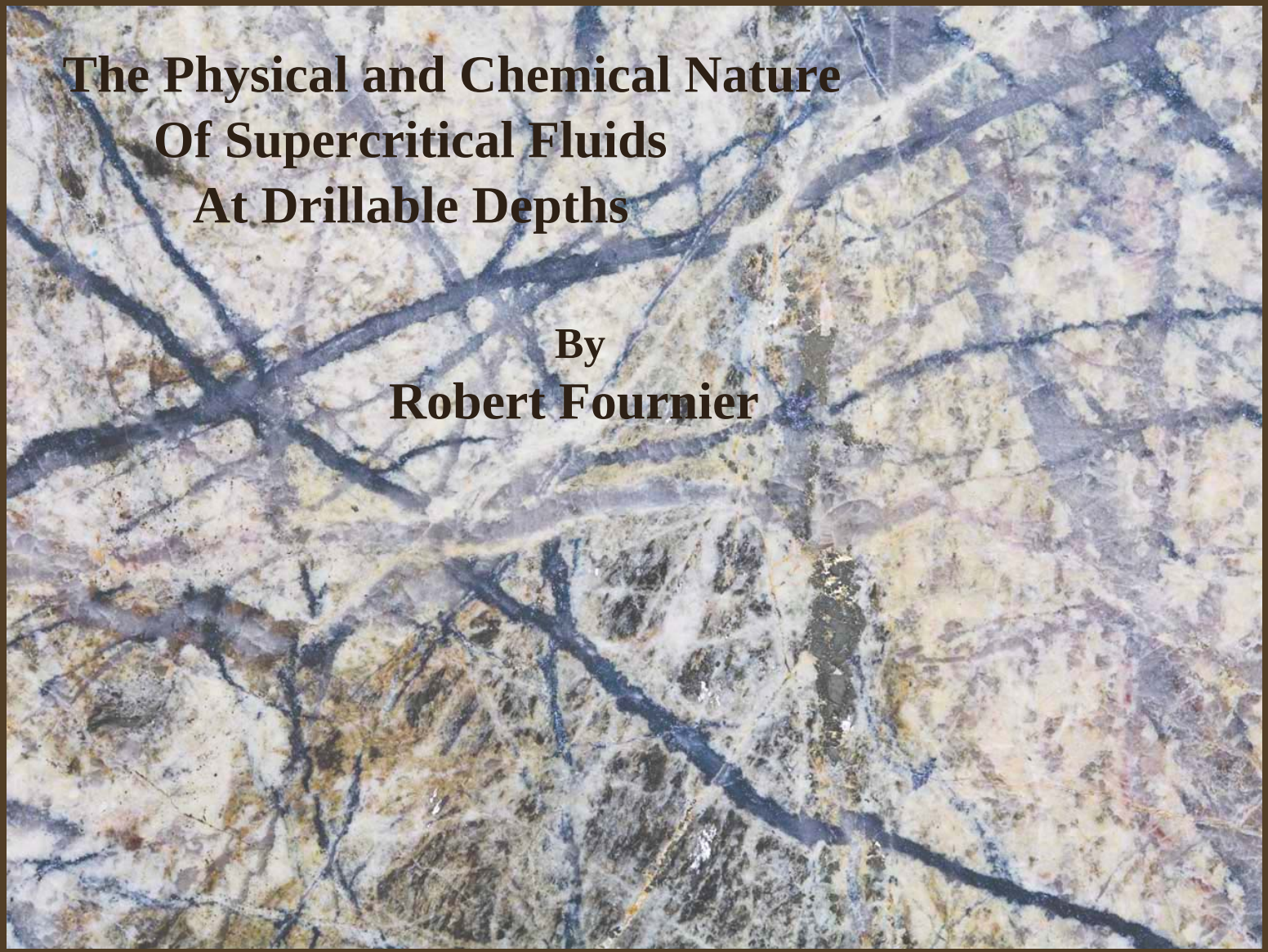
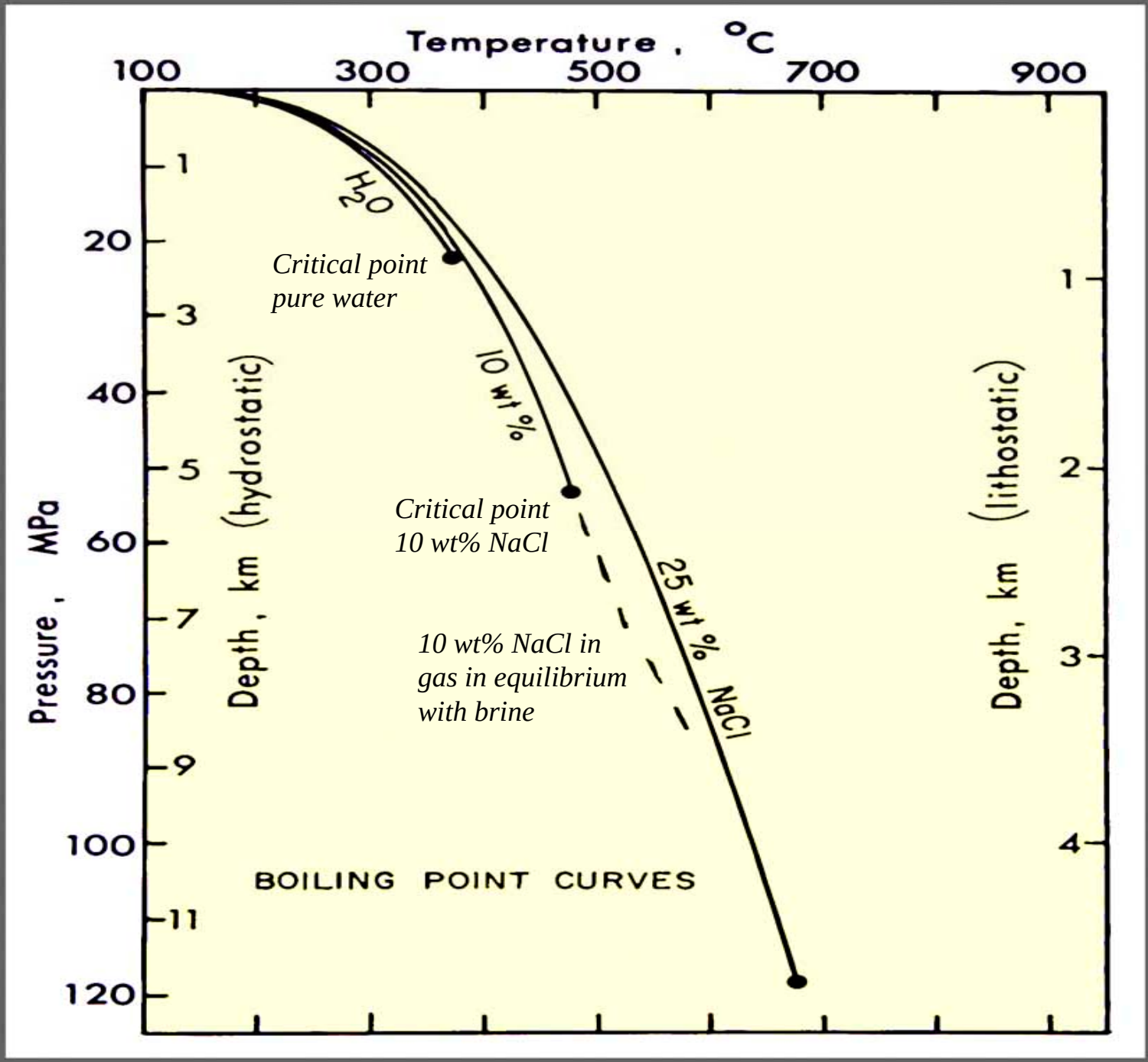
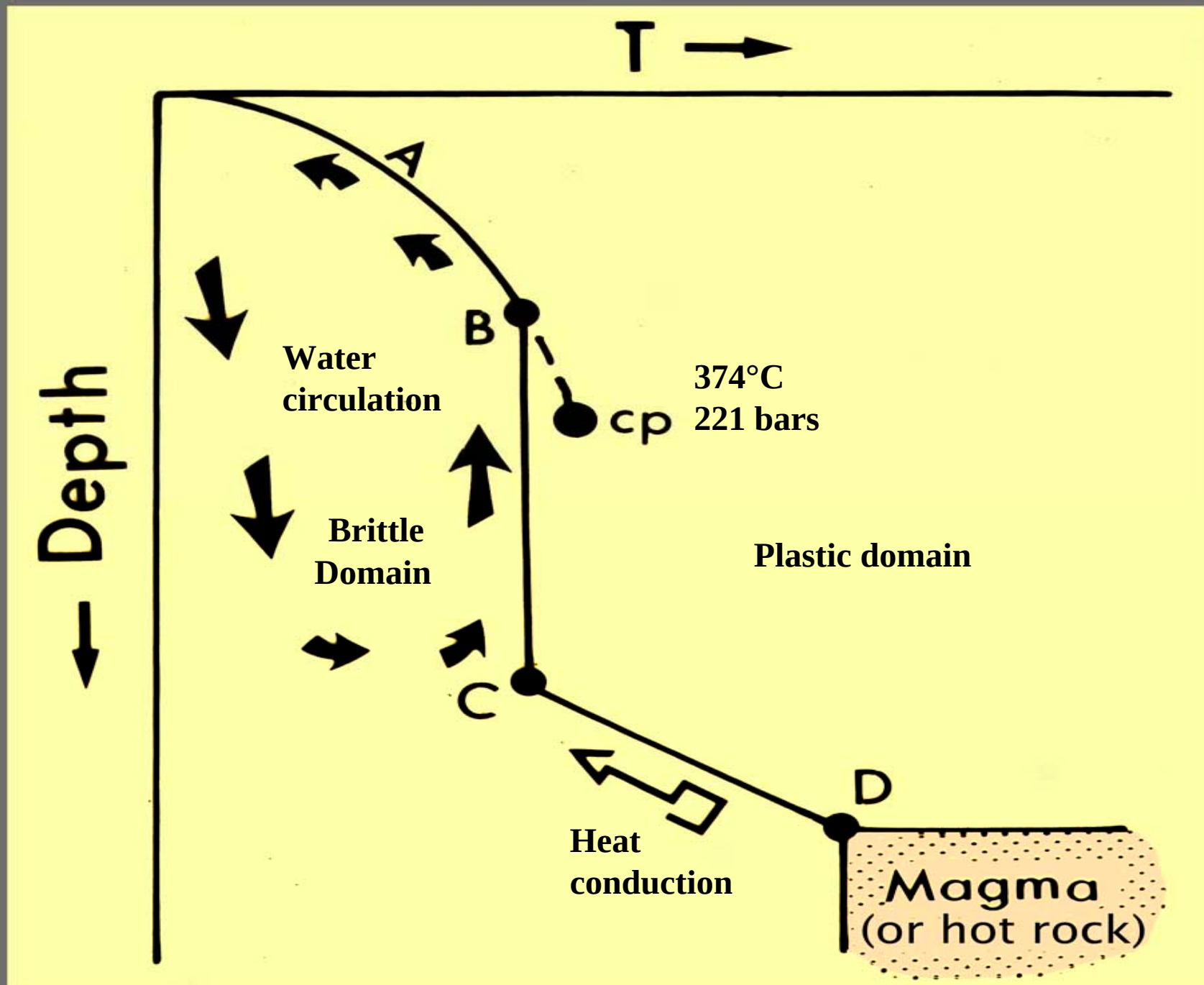


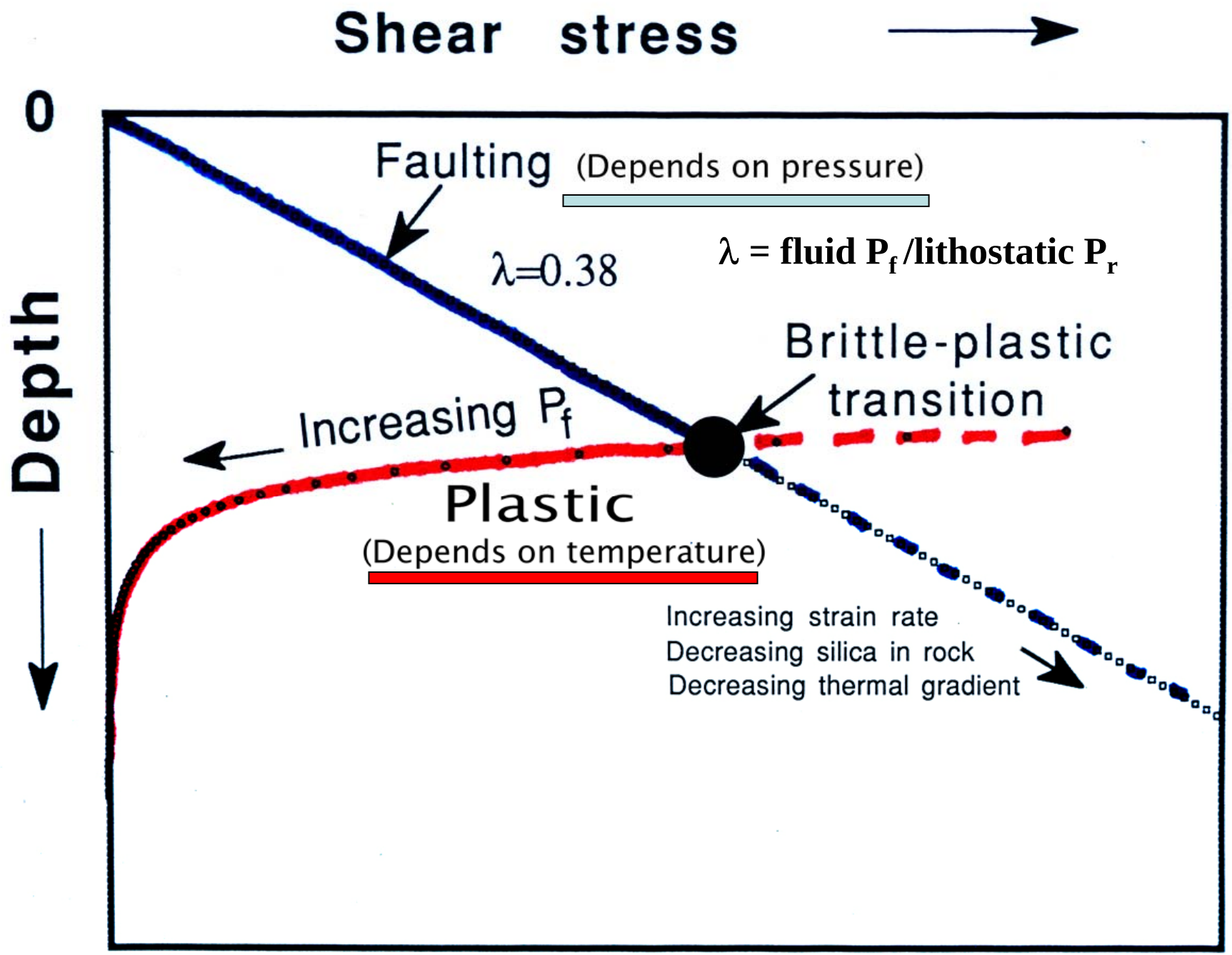
# The Physical and Chemical Nature Of Supercritical Fluids At Drillable Depths

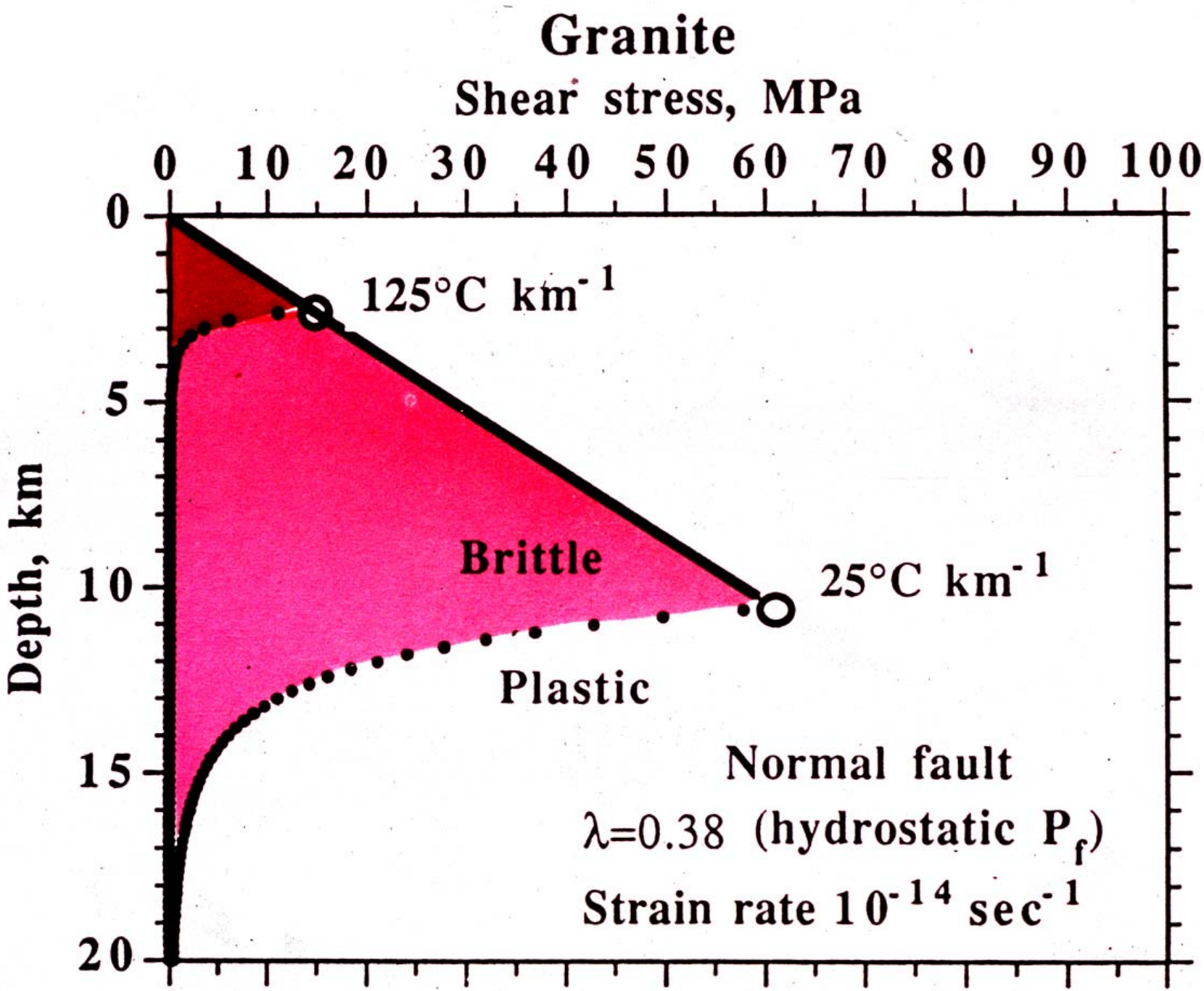
By

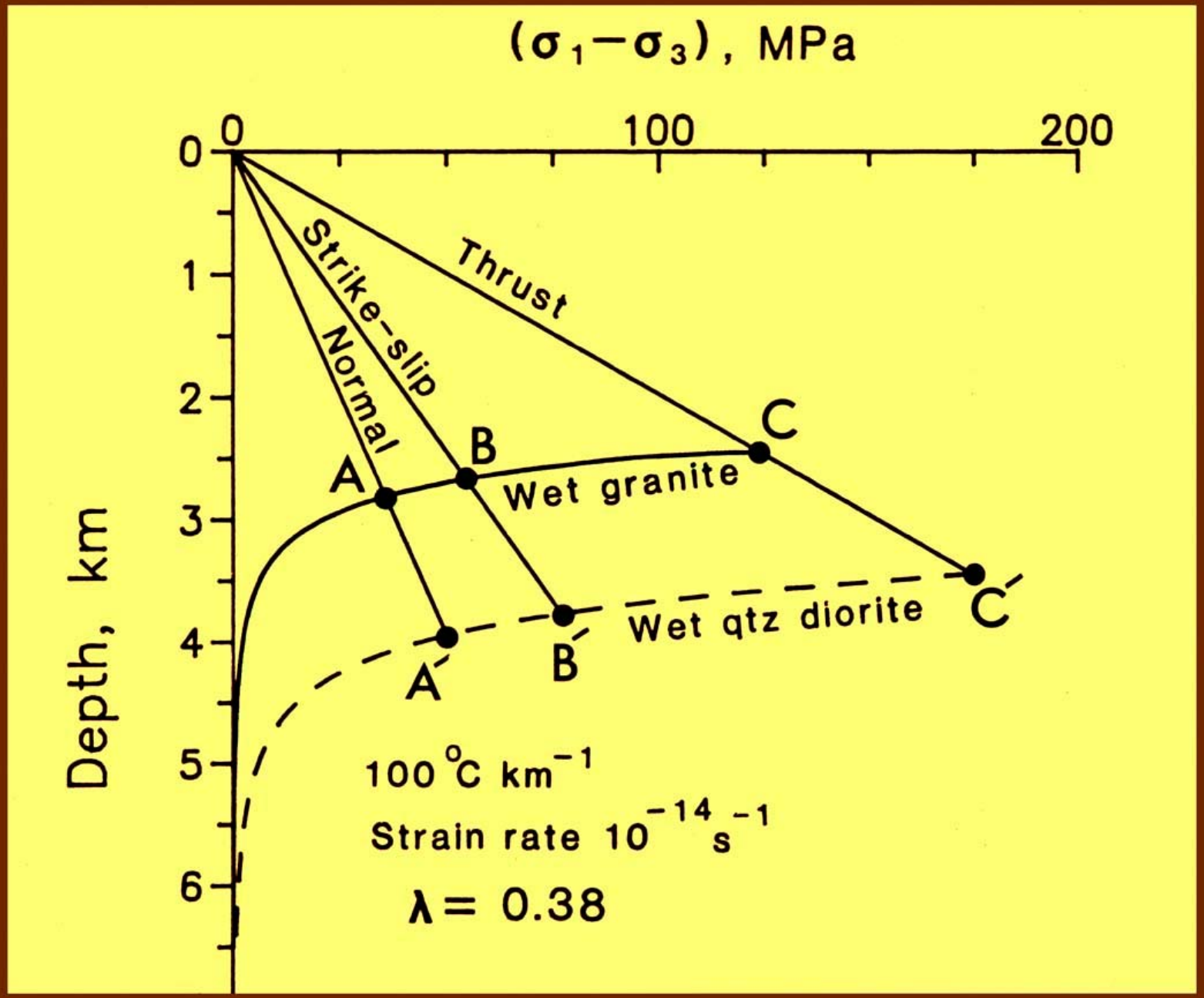
Robert Fournier

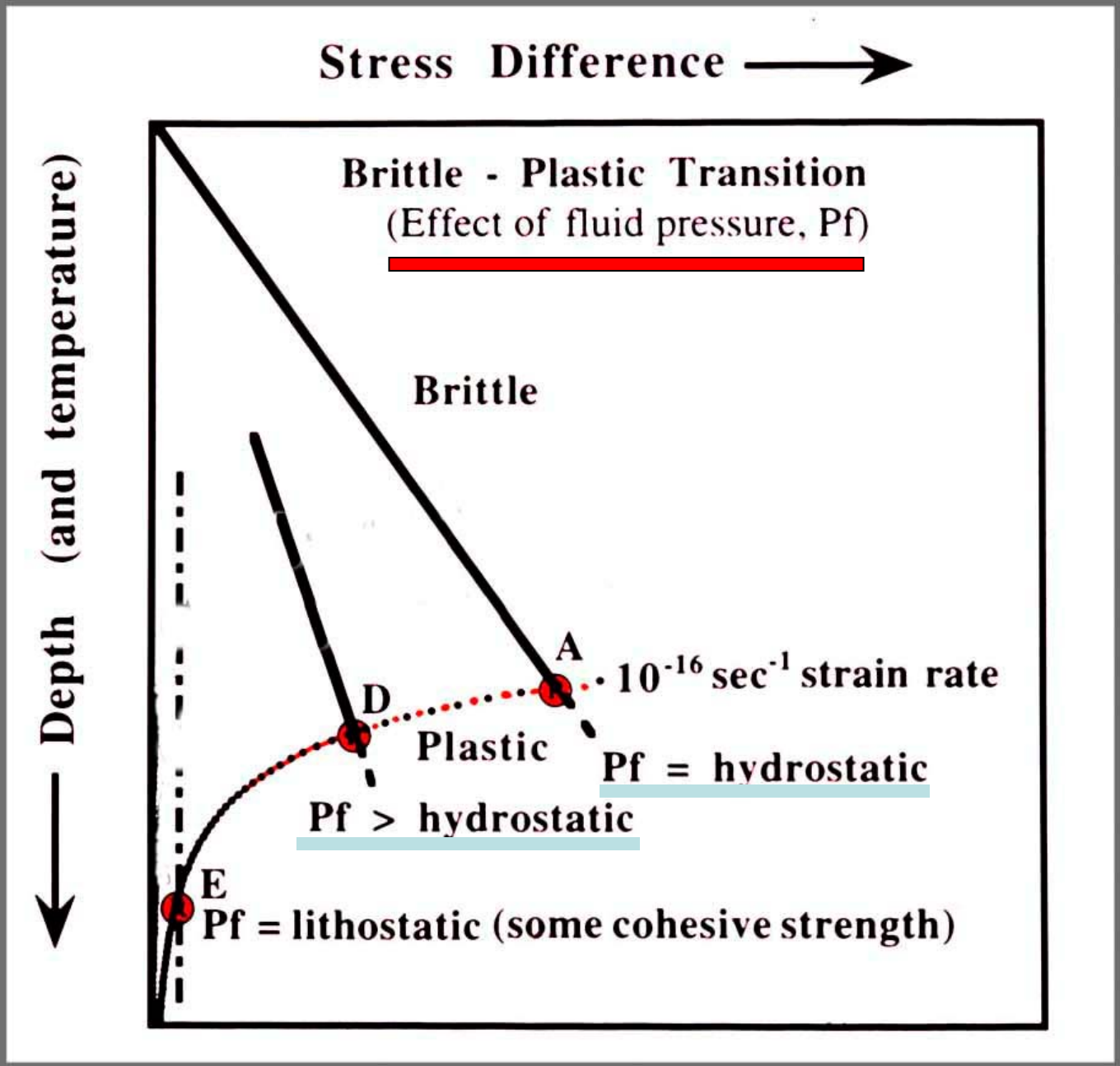

Temperature, °C
100
300
500
700
900
Pressure, MPa
20
40
60
80
100
120
Depth, km (hydrostatic)
1
3
5
7
9
11
Depth, km (lithostatic)
1
2
3
4
H2O
10 wt % NaCl
25 wt % NaCl
Critical point
pure water
Critical point
10 wt% NaCl
10 wt% NaCl in
gas in equilibrium
with brine
BOILING POINT CURVES


T
Depth
A
B
cp
C
D
Water
circulation
374°C
221 bars
Brittle
Domain
Plastic domain
Heat
conduction
Magma
(or hot rock)

