In Deep Water: New Insights into Geologic Fluids of the Deep Crust and Upper Mantle

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UCLA PTX LAB experimental petrology

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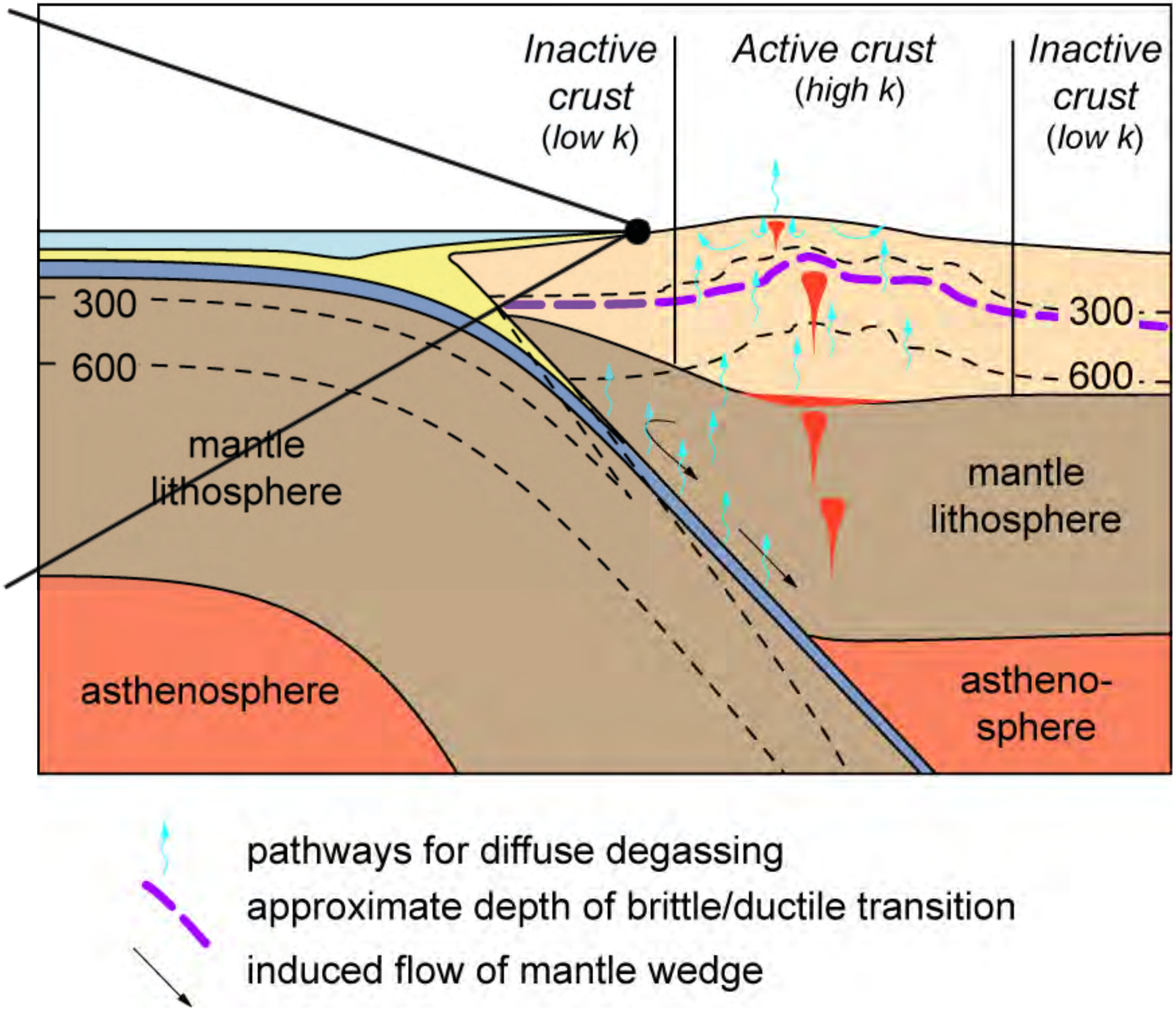
How deep is “deep”?



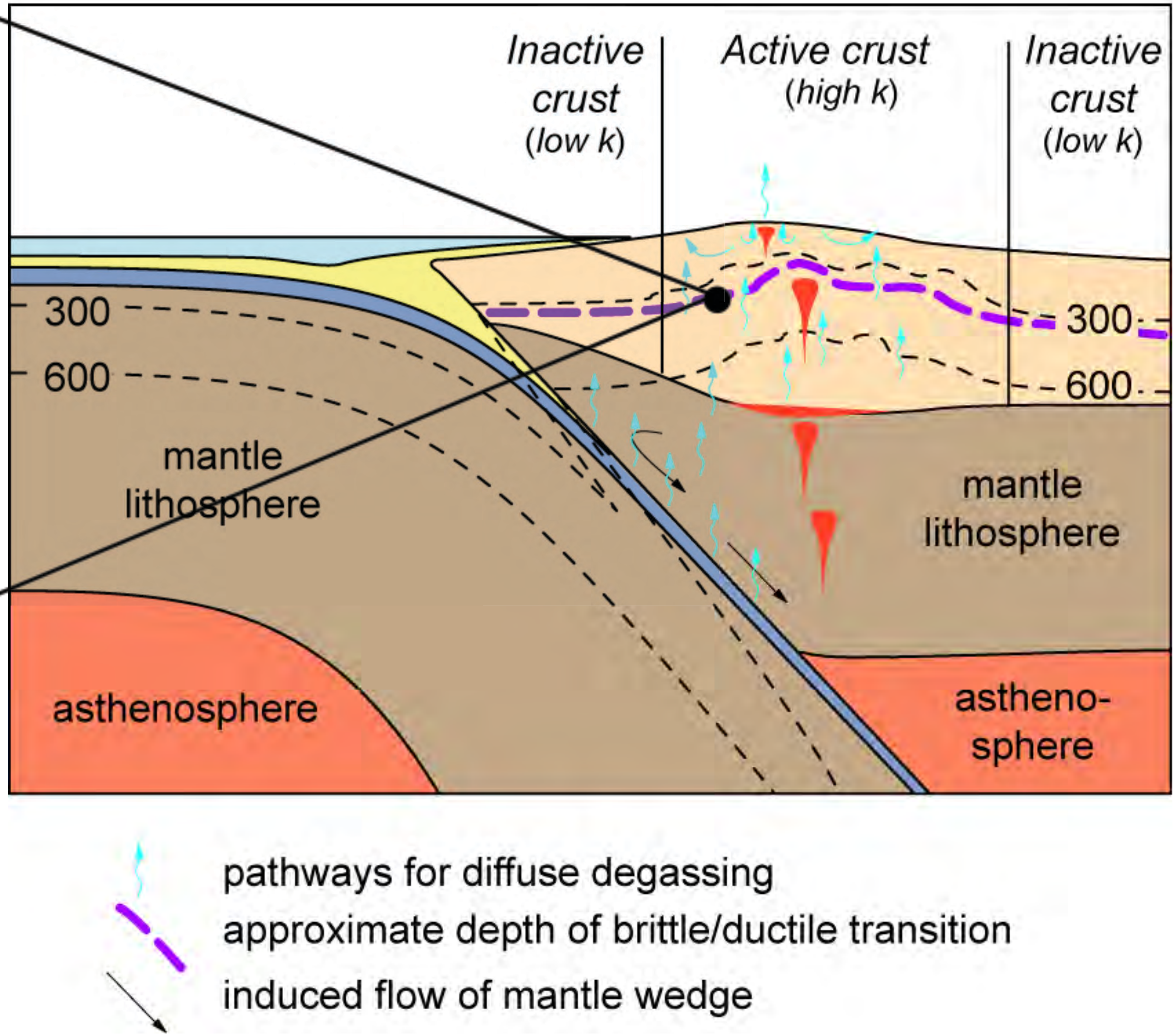
Surface & shallow subsurface:

Na^{+} Cl^{-} $Al(OH)_2^{+}$ $Al(OH)_4^{-}$

SiO_{2aq}

How deep is "deep"?

Metamorphism near brittle/ductile transition (~15 km):
NaCl° $Al(OH)_3$ SiO_{2aq}

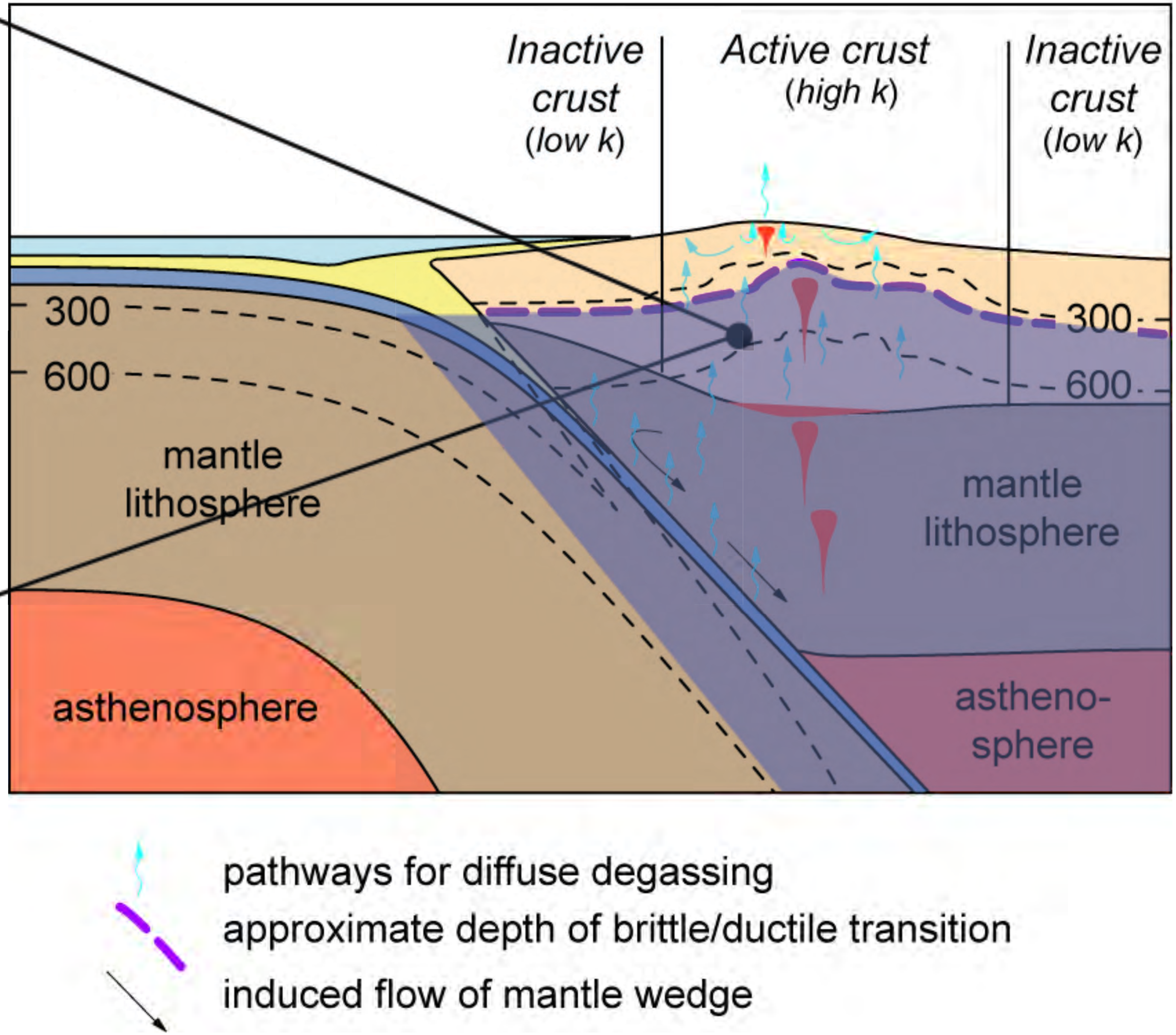


How deep is "deep"?

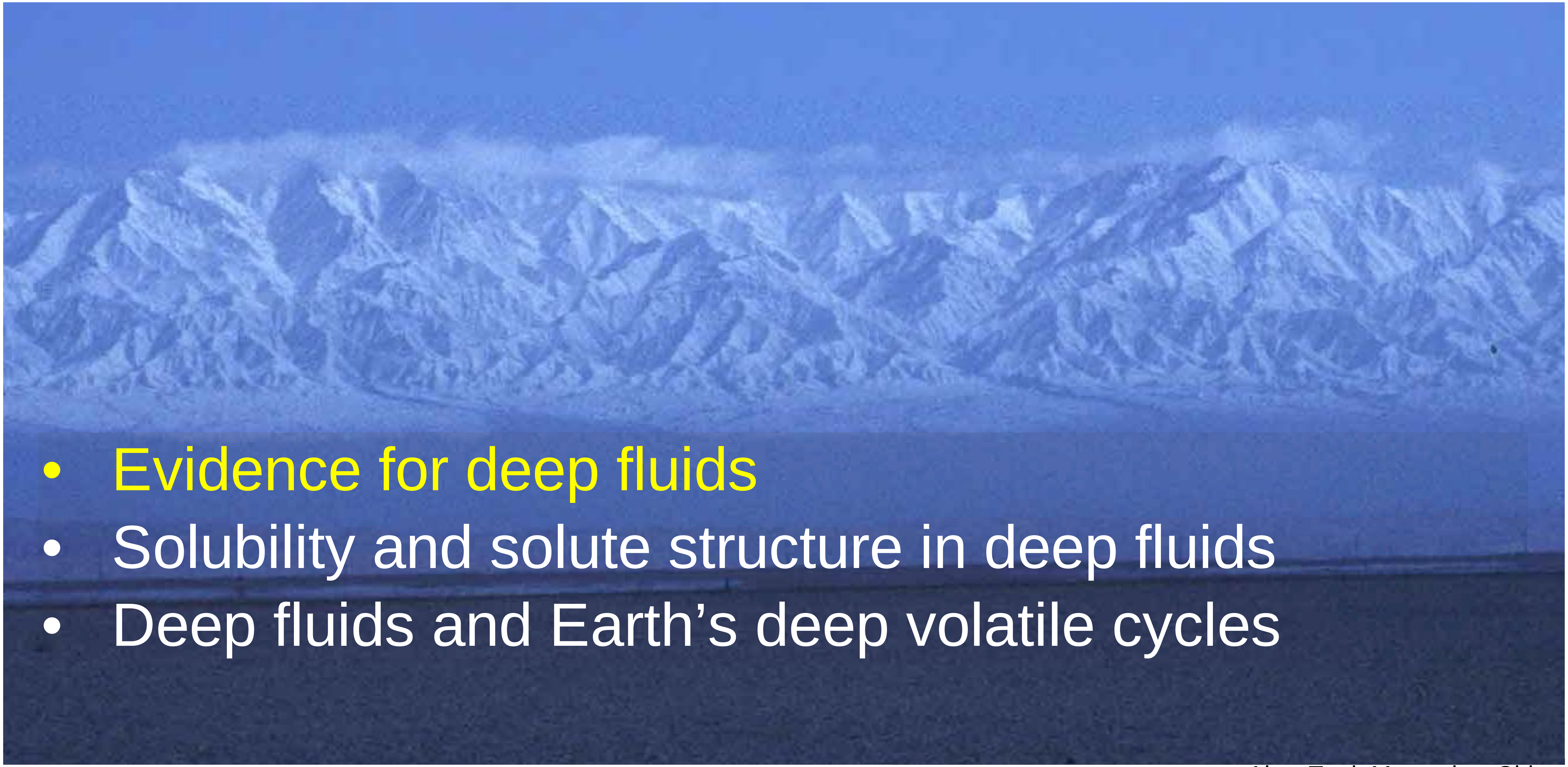
Major mass transfer in Barrovian metamorphsim

Metamorphism deeper than brittle/ductile transition (~15 km):

?



Outline

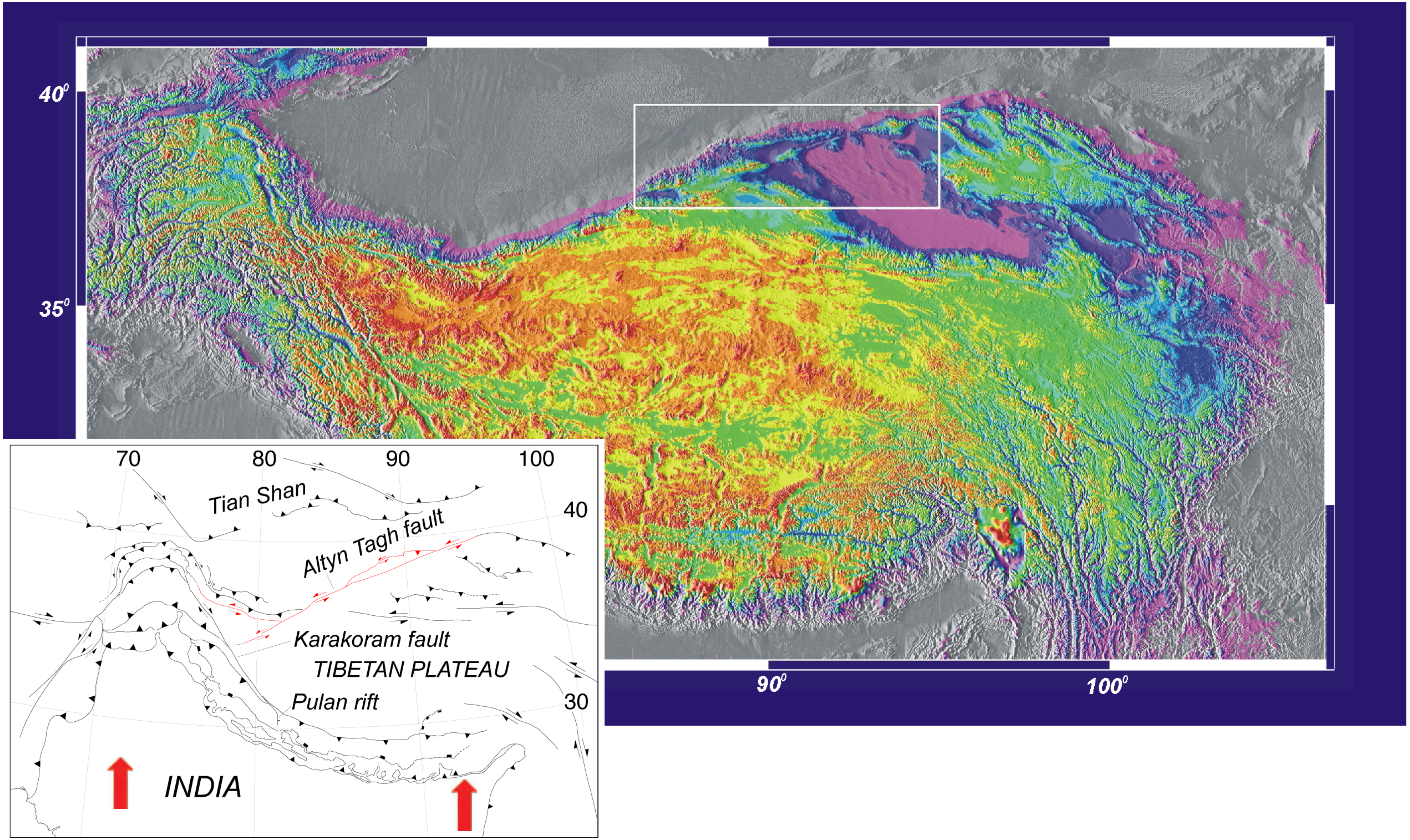


- Evidence for deep fluids
- Solubility and solute structure in deep fluids
- Deep fluids and Earth’s deep volatile cycles

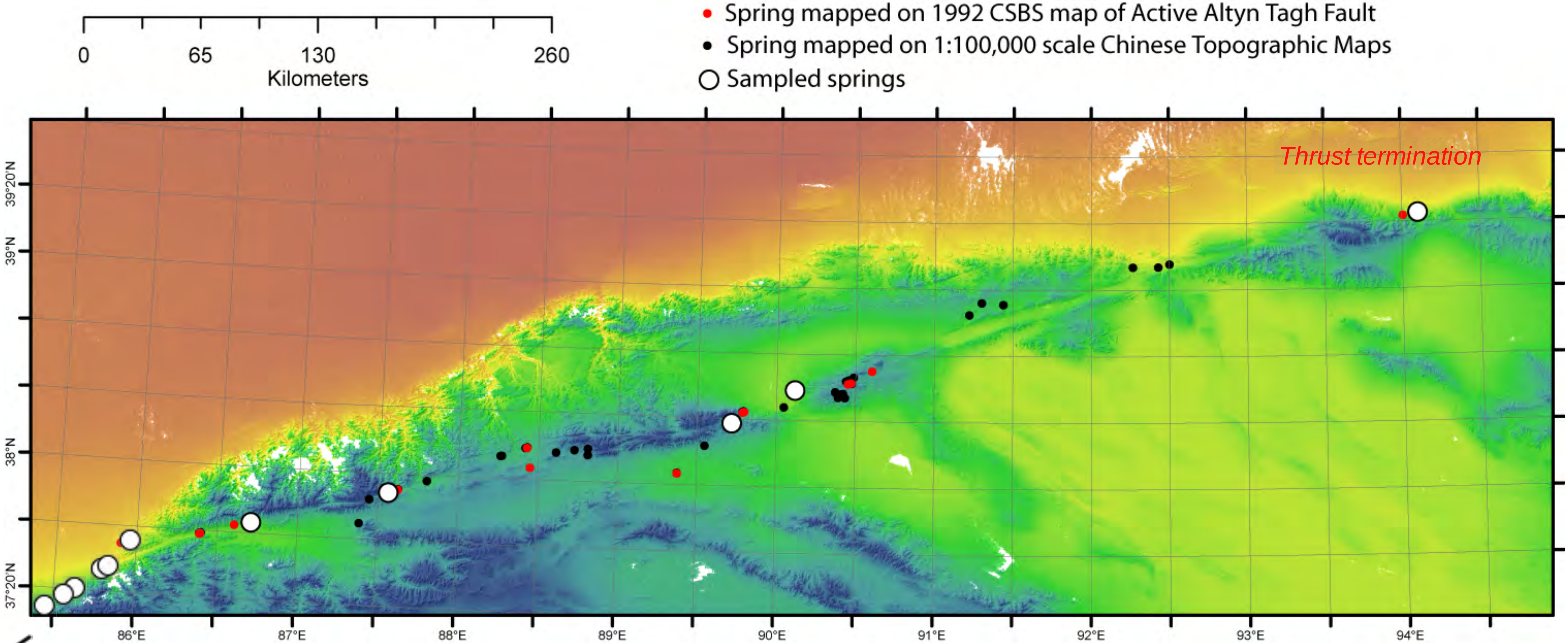
Altyn Tagh Mountains, China

How deep?

