Bulk-Diffusion of Fluids through quartz

Experimental Evidence?

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Question:

Can the properties of fluid inclusions change?

Are fluid inclusions flexible, open systems?

Answer:

No!, but .... (says the optimist)

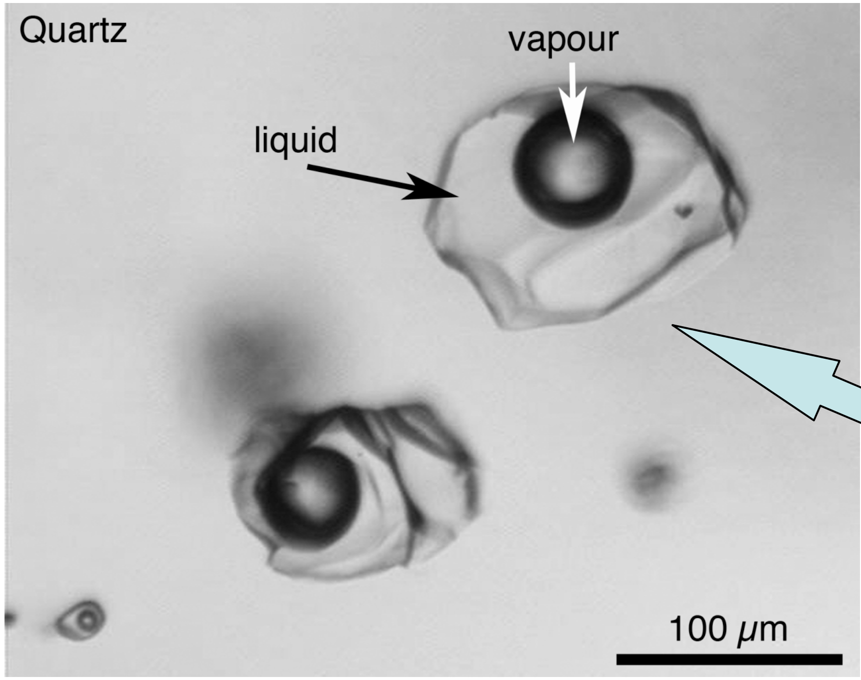
Yes!, but .... (says the pessimist)

So, what! .... (says the ignoramus)

Possible Processes Inclusion Alteration

process	*driving forces*
1. Recrystallization	surface forces
2. Deformation	tectonic forces
3. Diffusion	concentration gradients

Diffusion



Can fluids diffuse through quartz?