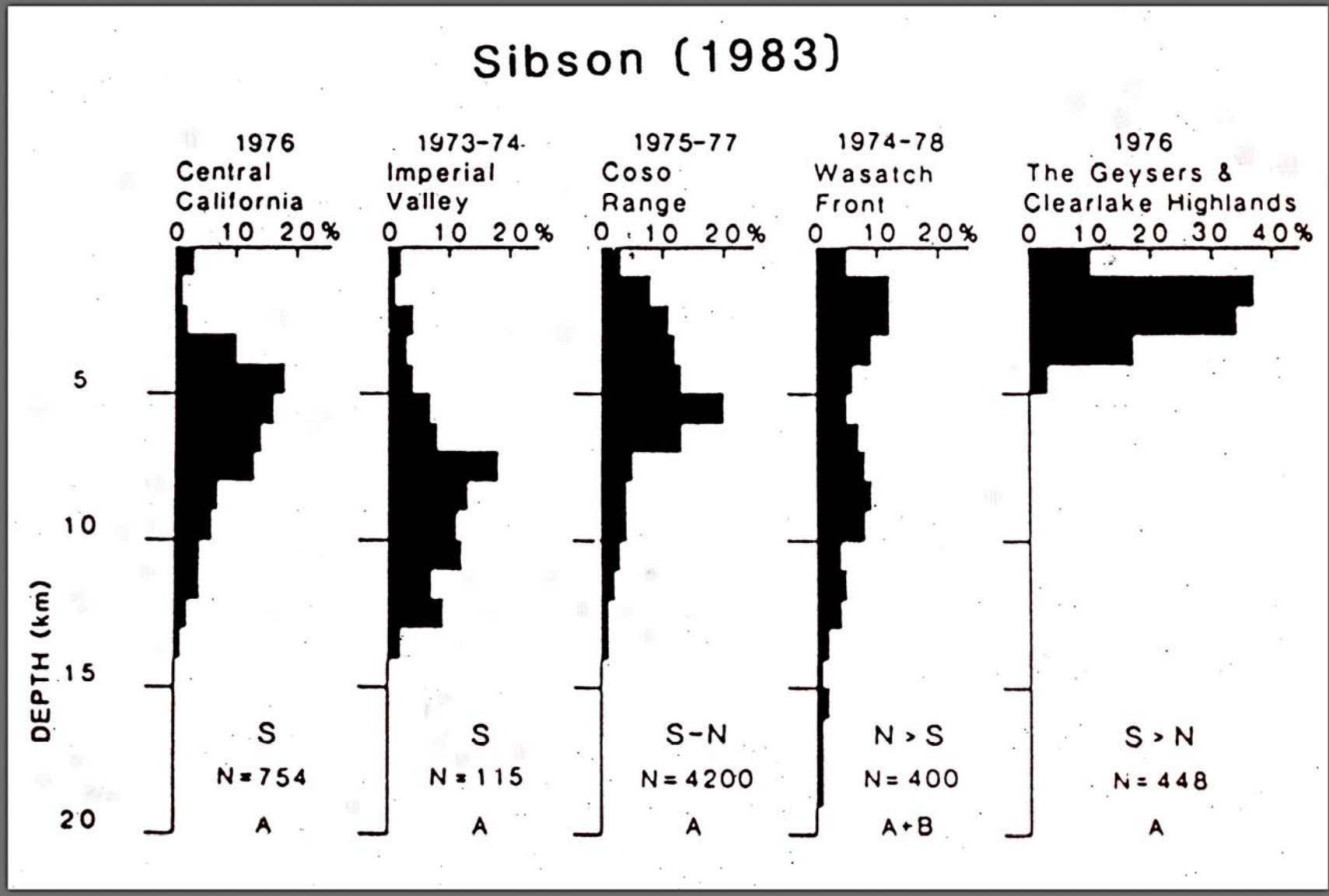

Shear stress
0
Depth
Faulting (Depends on pressure)
λ=0.38
λ = fluid $P_f$ /lithostatic $P_r$
Brittle-plastic transition
Increasing $P_f$
Plastic
(Depends on temperature)
Increasing strain rate
Decreasing silica in rock
Decreasing thermal gradient

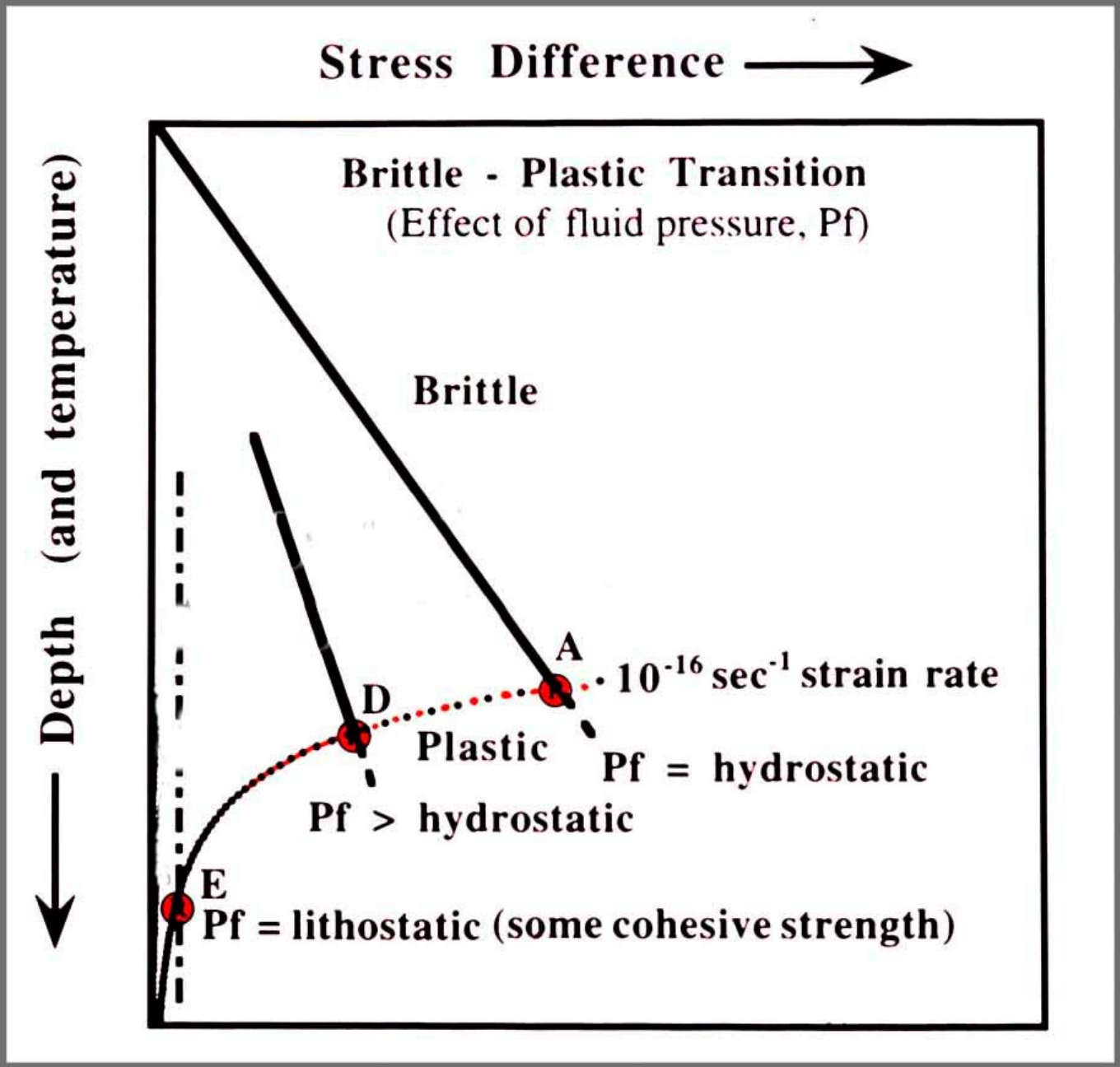

Granite
Shear stress, MPa
0 10 20 30 40 50 60 70 80 90 100
0
5
10
15
20
Depth, km
125°C km-1
25°C km-1
Brittle
Plastic
Normal fault
λ=0.38 (hydrostatic Pf)
Strain rate 10-14 sec-1

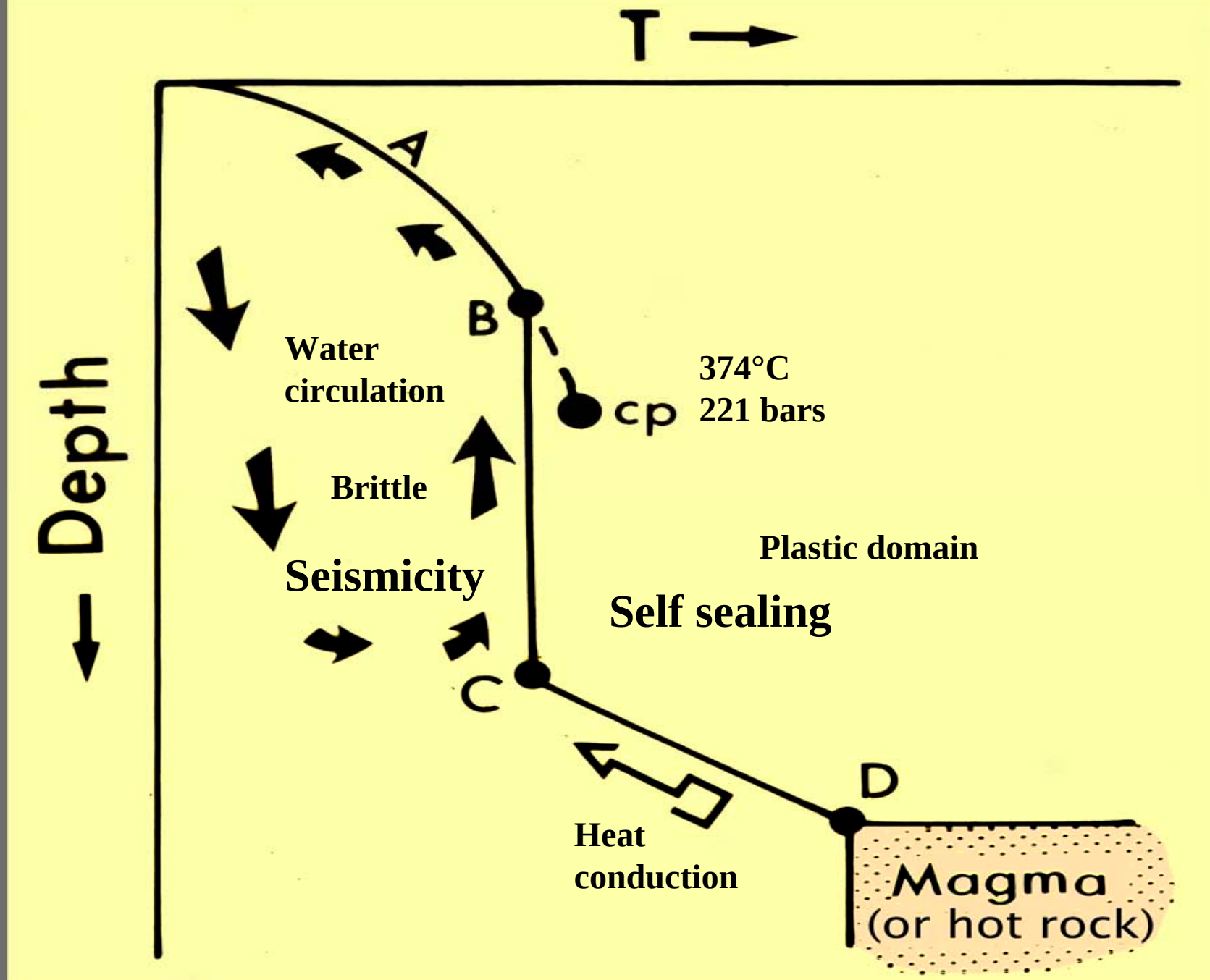

$(\sigma_1 - \sigma_3)$, MPa
0
100
200
0
1
2
3
4
5
6
Depth, km
Thrust
Strike-slip
Normal
A
B
C
Wet granite
Wet qtz diorite
A′
B′
C′
100 °C km$^{-1}$
Strain rate $10^{-14}$ s$^{-1}$
λ = 0.38

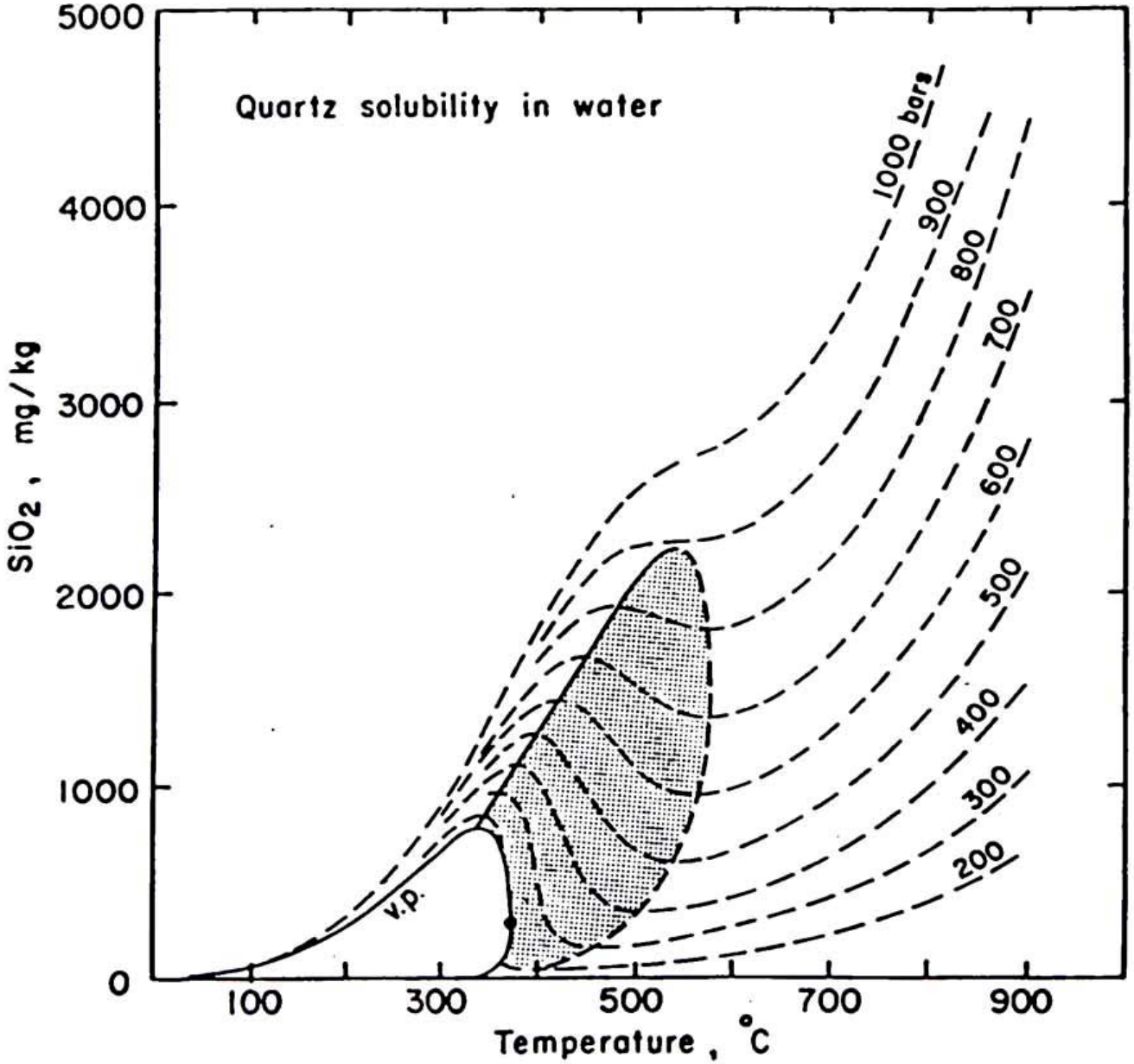

Stress Difference
Depth (and temperature)
Brittle - Plastic Transition
(Effect of fluid pressure, Pf)
Brittle
A
$10^{-16}$ $sec^{-1}$ strain rate
D
Plastic
Pf = hydrostatic
Pf > hydrostatic
E
Pf = lithostatic (some cohesive strength)

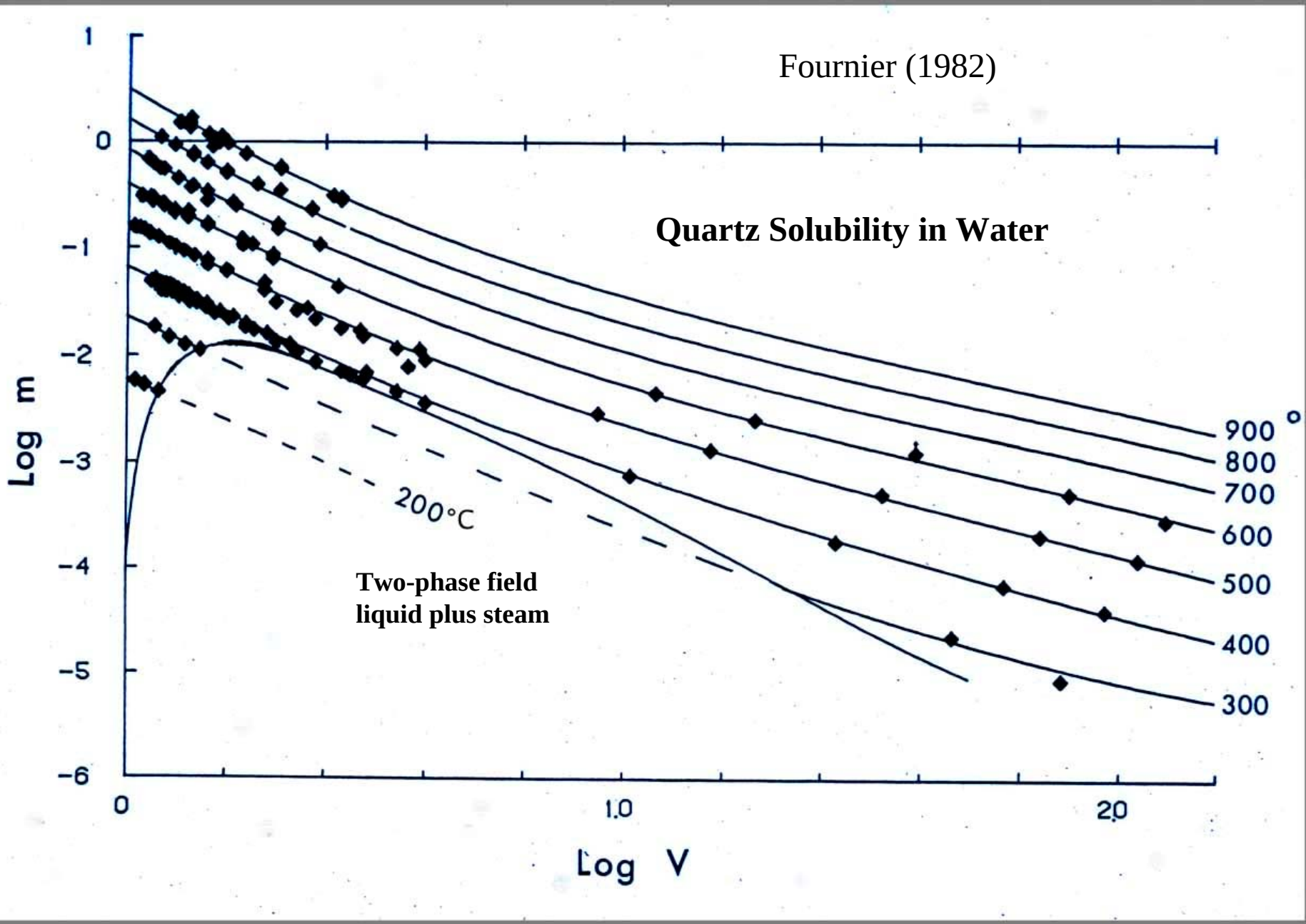
# Sibson (1983)


1976
Central
California
0 10 20%
1973-74
Imperial
Valley
0 10 20%
1975-77
Coso
Range
0 10 20%
1974-78
Wasatch
Front
0 10 20%
1976
The Geysers &
Clearlake Highlands
0 10 20 30 40%
DEPTH (km)
5
10
15
20
S
N=754
A
S
N=115
A
S-N
N=4200
A
N>S
N=400
A+B
S>N
N=448
A


Stress Difference
Depth (and temperature)
Brittle - Plastic Transition
(Effect of fluid pressure, Pf)
Brittle
A
$10^{-16}$ $sec^{-1}$ strain rate
D
Plastic
Pf = hydrostatic
Pf > hydrostatic
E
Pf = lithostatic (some cohesive strength)


T
Depth
A
B
C
D
cp
Water
circulation
374°C
221 bars
Brittle
Seismicity
Plastic domain
Self sealing
Heat
conduction
Magma
(or hot rock)


Quartz solubility in water
5000
4000
3000
2000
1000
0
SiO2 , mg/kg
100
300
500
700
900
Temperature , °C
1000 bars
900
800
700
600
500
400
300
200
v.p.


Fournier (1982)
Quartz Solubility in Water
Two-phase field
liquid plus steam
200°C
900 °
800
700
600
500
400
300
Log m
Log V
1
0
−1
−2
−3
−4
−5
−6
0
1.0
2.0

## Solubility of Quartz in Water

$$\text{Log } mSiO_2 = A + B(\text{Log } V) + C(\text{Log } V)^2$$

**(V is the specific volume of water or steam)**

$$A = -a_1 + a_2T + a_3T^{-1}$$

$$B = -b_1T - b_2T^{-1}$$

$$C = c_1T$$

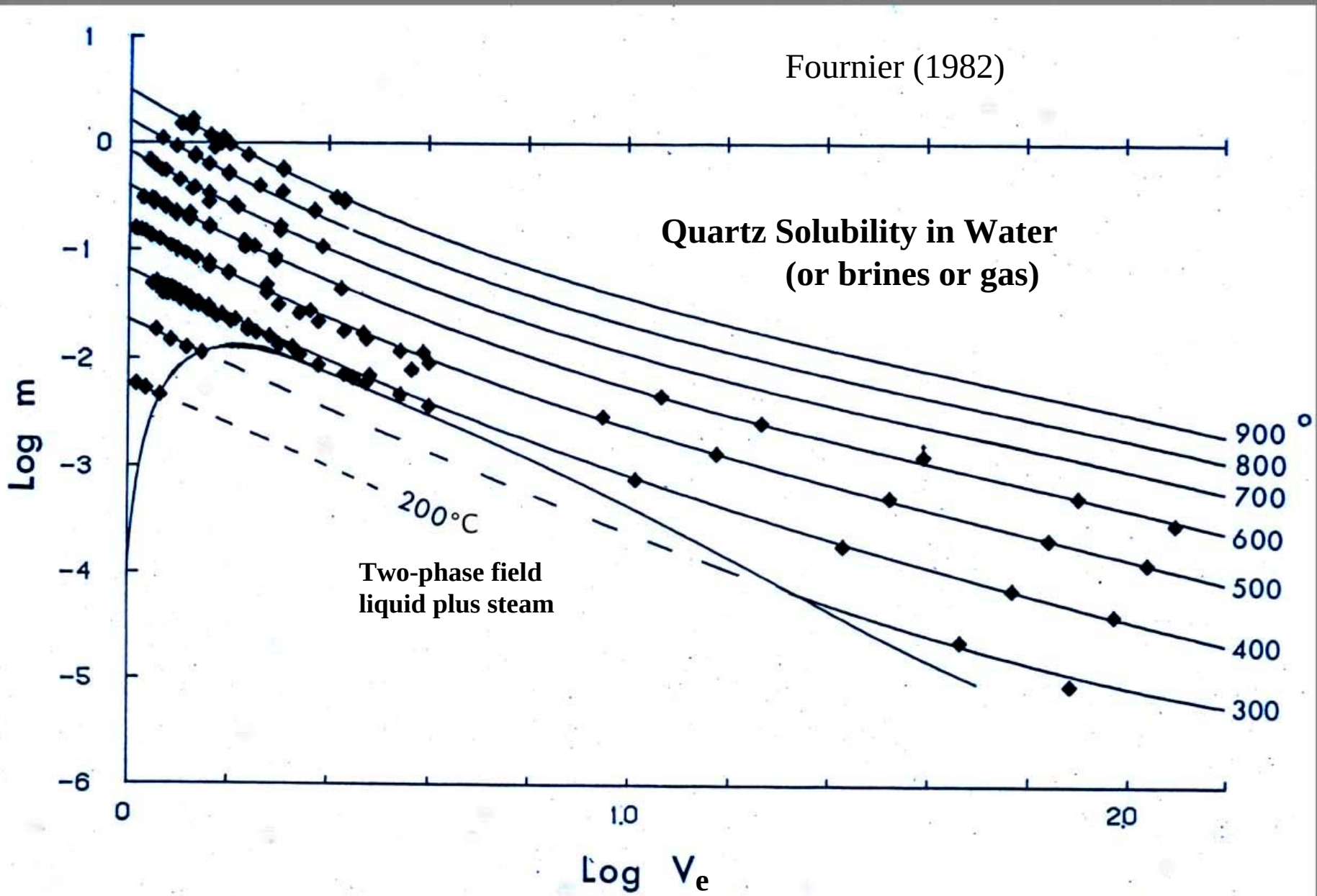
Fournier & Potter (1982)