Faults, fluids, and scale of flow: the Altyn Tagh fault, China



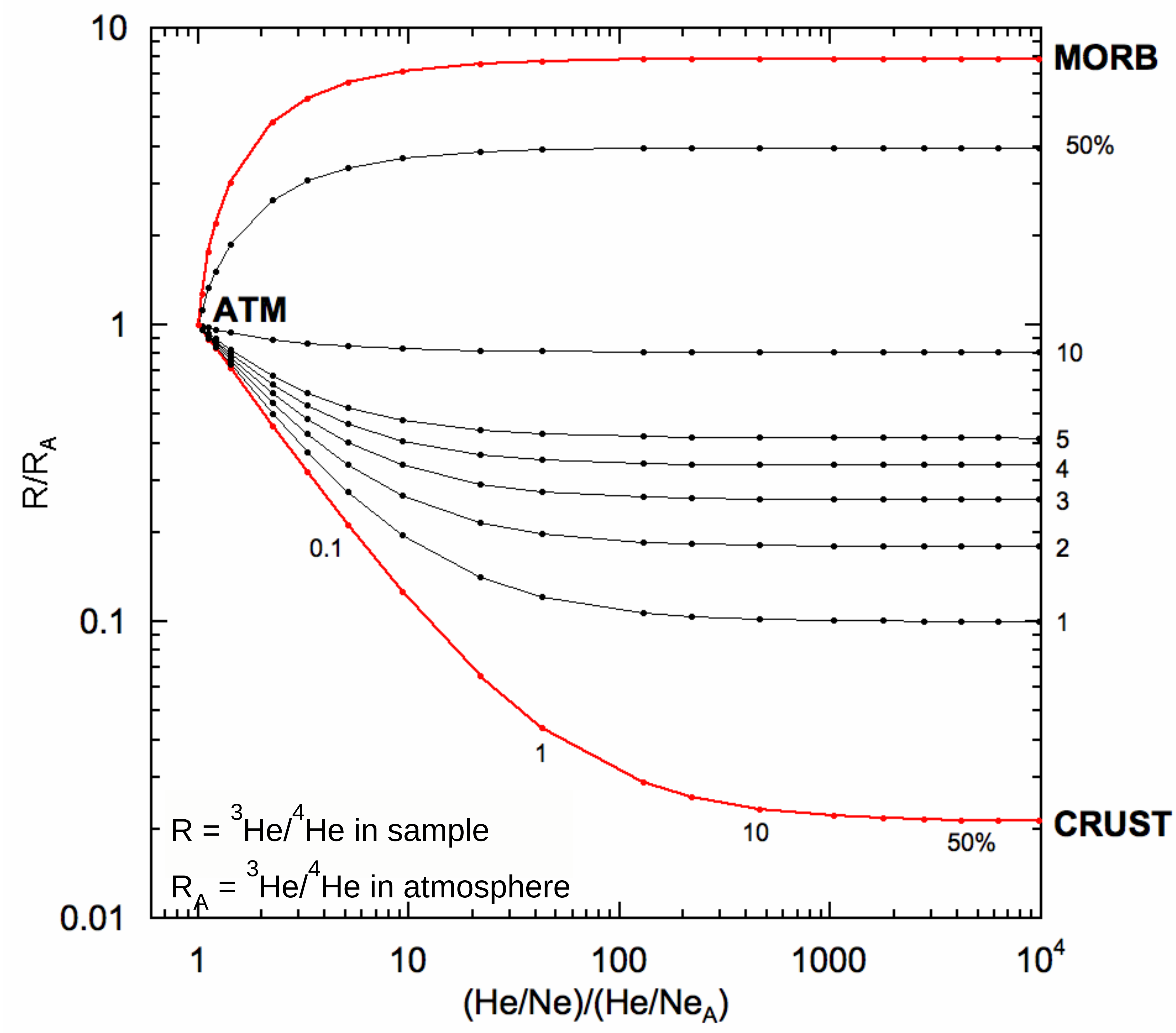
Faults and deep fluids



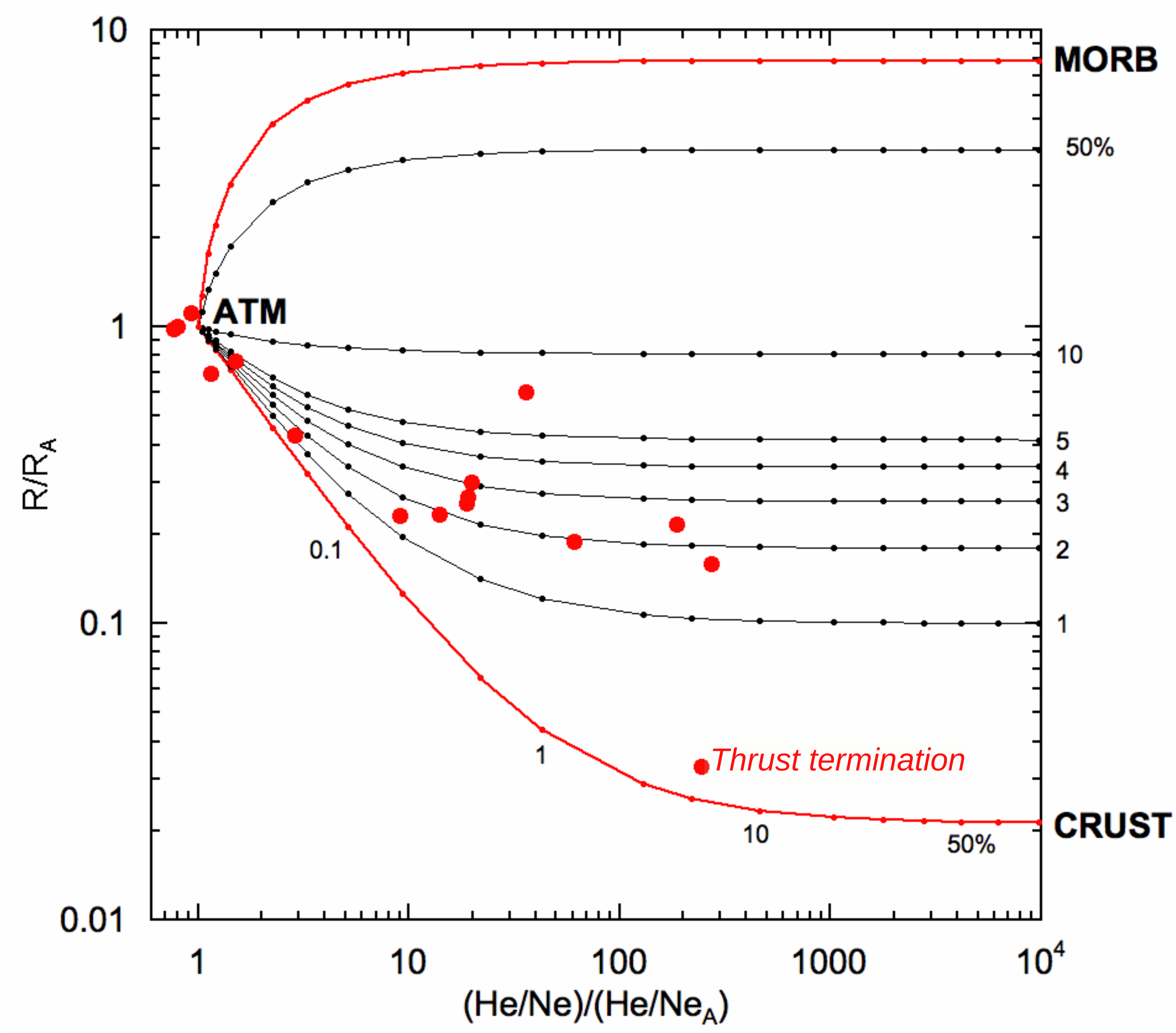
3 samples

Faults and deep fluids

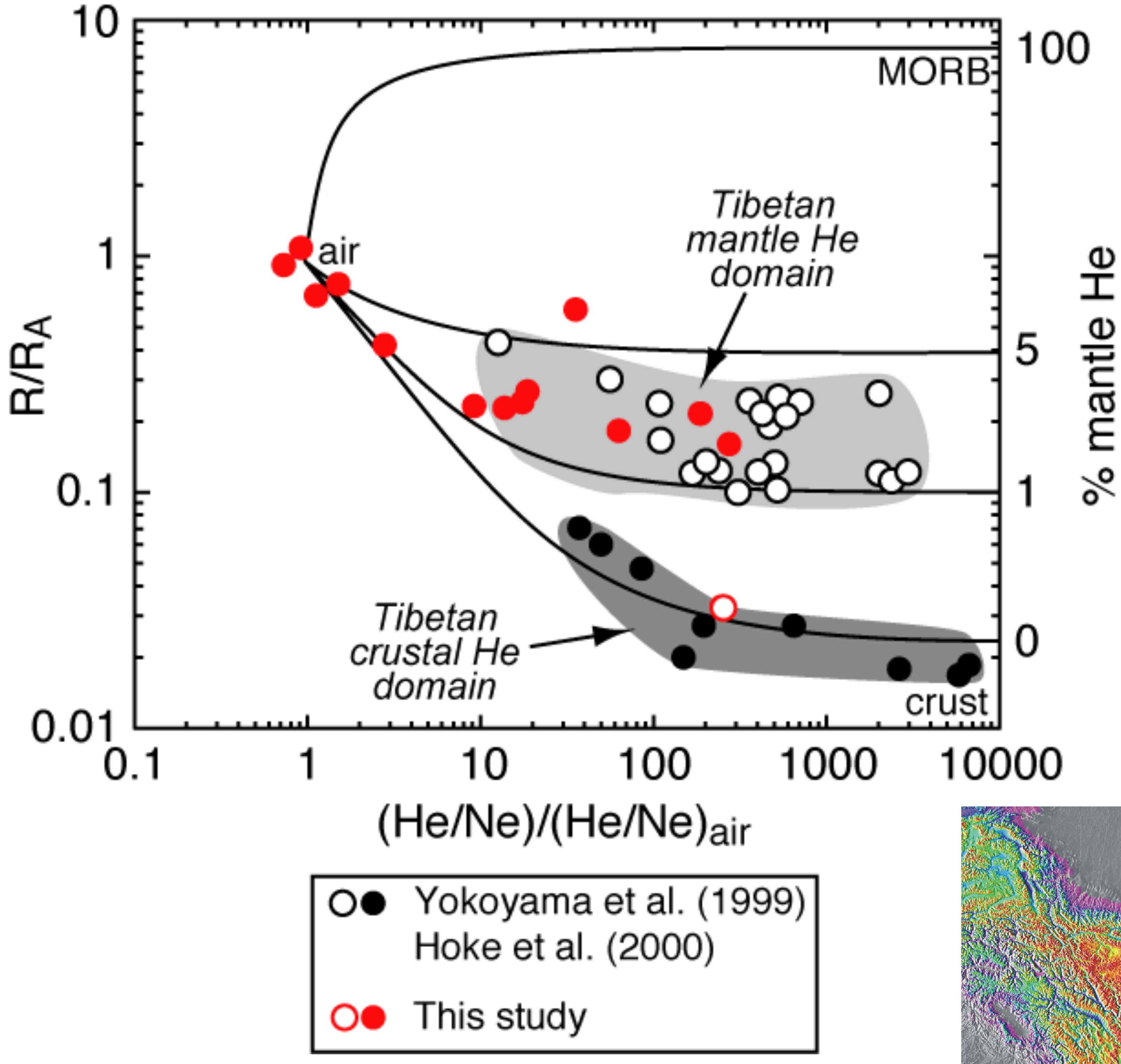
Faults and deep fluids

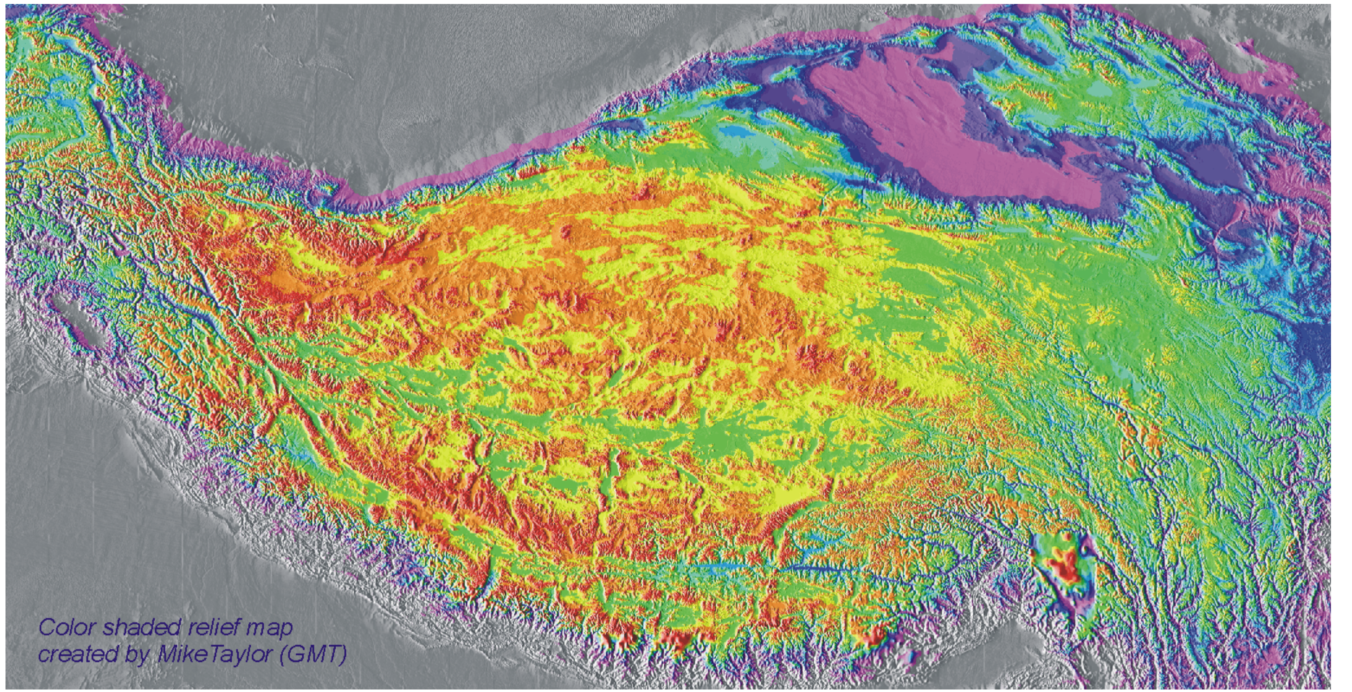


Faults and deep fluids

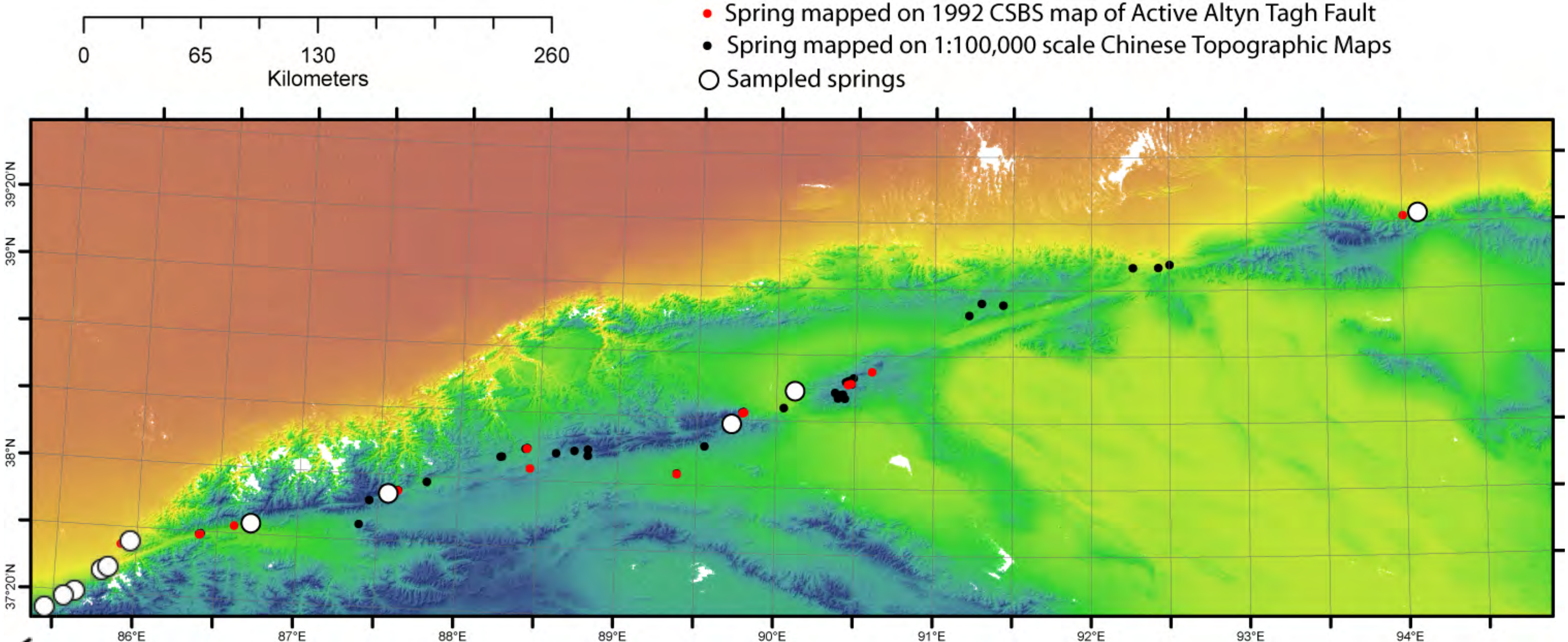


Faults and deep fluids





Faults and deep fluids

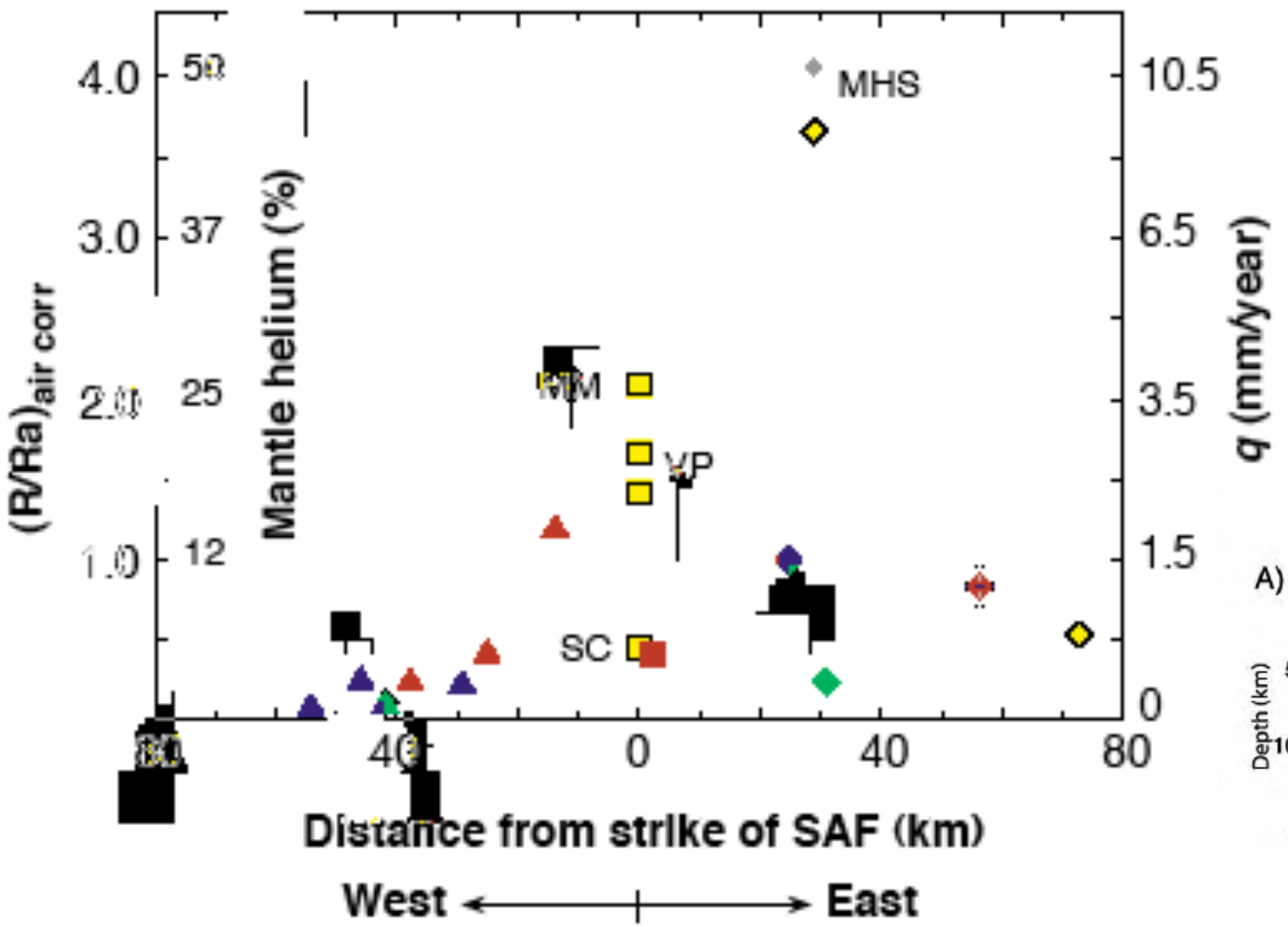


3 samples

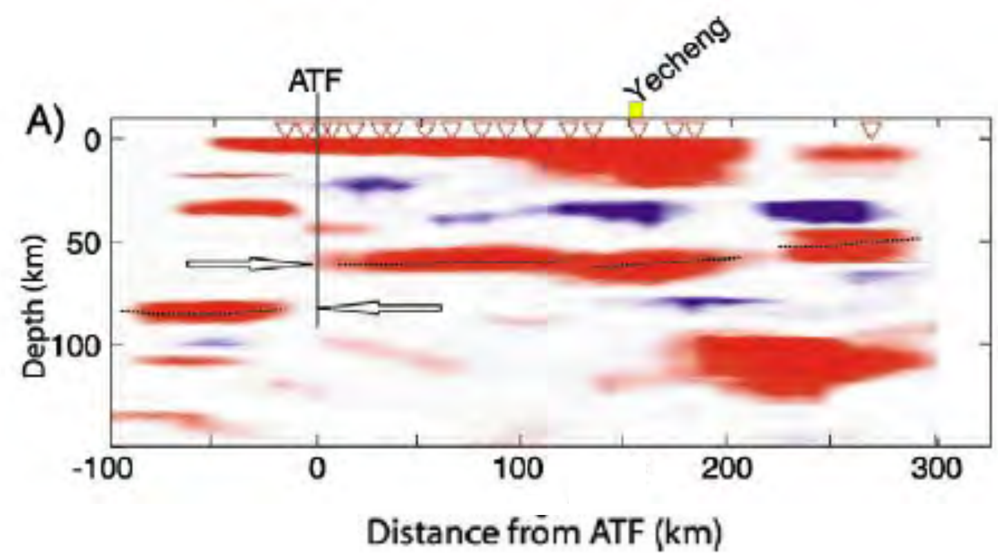
-no correlation with geology
-no recent volcanics
Conclusion: Altyn Tagh springs sample deep crust & mantle fluids

Faults and deep fluids

San Andreas vs. Altyn Tagh



$$q = \frac{H_{crust}\,\rho_s P(\mathrm{He})}{\rho_f [^4\mathrm{He}]_{f,mantle}} \times \left[\frac{(R/Ra)_{meas} - (R/Ra)_{crust}}{(R/Ra)_{mantle} - (R/Ra)_{meas}}\right]$$

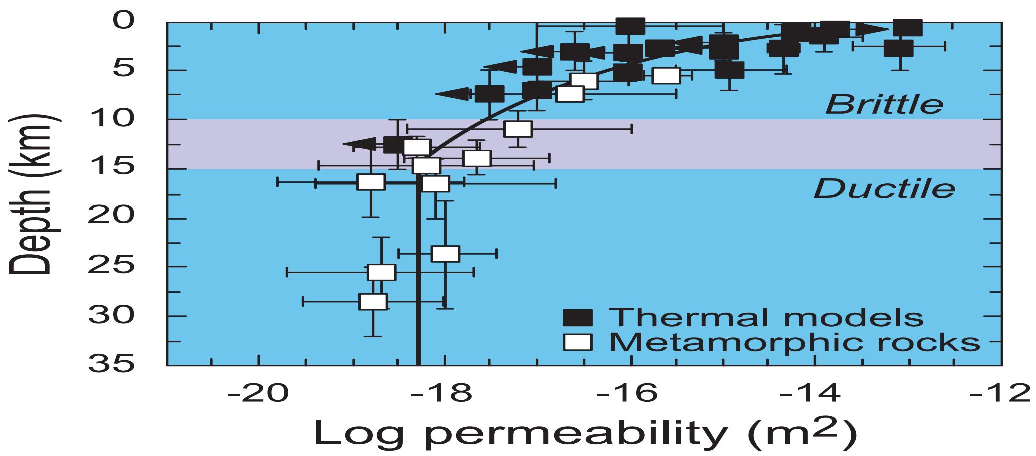