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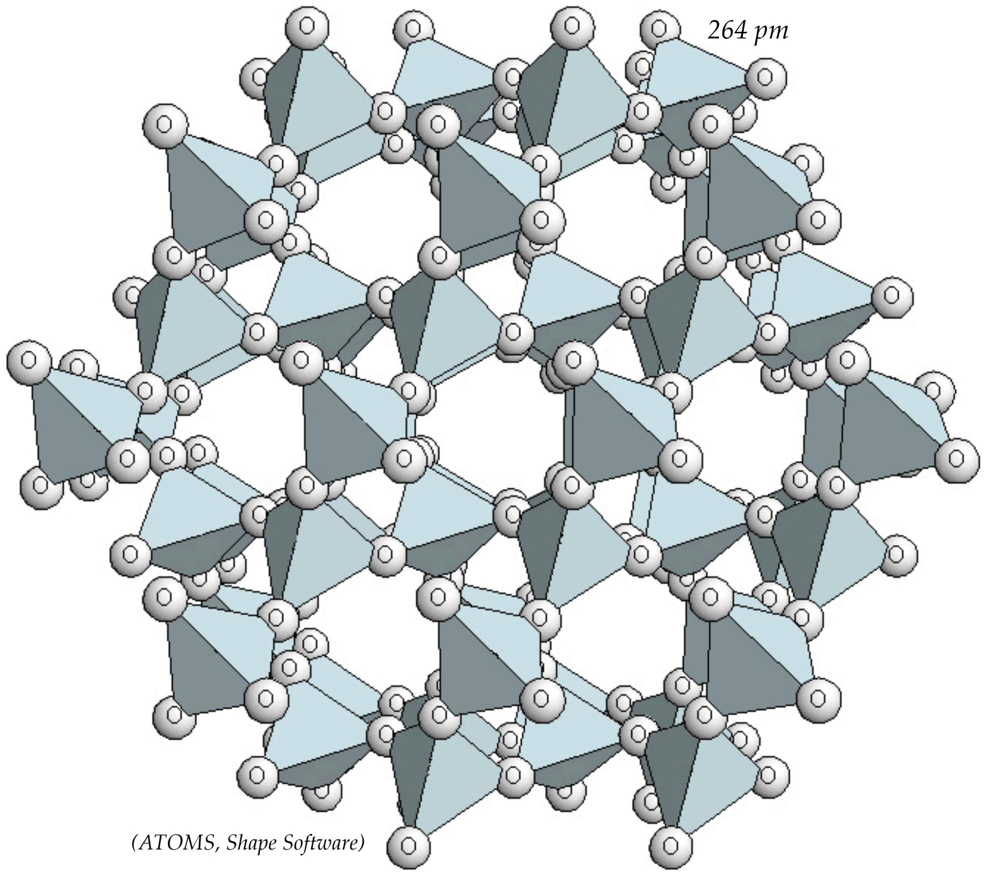
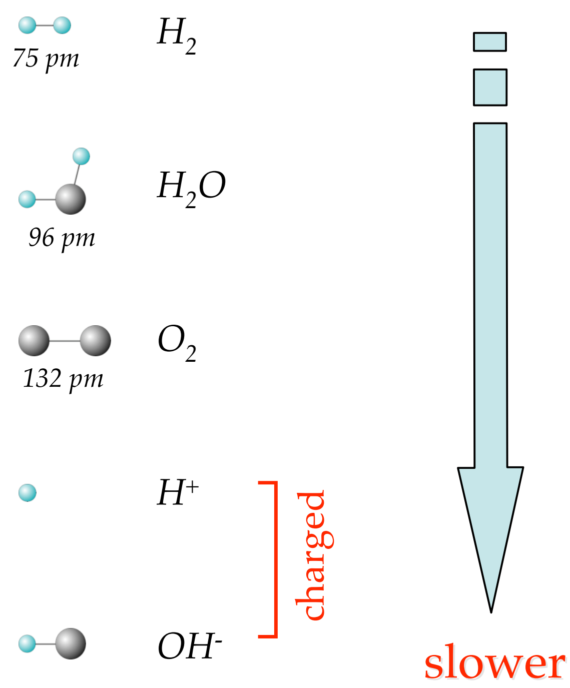
Quartz = highly dilute solid solution!

1. solvent = Si and O atoms in quartz lattice (solid phase)
2. solute = fluid components (H_2O, CO_2, etc)

Solubility of water

1. interstital impurity
2. substitutional impurity
3. fluid inclusions





Diffusion

Def.

Matter is transported from one part of a system to another as a result of „random“ molecular motions. In a dilute solution each molecule behaves independently of the others and is constantly undergoing collision with the solvent molecules. As a result it moves without preferred direction („random walk“).

Crank (1979)

There is a net transfer from the higher to the lower concentration side as a result of this „random walk“

Mathematical Theory

Fick‘s Laws

$$J = -D\frac{\partial C}{\partial x}$$

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

Diffusion Coefficient

D

Experimental Diffusion Coefficients

- Hydrothermal Experiments, Deformation Experiments

- What was measured: Isotopic variation of quartz (oxygen isotopes)
  Tracer particles in quartz
  Deformation Phenomena (hydrolitic weakening)

- Detection method: Infrared Spectroscopy → H_2O and OH^-
  Mass Spectroscopy (secondary ions) → ^{18}O and ^{16}O
  Optical Microscopy

- What was modelled: Concentration Profile
  One-dimensional diffusion model

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Diffusion Coefficients: numbers .....?