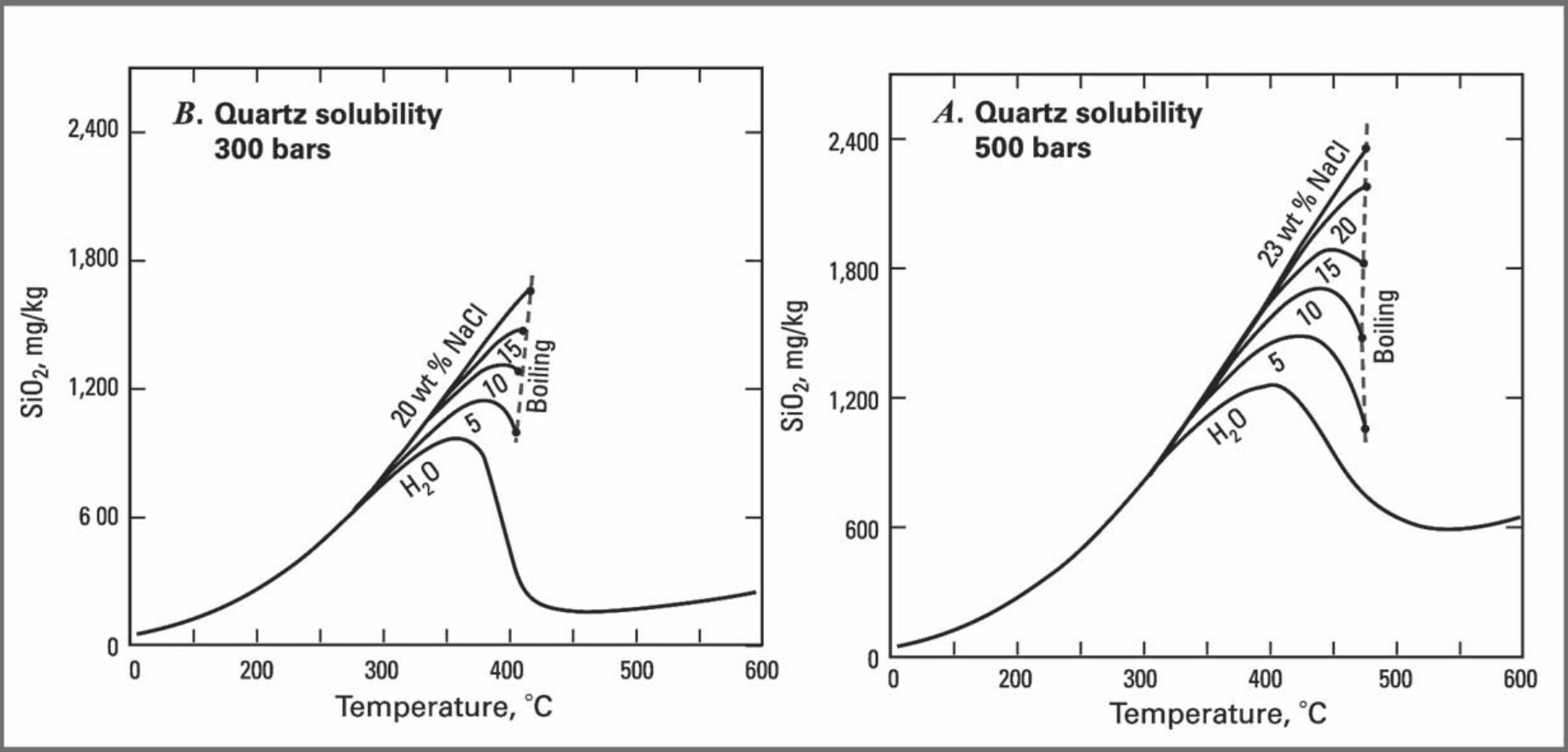
# Calculation of Quartz Solubilities

## For Steam-Gas Mixtures or Brines

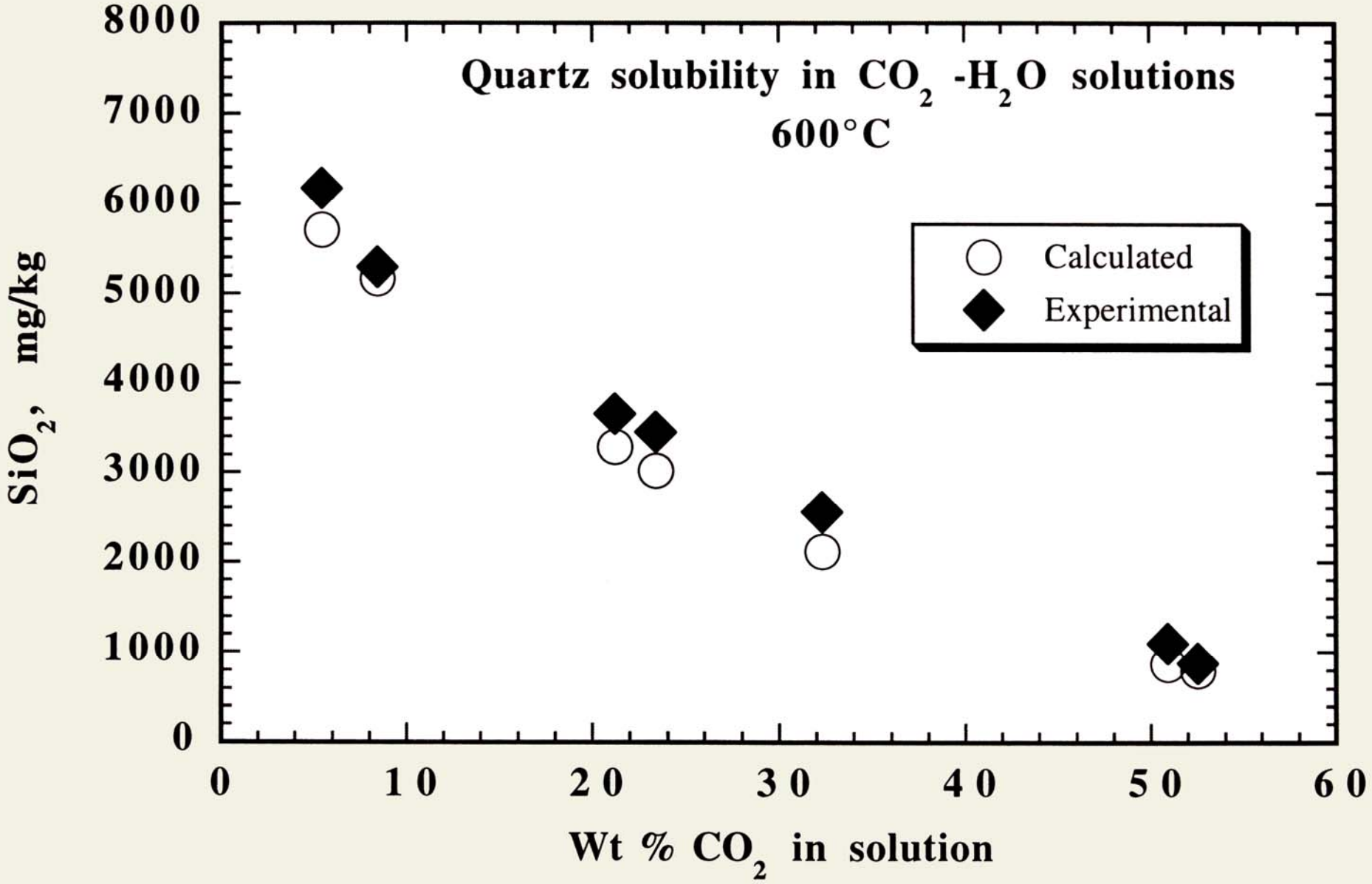
**Instead of the specific volume of pure water:**

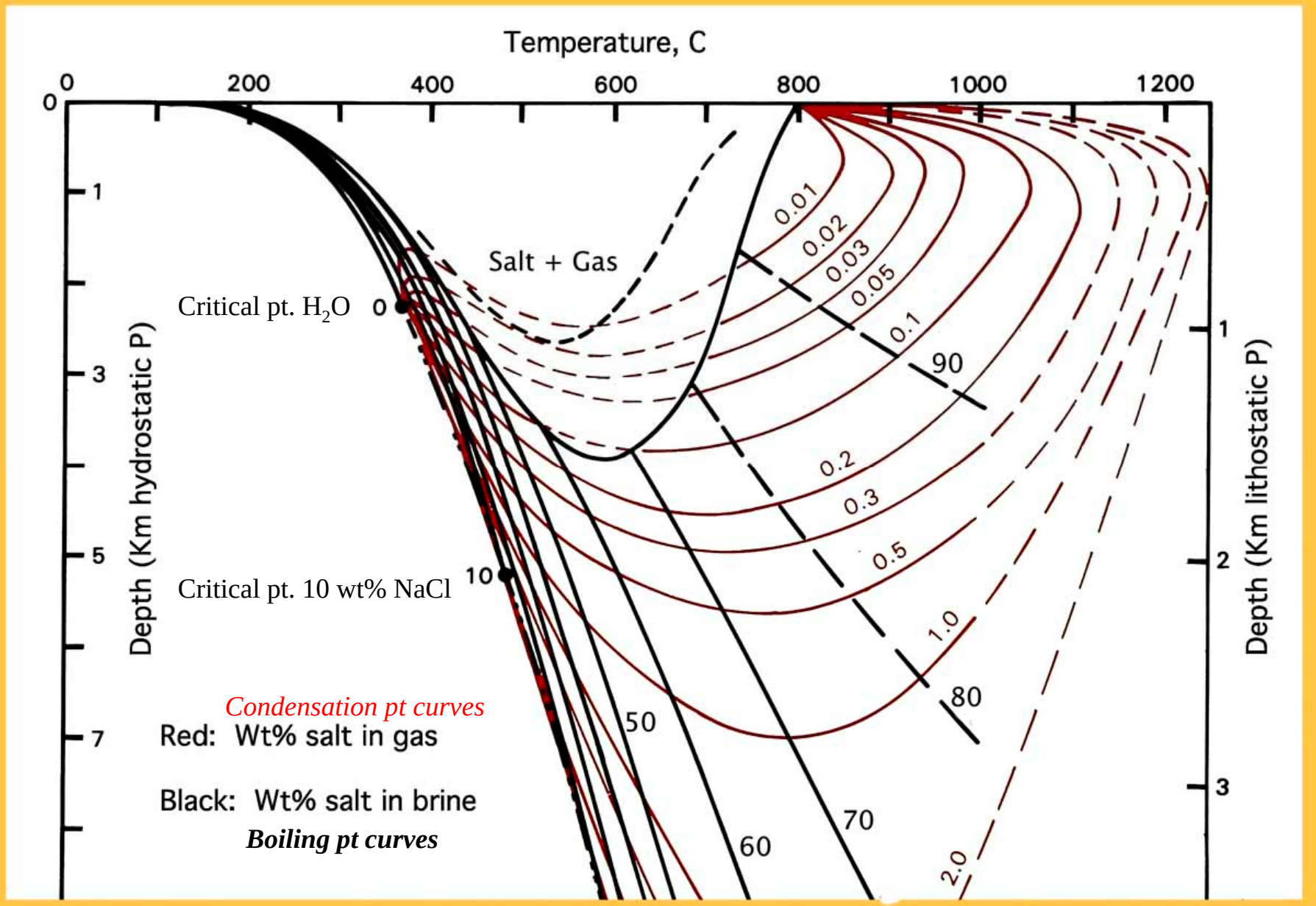
**Use the specific volume of the mixture**
**times the weight fraction of water in the mixture**


Fournier (1982)
Quartz Solubility in Water
(or brines or gas)
Two-phase field
liquid plus steam
200°C
900 °
800
700
600
500
400
300
Log m
Log Ve
1
0
-1
-2
-3
-4
-5
-6
0
1.0
2.0

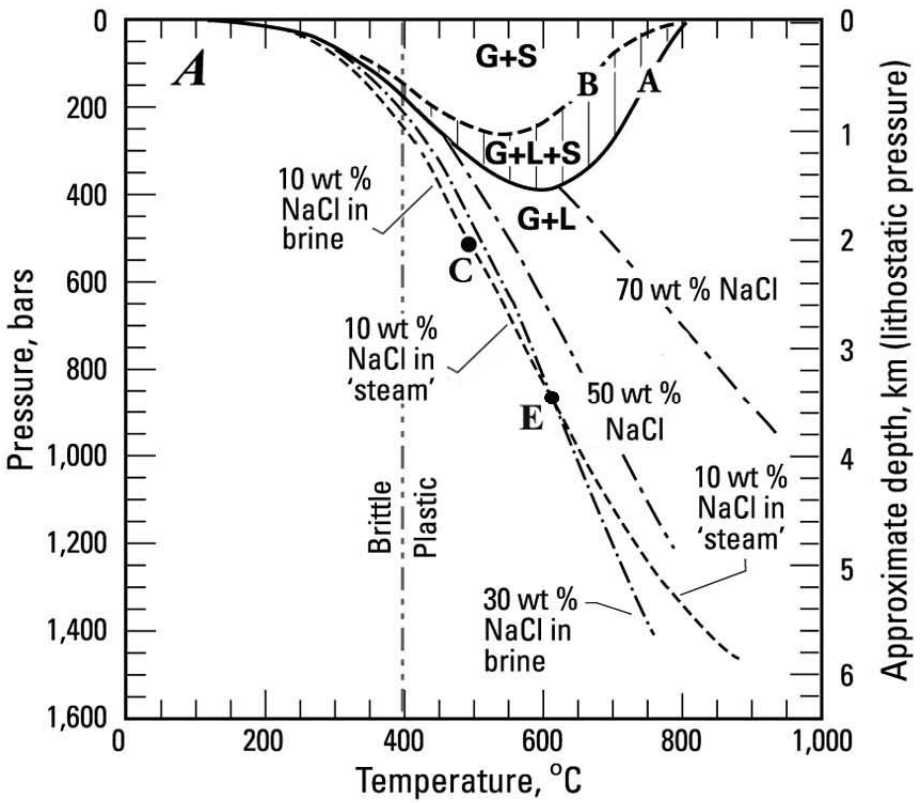

B. Quartz solubility
300 bars
2,400
1,800
1,200
6 00
0
SiO2, mg/kg
20 wt % NaCl
15
10
5
H2O
Boiling
0
200
300
400
500
600
Temperature, °C
A. Quartz solubility
500 bars
2,400
1,800
1,200
600
0
SiO2, mg/kg
23 wt % NaCl
20
15
10
5
H2O
Boiling
0
200
300
400
500
600
Temperature, °C

Shibue (1997)

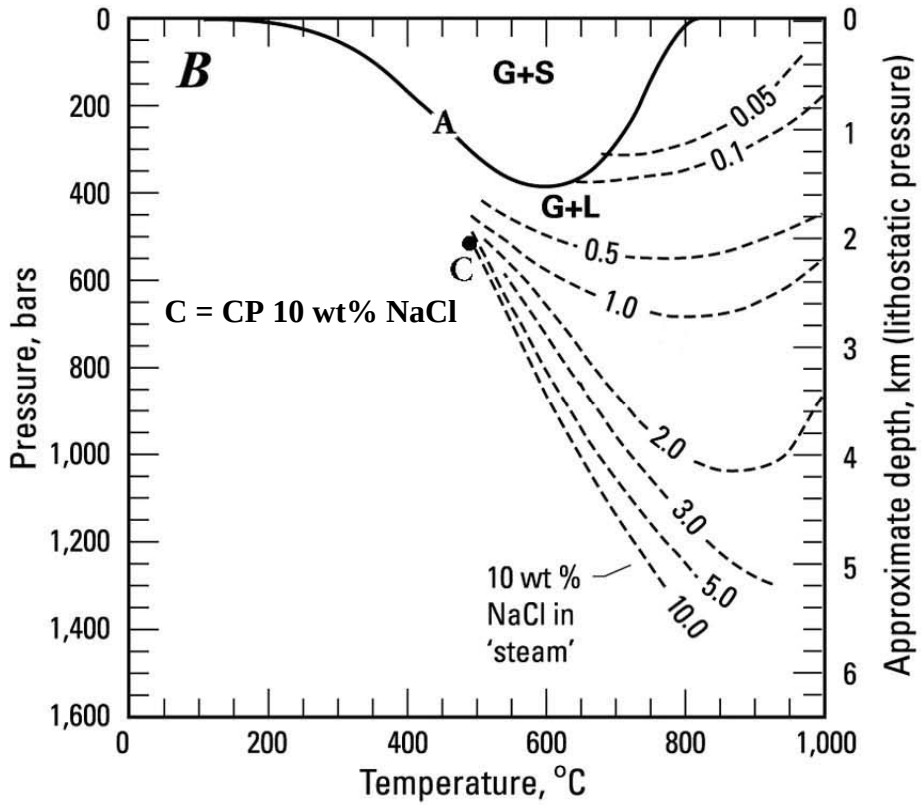

Quartz solubility in $CO_2$ -$H_2O$ solutions
600°C
Calculated
Experimental
$SiO_2$, mg/kg
Wt % $CO_2$ in solution
8000
7000
6000
5000
4000
3000
2000
1000
0
0
10
20
30
40
50
60

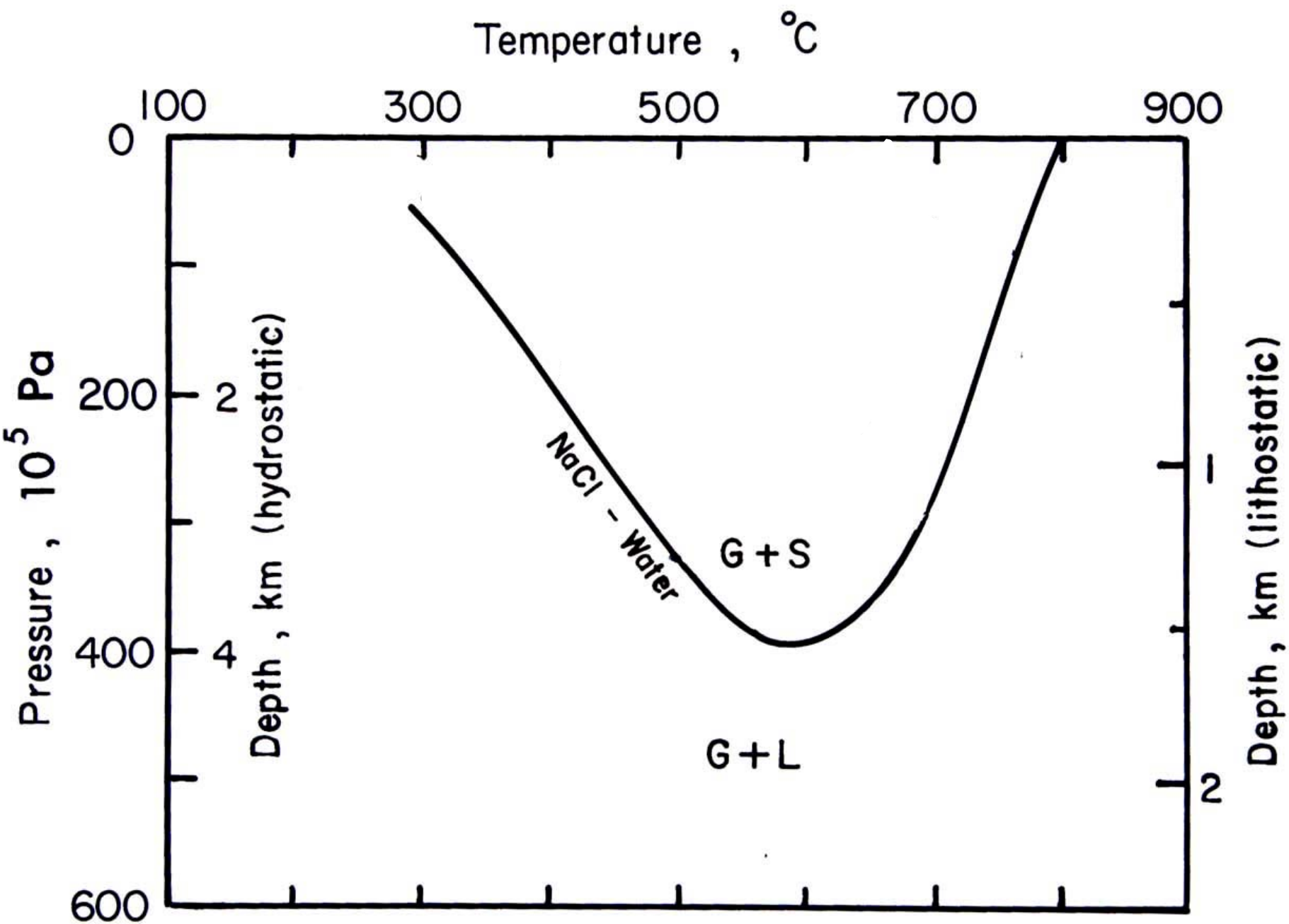

Temperature, C
0
200
400
600
800
1000
1200
Depth (Km hydrostatic P)
Depth (Km lithostatic P)
1
3
5
7
1
2
3
Salt + Gas
Critical pt. $H_2O$
0
Critical pt. 10 wt% NaCl
10
0.01
0.02
0.03
0.05
0.1
90
0.2
0.3
0.5
1.0
80
50
60
70
2.0
Condensation pt curves
Red: Wt% salt in gas
Black: Wt% salt in brine
Boiling pt curves

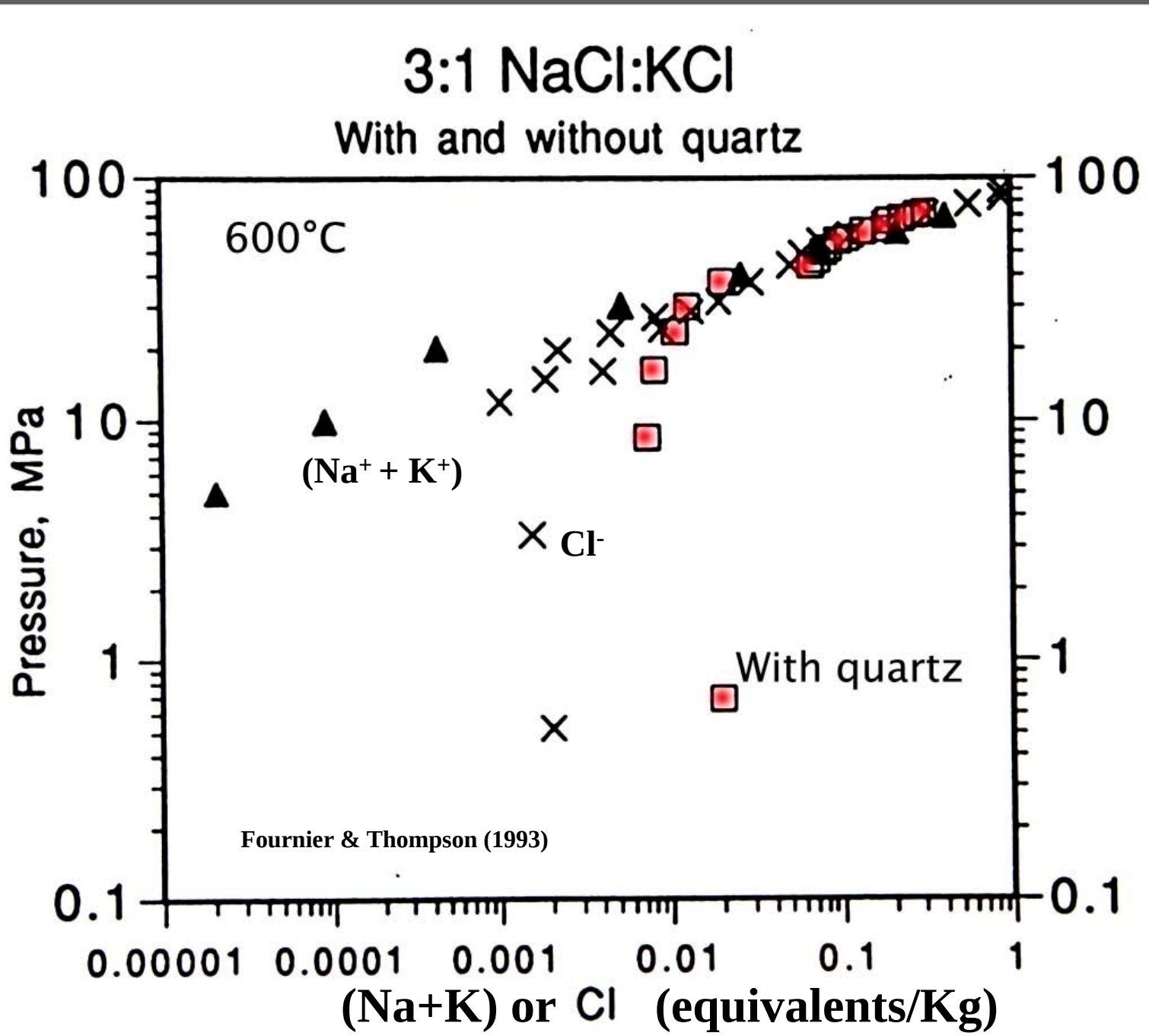
**Brines boil and become more concentrated with increasing temperature or decreasing pressure**




**Salt dissolved in gas or "steam" becomes less concentrated (brine condenses) with increasing temperature or decreasing pressure**



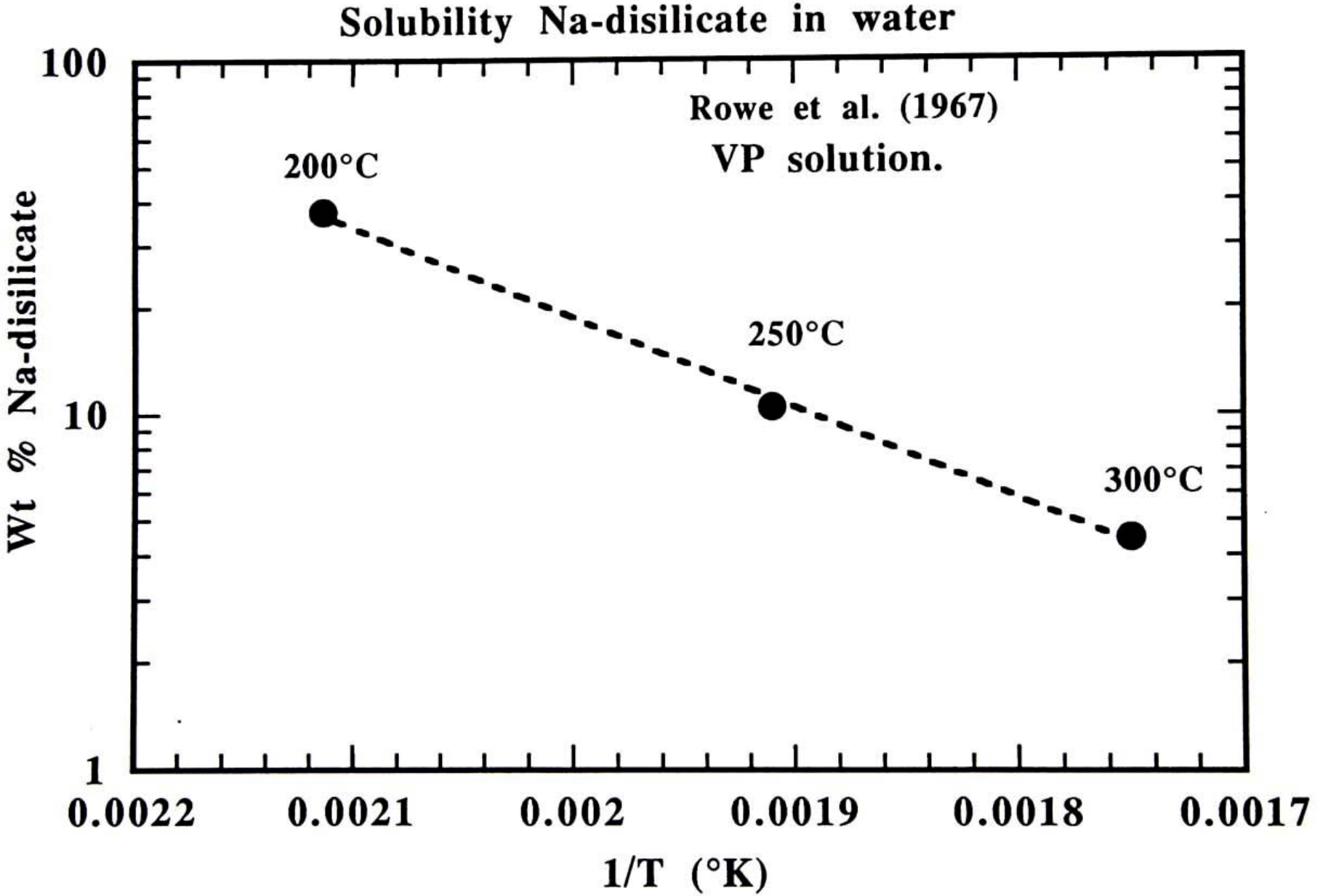

Temperature , °C
100
300
500
700
900
0
200
400
600
Pressure , $10^5$ Pa
Depth , km (hydrostatic)
2
4
Depth, km (lithostatic)
1
2
NaCl - Water
G+S
G+L