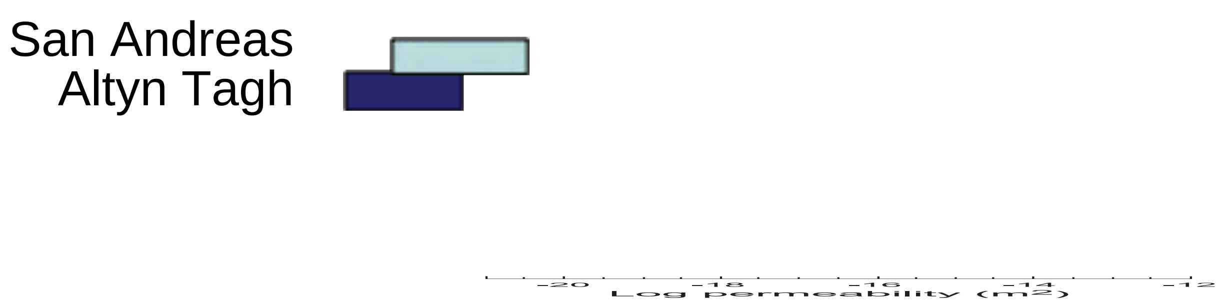
Kennedy et al (1997), Pili et al (2011)

Wittlinger et al (1997)

Faults and deep fluids

Average permeability of “active” crust

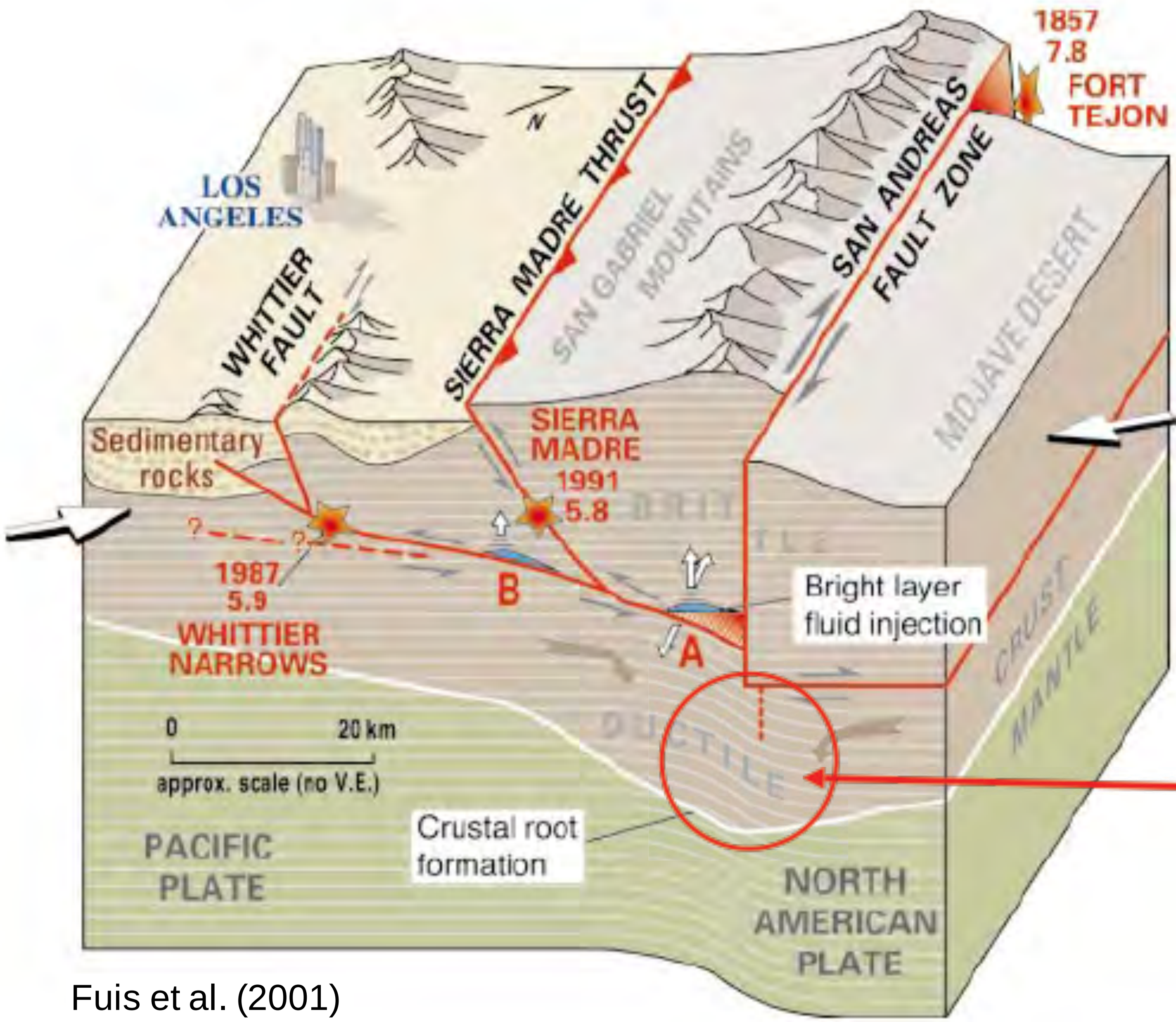




Ingebritsen & Manning (2002)

Faults and deep fluids

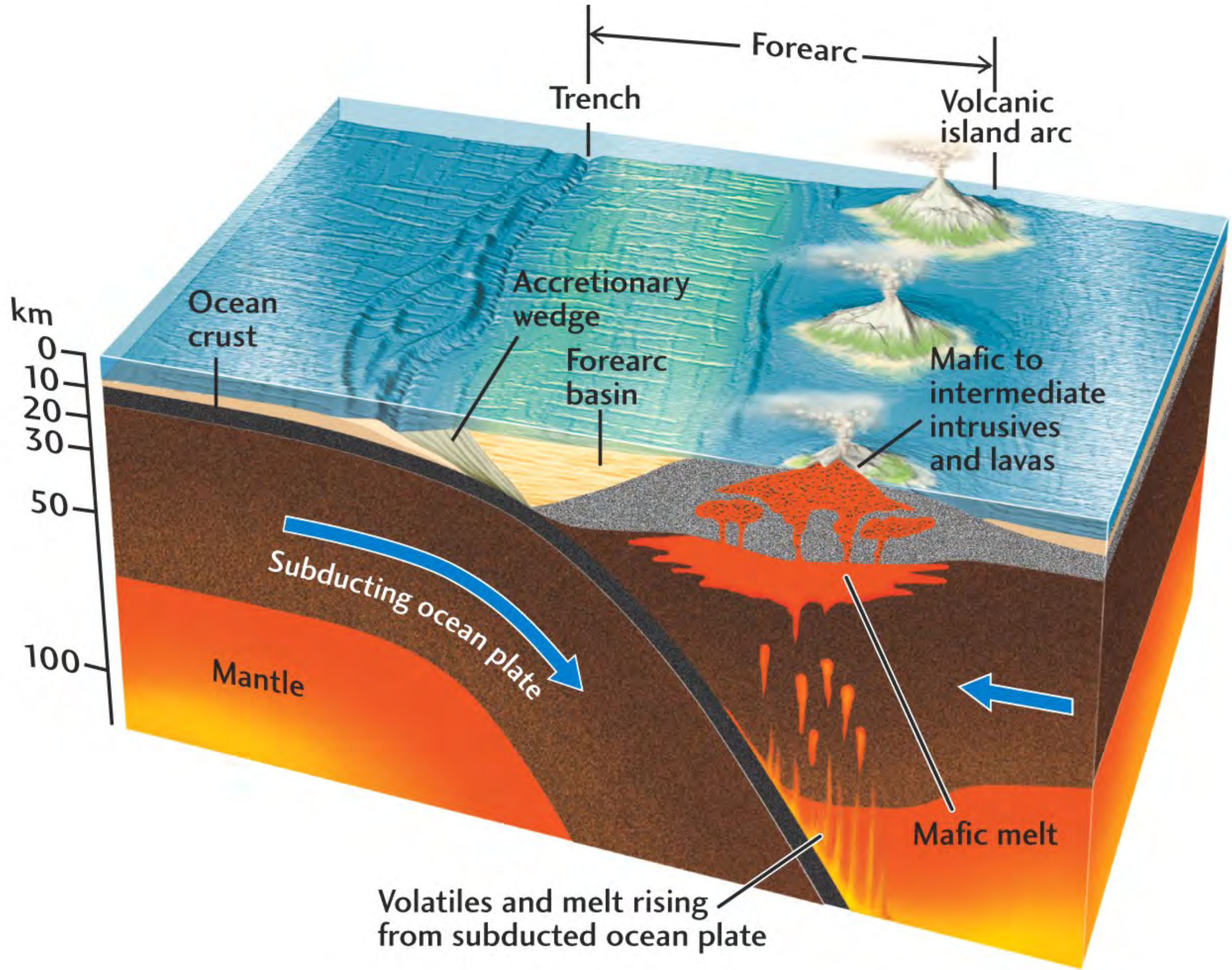
Mantle-derived ^{3}He implies crustal-scale permeability



Fuis et al. (2001)

Elevated ^{3}He suggests crustal-scale faults...

- Evidence for deep fluids
- Deep fluids: solubility and solute structure
- Deep fluids and Earth’s deep volatile cycles

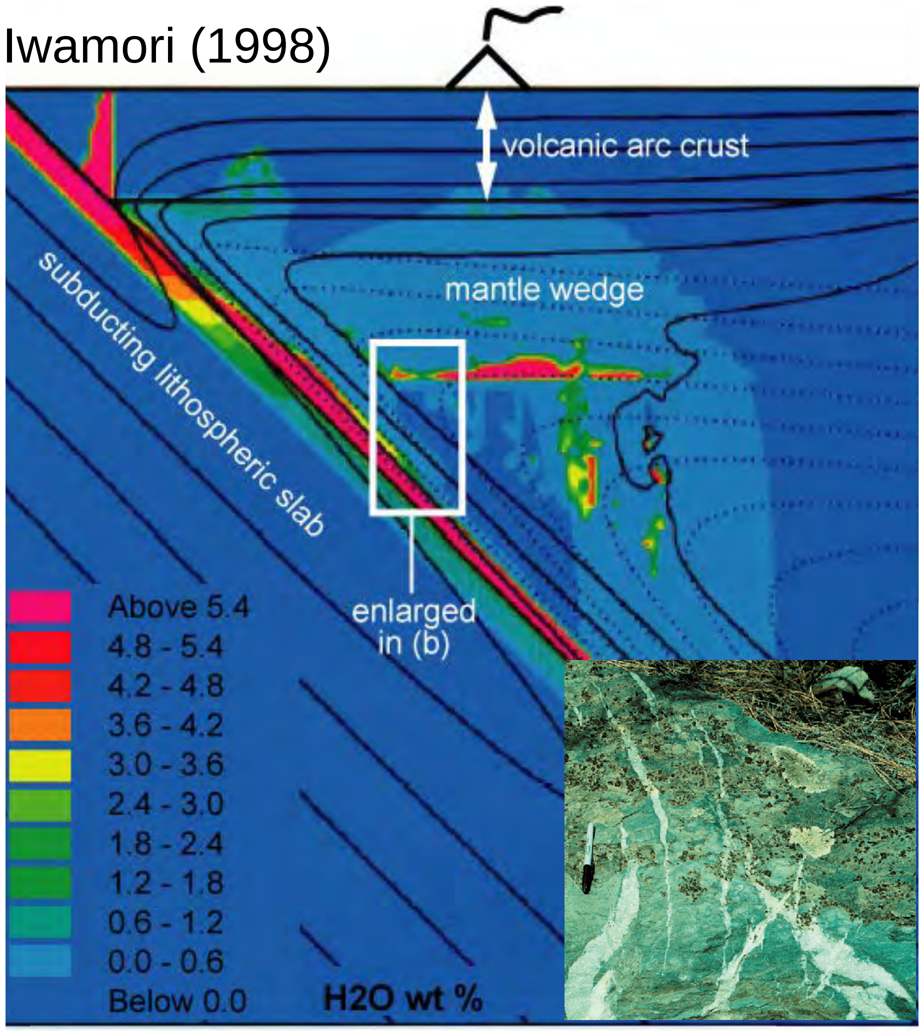


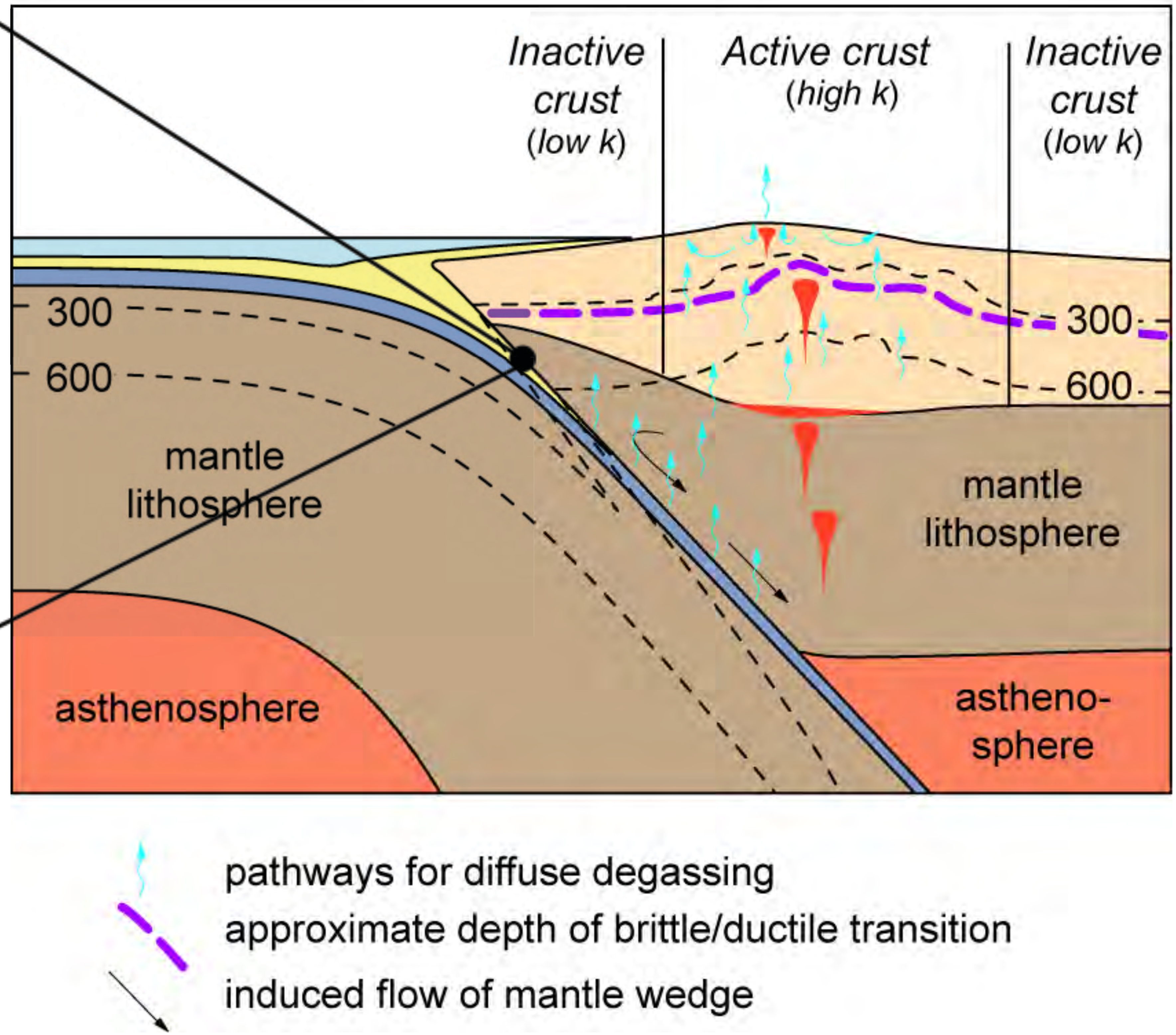
Forearc
Trench
Volcanic
island arc
km
0
10
20
30
50
100
Ocean
crust
Accretionary
wedge
Forearc
basin
Mafic to
intermediate
intrusives
and lavas
Subducting ocean plate
Mantle
Mafic melt
Volatiles and melt rising
from subducted ocean plate