Deformation experiments

1. Diffusion of H_2O is too slow within the limits of experimentation

Ref. Kronenberg et al. (1986)
Gerretsen et al. (1989)

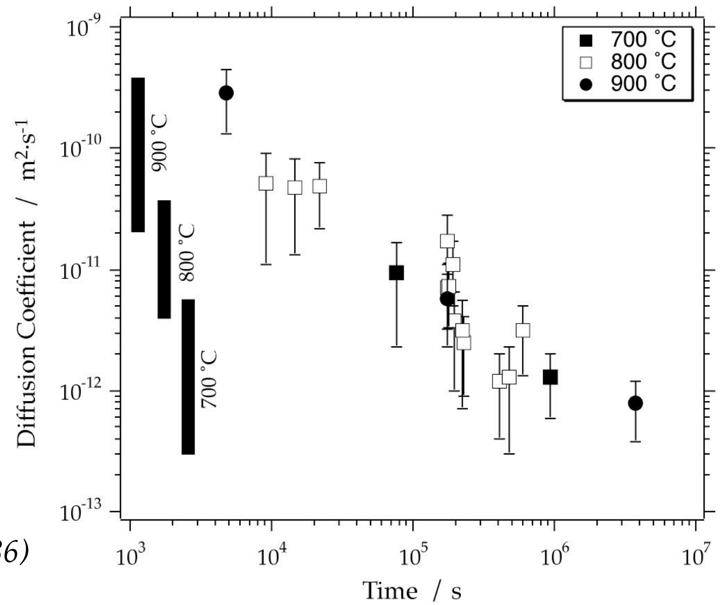
2. Synthetic quartz behaves completely different

⇨ grown-in water defects during synthesis

Hypothesis: crack-assistent diffusion

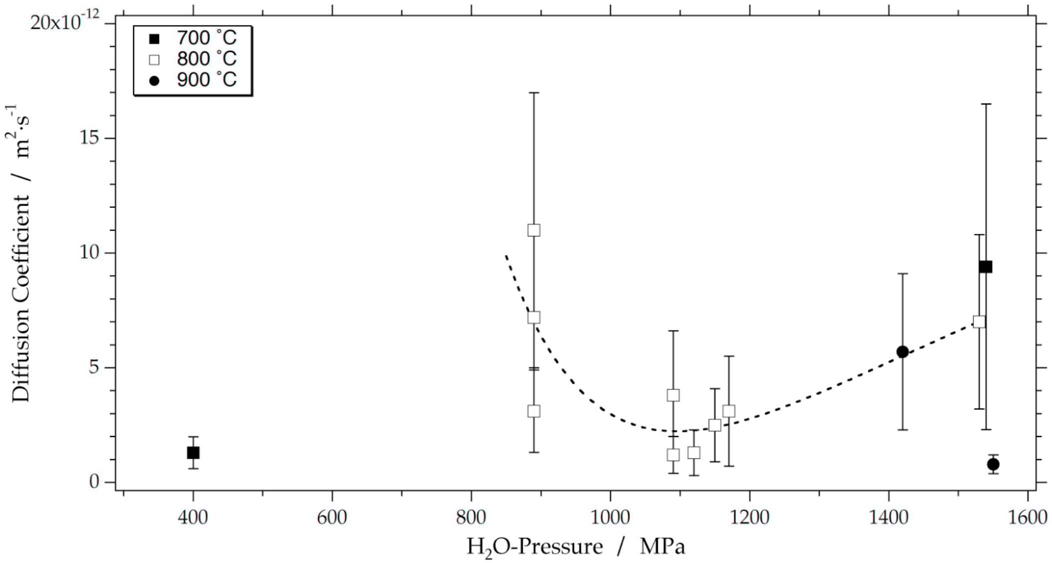
Diffusion Coefficients: numbers .....?

Temperature dependence?



re-evaluated data Kronenberg et al. (1986)

Pressure dependence?



Diffusion Coefficients: numbers .....?

1. rate-defining step: diffusion
   or
   isotope exchange reaction

$$Si^{16}O_2 + 2H_2{}^{18}O \Leftrightarrow Si^{18}O_2 + 2H_2{}^{16}O$$

2. what are the diffusing species?