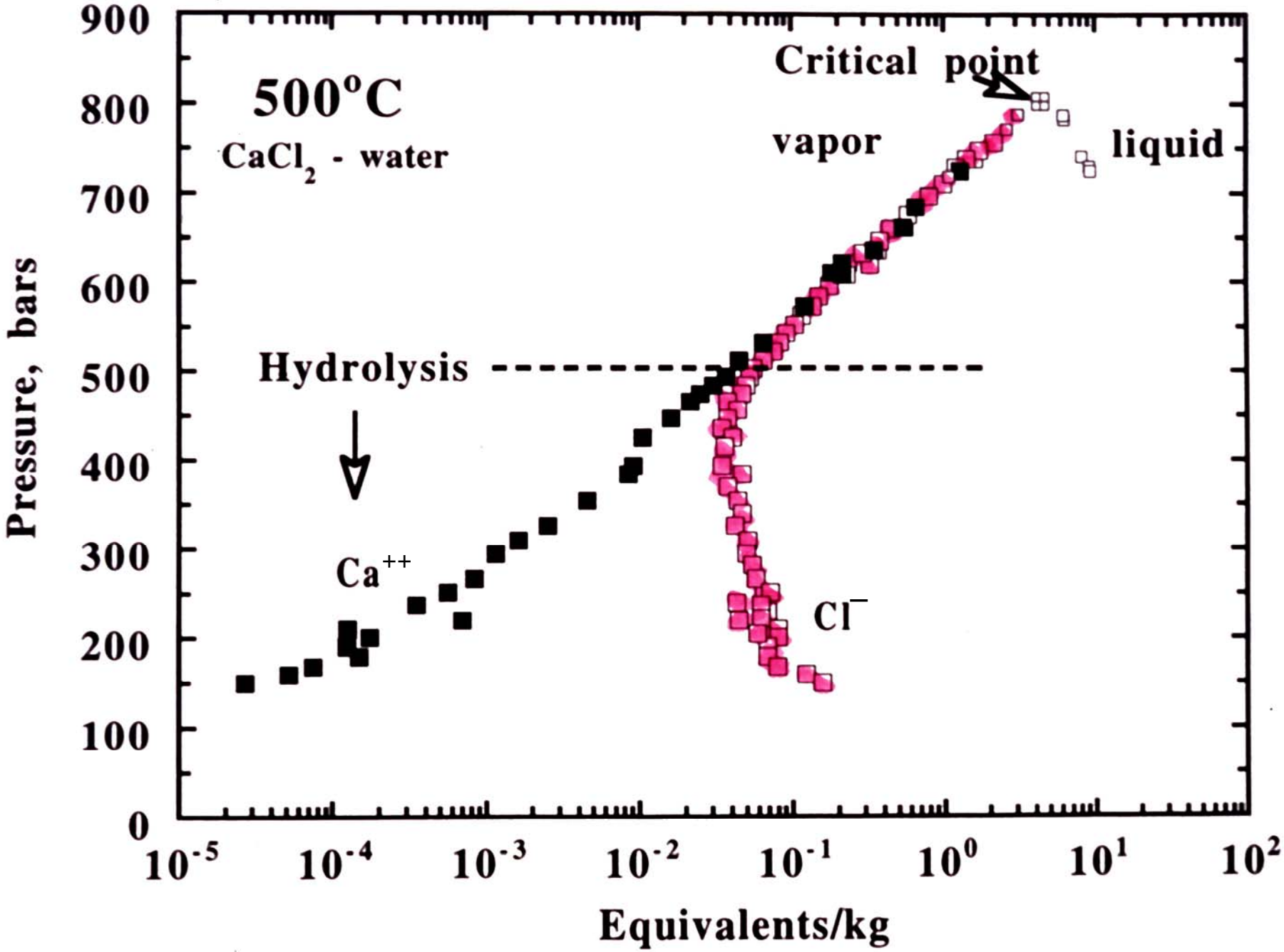

3:1 NaCl:KCl
With and without quartz
600°C
(Na+ + K+)
Cl-
With quartz
Fournier & Thompson (1993)
Pressure, MPa
100
10
1
0.1
0.00001
0.0001
0.001
0.01
0.1
1
(Na+K) or Cl (equivalents/Kg)

$$NaCl + H_2O = NaOH + HCl°$$

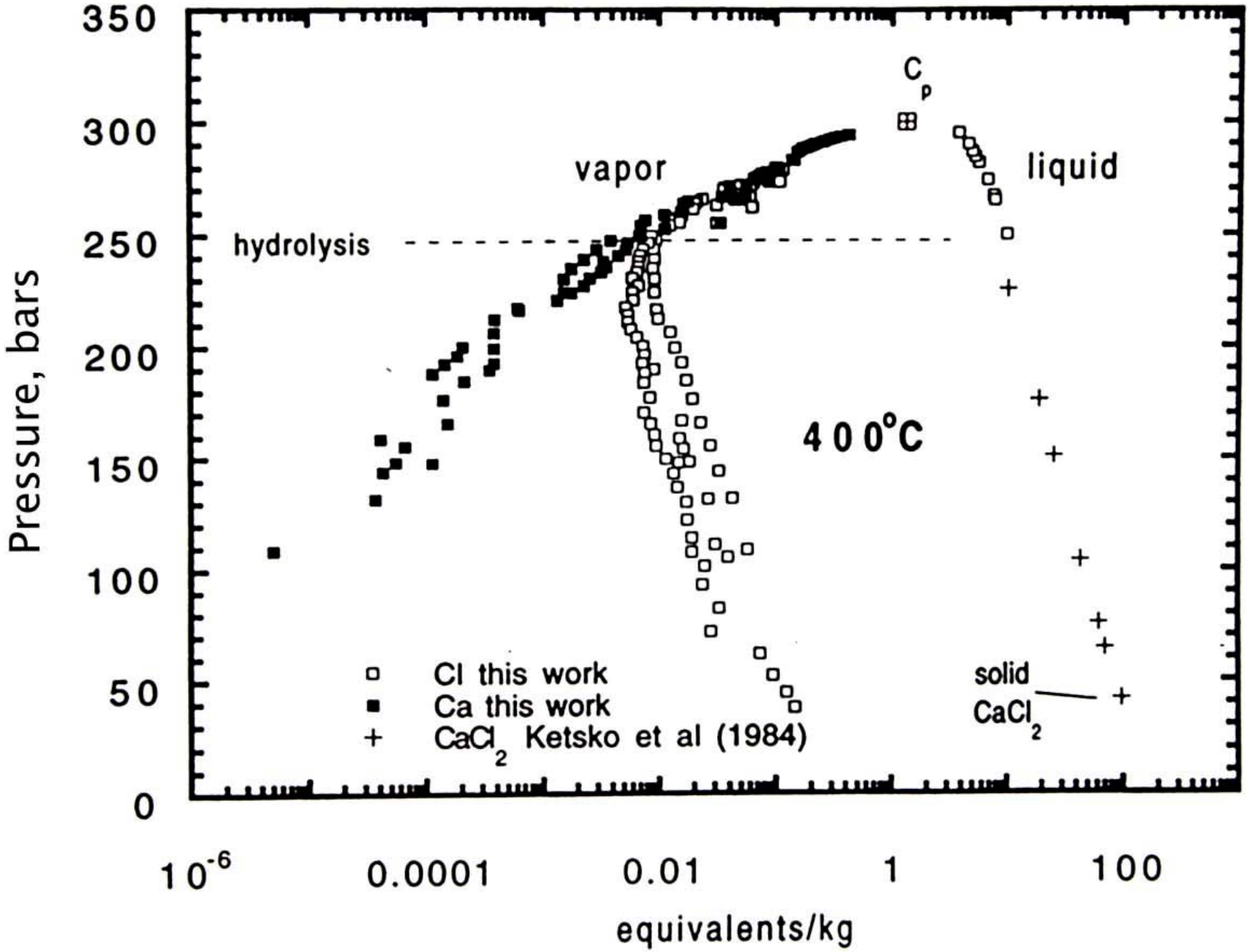
$$2NaCl + SiO_2 + H_2O = Na_2Si_2O_5 + 2HCl°$$

$Na_2Si_2O_5$ **is less soluble at higher temperatures**


Solubility Na-disilicate in water
Rowe et al. (1967)
VP solution.
200°C
250°C
300°C
100
10
1
Wt % Na-disilicate
0.0022
0.0021
0.002
0.0019
0.0018
0.0017
1/T (°K)


From Bischoff, Rosenbauer, & Fournier (1996)
500°C
CaCl2 - water
Critical point
vapor
liquid
Hydrolysis
Ca++
Cl−
Pressure, bars
Equivalents/kg
900
800
700
600
500
400
300
200
100
0
10-5
10-4
10-3
10-2
10-1
100
101
102

From Bischoff, Rosenbauer, & Fournier (1996)



$$CaCl_2 + 2H_2O = Ca(OH)_2 + 2HCl°$$

**With silica present that reacts with $Ca(OH)_2$ , expect a greater yield of HCl°**

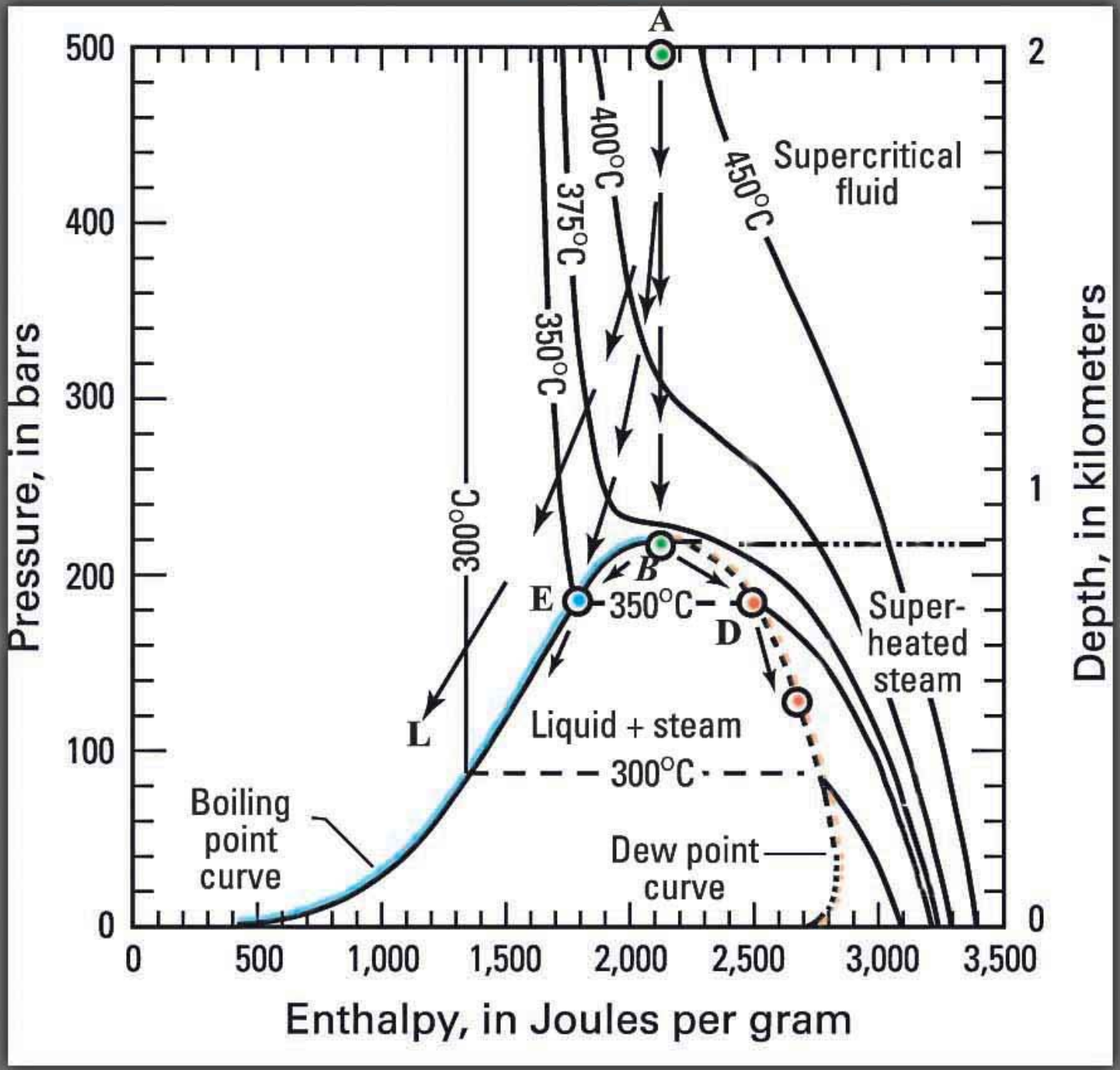
$$CaCl_2 + SiO2 + H_2O = CaSiO_3 + 2HCl°$$

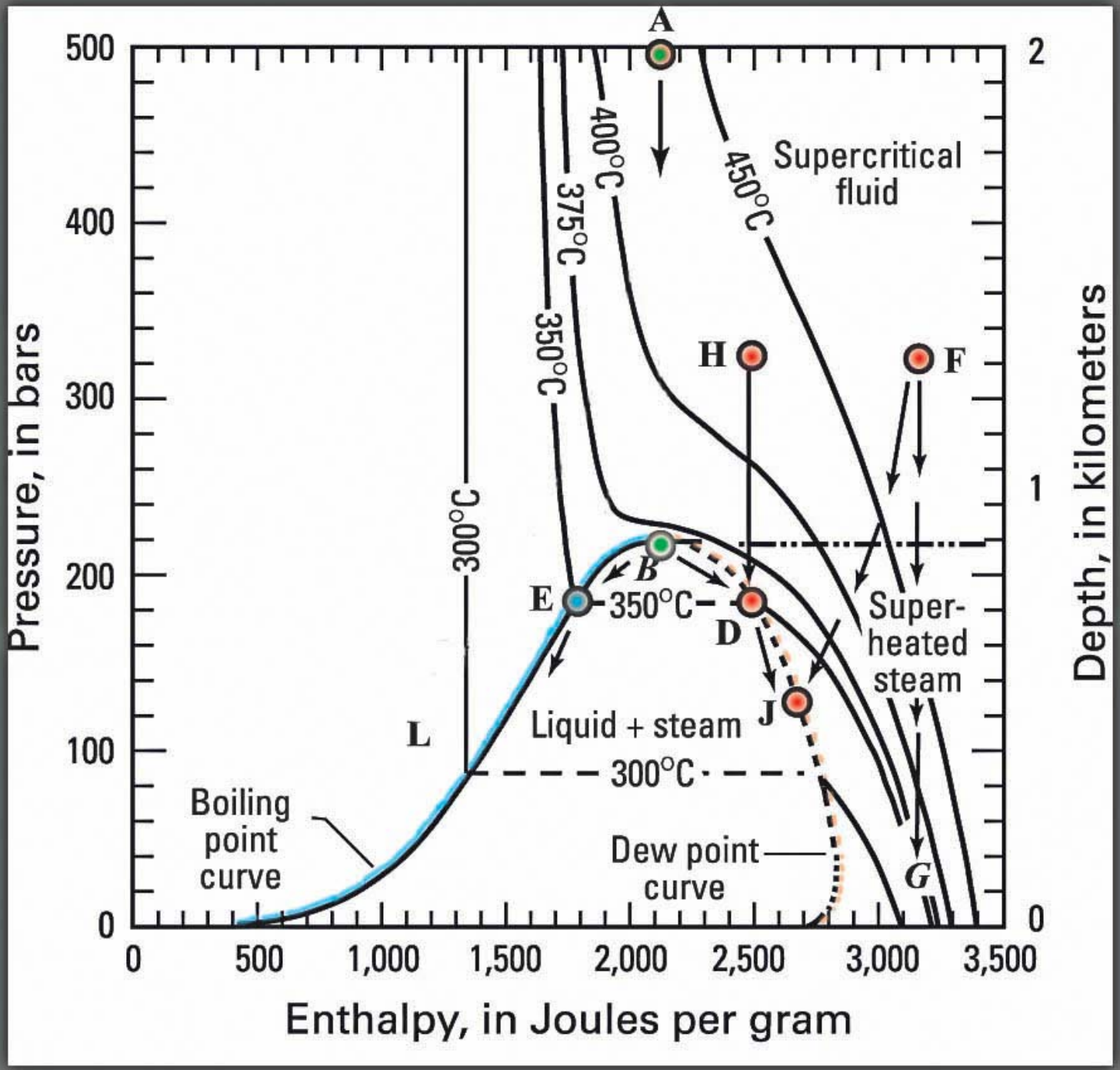
# Generation of HCl During Alteration of Plagioclase to Alkali Feldspar and/or Epidote

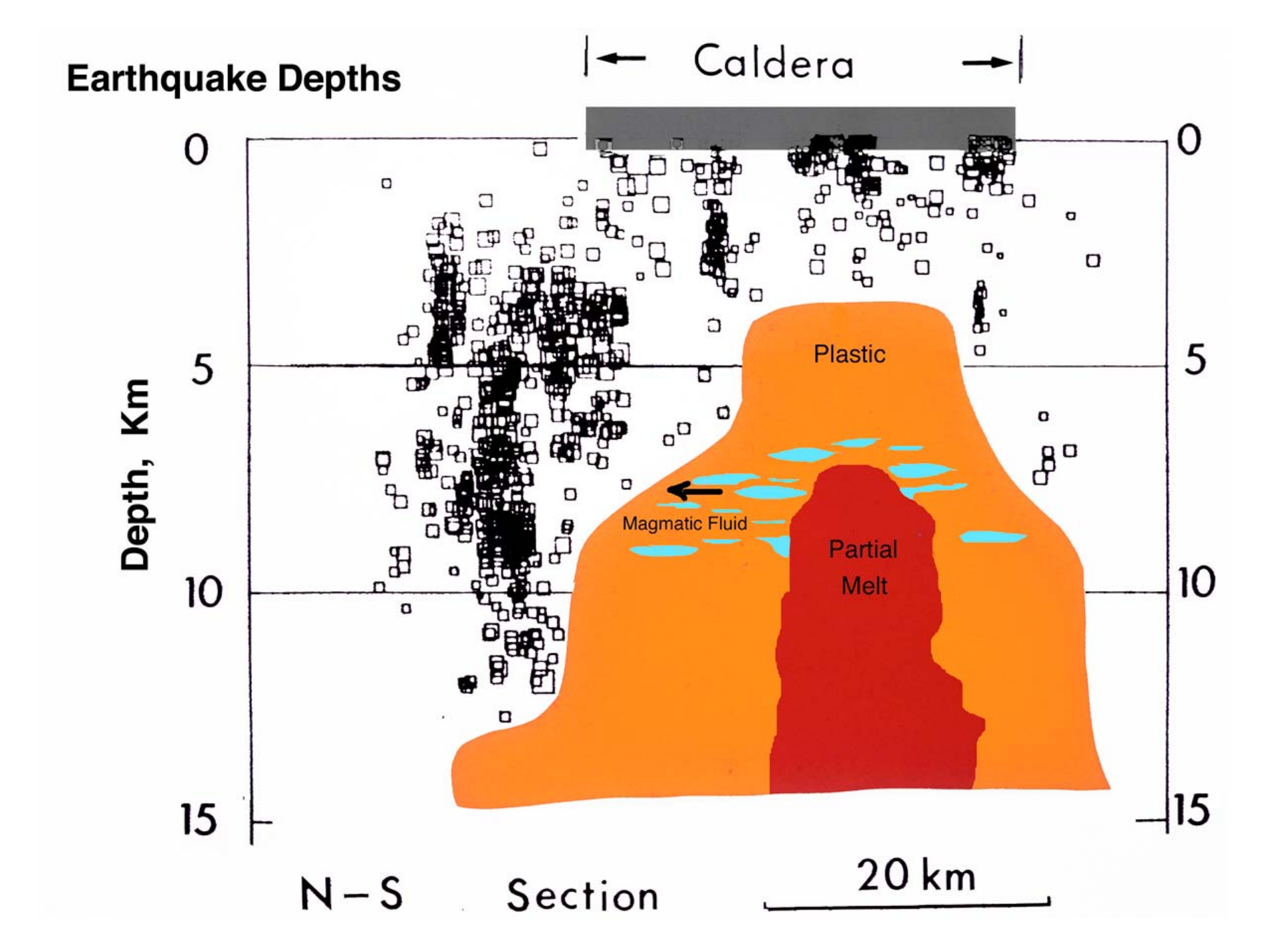
**2Anorthite + 2 Qtz +NaCl + $H_2O$ = Albite + Epidote + HCl°**

**2Anorthite + 2 Qtz +KCl + $H_2O$ = K-Feldspar + Epidote + HCl°**

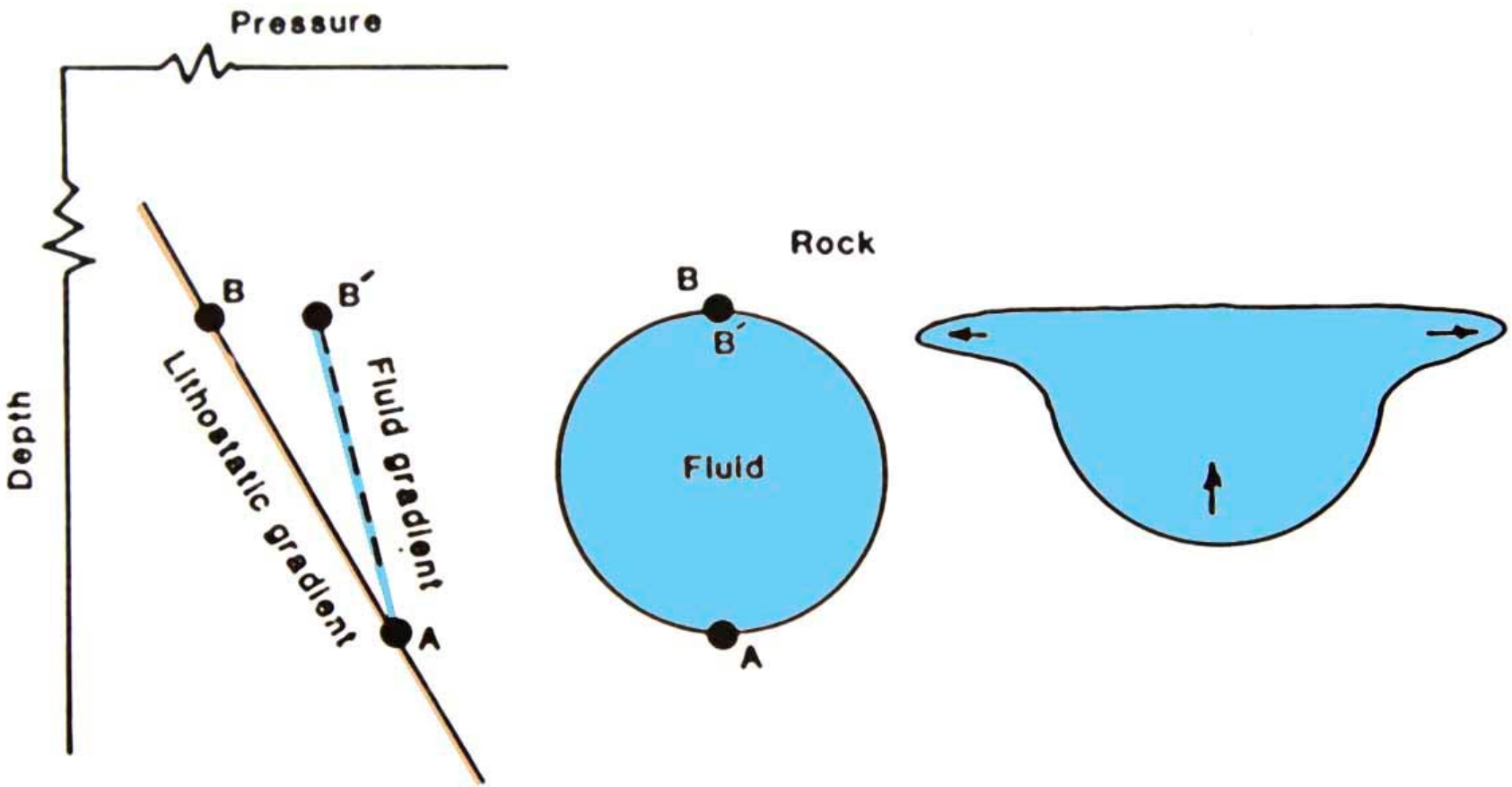
**3Anorthite + 2 Qtz + 2$CaCl_2$ + 2$H_2O$ = 2Epidote + 4HCl°**

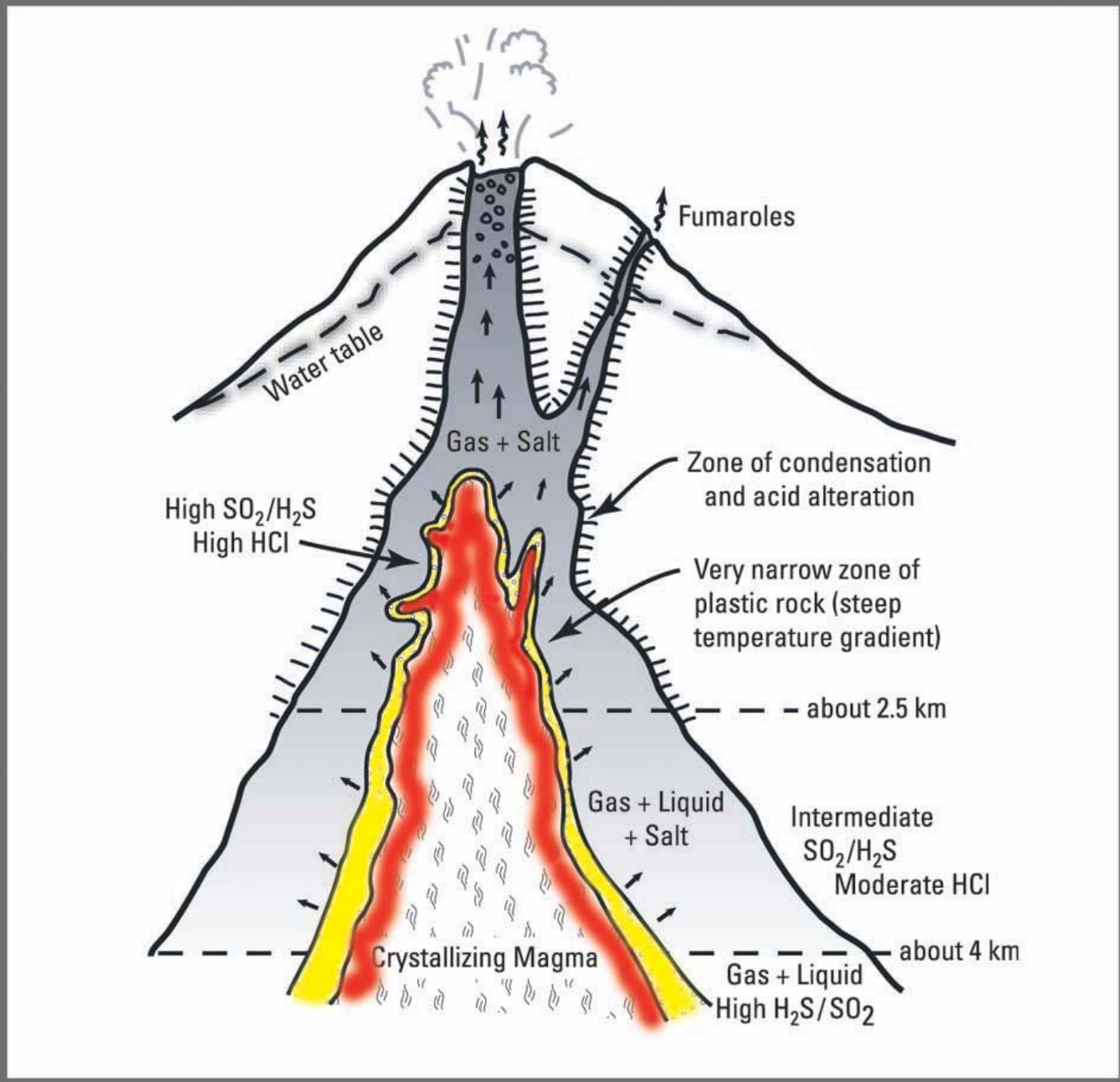

A
500
400
300
200
100
0
2
1
0
400°C
375°C
350°C
300°C
450°C
Supercritical fluid
B
E
350°C
D
L
Super-heated steam
Liquid + steam
300°C
Boiling point curve
Dew point curve
Pressure, in bars
Depth, in kilometers
0
500
1,000
1,500
2,000
2,500
3,000
3,500
Enthalpy, in Joules per gram


A
500
400
300
200
100
0
2
1
0
400°C
375°C
350°C
300°C
450°C
Supercritical fluid
H
F
B
E
350°C
D
Super-heated steam
J
L
Liquid + steam
300°C
Boiling point curve
Dew point curve
G
0
500
1,000
1,500
2,000
2,500
3,000
3,500
Pressure, in bars
Depth, in kilometers
Enthalpy, in Joules per gram