Deep fluids: solubility & solute structure

Focus on subduction zones

Iwamori (1998)





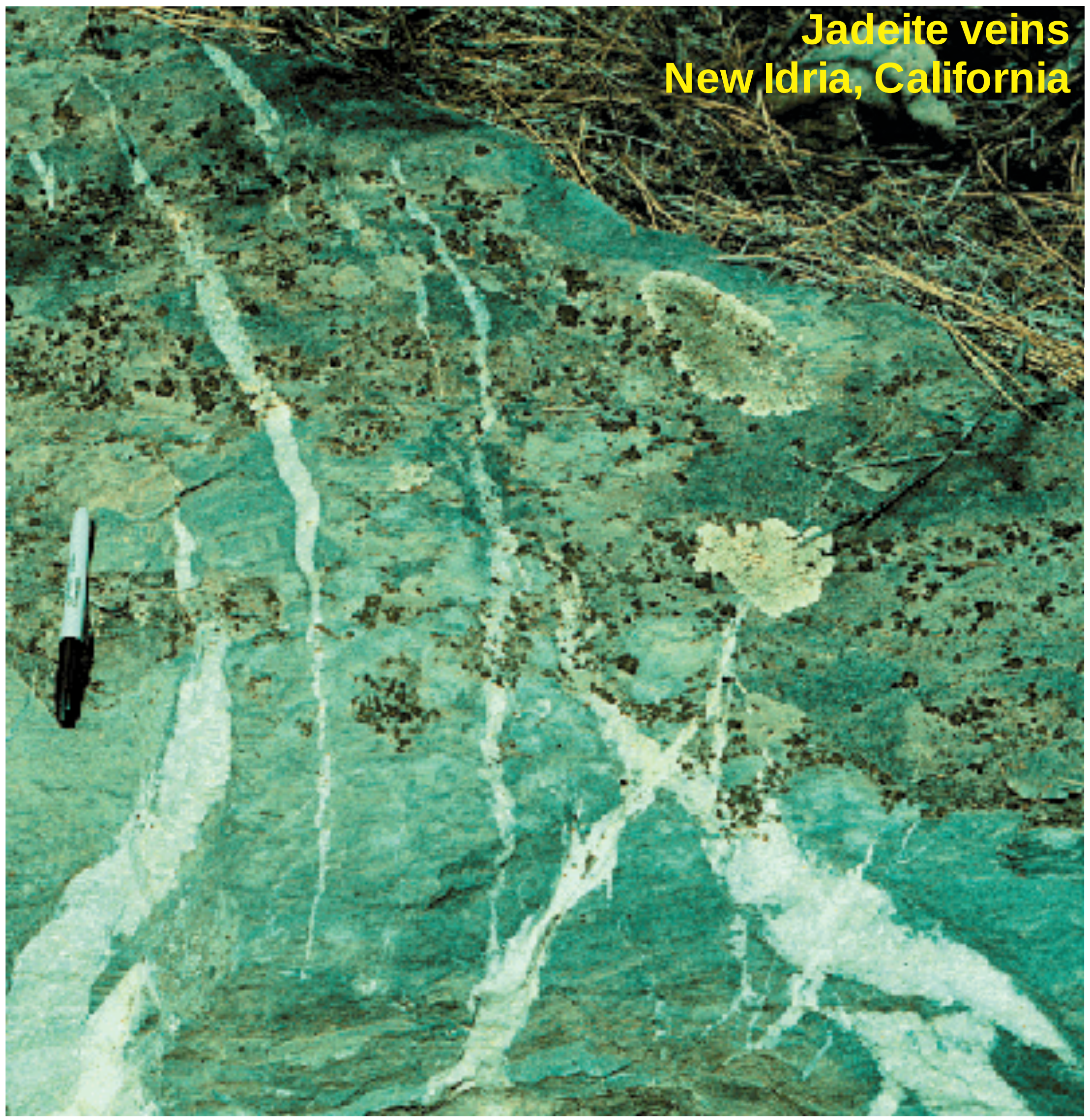
Metamorphism deeper than brittle/ductile transition (~15 km):

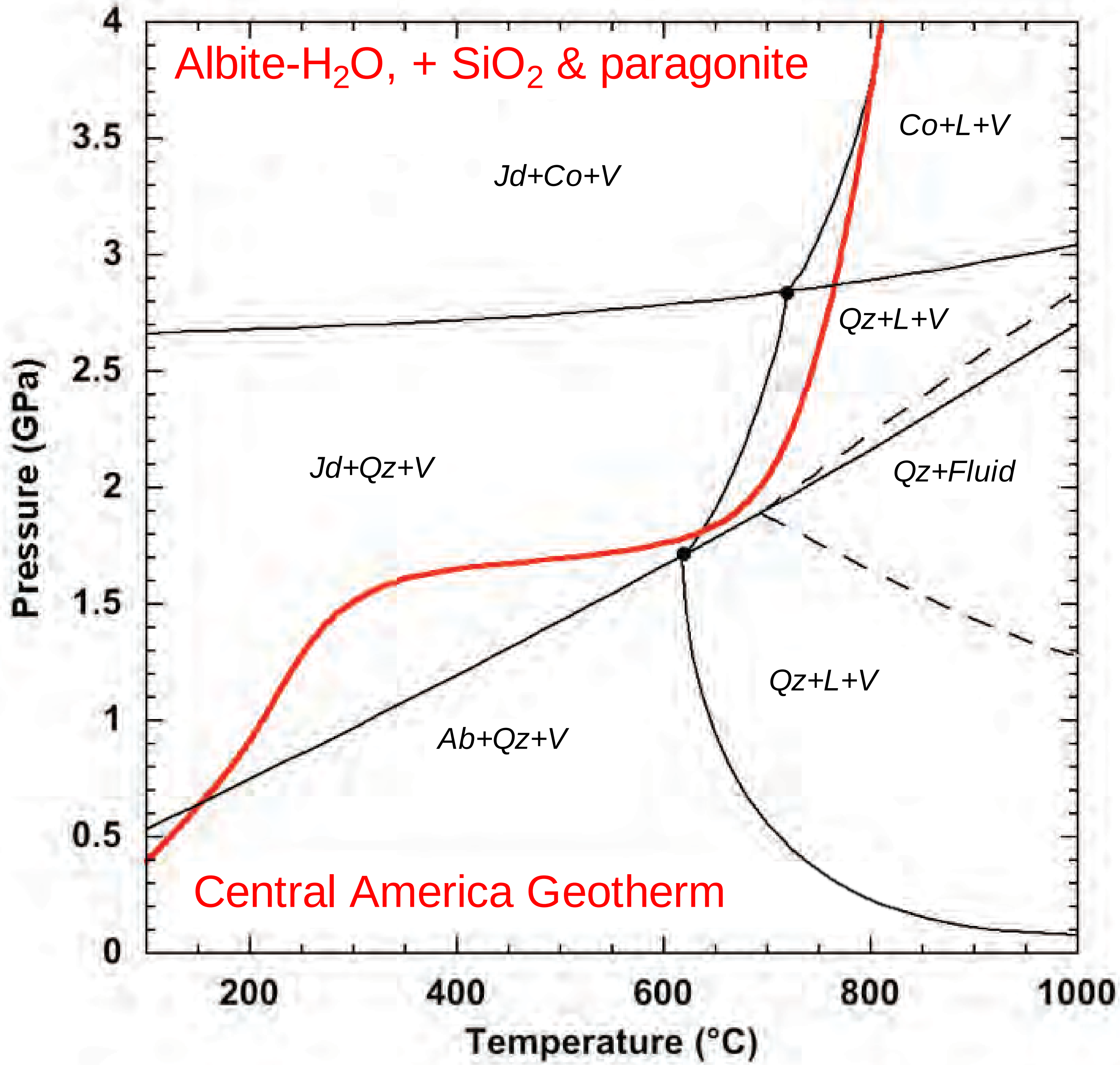
?

Approaches: prediction & experiment

Simple system approach for comparison to nature & experiment

Na_2O-Al_2O_3-SiO_2-H_2O = "NASH"

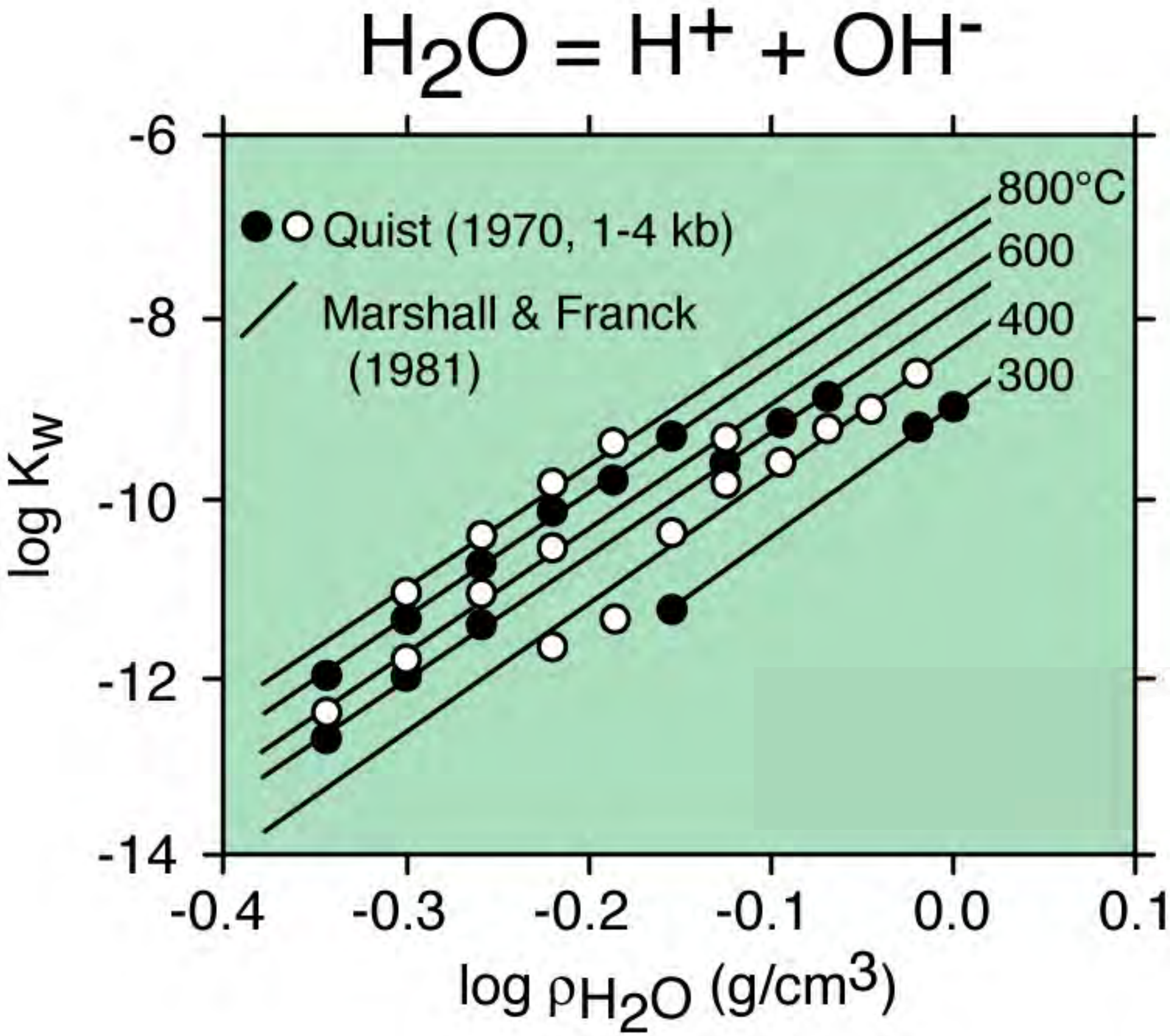




Boettcher & Wyllie (1968), Holland & Powell (2002), Manning et al. (2010), Hayden & Manning (2011)

Prediction of slab-fluid composition

Theoretical background for unconstrained fluid components



Slopes of isotherms:

Permits extrapolation of thermodynamic properties of reactions such as

$$NaAlSi_2O_6 + 4H^+ \rightarrow Na^+ + Al^{+3} + 2SiO_{2,aq} + 2H_2O$$

jadeite

Consider:

ionic species (eg Na^+ $Al(OH)_4^-$)

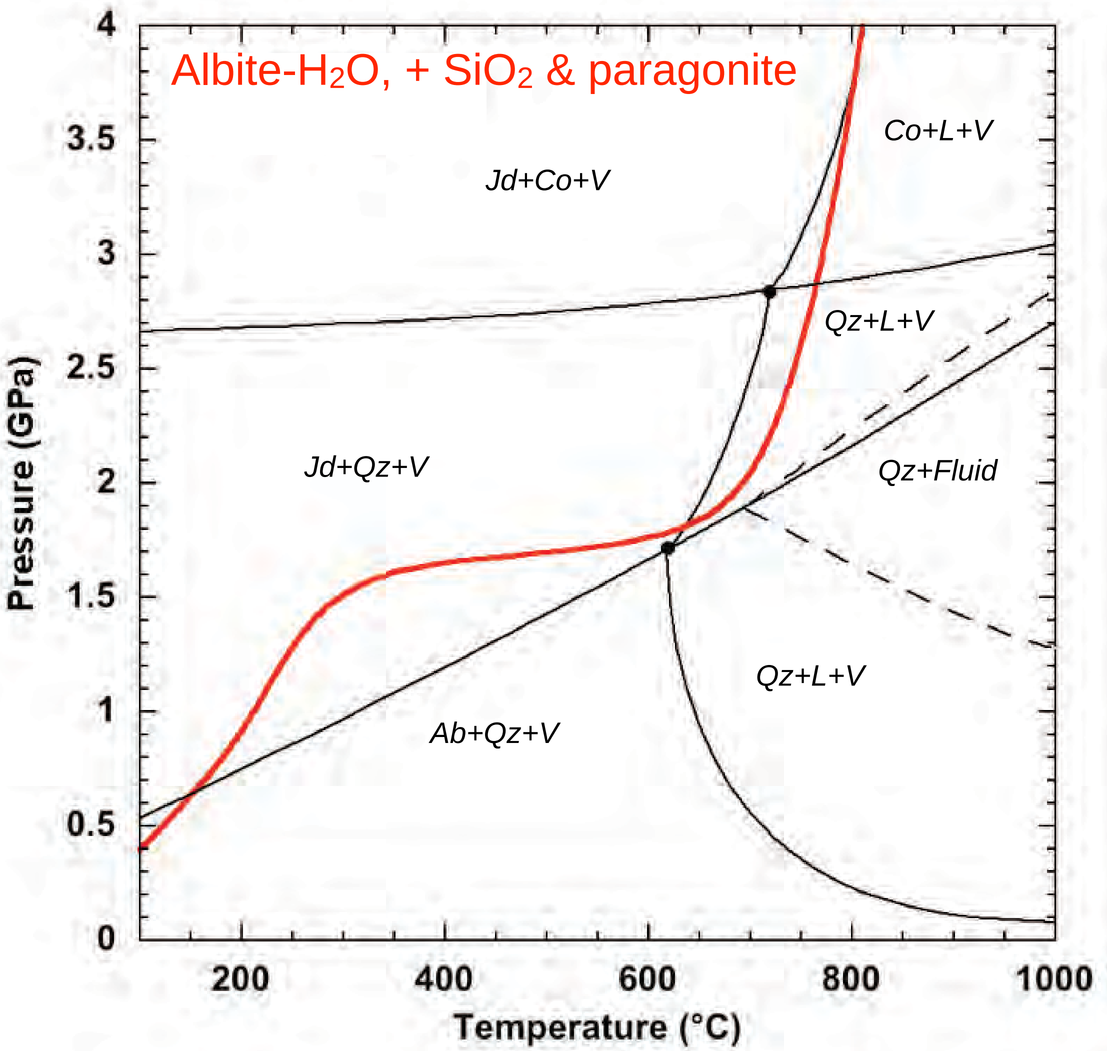
monomeric neutrals (eg SiO_{2aq})

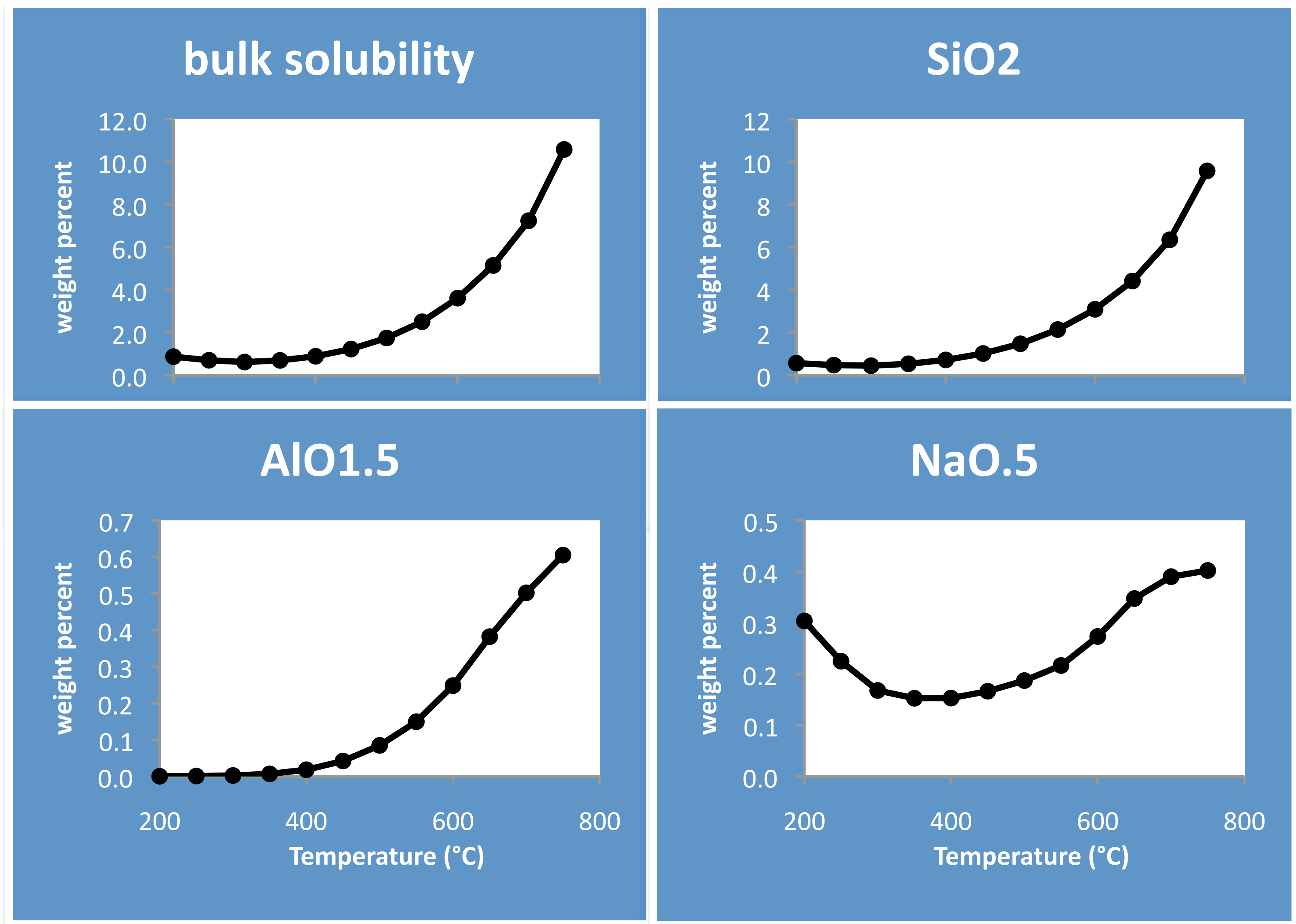
silica dimer (Si_2O_{4aq})