3. experimental quenching technique

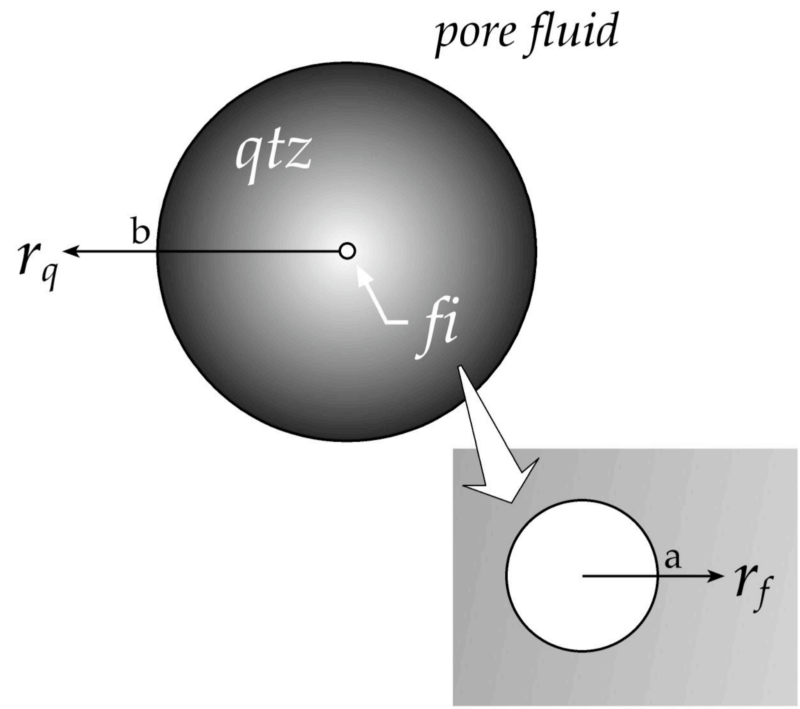
4. three-dimensional diffusion model

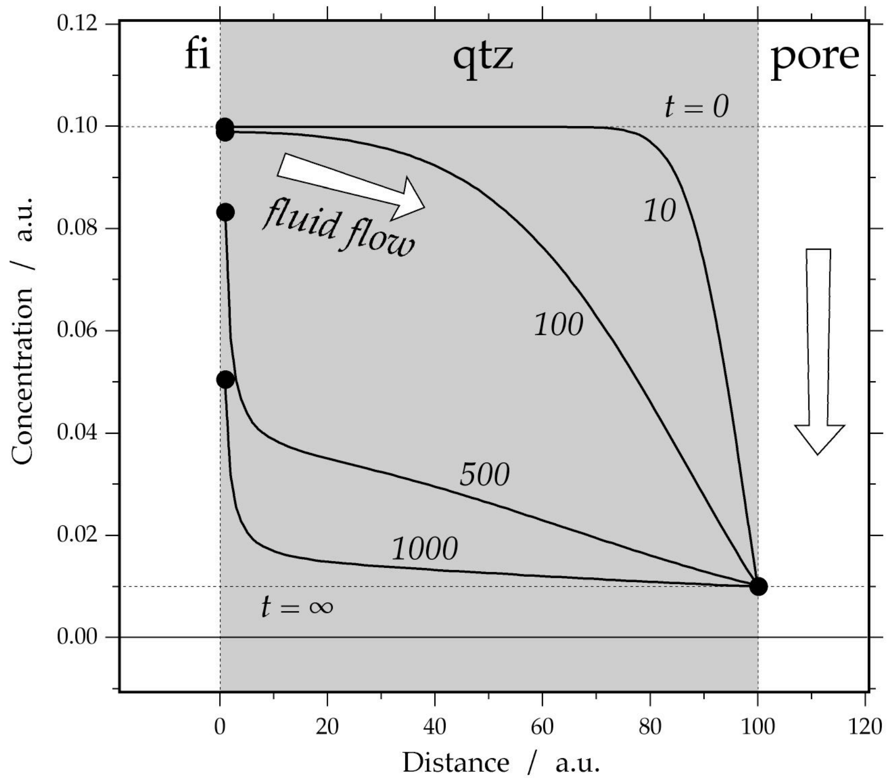
Mathematical Diffusion Model for Fluid / Melt Inclusions

Qin, Lu & Anderson (1992)