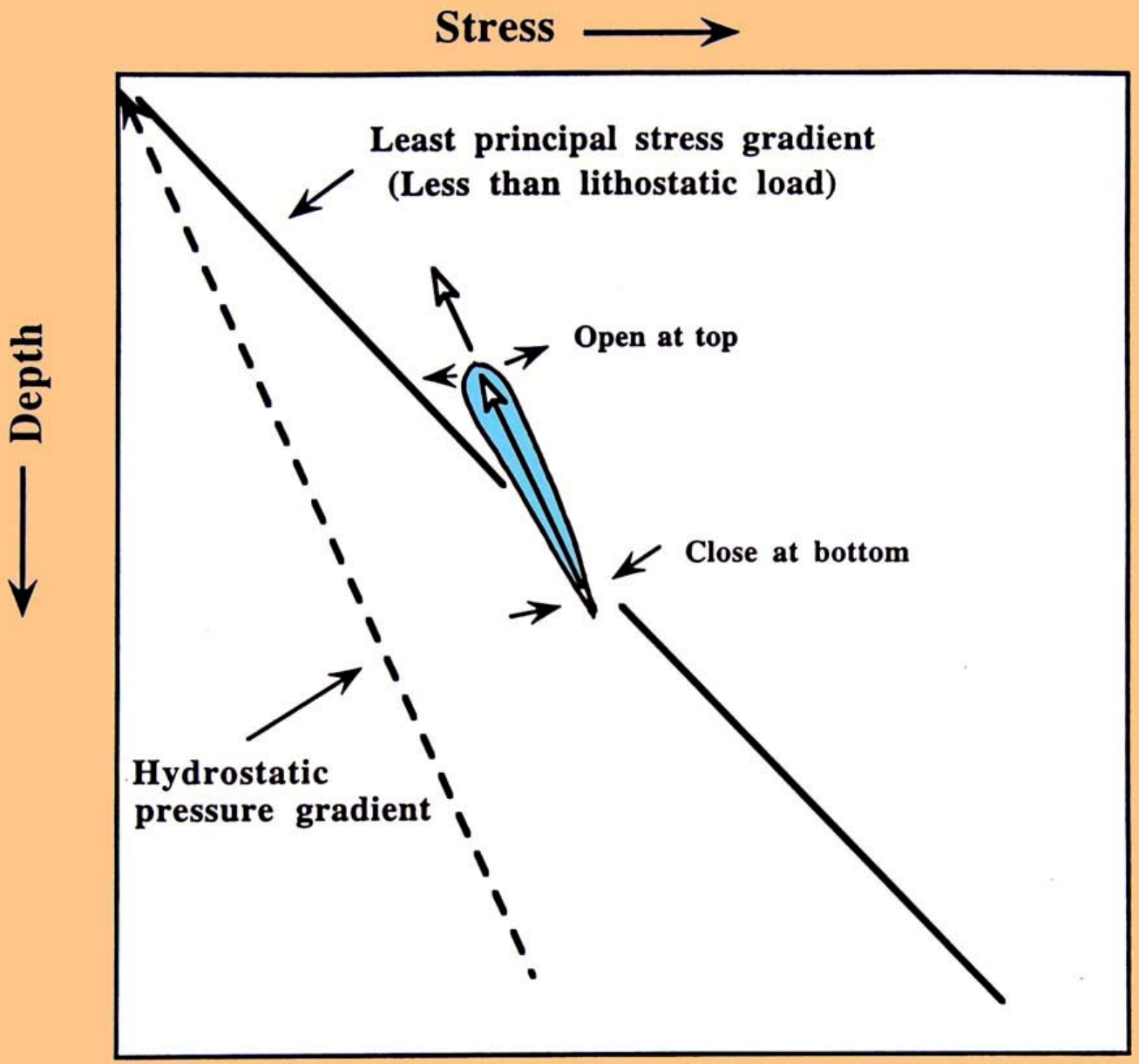

Earthquake Depths
Caldera
0
5
10
15
Depth, Km
Plastic
Magmatic Fluid
Partial
Melt
N – S Section
20 km

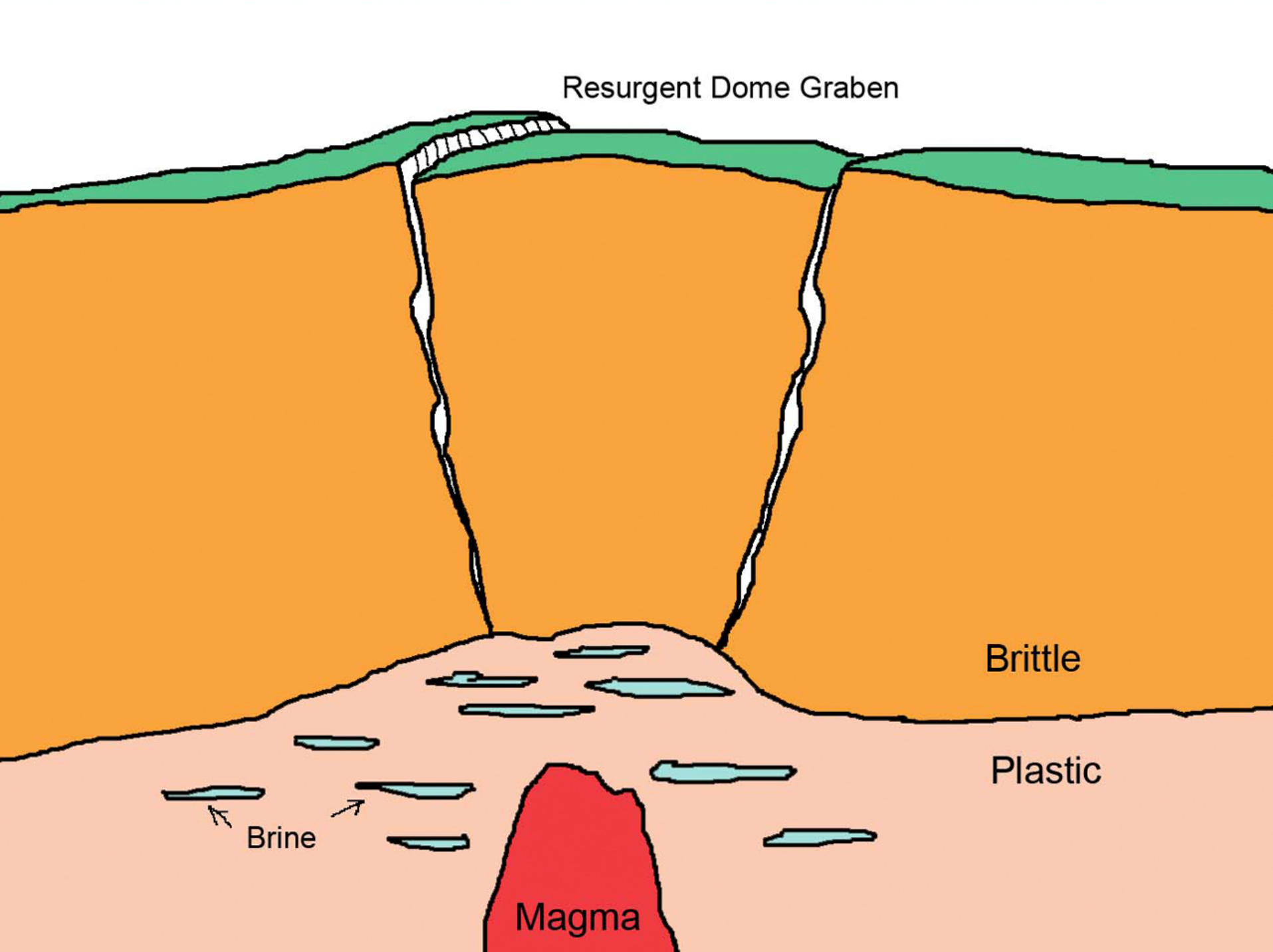
# Least Principal Stress is the Lithostatic Load

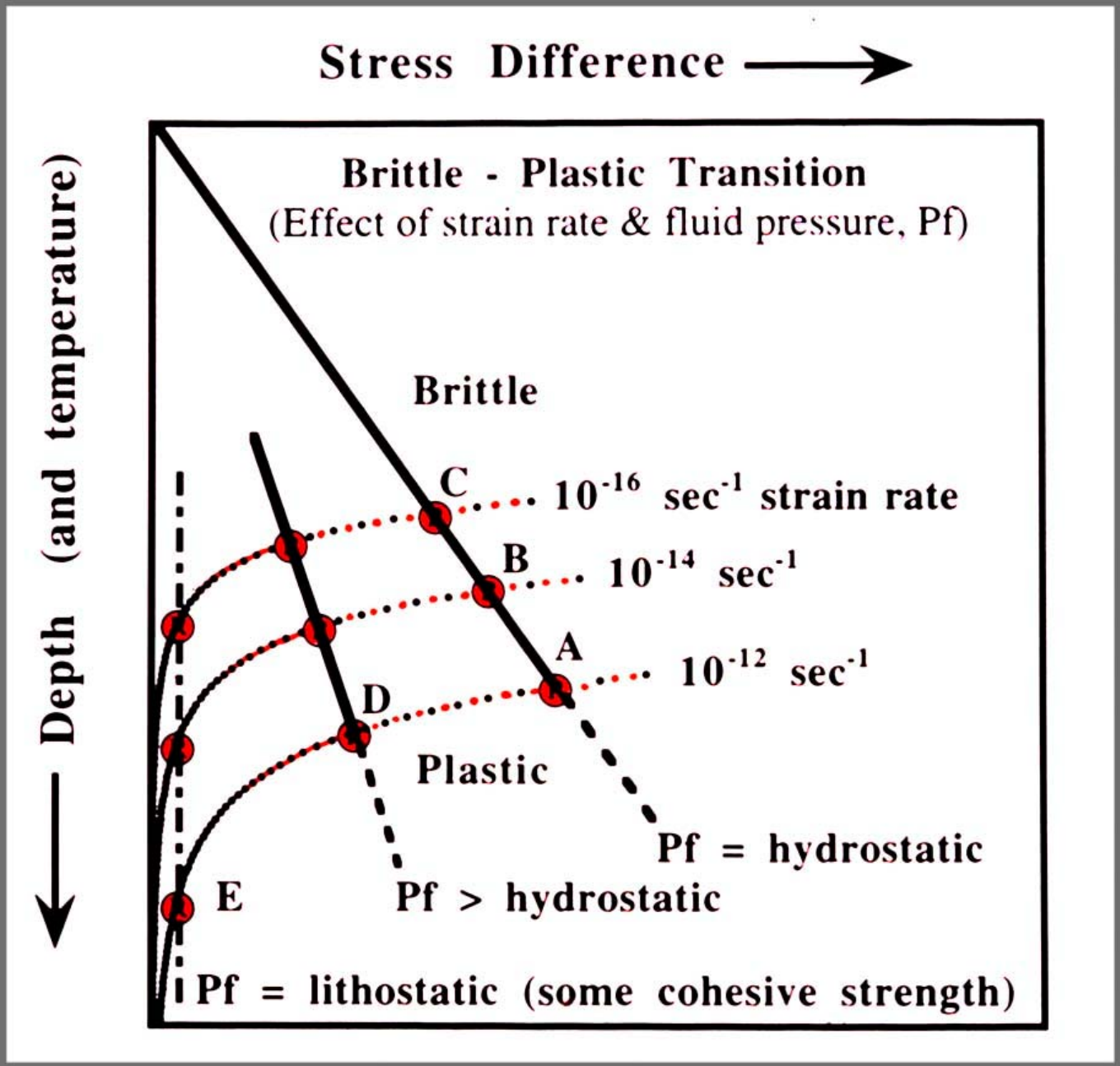


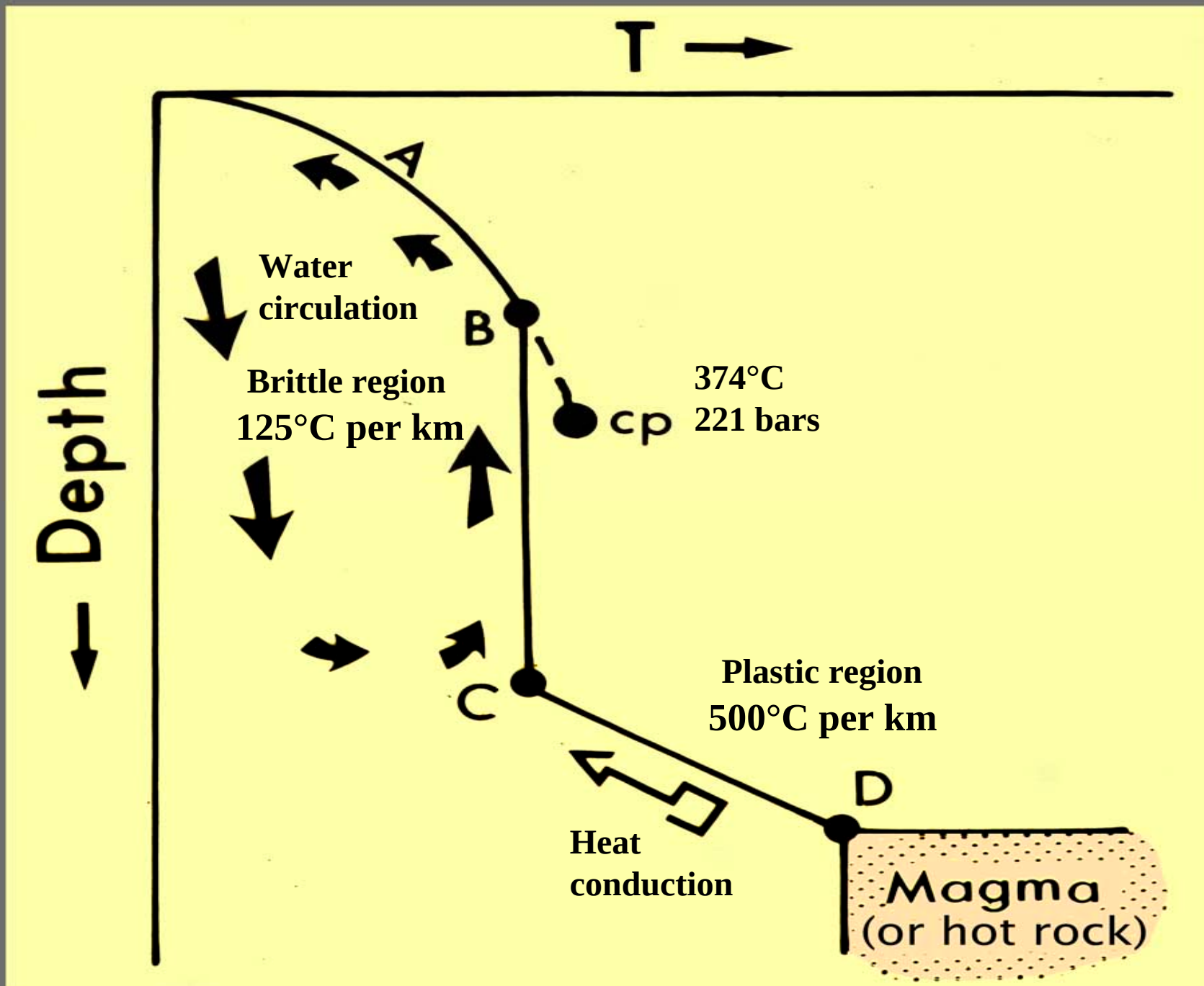

Fumaroles
Water table
Gas + Salt
Zone of condensation
and acid alteration
High $SO_2/H_2S$
High HCl
Very narrow zone of
plastic rock (steep
temperature gradient)
about 2.5 km
Gas + Liquid
+ Salt
Intermediate
$SO_2/H_2S$
Moderate HCl
about 4 km
Crystallizing Magma
Gas + Liquid
High $H_2S/SO_2$

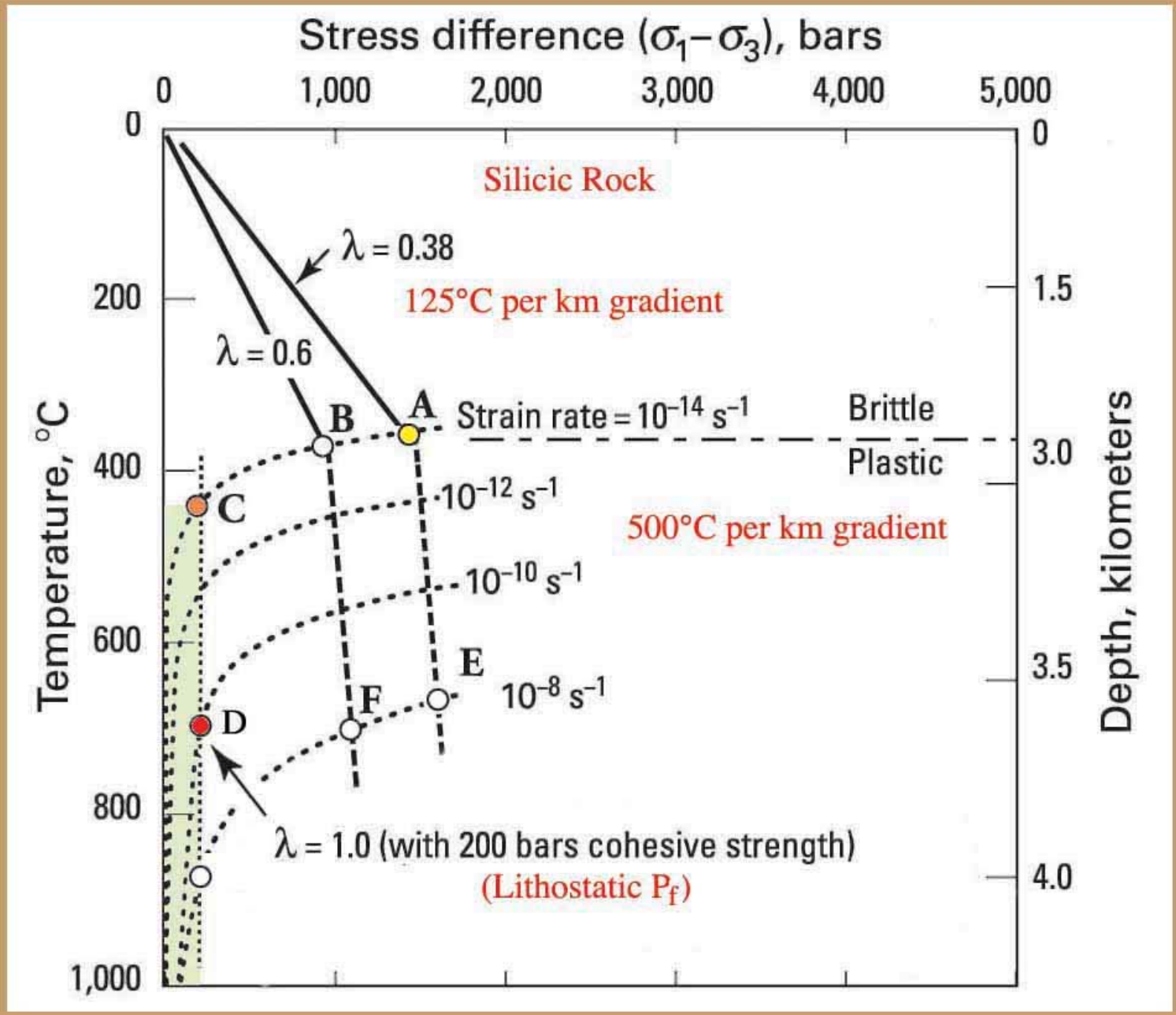
# Hydraulic Fracture Moves Upward By Opening At Top And Closing At Bottom

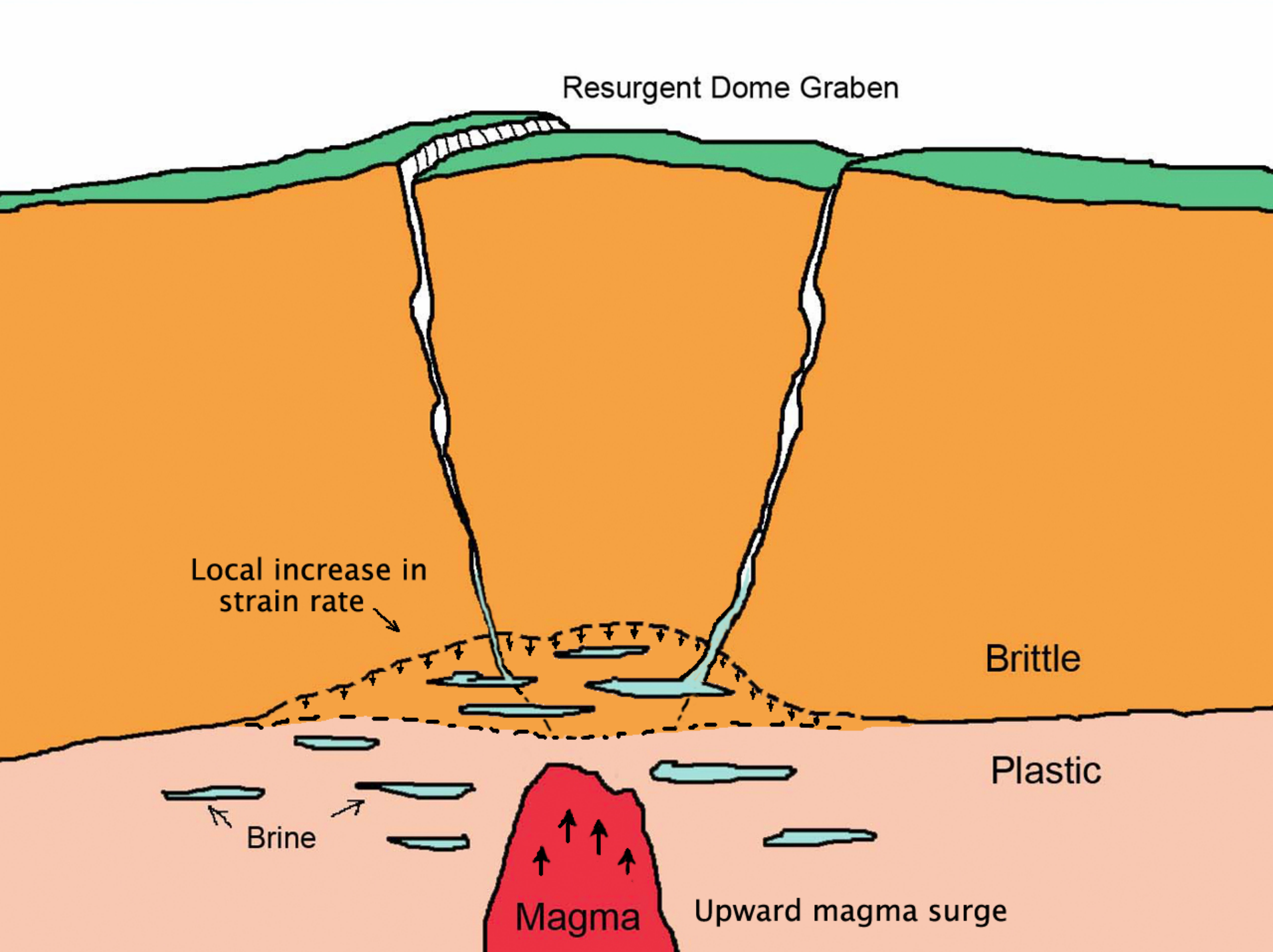



Resurgent Dome Graben
Brittle
Plastic
Brine
Magma


Stress Difference
Depth (and temperature)
Brittle - Plastic Transition
(Effect of strain rate & fluid pressure, Pf)
Brittle
C
$10^{-16}$ $sec^{-1}$ strain rate
B
$10^{-14}$ $sec^{-1}$
A
$10^{-12}$ $sec^{-1}$
D
Plastic
Pf = hydrostatic
E
Pf > hydrostatic
Pf = lithostatic (some cohesive strength)

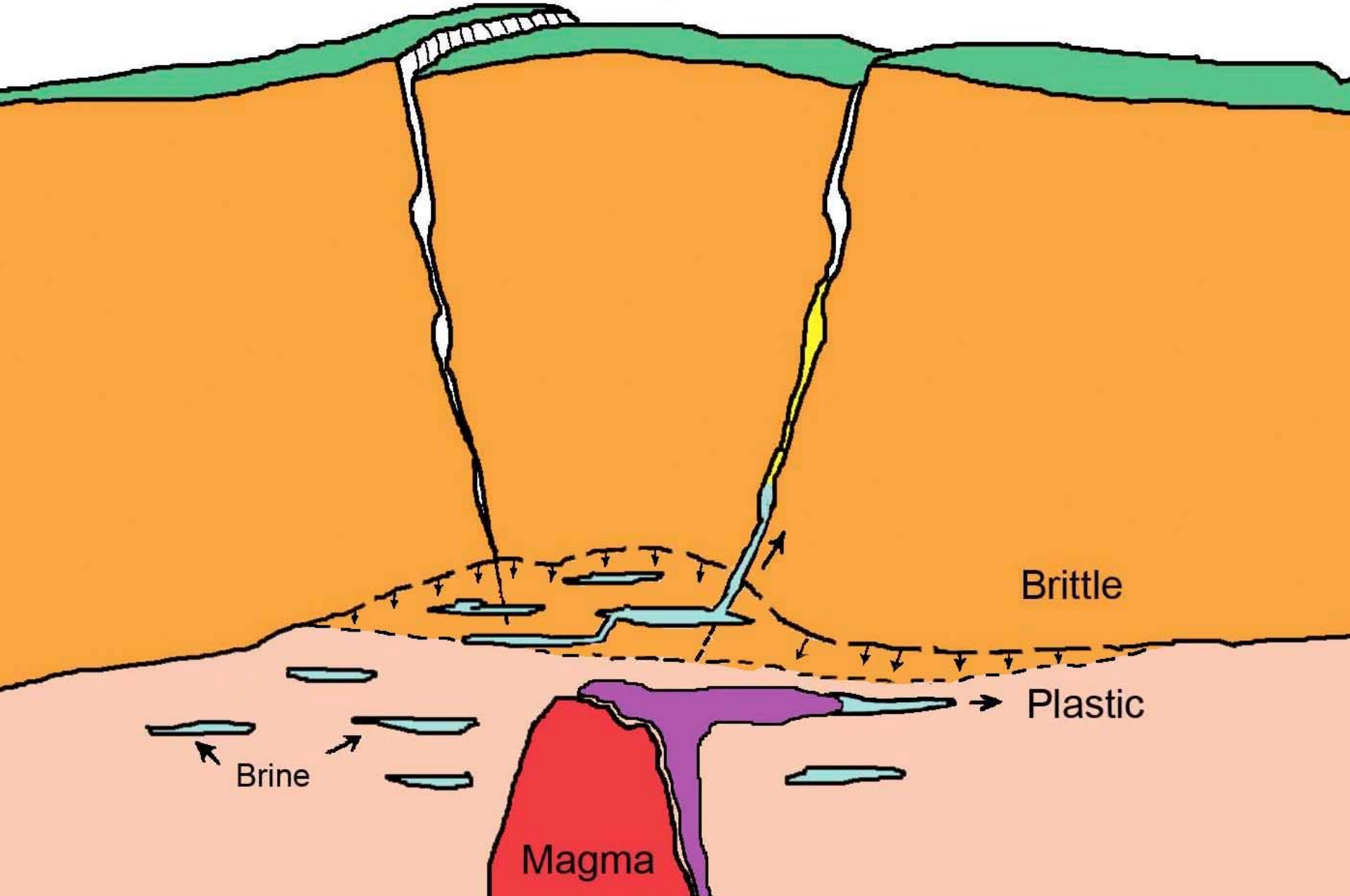

T
A
Water
circulation
B
Brittle region
125°C per km
cp
374°C
221 bars
Depth
C
Plastic region
500°C per km
D
Heat
conduction
Magma
(or hot rock)


Stress difference ($\sigma_1 - \sigma_3$), bars
0
1,000
2,000
3,000
4,000
5,000
Temperature, °C
0
200
400
600
800
1,000
Depth, kilometers
0
1.5
3.0
3.5
4.0
Silicic Rock
$\lambda = 0.38$
125°C per km gradient
$\lambda = 0.6$
A
B
Strain rate = $10^{-14}$ $s^{-1}$
Brittle
Plastic
C
$10^{-12}$ $s^{-1}$
500°C per km gradient
$10^{-10}$ $s^{-1}$
E
$10^{-8}$ $s^{-1}$
F
D
$\lambda = 1.0$ (with 200 bars cohesive strength)
(Lithostatic $P_f$)