Which allows calculation of fluid compostions…

Prediction of slab-fluid composition

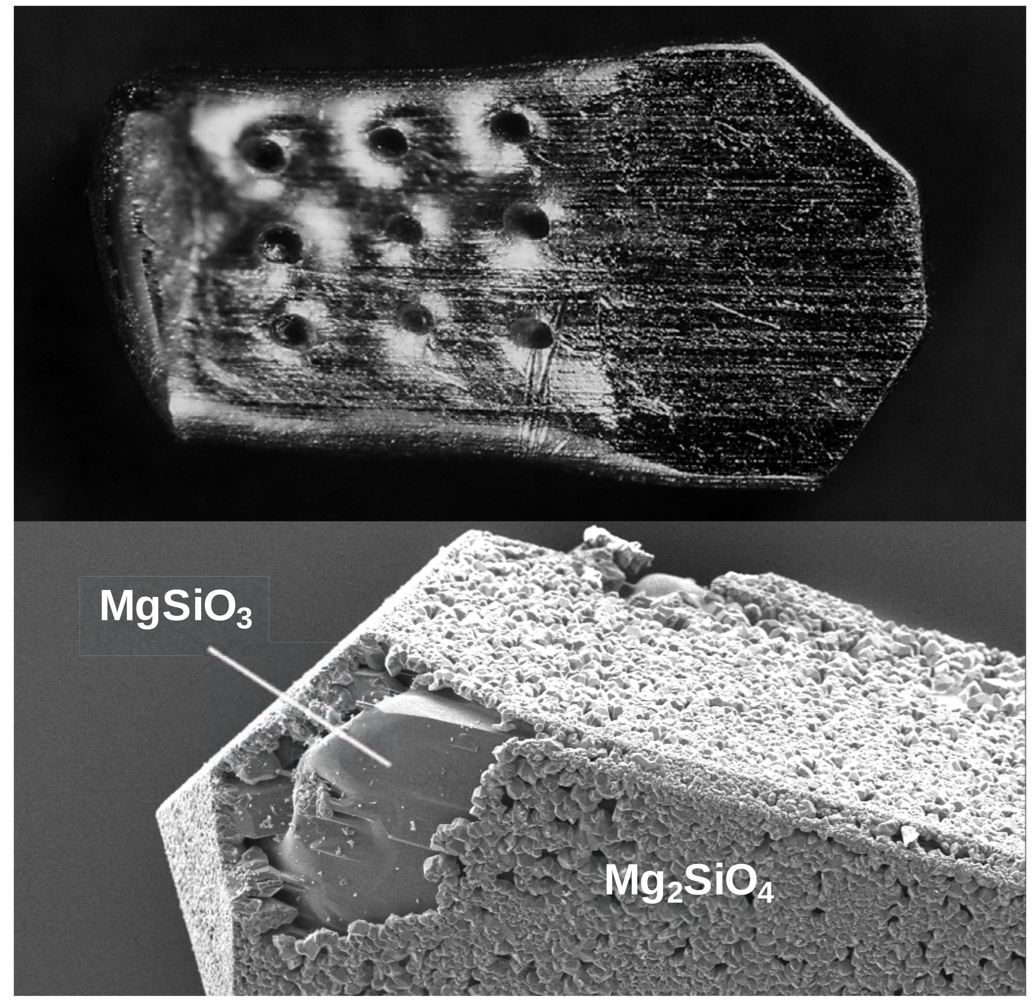
Central America slab-top geotherm





Experimental Approach

Rapid-quench, hydrothermal piston-cylinder apparatus



Experimental constraints on slab-top fluids

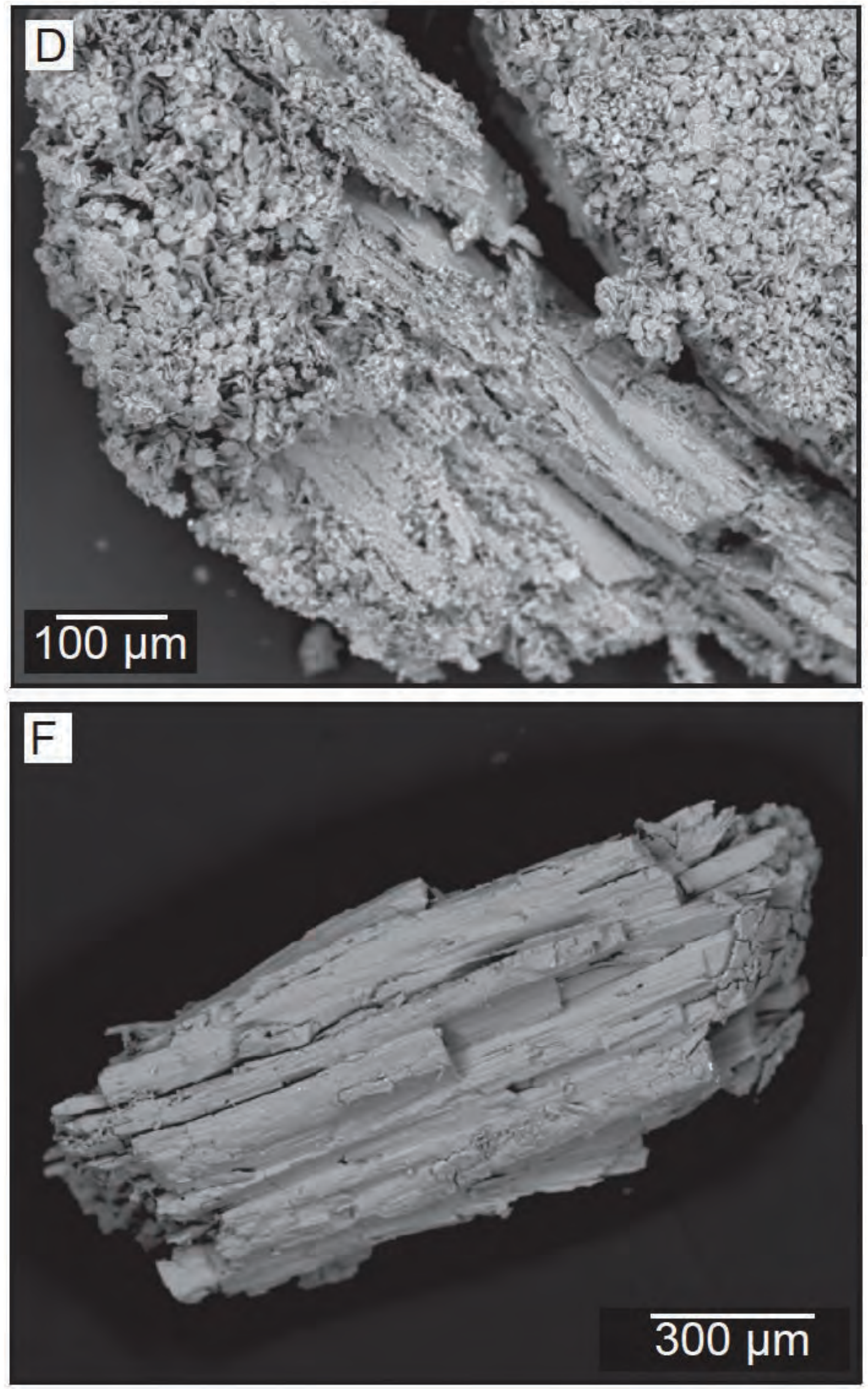
Investigation of the NASH system

-Solubility determination:

Direct analysis of quench fluid (350-500°C, 1 GPa)

Weight loss & mass balance (580-620°C, 1 GPa)

Phase-boundary bracketing(500-600°C, 1-2.25 GPa)



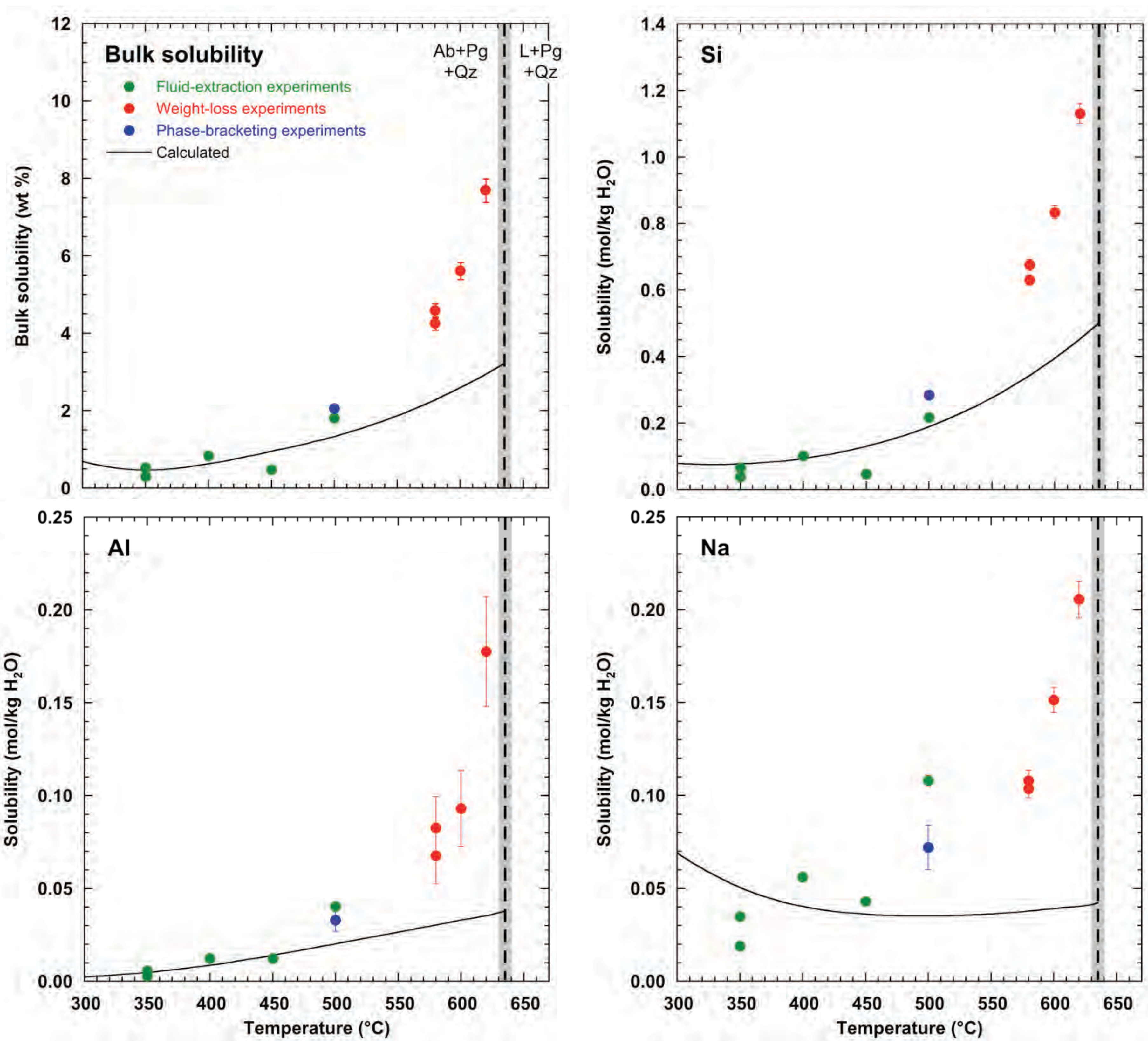
jadeite
+
paragonite

jadeite
without
paragonite

Manning et al. (2010), Wohlers et al. (2011)

Experimental constraints

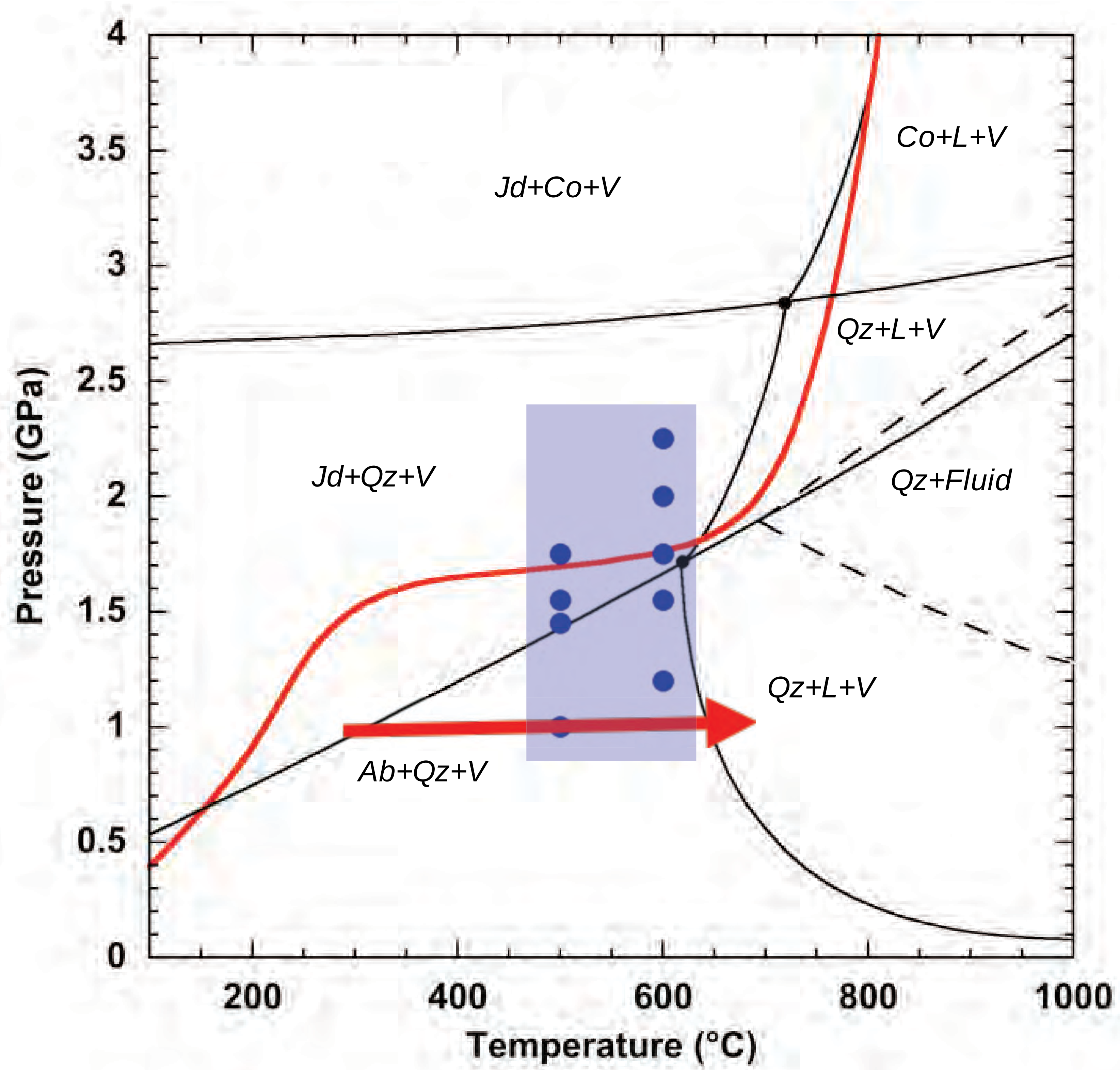
Results at 1 GPa: albite + paragonite + quartz



Manning et al. (2010), Wohlers et al. (2011)

Experimental constraints

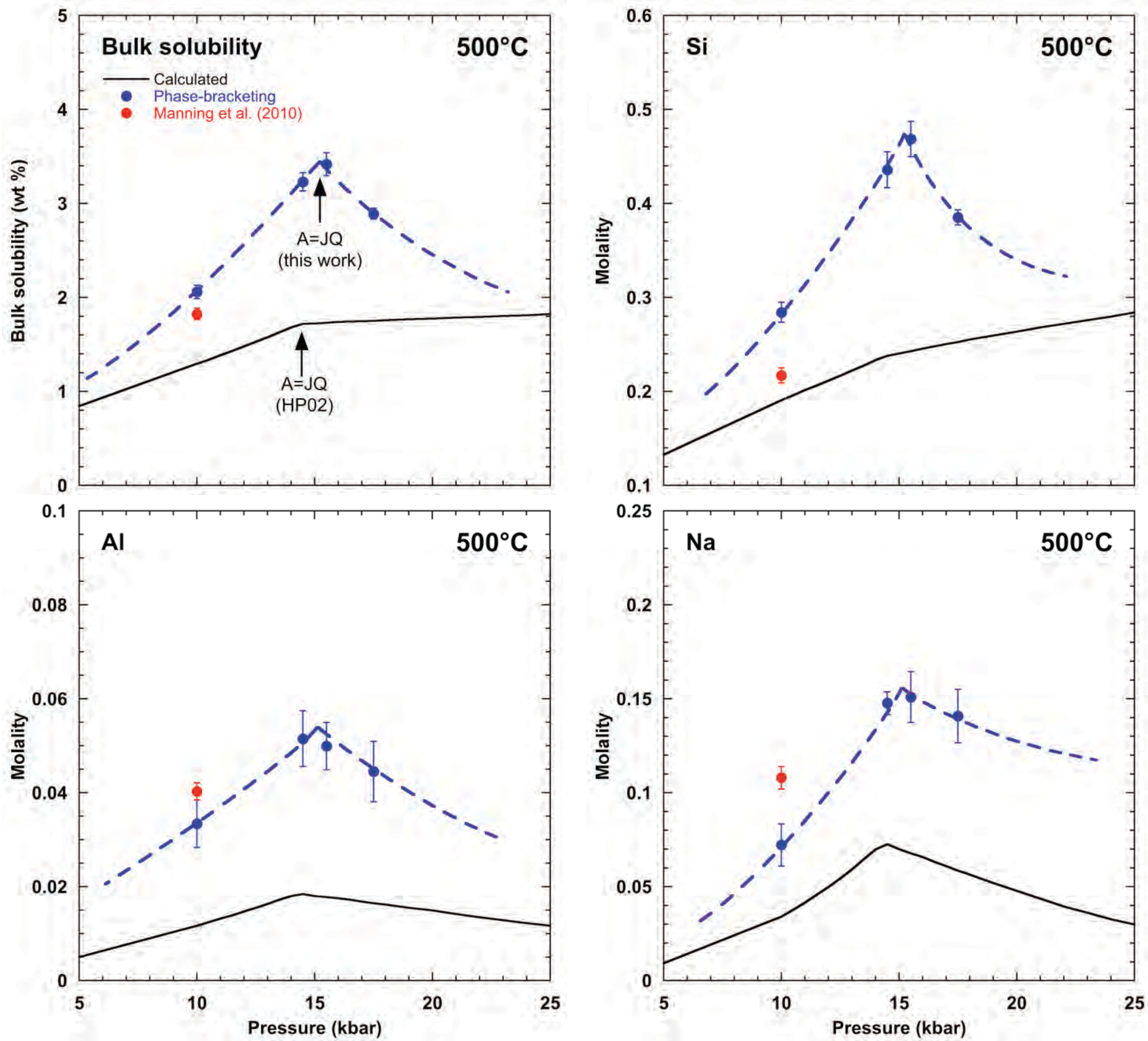
500 and 600°C isotherms



Wohlers et al. (2011)

