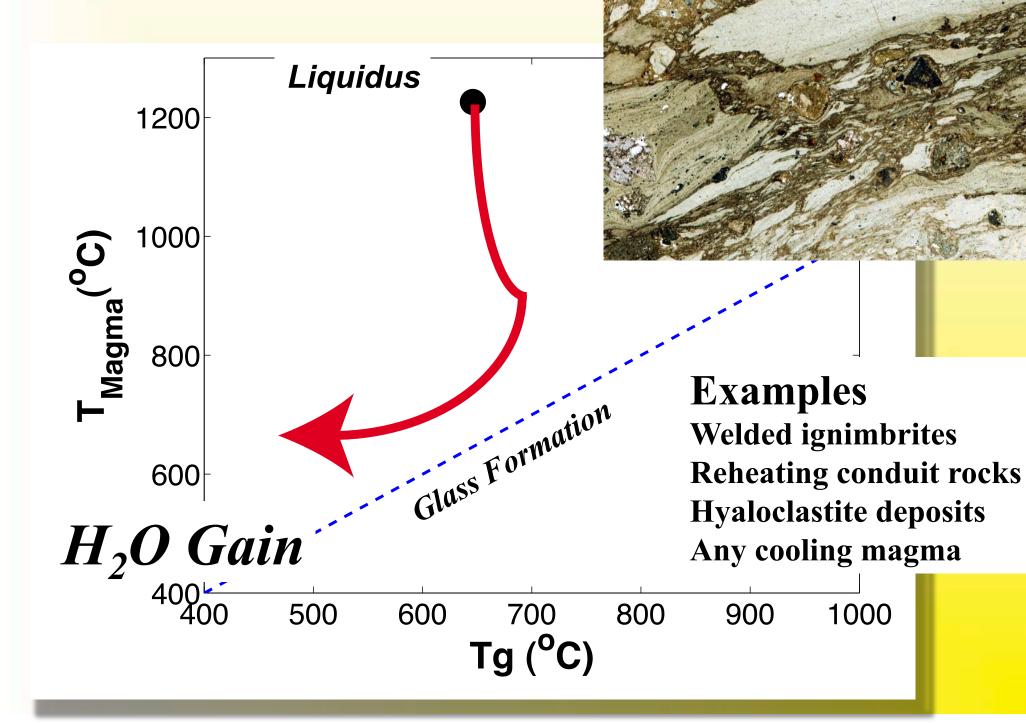
Need partial molar H<sub>H2O</sub> melts/glasses

D.B. Dingwell / Physics of the Earth and Planetary Interiors 107 (1998) 1-8





# **Tg & REHYDRATION**



**SUMMARY** Glass formation is a boundary between changing environmental states.

A) Above Tg, rates of crystallization & vesiculation are sufficiently fast to affect magmatic processes

B) Where liquid lines of decent intersect the Tg of the melt, glass forms and many processes cease.

## MIXING & ASCENT .... Hmm ??