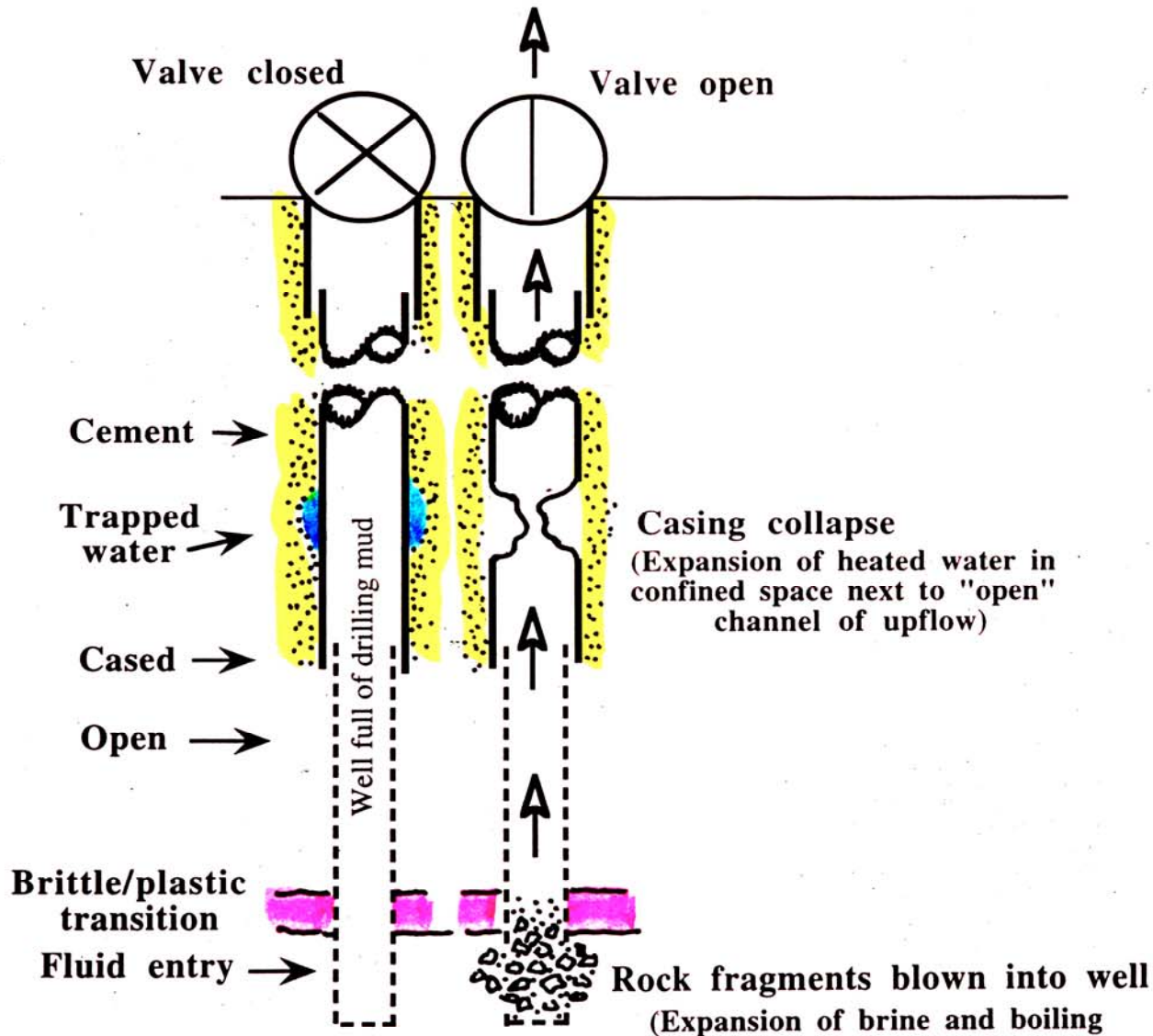

Resurgent Dome Graben
Local increase in strain rate
Brittle
Plastic
Brine
Magma
Upward magma surge

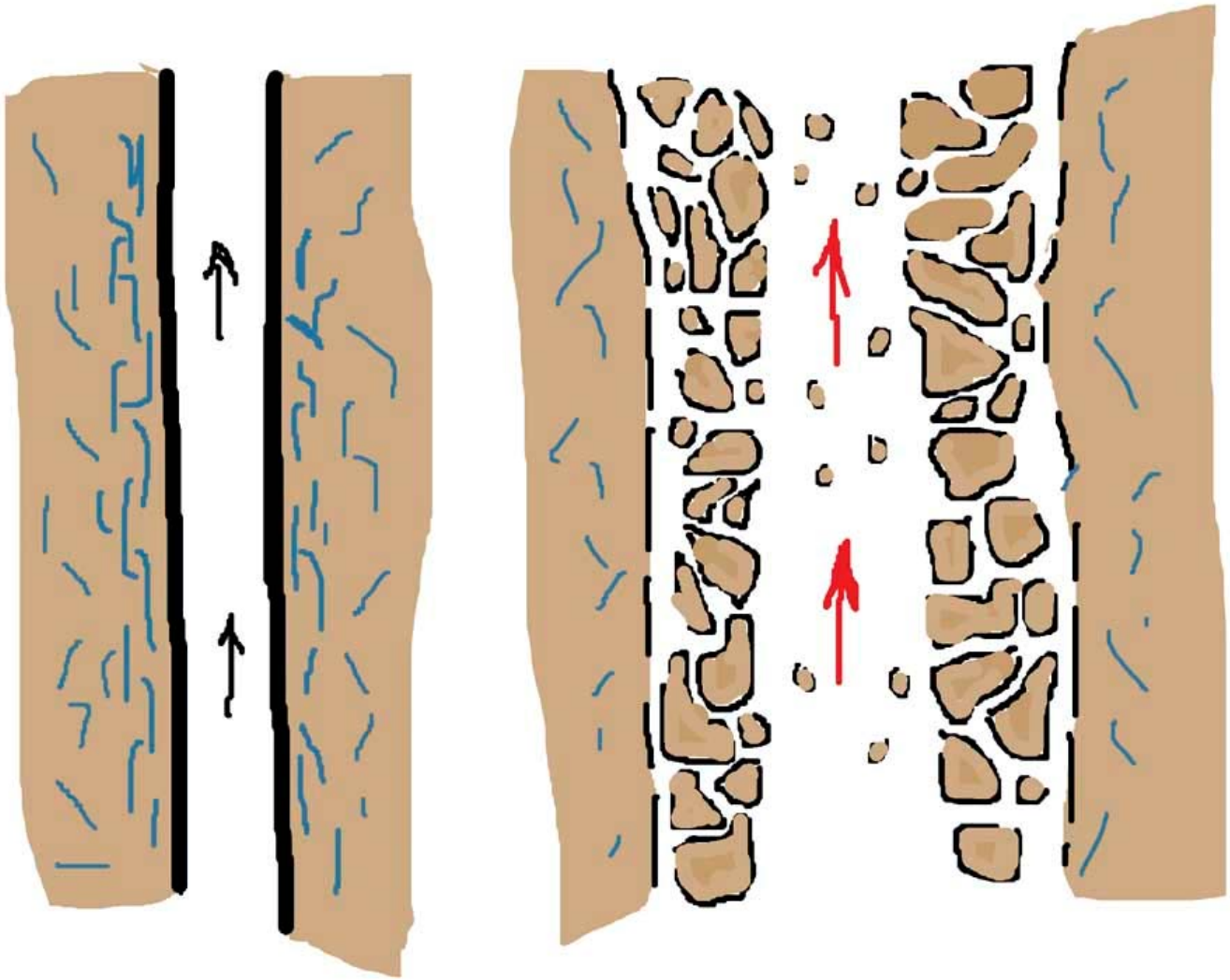
Effect Of High Strain Rate During Intrusion

Resurgent Dome Graben



# Deep ≈ 400°C well before and during fluid production

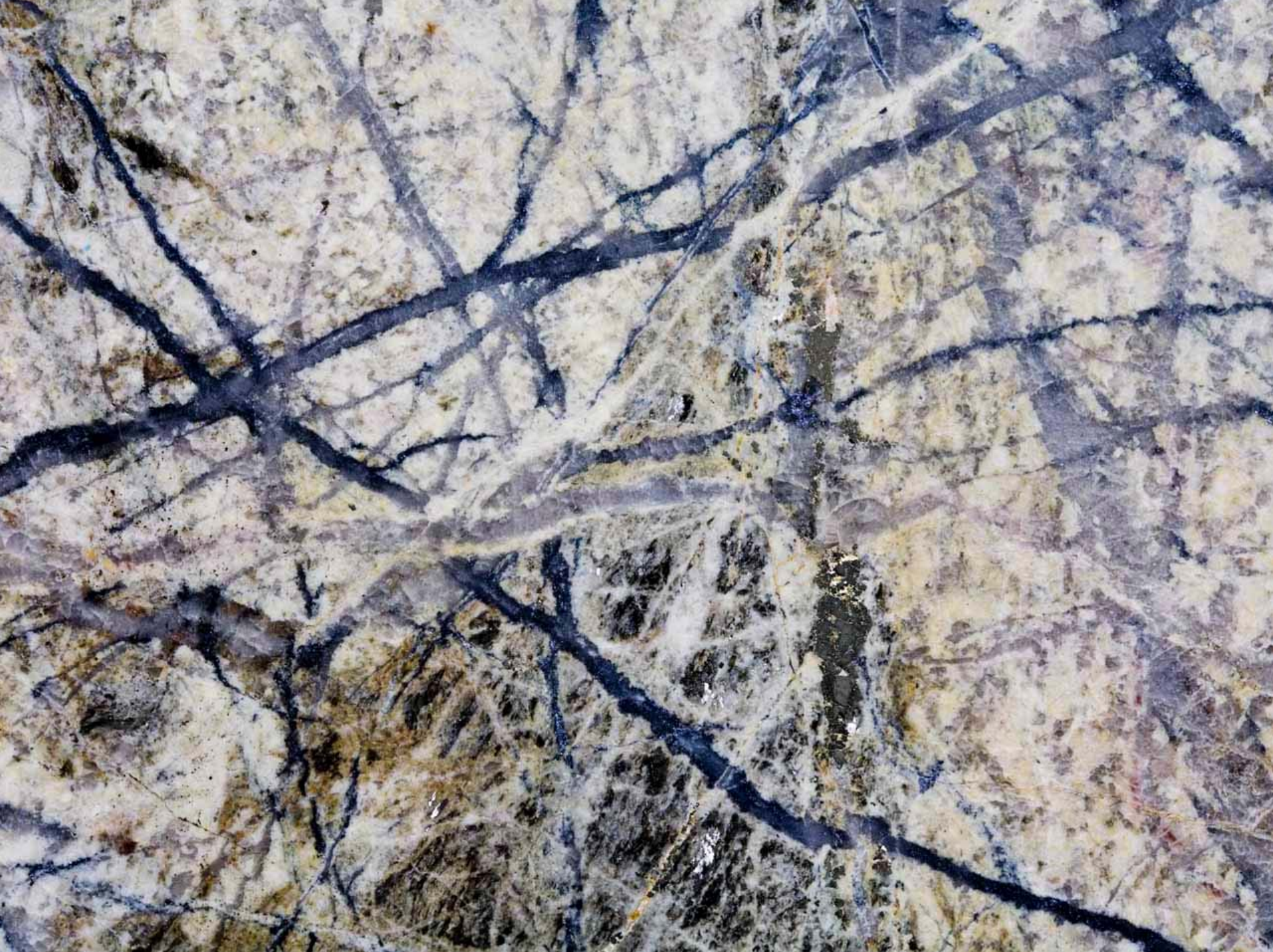


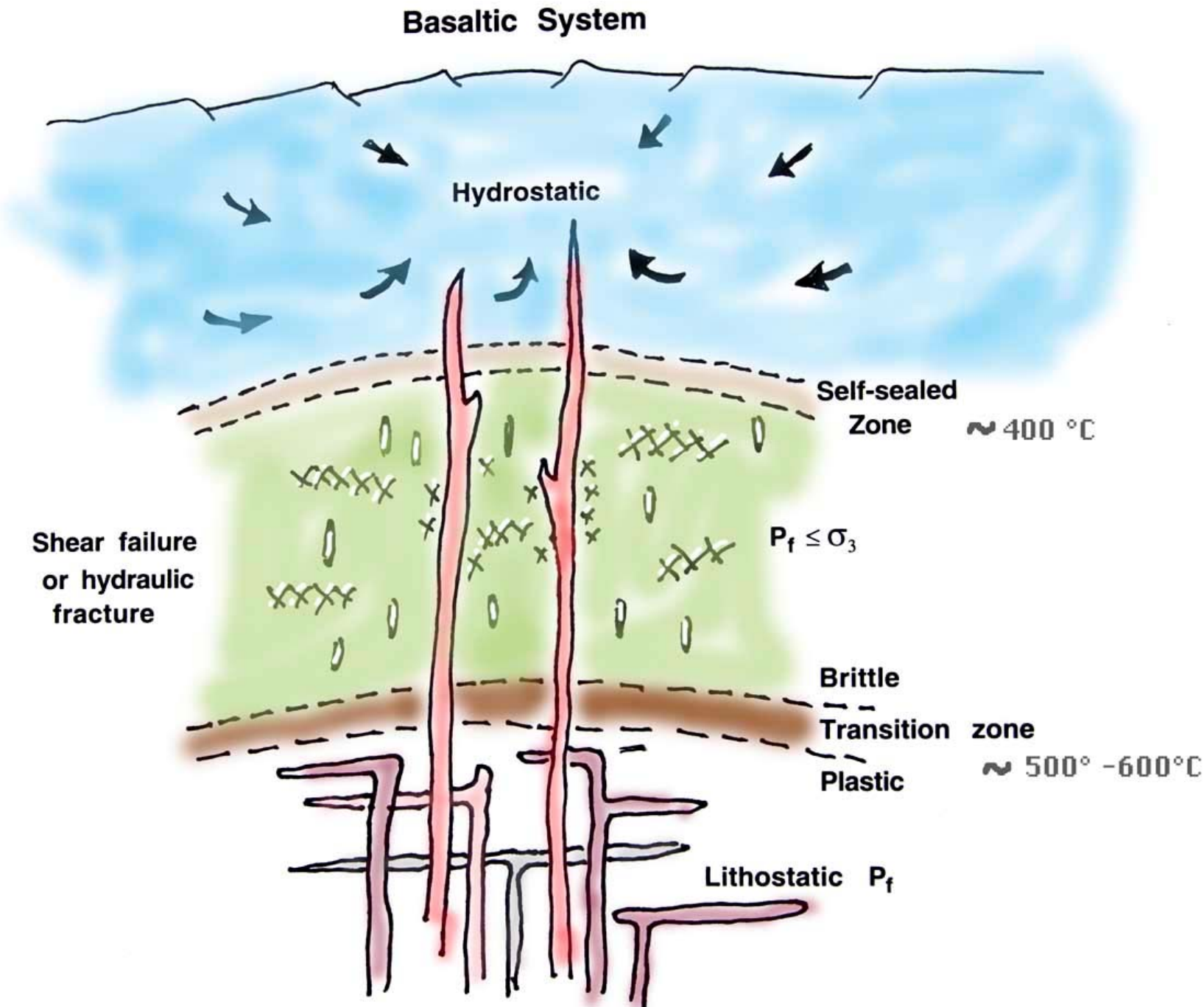


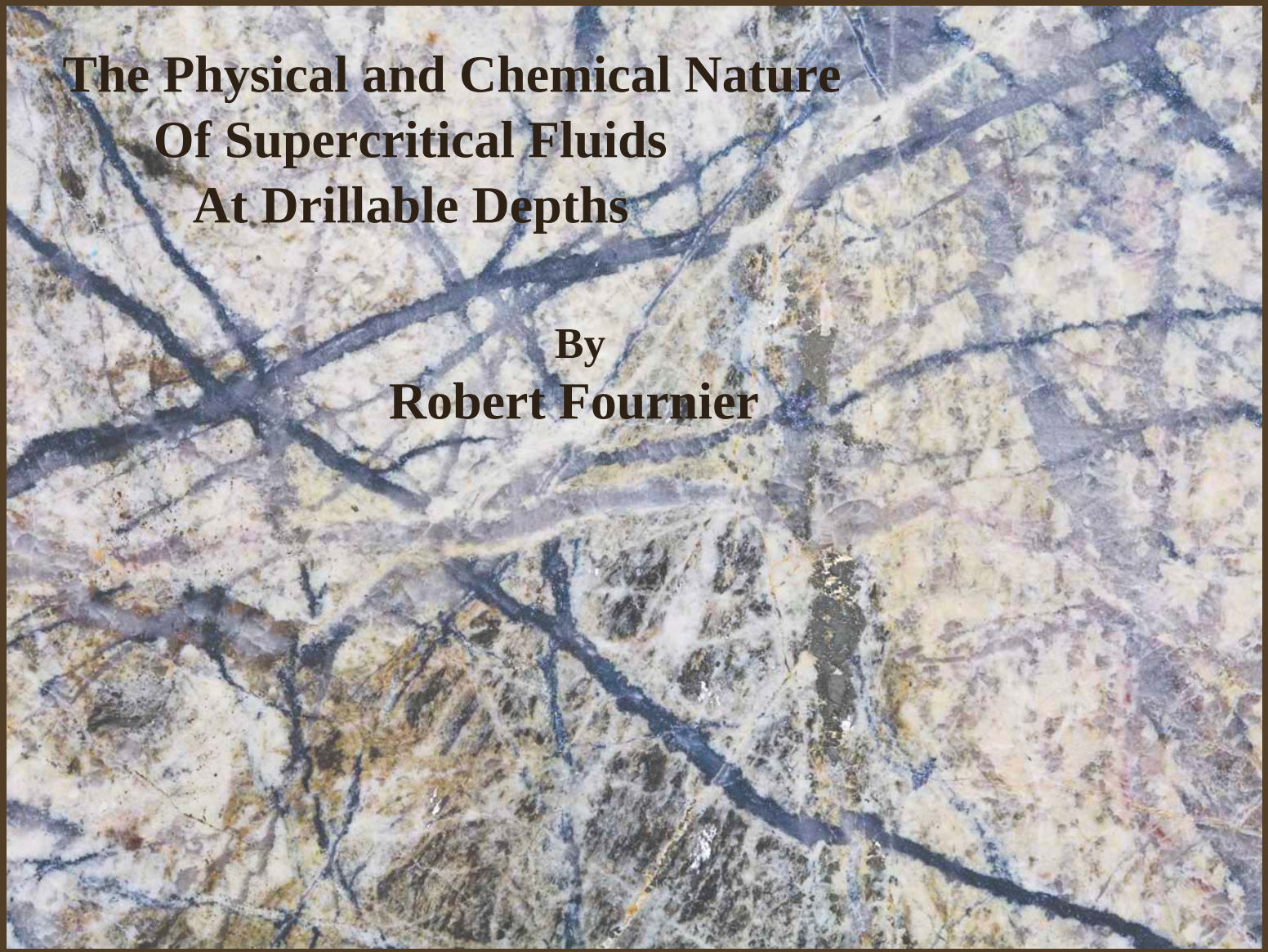
Breccia Dike Or Pipe Formation By Heating Water Trapped

In Rock adjacent To Channel Of Upflow

(Hydraulic Fracture)



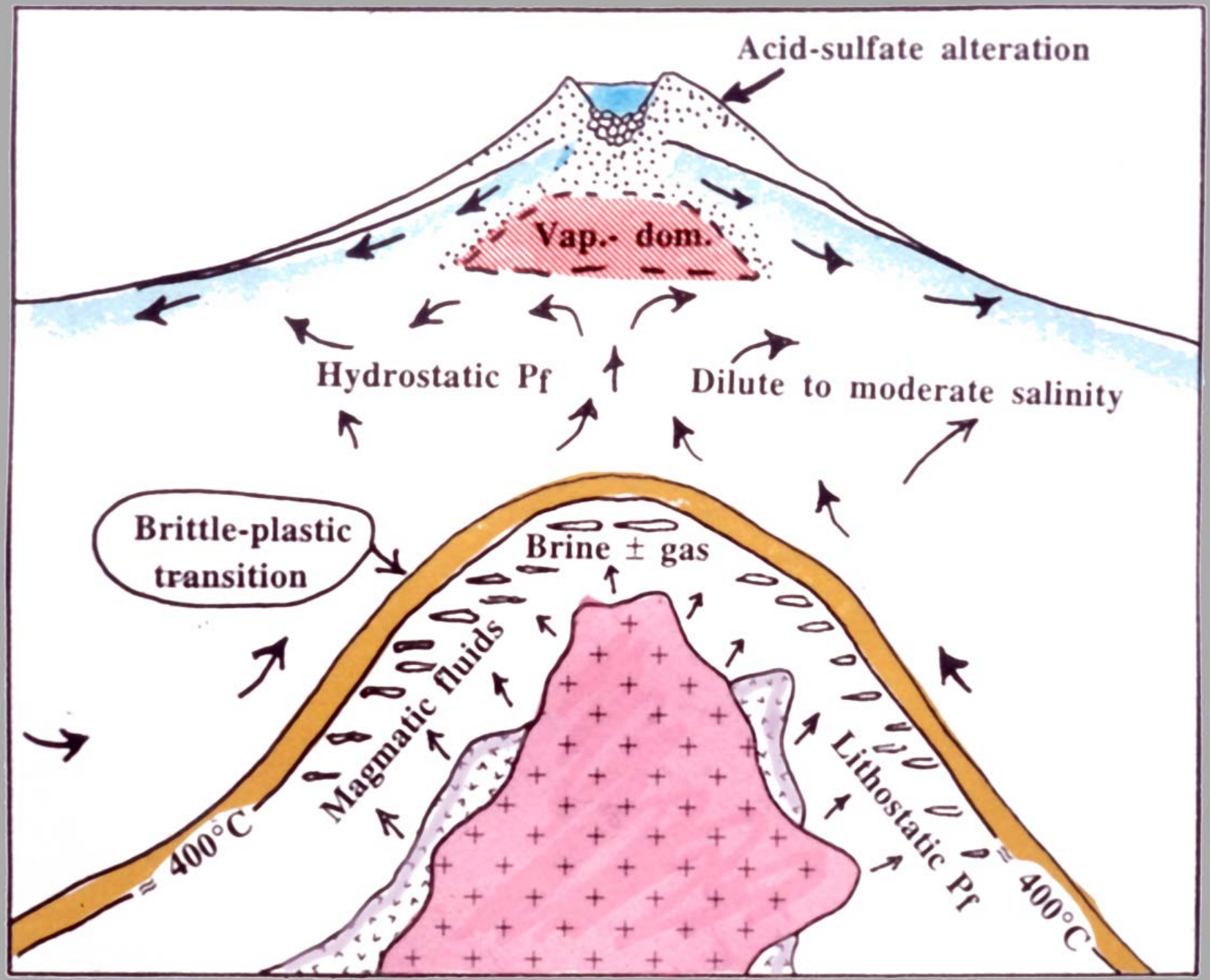

Basaltic System
Hydrostatic
Self-sealed
Zone
~ 400 °C
Shear failure
or hydraulic
fracture
$P_f \leq \sigma_3$
Brittle
Transition zone
Plastic
~ 500° -600°C
Lithostatic $P_f$

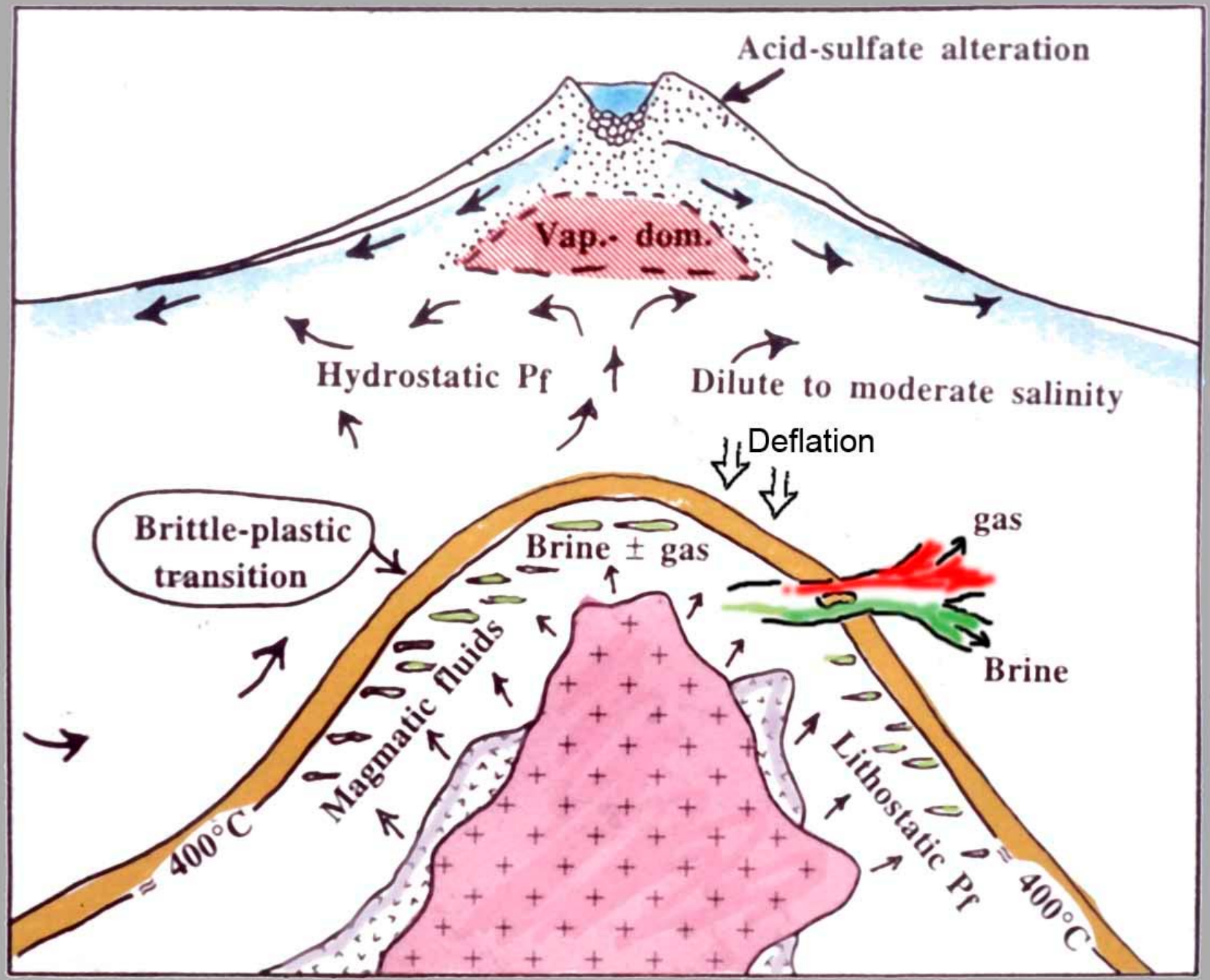


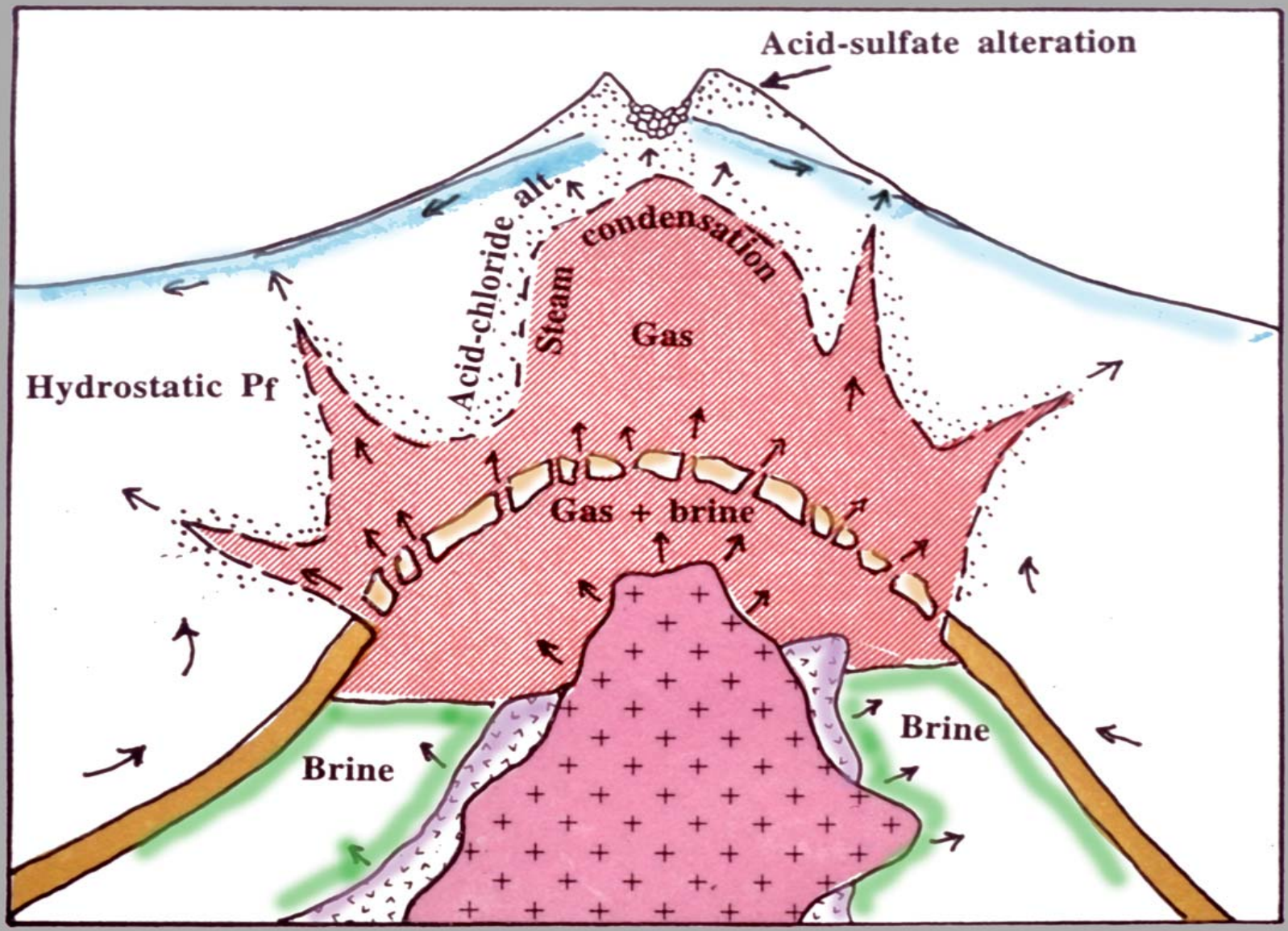
# The Physical and Chemical Nature Of Supercritical Fluids At Drillable Depths