Experimental constraints

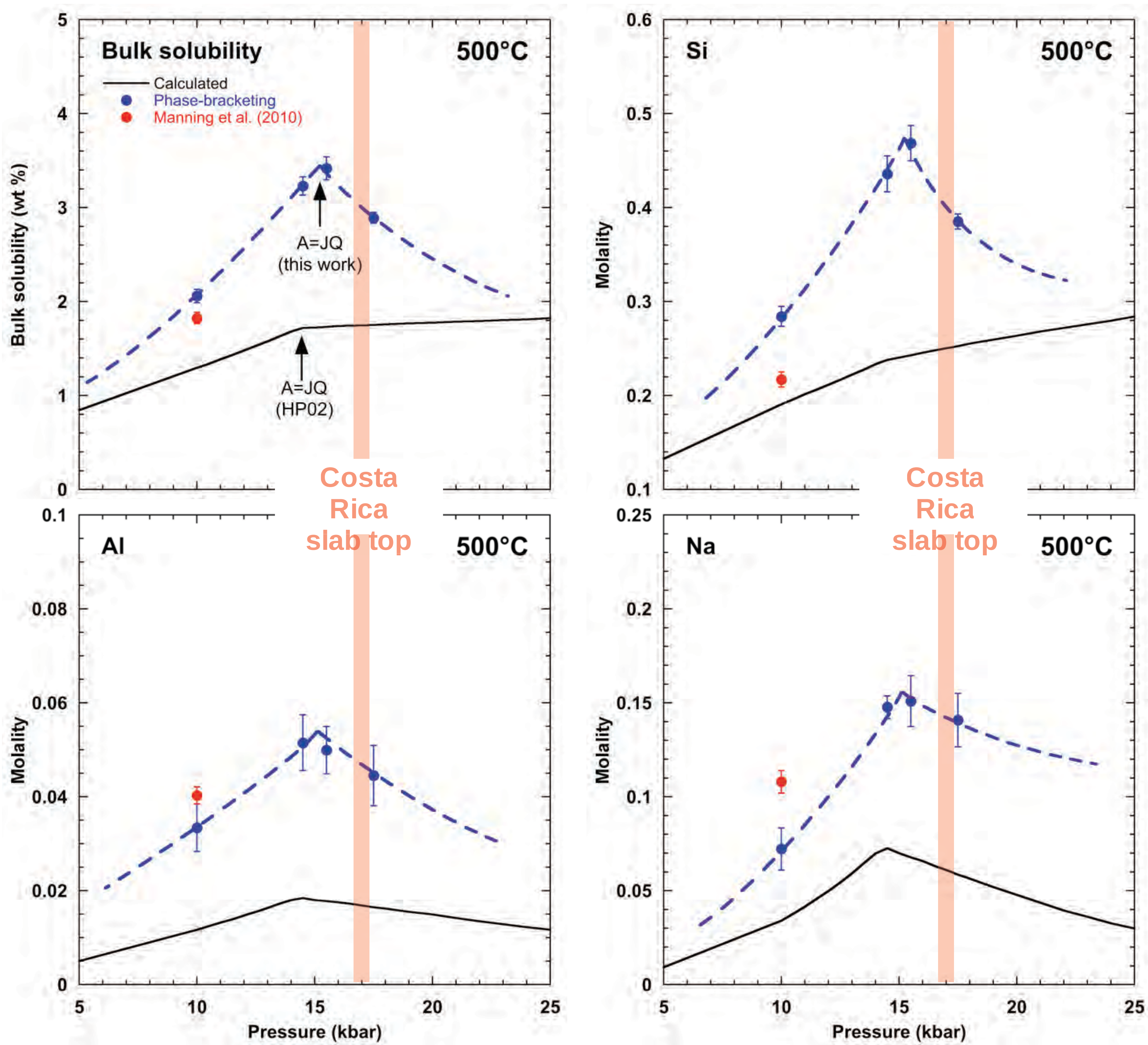
Results at 500°C



Wohlers et al. (2011)

Experimental constraints

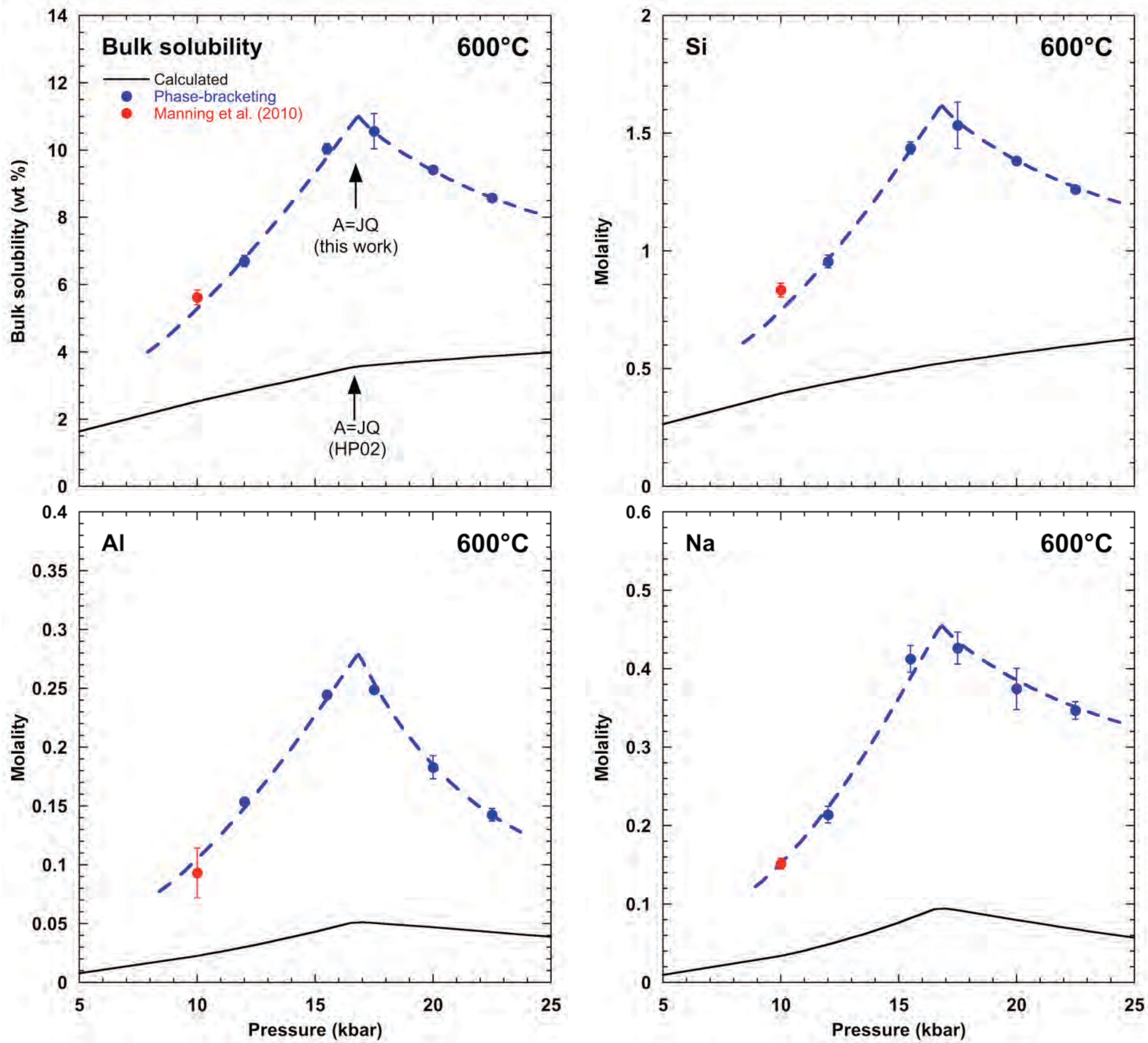
Results at 500°C



Wohlers et al. (2011)

Experimental constraints

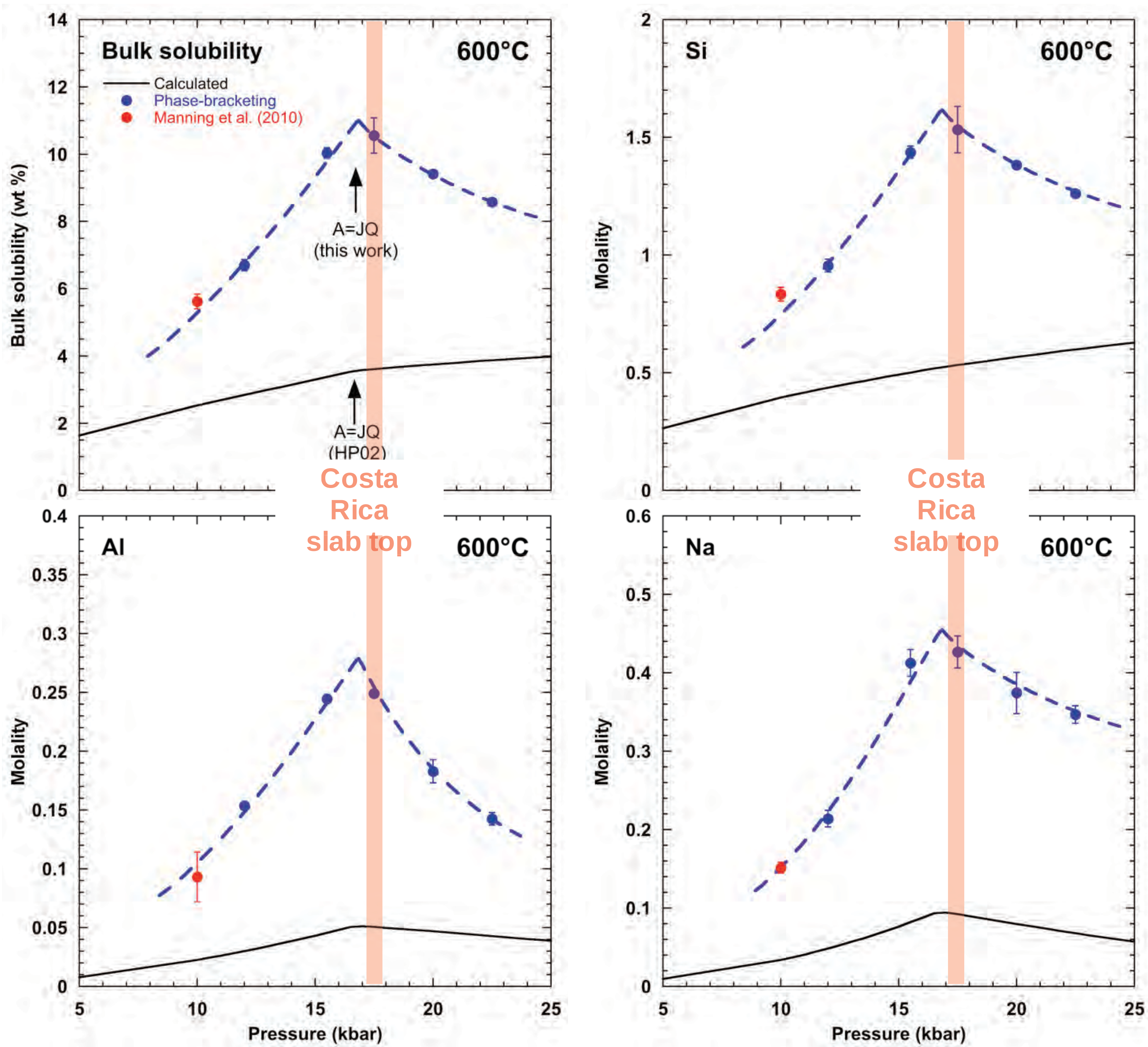
Results at 600°C



Wohlers et al. (2011)

Experimental constraints

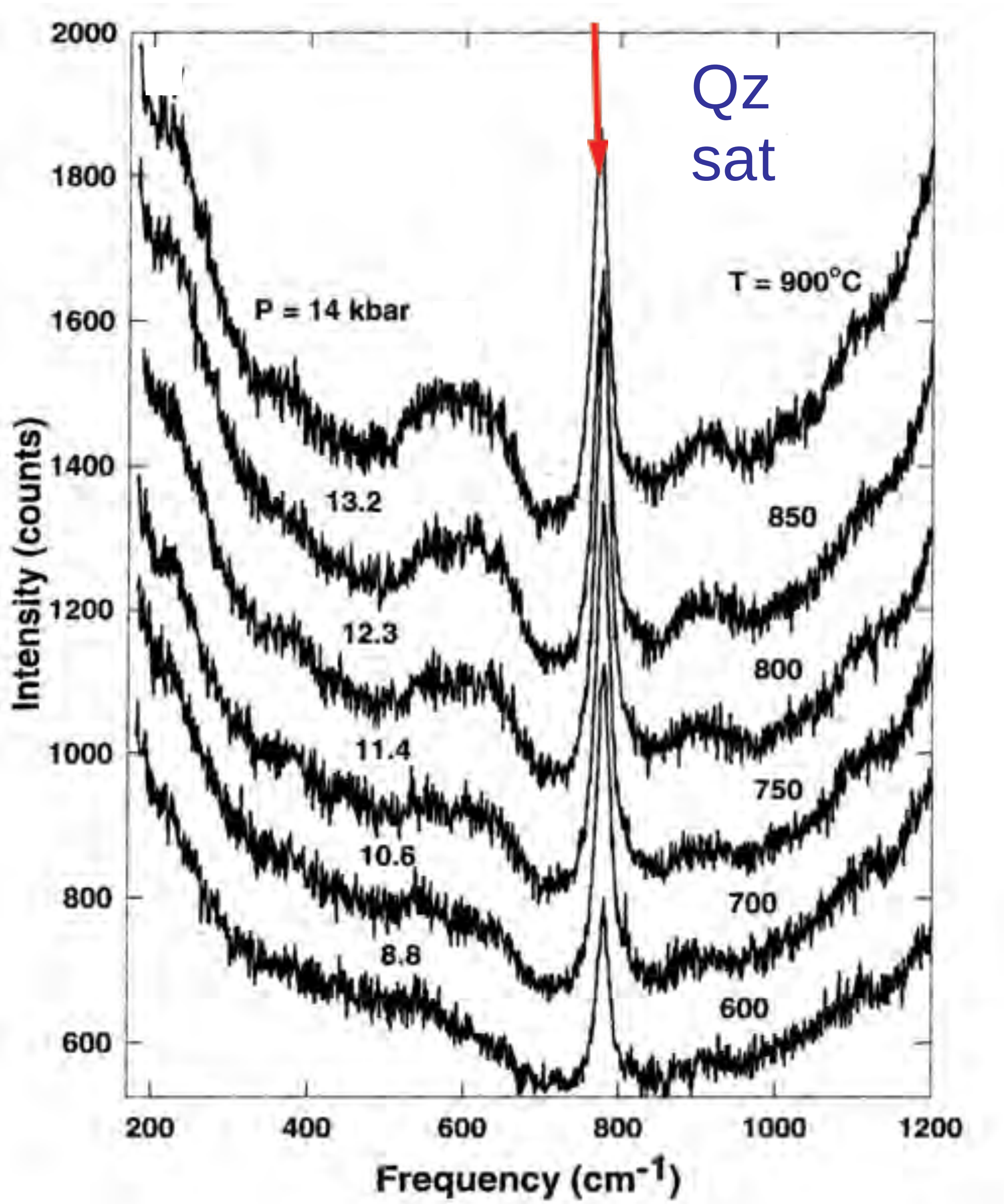
Results at 600°C



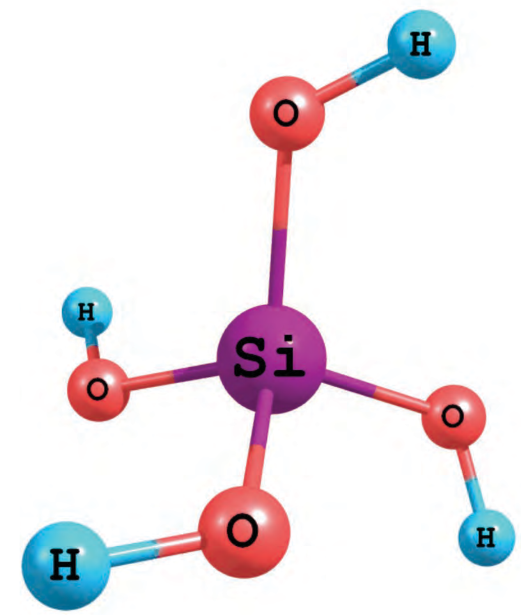
Wohlers et al. (2011)

Why the difference beteween experiment & theory?

Dissolved SiO_2 polymerizes at high P & T



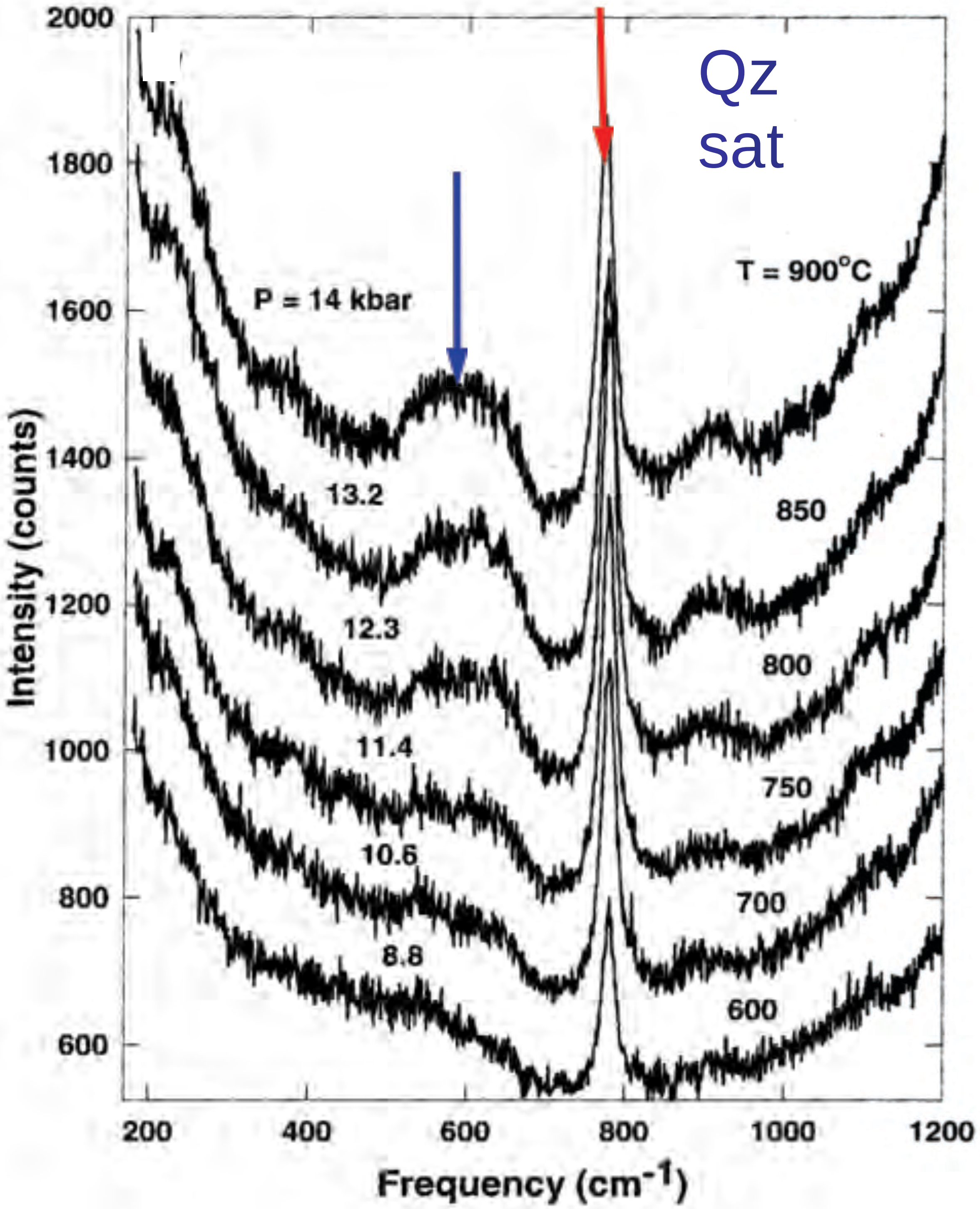
Zotov & Keppler (2000, 2002)