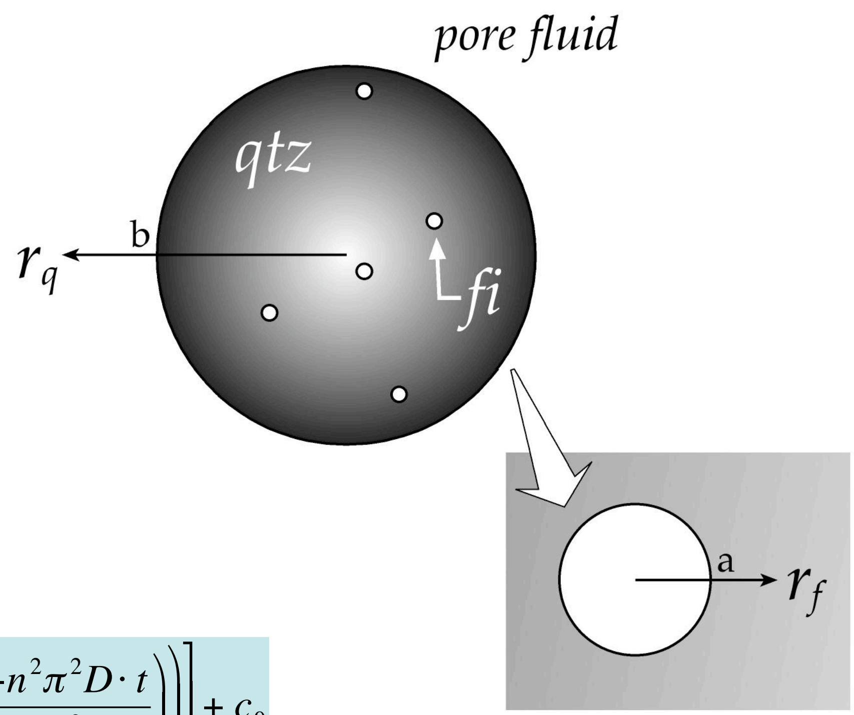
Radial diffusion
Inclusion in center of crystal
Pore fluid concentration is constant

$$C_1(t) = C_e + \frac{2\beta}{\alpha}\left(C_0 - C_e\right)\cdot\sum_{n=1}^{\infty}\frac{\exp\left(-q_n^{\,2}Dt/b^2\right)}{\gamma q_n \sin\left[q_n(1-\alpha)\right] + \left[\alpha(1-\alpha)q_n^{\,2} - \beta/\alpha\right]\cos\left[q_n(1-\alpha)\right]}$$





New Diffusion Model



1. diffusion pores → quartz

infinite external source

$$c = (c_1 - c_0)\cdot\left[1 + \frac{2b}{\pi\cdot r_q}\sum_{n=1}^{\infty}\left(\frac{(-1)^n}{n}\sin\left(\frac{n\cdot\pi\cdot r_q}{b}\right)\exp\left(\frac{-n^2\pi^2 D\cdot t}{b^2}\right)\right)\right] + c_0$$

2. diffusion quartz → inclusions

instantaneous point source

$$c = c_0 + \frac{(c_1 - c_0)}{2}\cdot\left[erf\left(\frac{a + r_f}{2\sqrt{D\cdot t}}\right) + erf\left(\frac{a - r_f}{2\sqrt{D\cdot t}}\right)\right] - \frac{(c_1 - c_0)}{2}\sqrt{\frac{D\cdot t}{\pi}}\cdot\left(\exp\left(\frac{-(a - r_f)^2}{4\cdot D\cdot t}\right) - \exp\left(\frac{-(a + r_f)^2}{4\cdot D\cdot t}\right)\right)$$