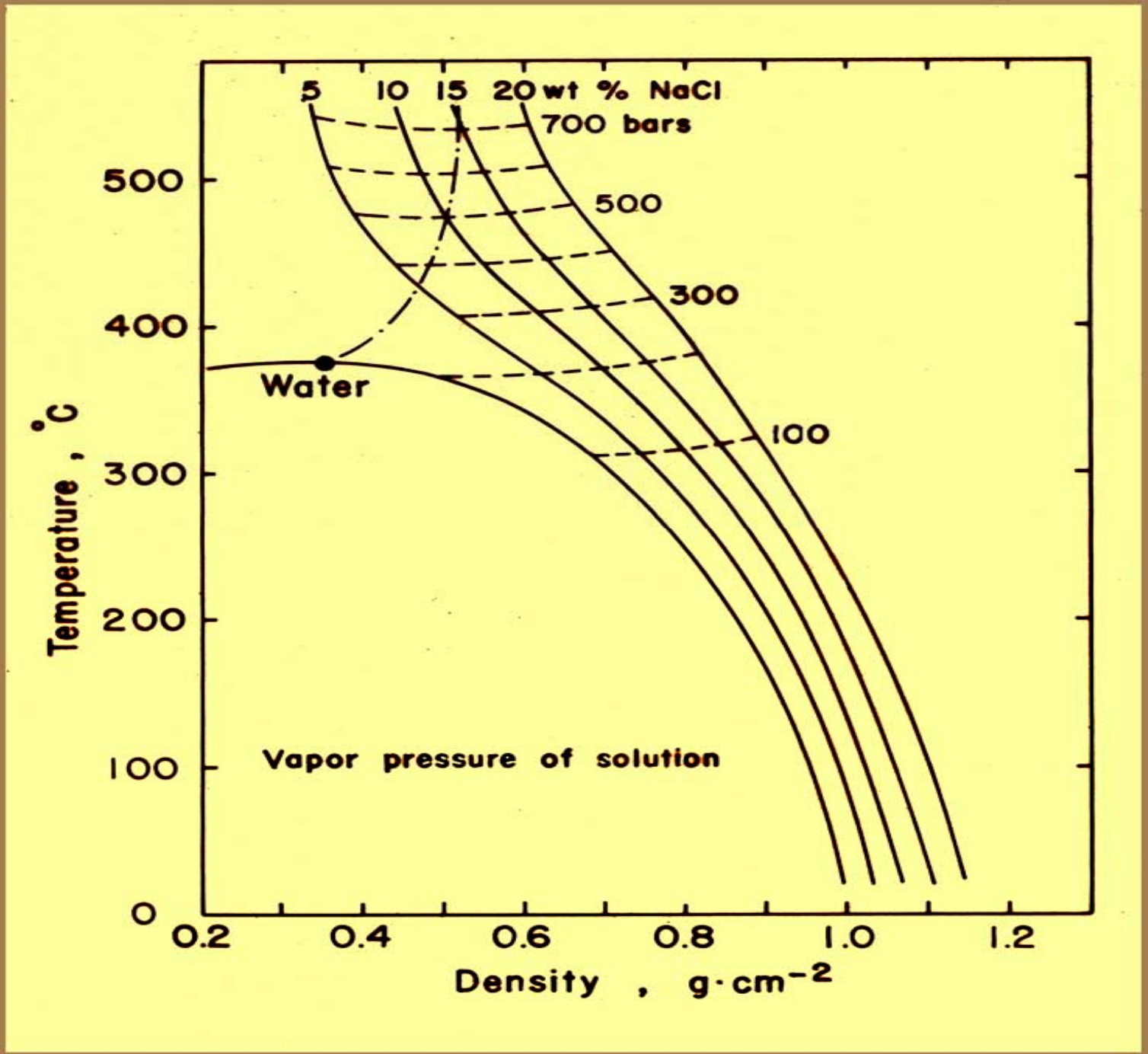
By

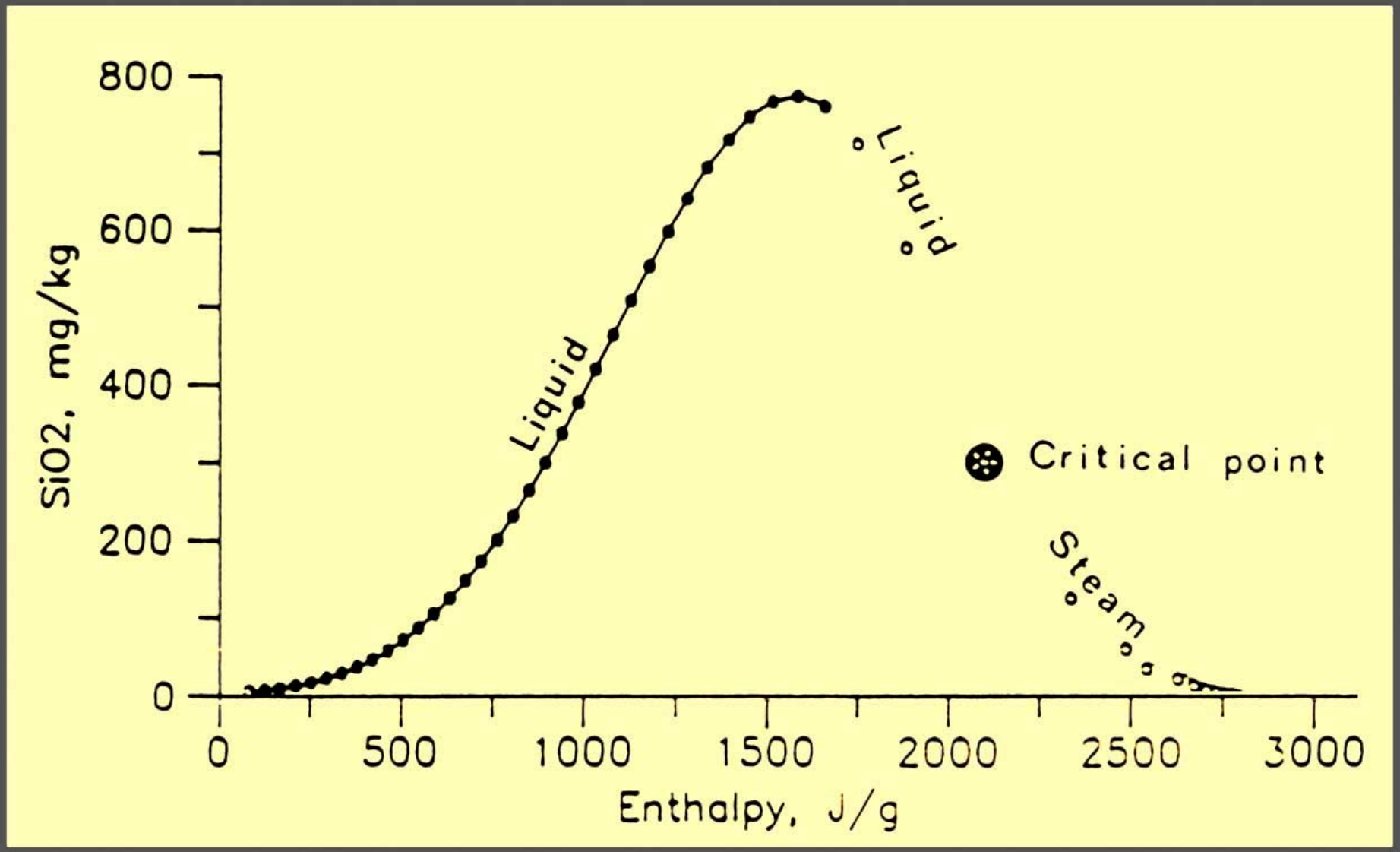
Robert Fournier

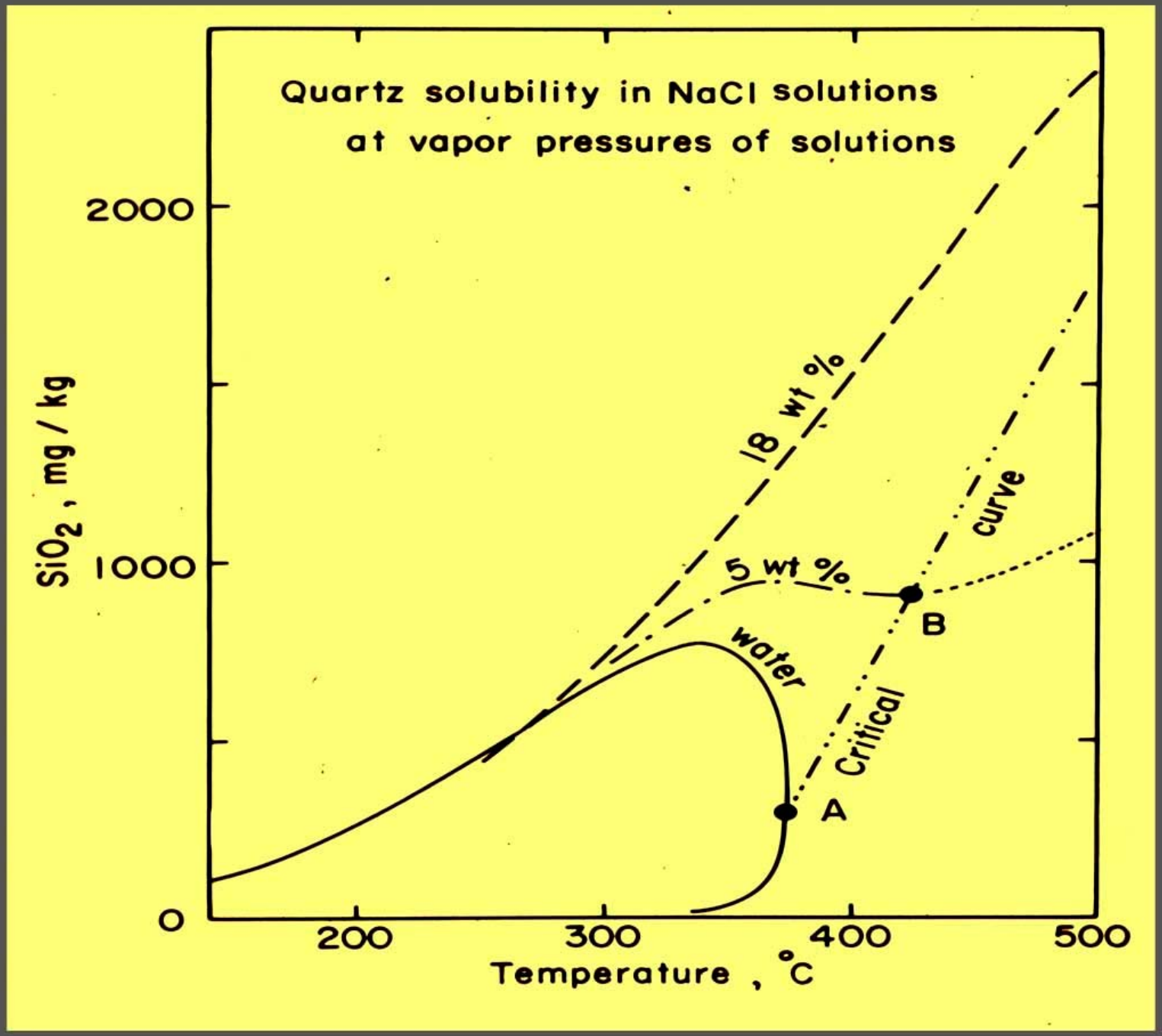

Acid-sulfate alteration
Vap.- dom.
Hydrostatic Pf
Dilute to moderate salinity
Brittle-plastic transition
Brine ± gas
Magmatic fluids
Lithostatic Pf
≈ 400°C
≈ 400°C

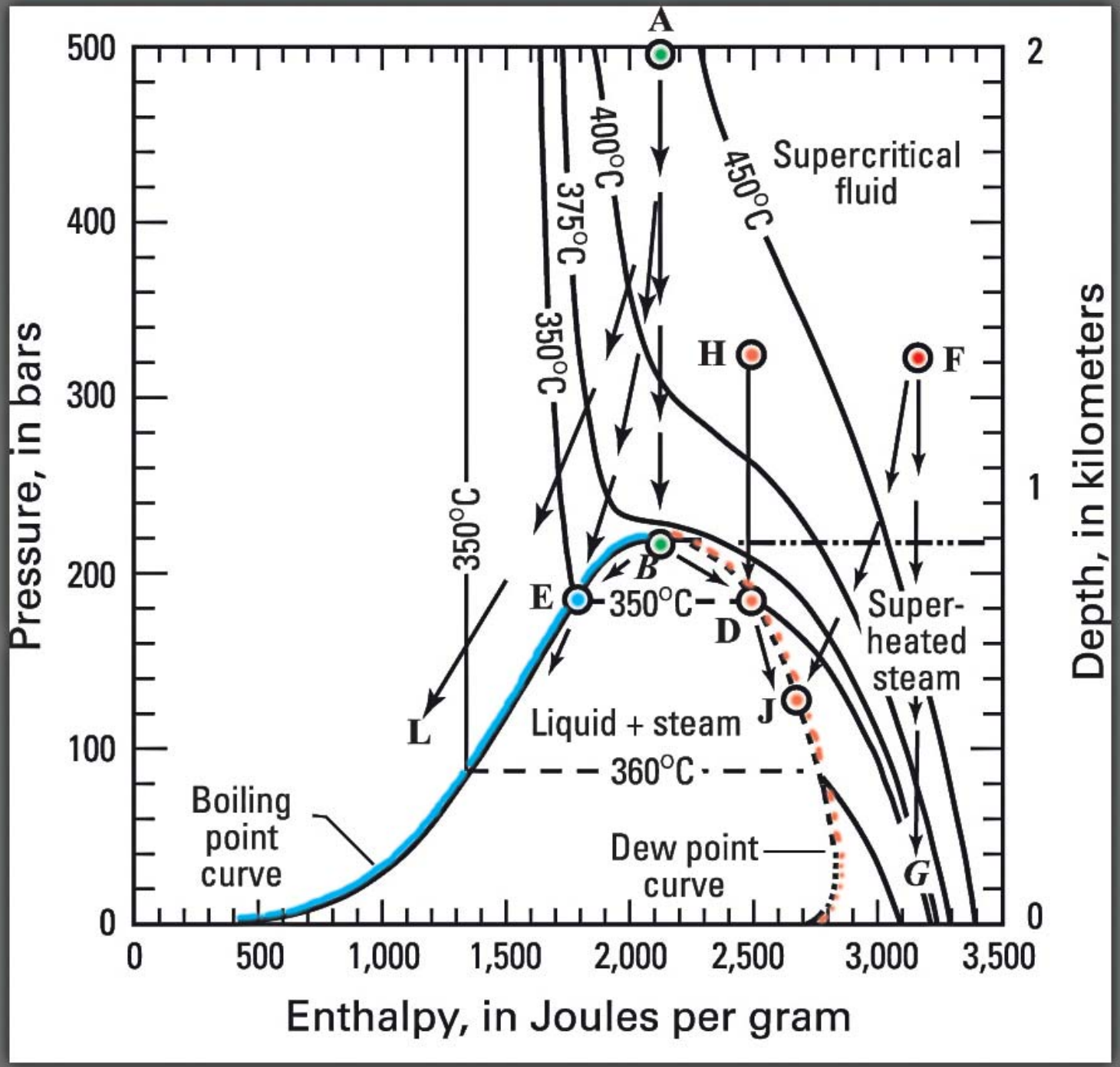

Acid-sulfate alteration
Vap.- dom.
Hydrostatic Pf
Dilute to moderate salinity
Deflation
Brittle-plastic transition
Brine ± gas
gas
Brine
Magmatic fluids
Lithostatic Pf
≈ 400°C
≈ 400°C

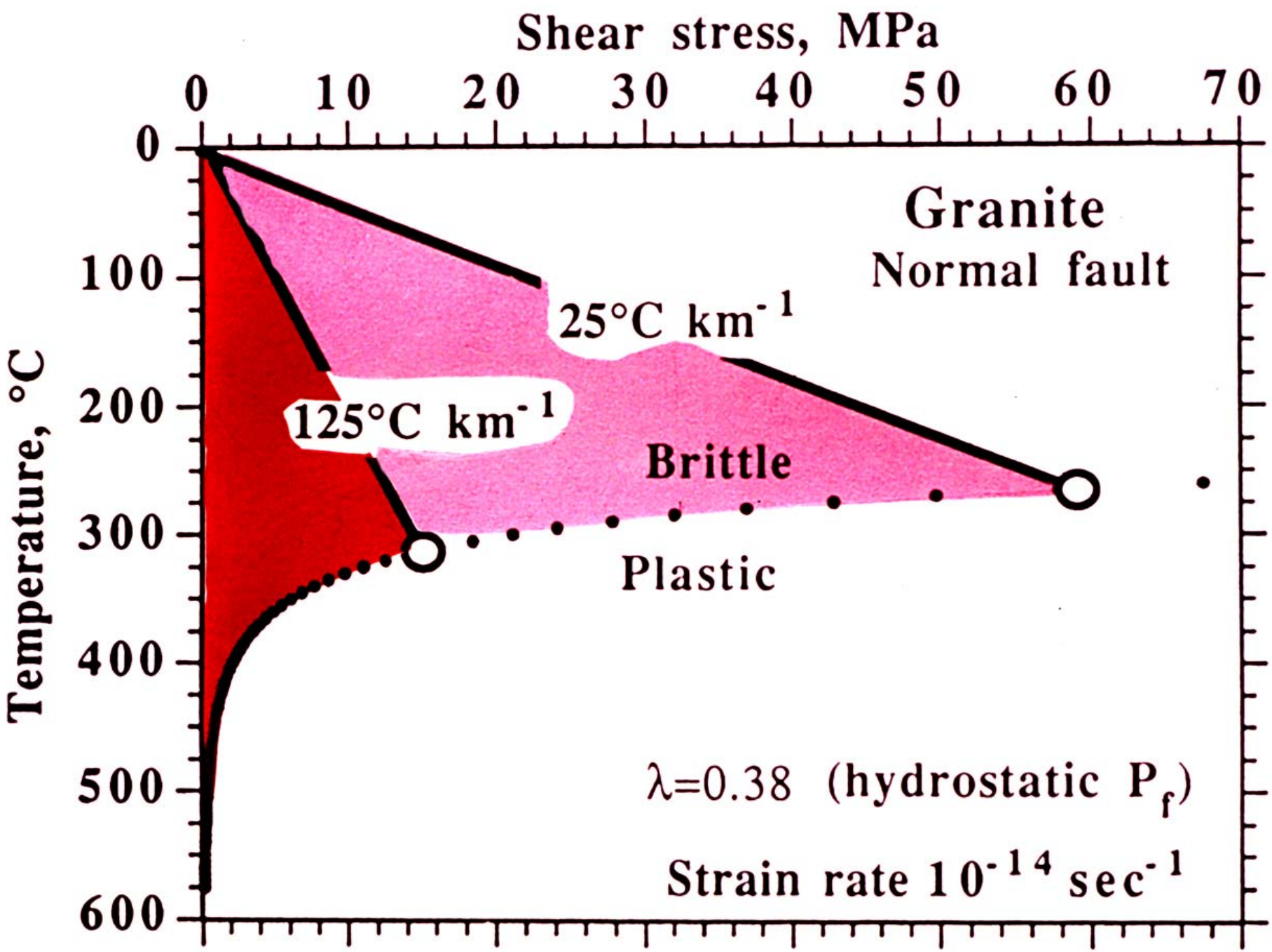

Acid-sulfate alteration
Acid-chloride alt.
Steam condensation
Gas
Hydrostatic Pf
Gas + brine
Brine
Brine


5 10 15 20 wt % NaCl
700 bars
500
300
100
Water
Vapor pressure of solution
Temperature , °C
0
100
200
300
400
500
0.2
0.4
0.6
0.8
1.0
1.2
Density , g·cm⁻²

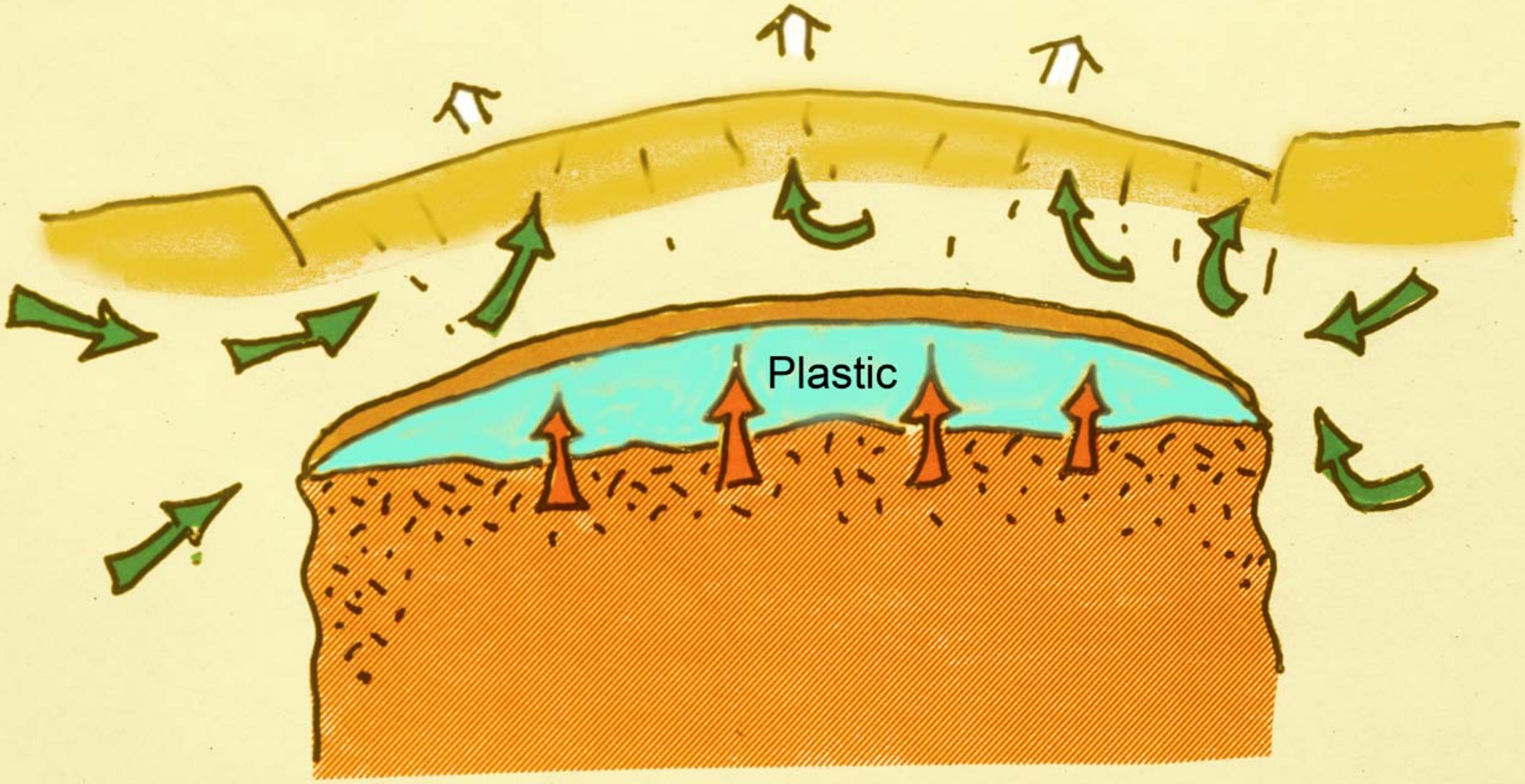

800
600
400
200
0
SiO2, mg/kg
Liquid
Liquid
Critical point
Steam
0
500
1000
1500
2000
2500
3000
Enthalpy, J/g


Quartz solubility in NaCl solutions
at vapor pressures of solutions
2000
1000
0
$SiO_2$, mg / kg
18 wt %
5 wt %
curve
B
water
Critical
A
200
300
400
500
Temperature, °C