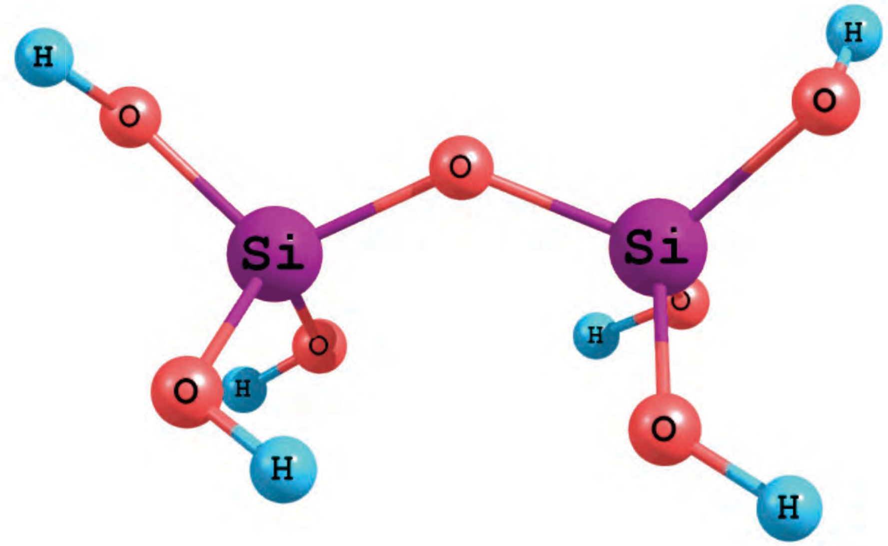
Monomer
Symmetric stretch
~785 cm^{-1}

Experiment vs. theory

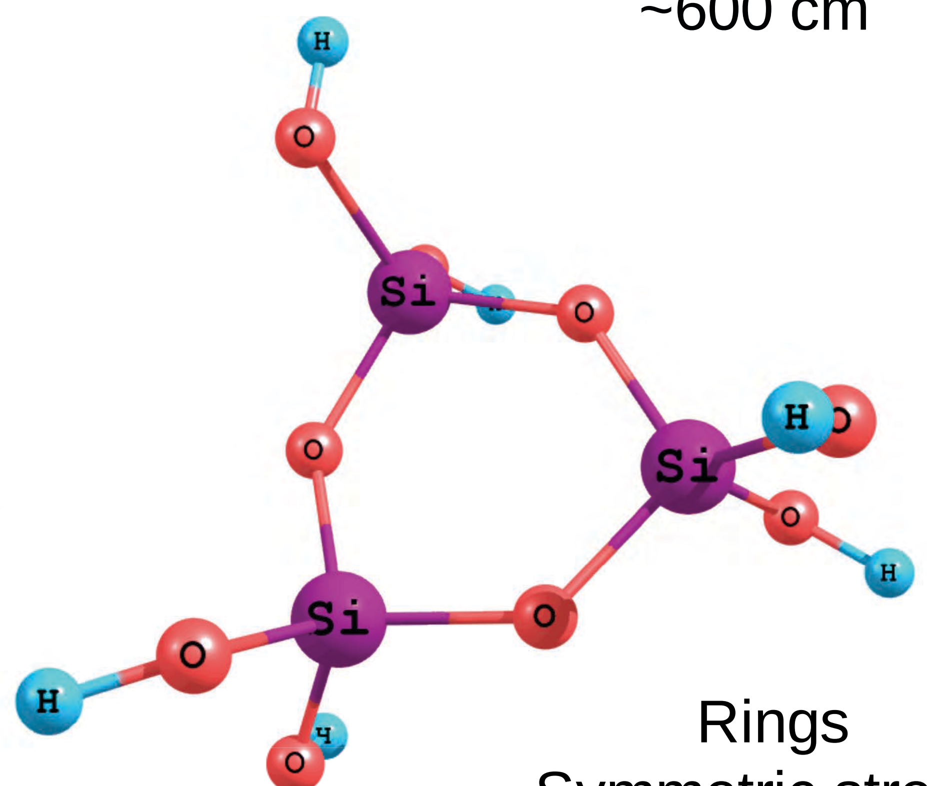
Dissolved SiO_2 polymerizes at high P & T



Zotov & Keppler (2000, 2002)



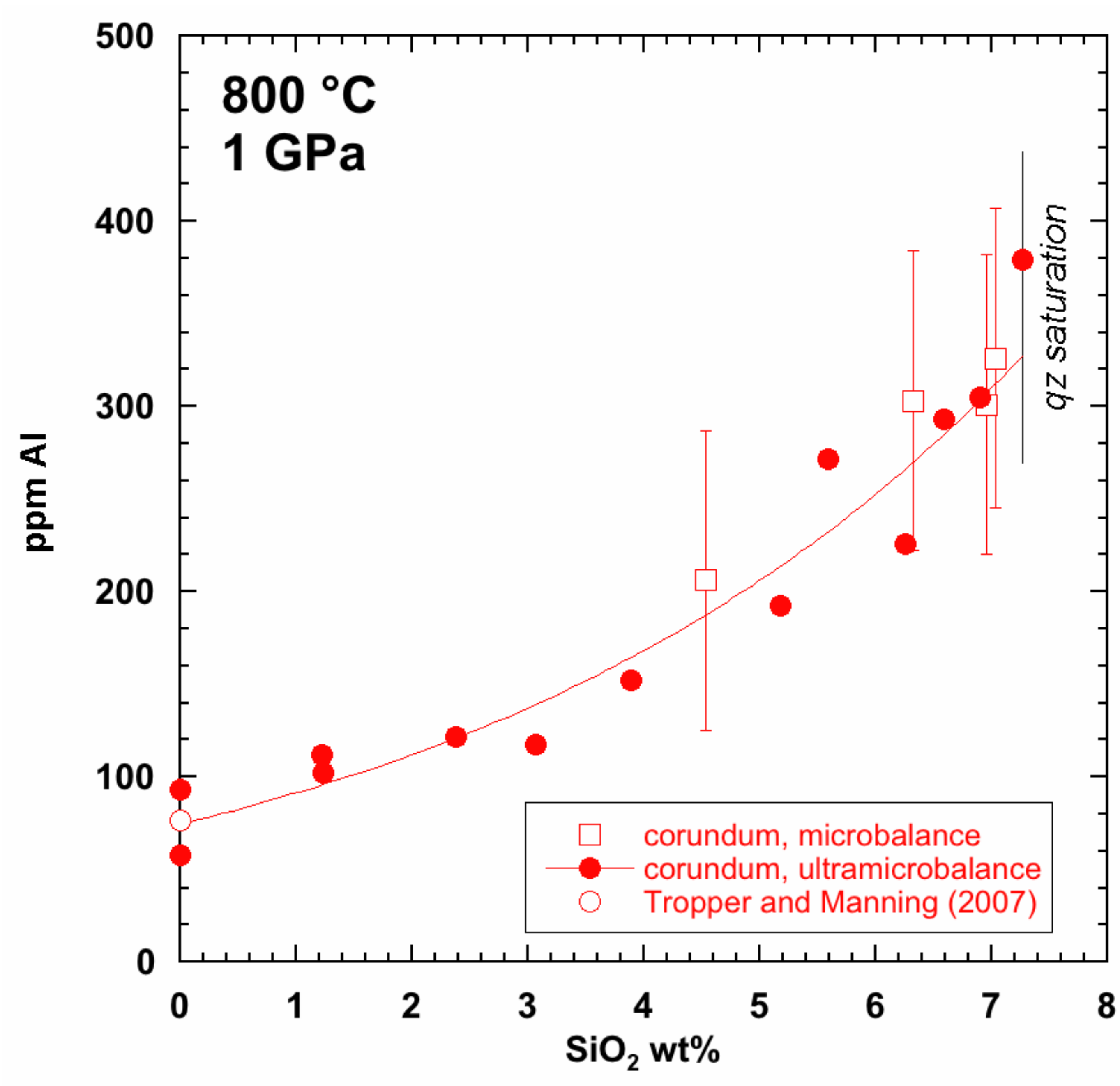
Dimers & oligomers
Bridging O bend
~600 cm^{-1}



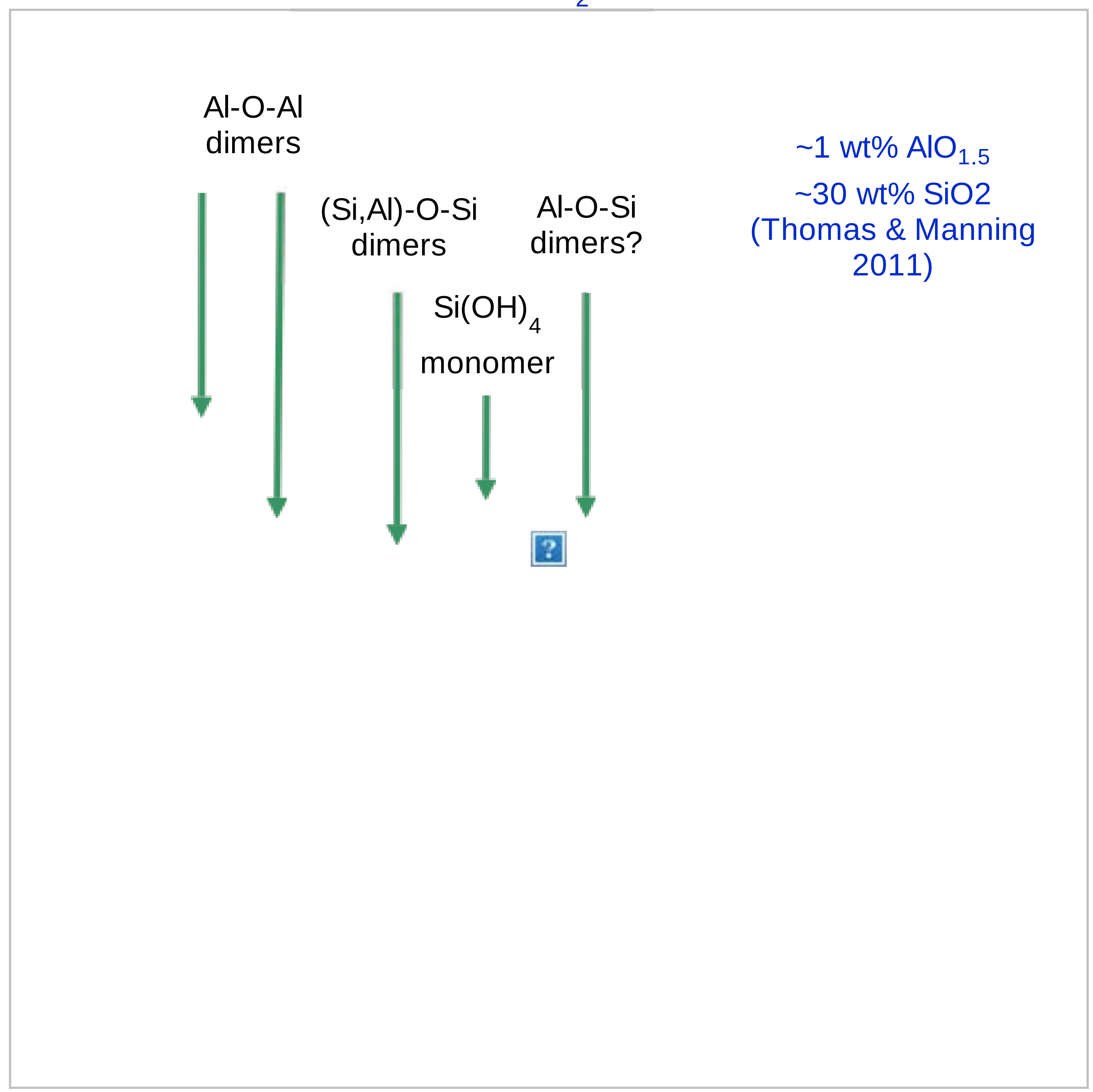
Rings
Symmetric stretch
~500-600 cm^{-1}

Experiment vs. theory

Si-Al polymerization in pure H_2O



Qtz-saturated H_2O



Manning et al. (in prep)

Mookherjee, Keppler & Manning (in review)

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Food and Chemical Toxicology 46 (2008) 49–56

www.elsevier.com/locate/foodchemtox

Role of beer as a possible protective factor in preventing Alzheimer's disease

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Received 13 December 2005; accepted 20 June 2007

Al is a neuorotoxin implicated as a cause of Alzheimer's disease.

Remove Al from body by $Si(OH)_4$? Or other source - eg, beer?

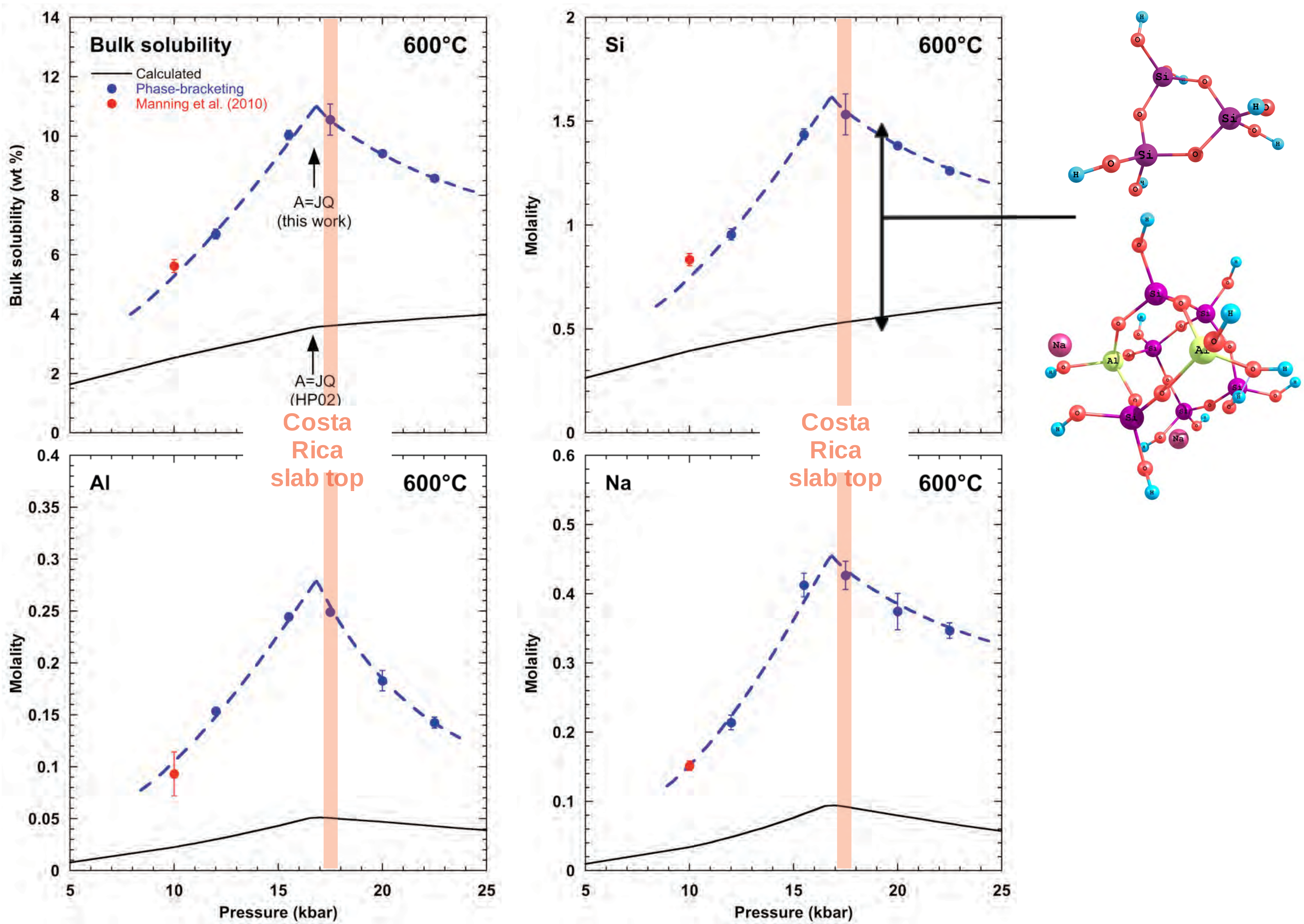
"The higher faecal levels of Al and Si in [mice]… fed beer or silicic acid … support the hypothesis that Al and Si combine to form compounds that are not taken up by the digestive tract."

"Beer would indeed seem to exert protective action against dietary Al intake by curtailing uptake of Al in the digestive tract."

Conclusion: Enjoy your beer!

Solute polymerization in high P-T fluids

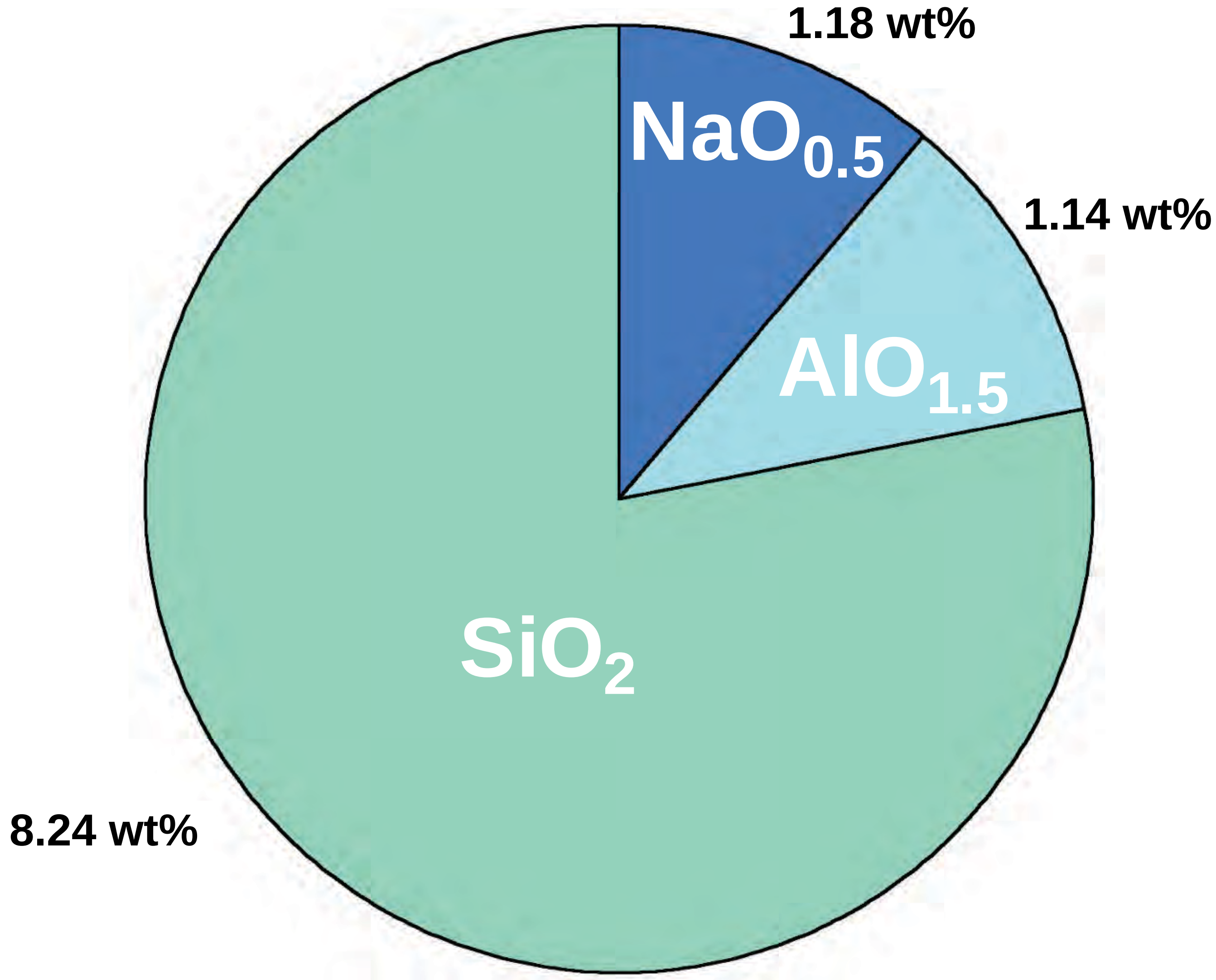
Excess solubility due to Si-Al-Na polymeric species



Wohlers et al. (2011)