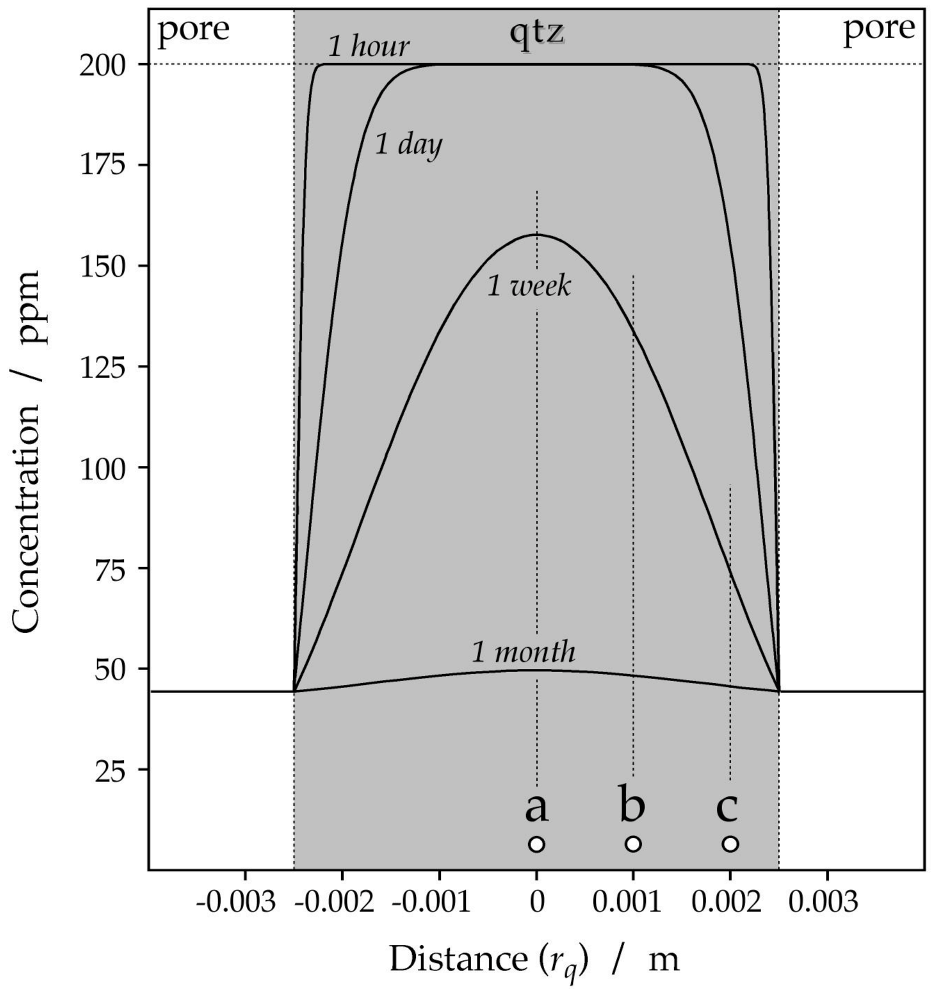
Example calculation

Fluid Inclusions (a, b, c) trapped at 500 ˚C and 500 MPa

uplift to 100 MPa

D = 10^{-12} $m^2 \cdot s^{-1}$

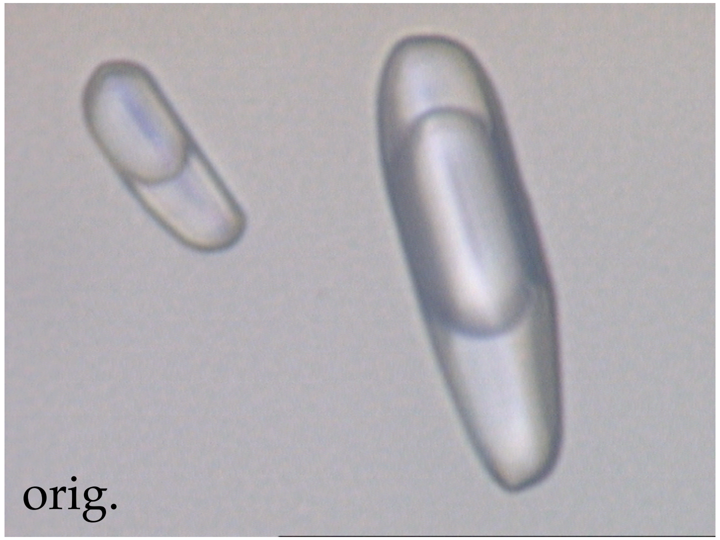
too fast!