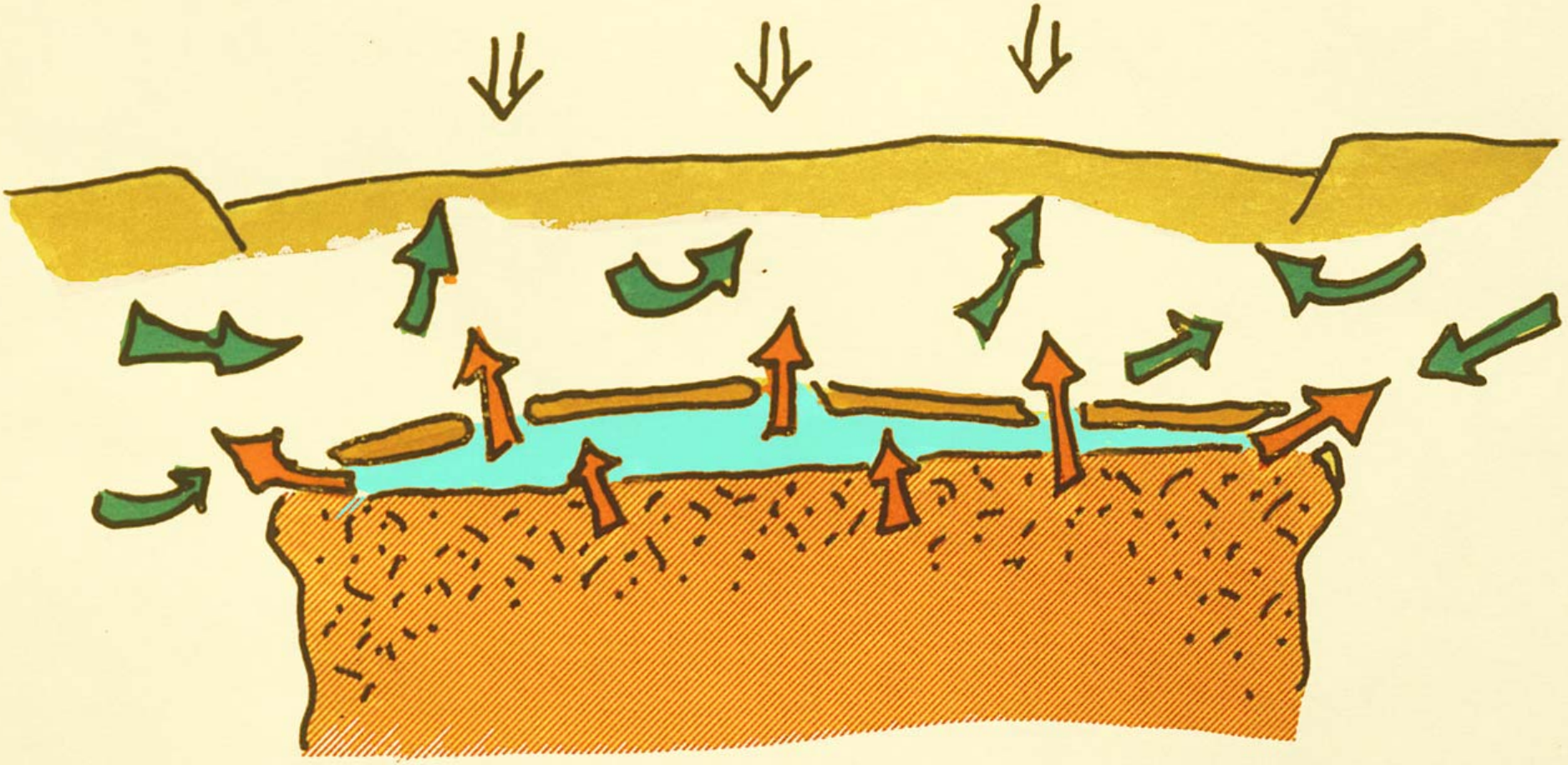

A
500
400
300
200
100
0
2
1
0
400°C
375°C
350°C
450°C
Supercritical fluid
H
F
350°C
B
E
350°C
D
Super-heated steam
J
L
Liquid + steam
360°C
Boiling point curve
Dew point curve
G
0
500
1,000
1,500
2,000
2,500
3,000
3,500
Pressure, in bars
Depth, in kilometers
Enthalpy, in Joules per gram


Shear stress, MPa
0
10
20
30
40
50
60
70
Temperature, °C
0
100
200
300
400
500
600
Granite
Normal fault
25°C km-1
125°C km-1
Brittle
Plastic
λ=0.38 (hydrostatic Pf)
Strain rate 10-14 sec-1

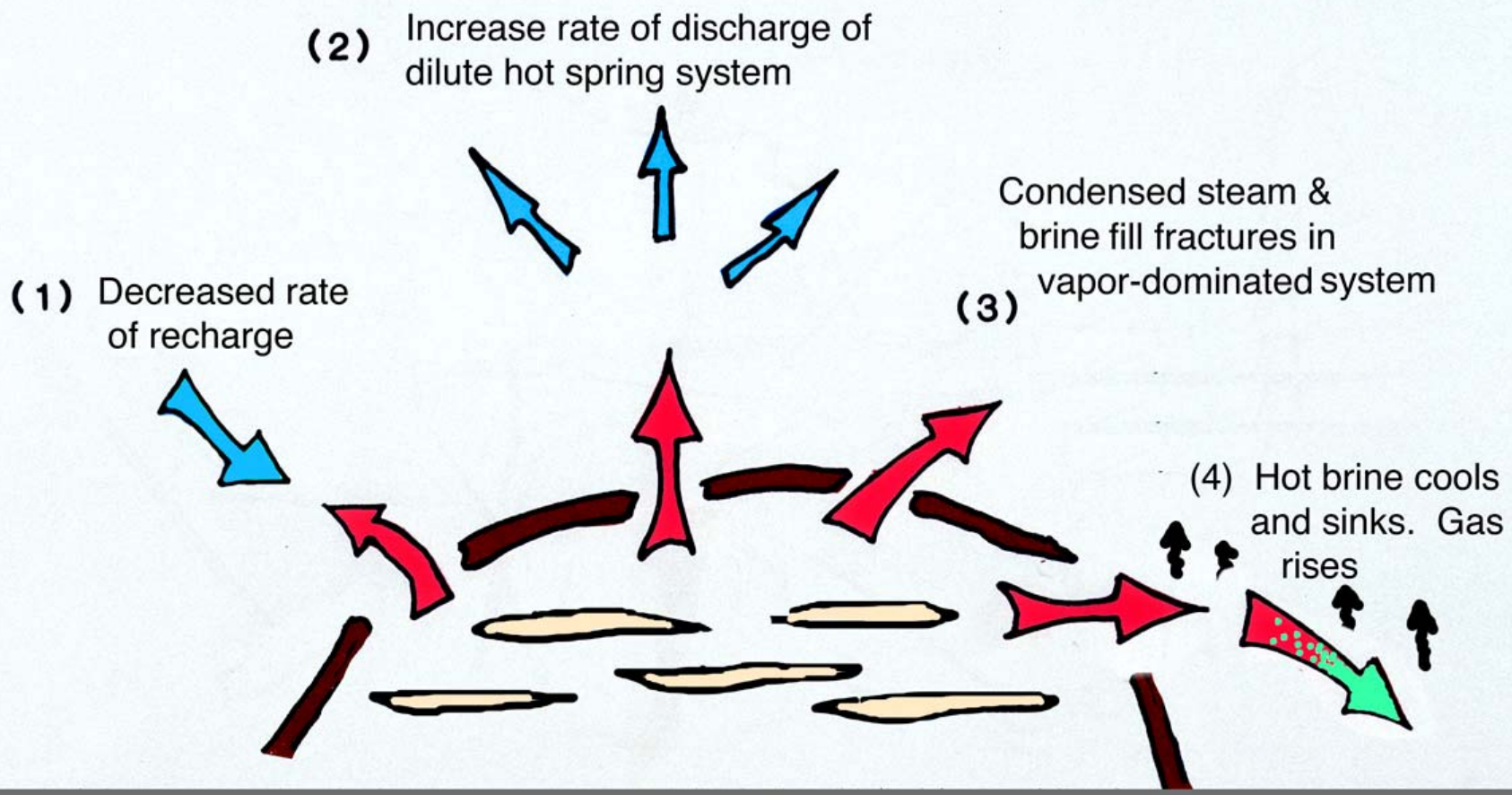
Inflation when magmatic fluids are trapped in plastic rock at lithostatic pressure

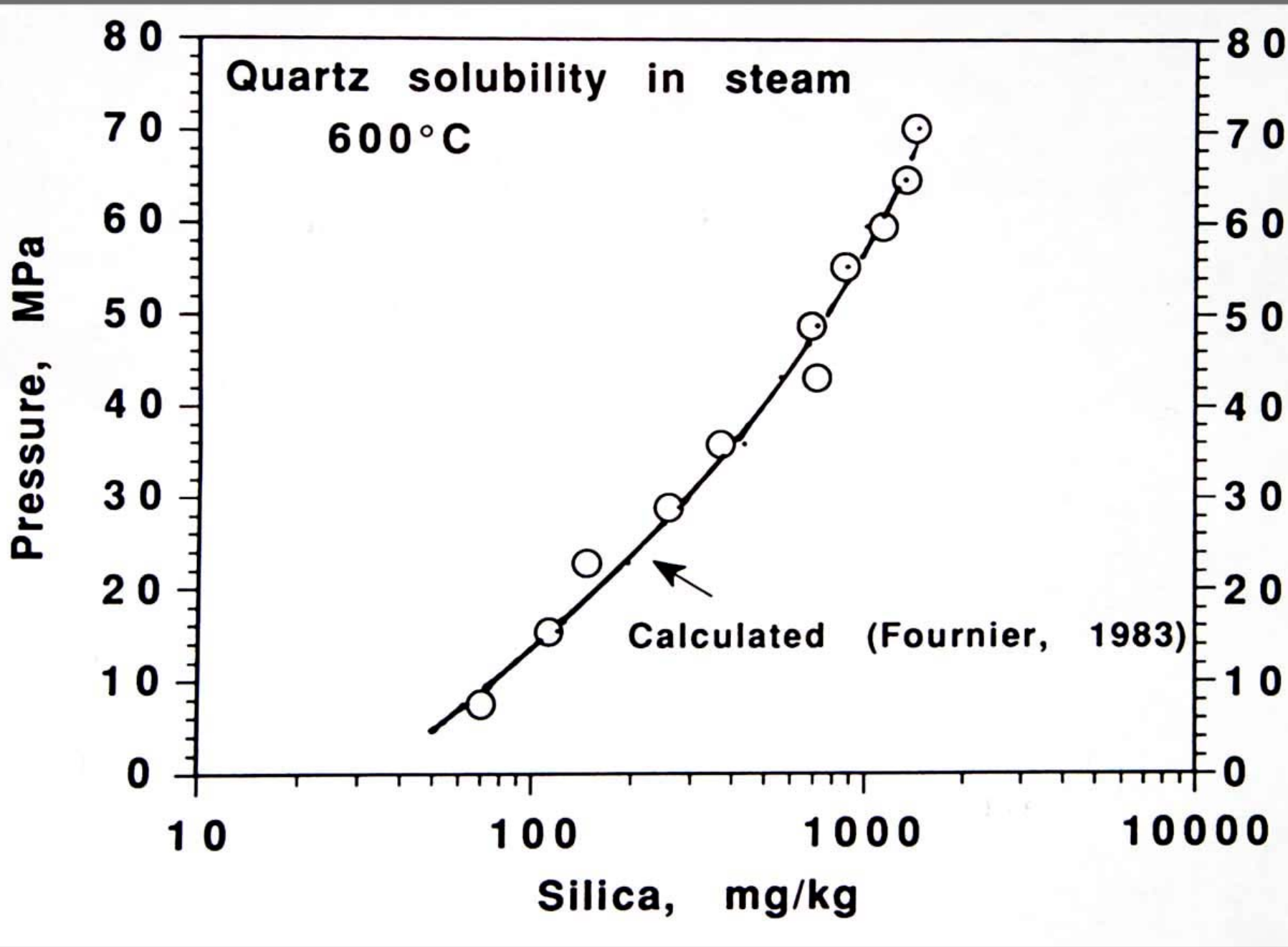


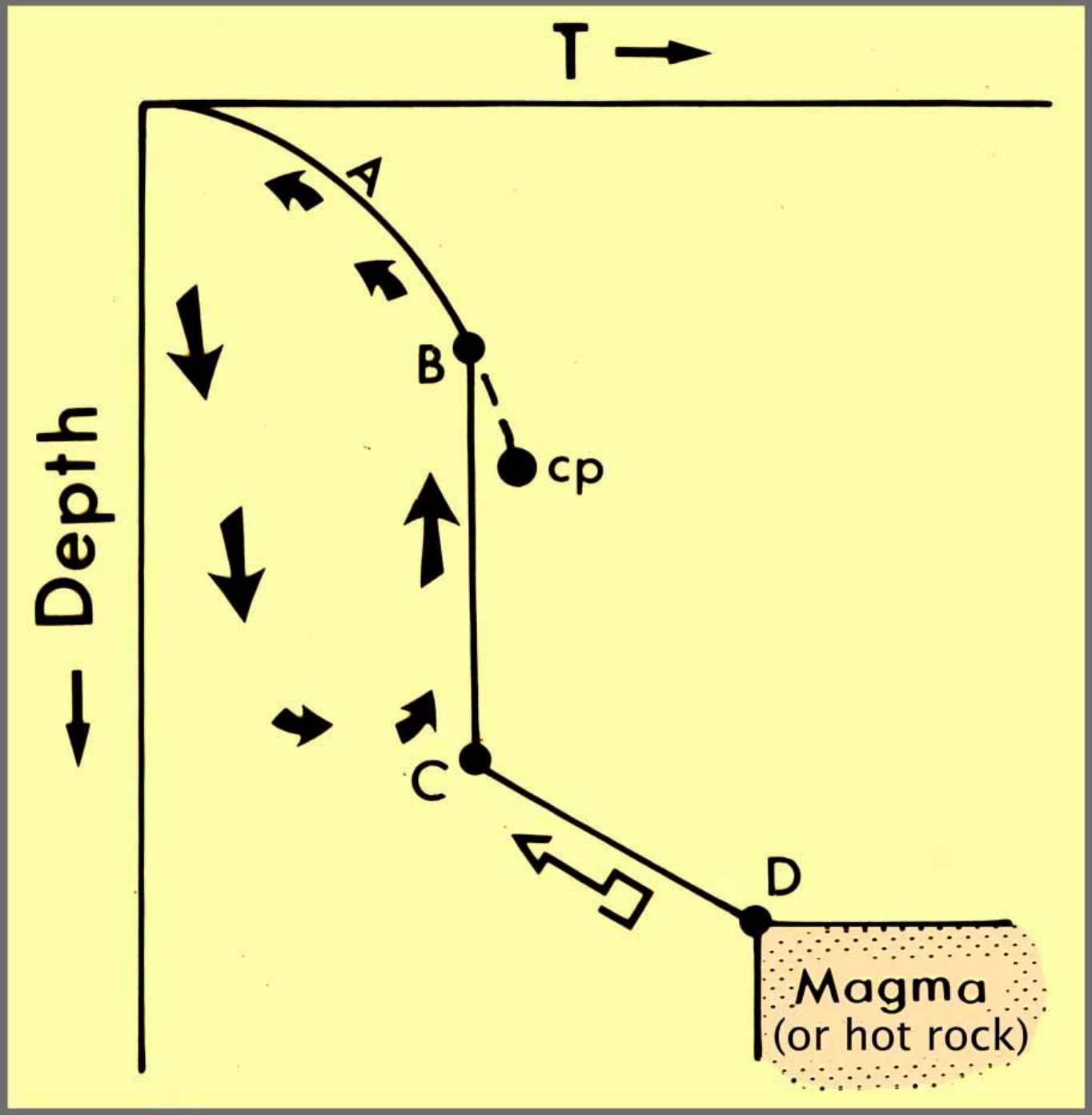
Deflation when significant leakage through seal occurs



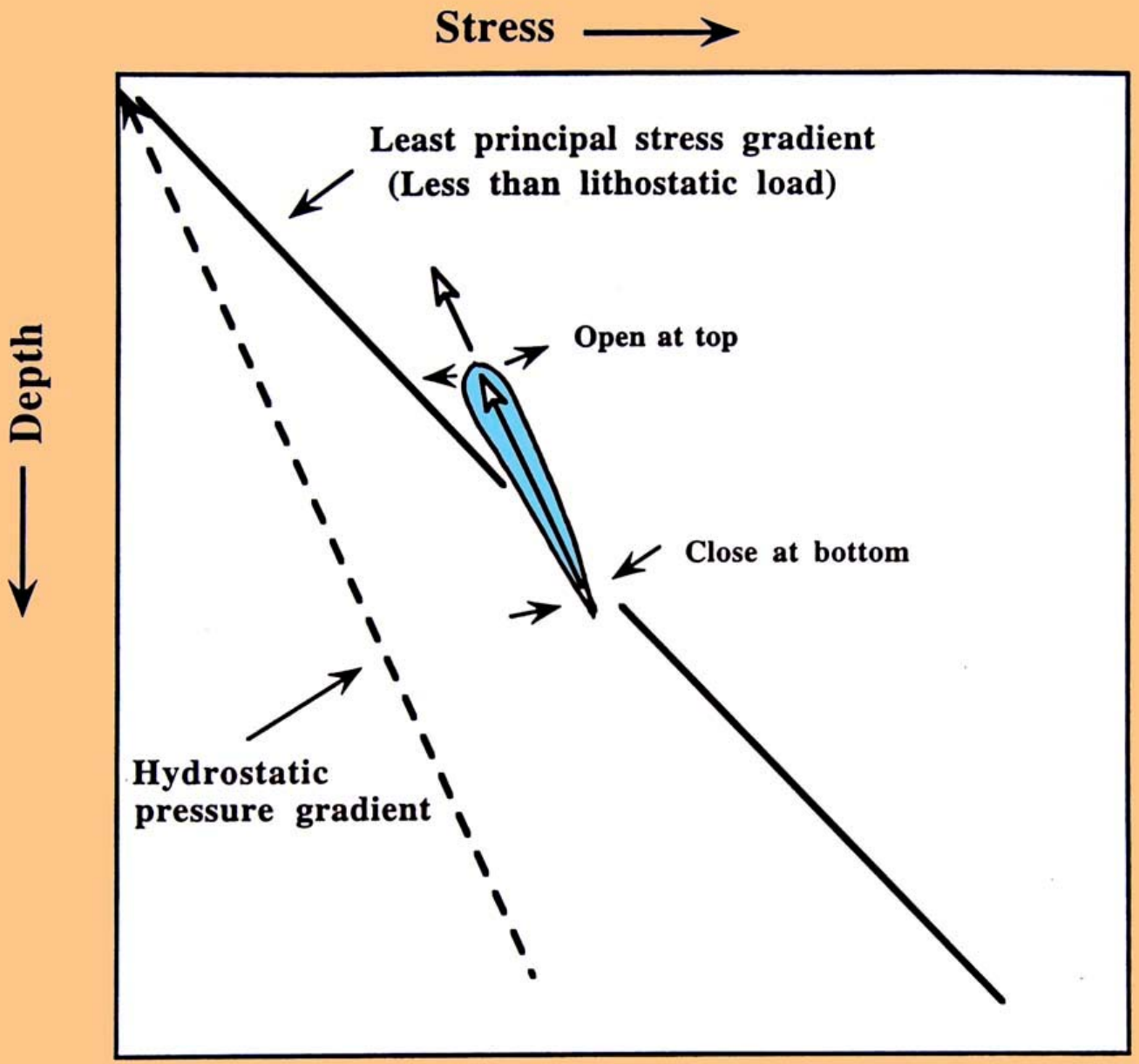
## Deflation by Break in High-Pressure Seal



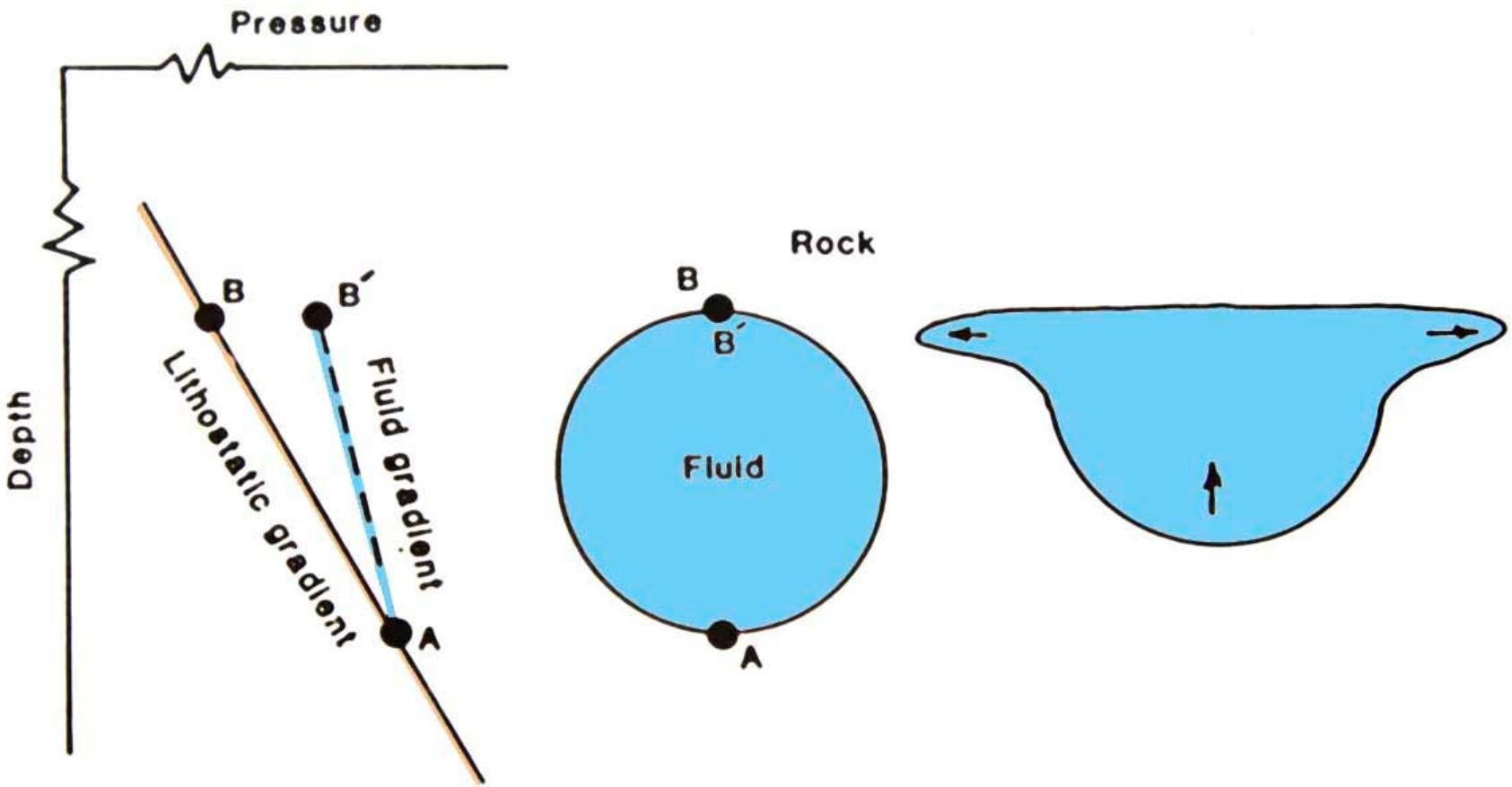

Quartz solubility in steam
600°C
Calculated (Fournier, 1983)
Pressure, MPa
Silica, mg/kg
0
10
20
30
40
50
60
70
80
10
100
1000
10000

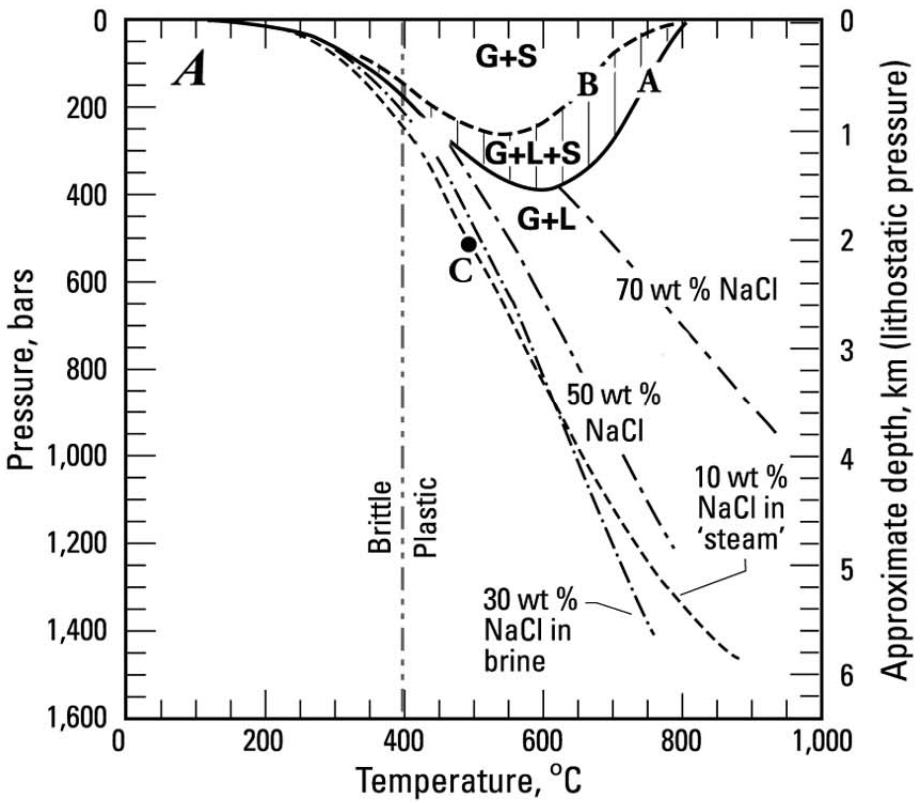

T
Depth
A
B
cp
C
D
Magma
(or hot rock)

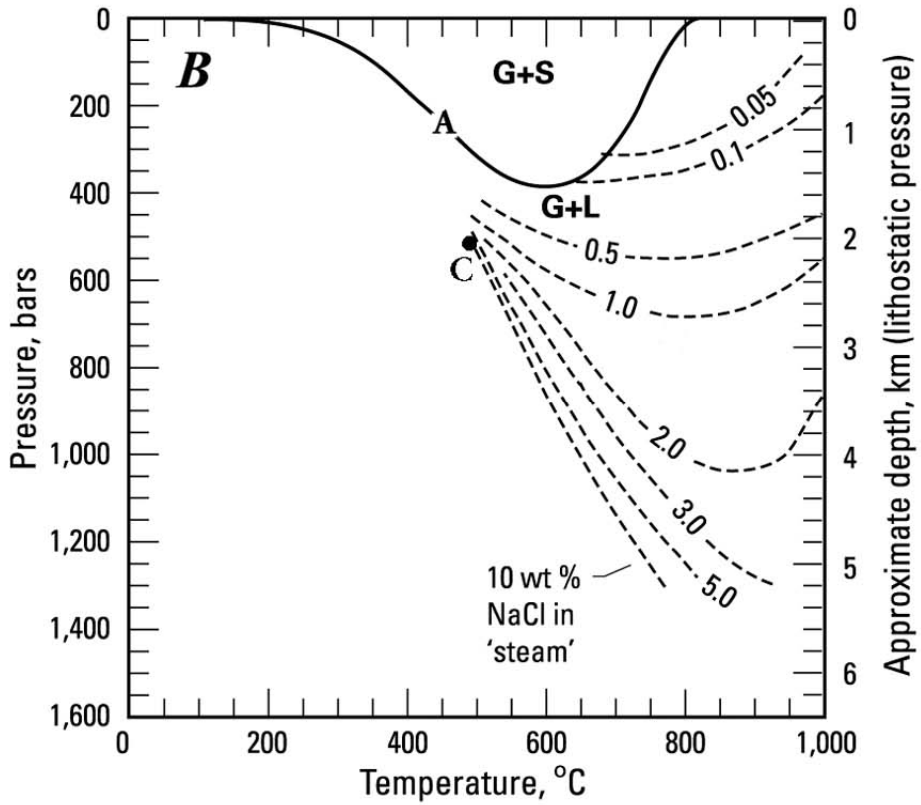
# Hydraulic Fracture Moves Upward By Opening At Top And Closing At Bottom



# Least Principal Stress is the Lithostatic Load




A
G+S
B
A
G+L+S
G+L
C
70 wt % NaCl
50 wt %
NaCl
10 wt %
NaCl in
'steam'
30 wt %
NaCl in
brine
Brittle
Plastic
Pressure, bars
Approximate depth, km (lithostatic pressure)
Temperature, °C
0
200
400
600
800
1,000
1,200
1,400
1,600
1
2
3
4
5
6


B
G+S
A
0.05
0.1
G+L
0.5
C
1.0
2.0
3.0
5.0
10 wt %
NaCl in
'steam'
Pressure, bars
Approximate depth, km (lithostatic pressure)
Temperature, °C
0
200
400
600
800
1,000
1,200
1,400
1,600
1
2
3
4
5
6