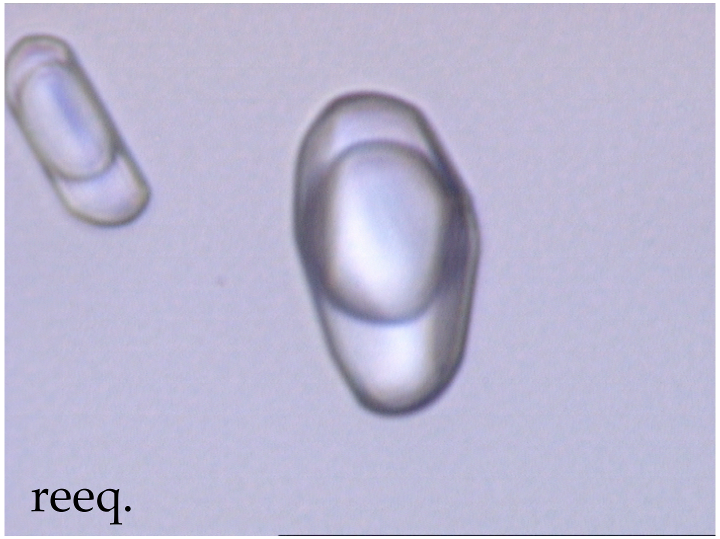


New method

Properties of Fluid Inclusions (alterations in composition and density)

Re-equilibration experiments

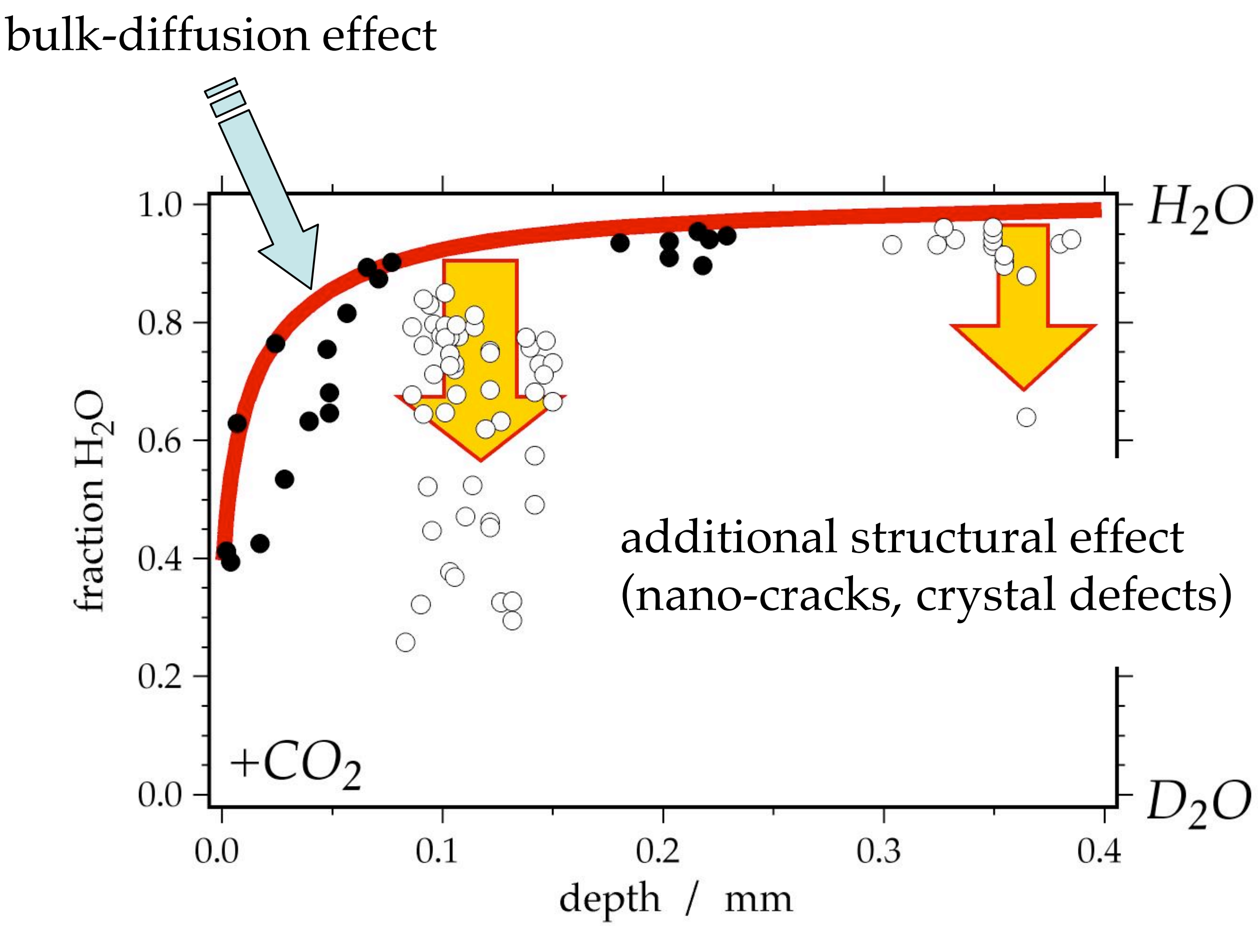




H_2O - CO_2

H_2O - CO_2
$\pm D_2O$

Fluid Inclusions Properties



my guess: D ≈ 10^{-14} to 10^{-15} $m^2 \cdot s^{-1}$

Conclusions

1. Solubility, Diffusion Coefficients of Fluids in Quartz

   no substantial knowledge available!

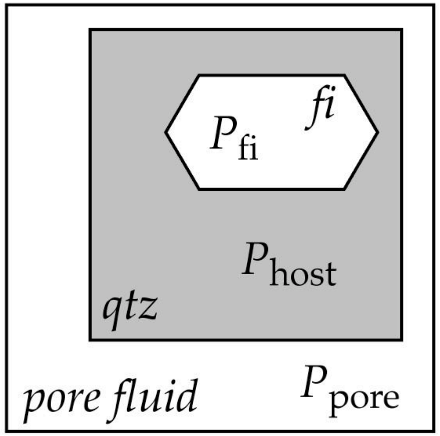
2. Fluid Inclusions

   new tool to examine diffusion

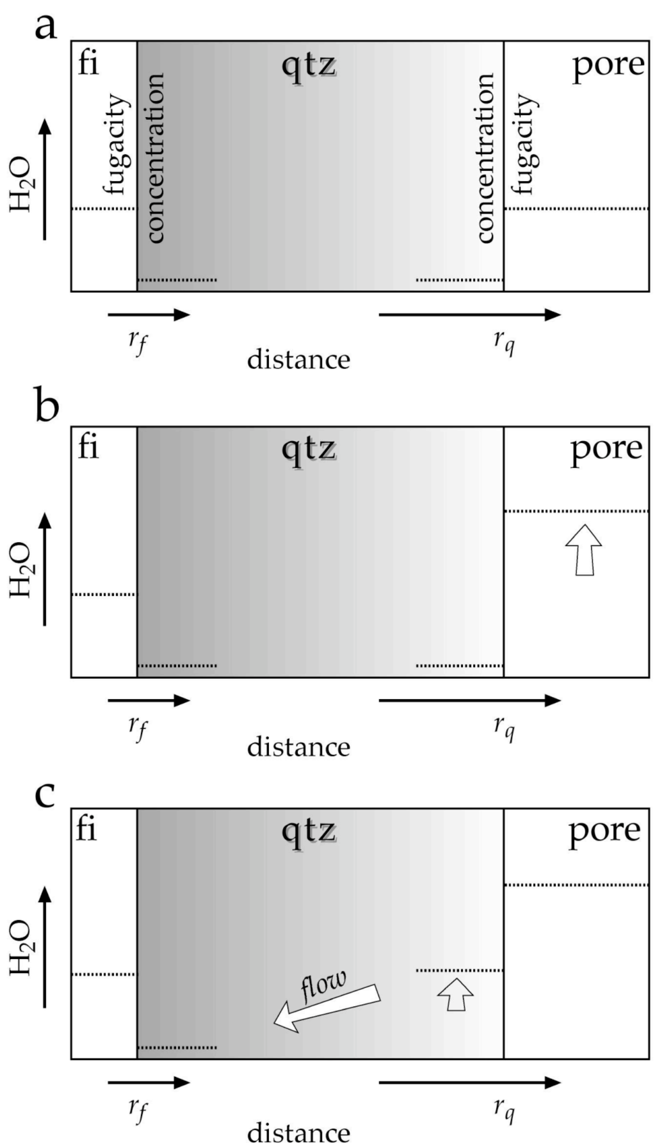
   + reliability of natural fluid inclusions

[redacted]

System Definition



Fugacity Gradients



Pressure Gradients