Solute polymerization in high P-T fluids

Central America slab-top fluid, 600°C, 1.75 GPa



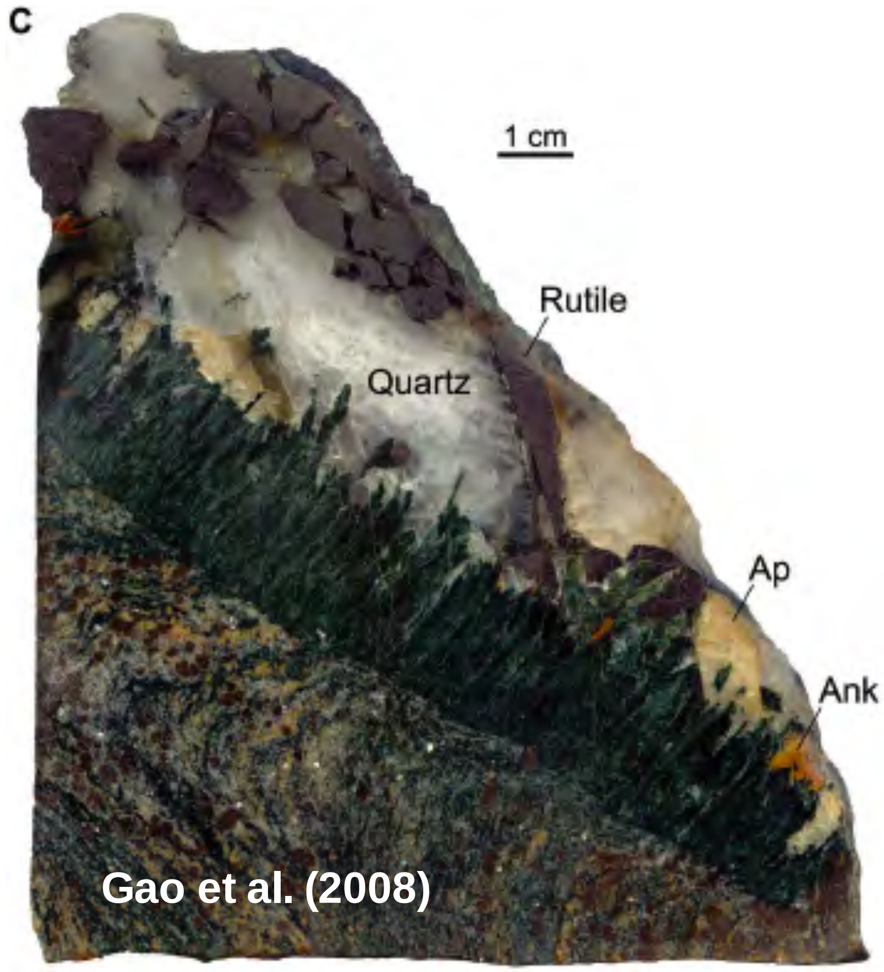
Bulk solubility
10.56 wt% oxides

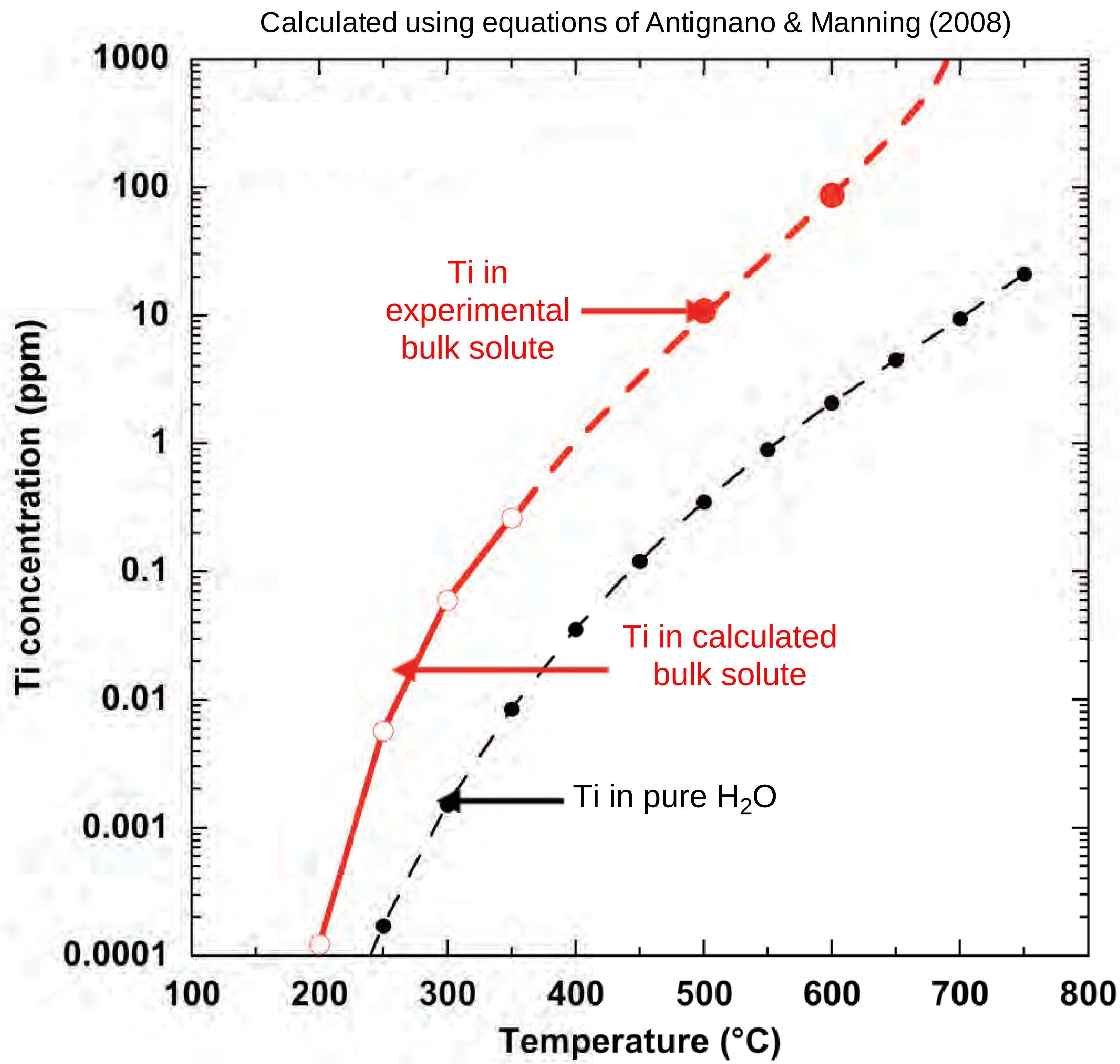
- 76% polymerized
- molar Na/Al = 1.7
- molar Si/(Na+Al) = 2.27
- Si > Qz saturation by 2.9X
- Al > Corundum sat by 200X

Wohlers et al. (2011)

Implications: 1

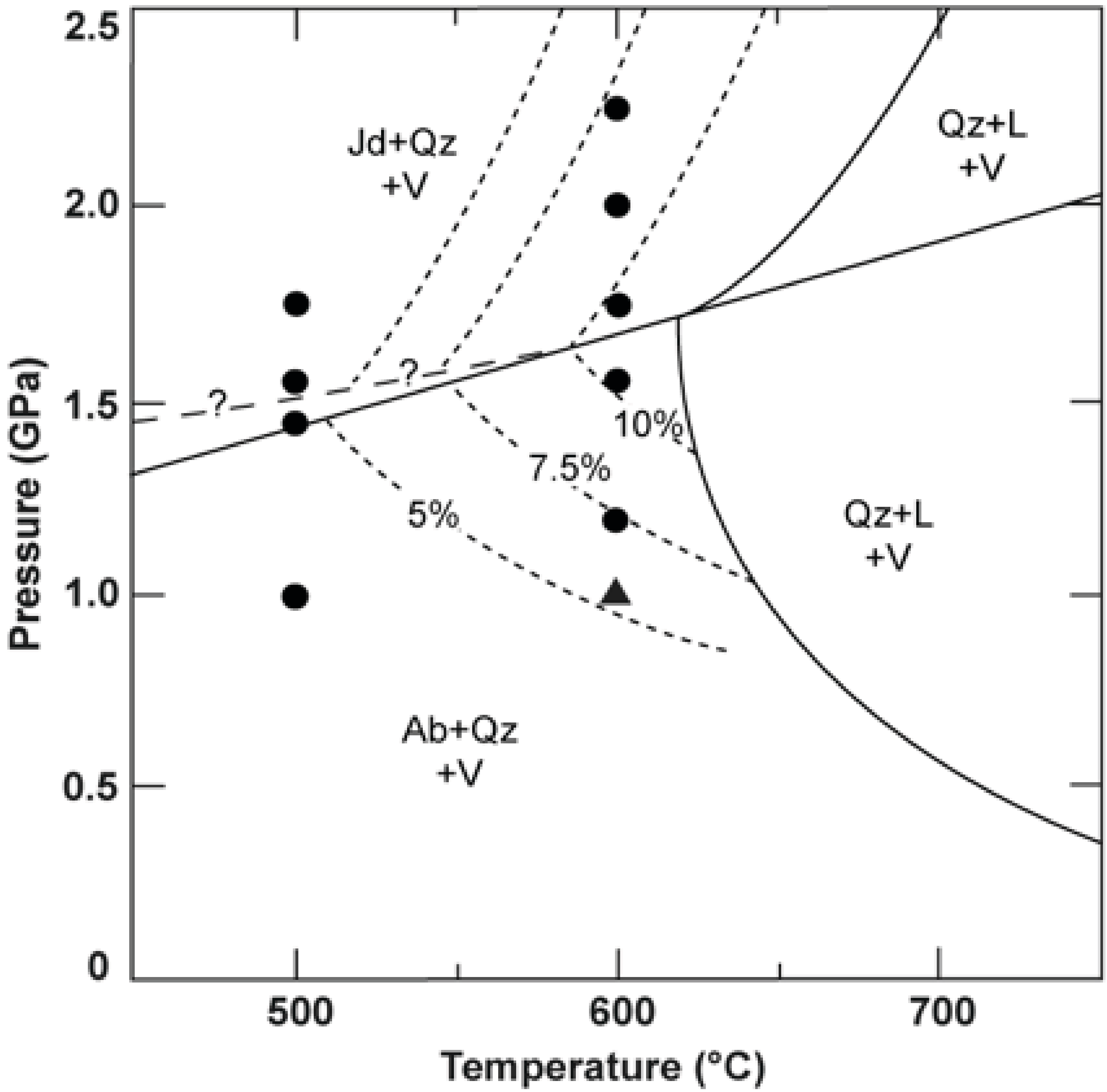
Trace element mobility: Ti in Central America slab-top fluid

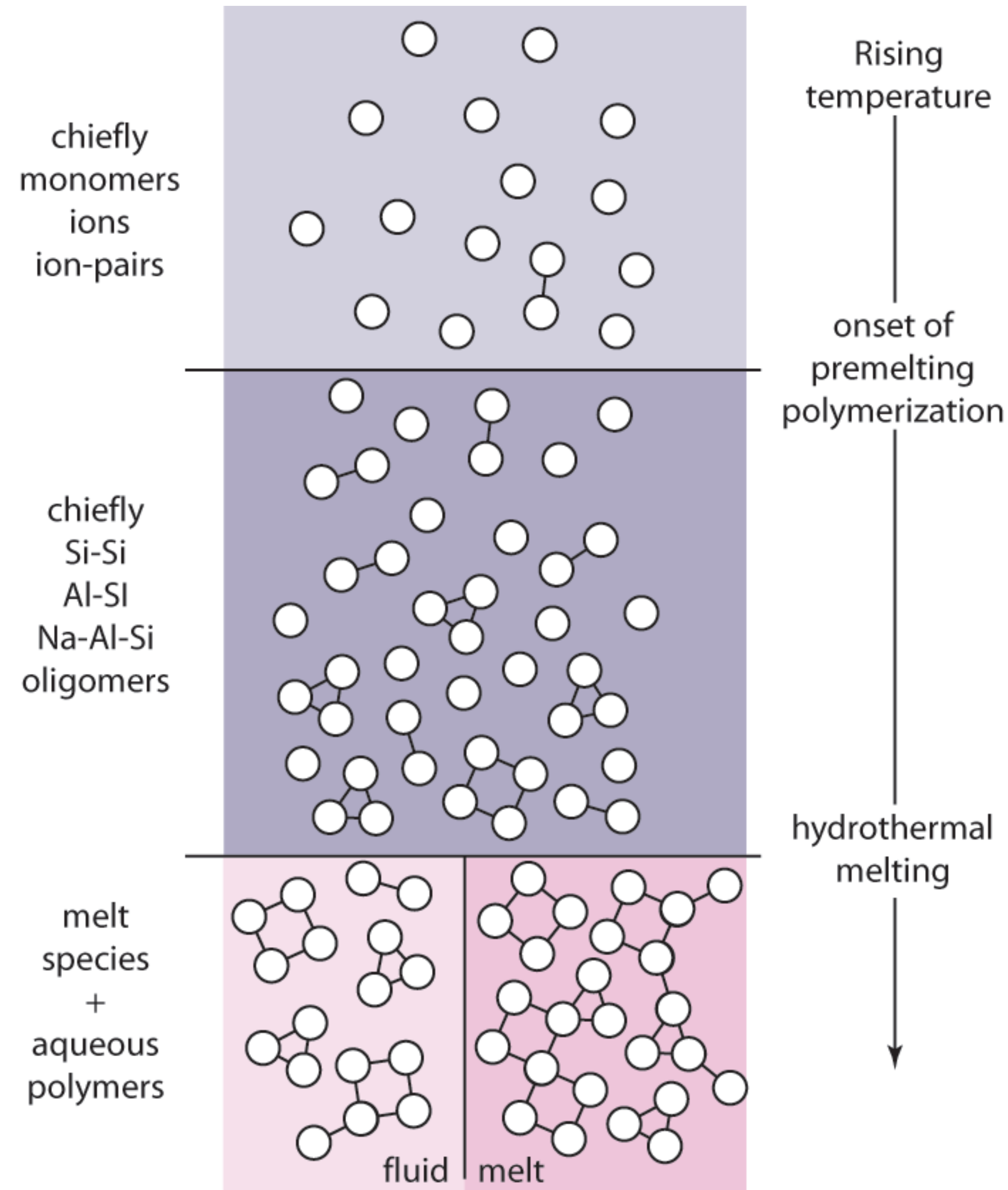




Implications: 2

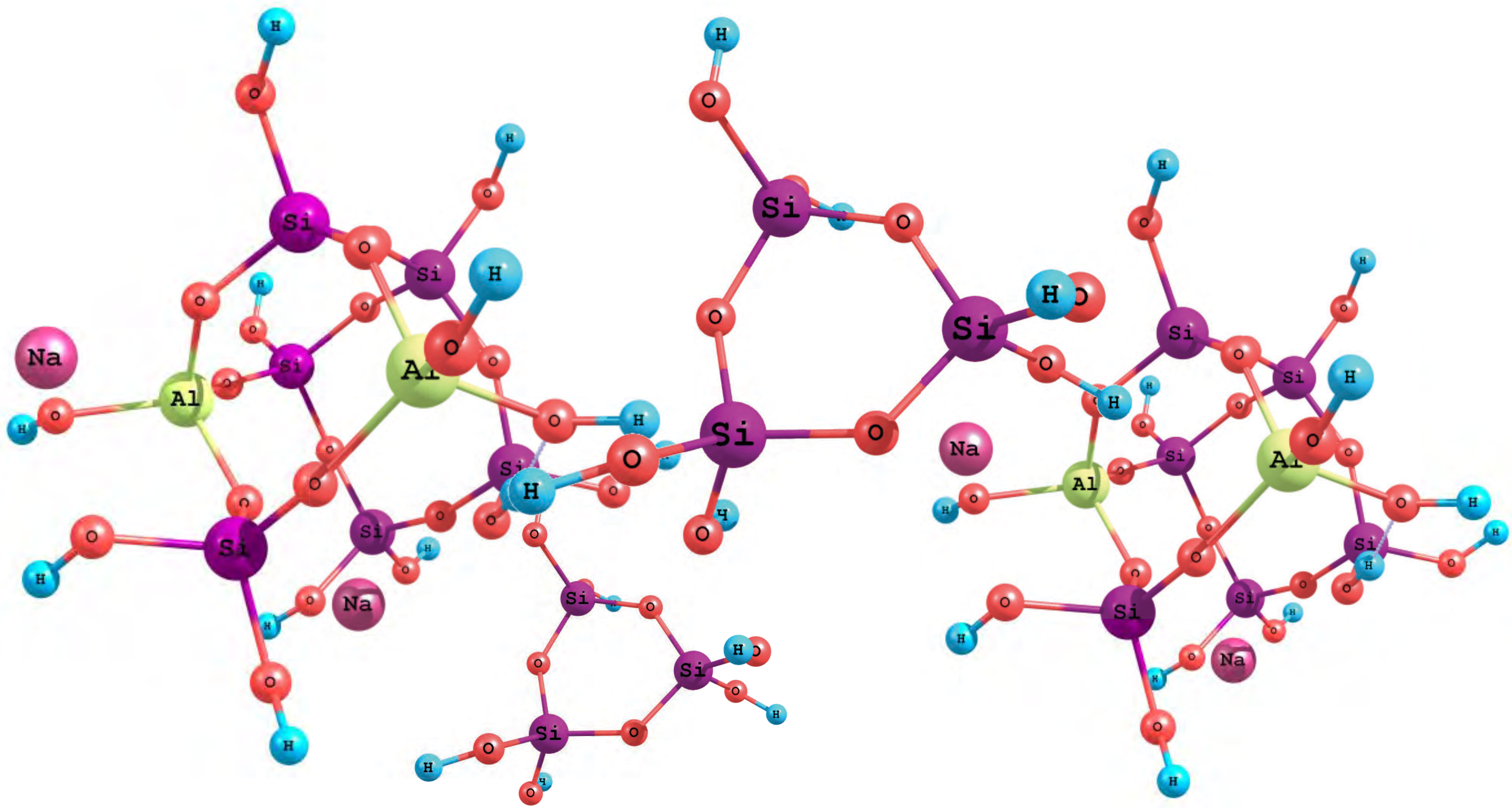
Polymerization as a "premelting effect"

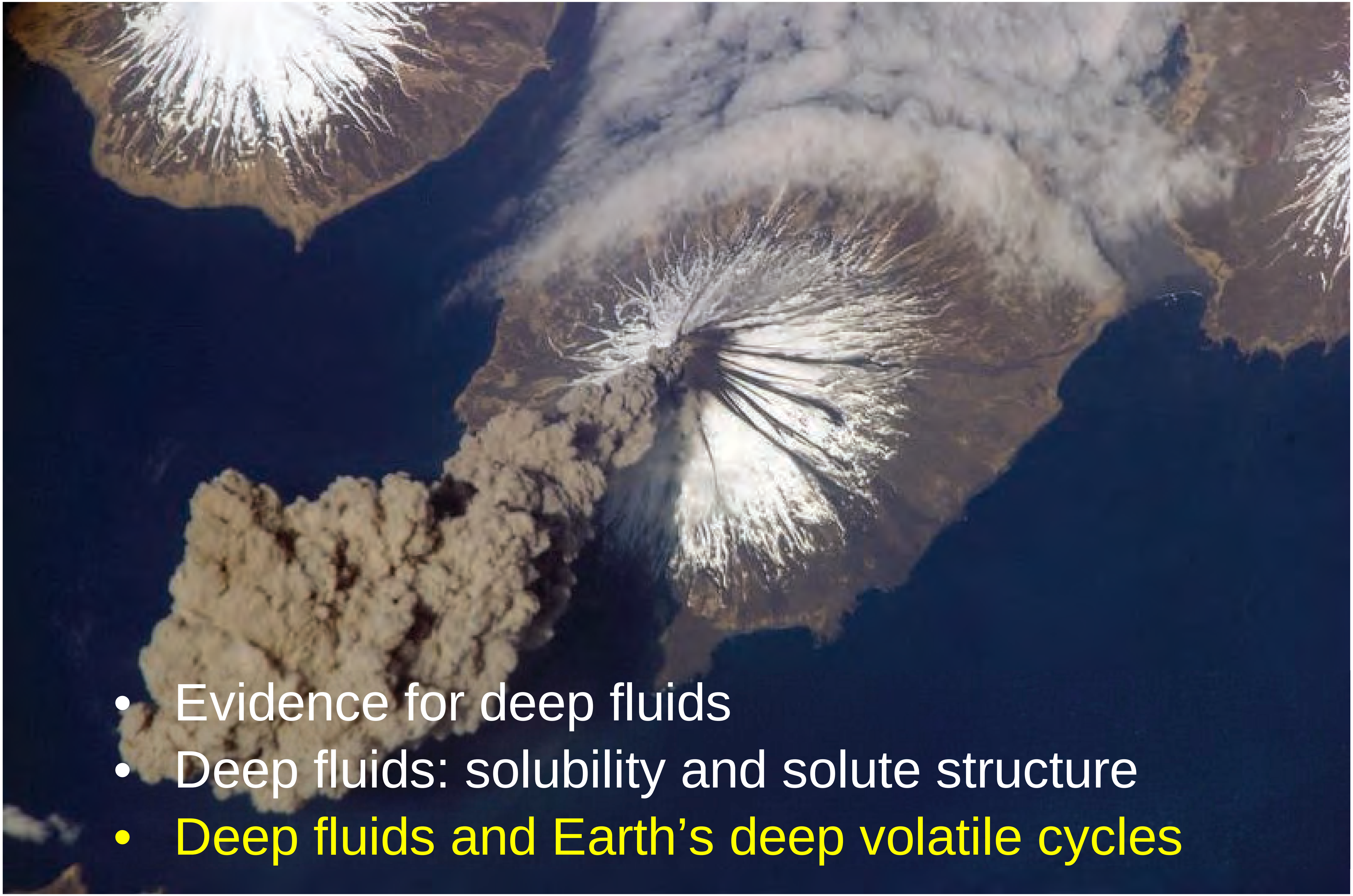




Implications: 2

Polymerization as a “premelting effect”





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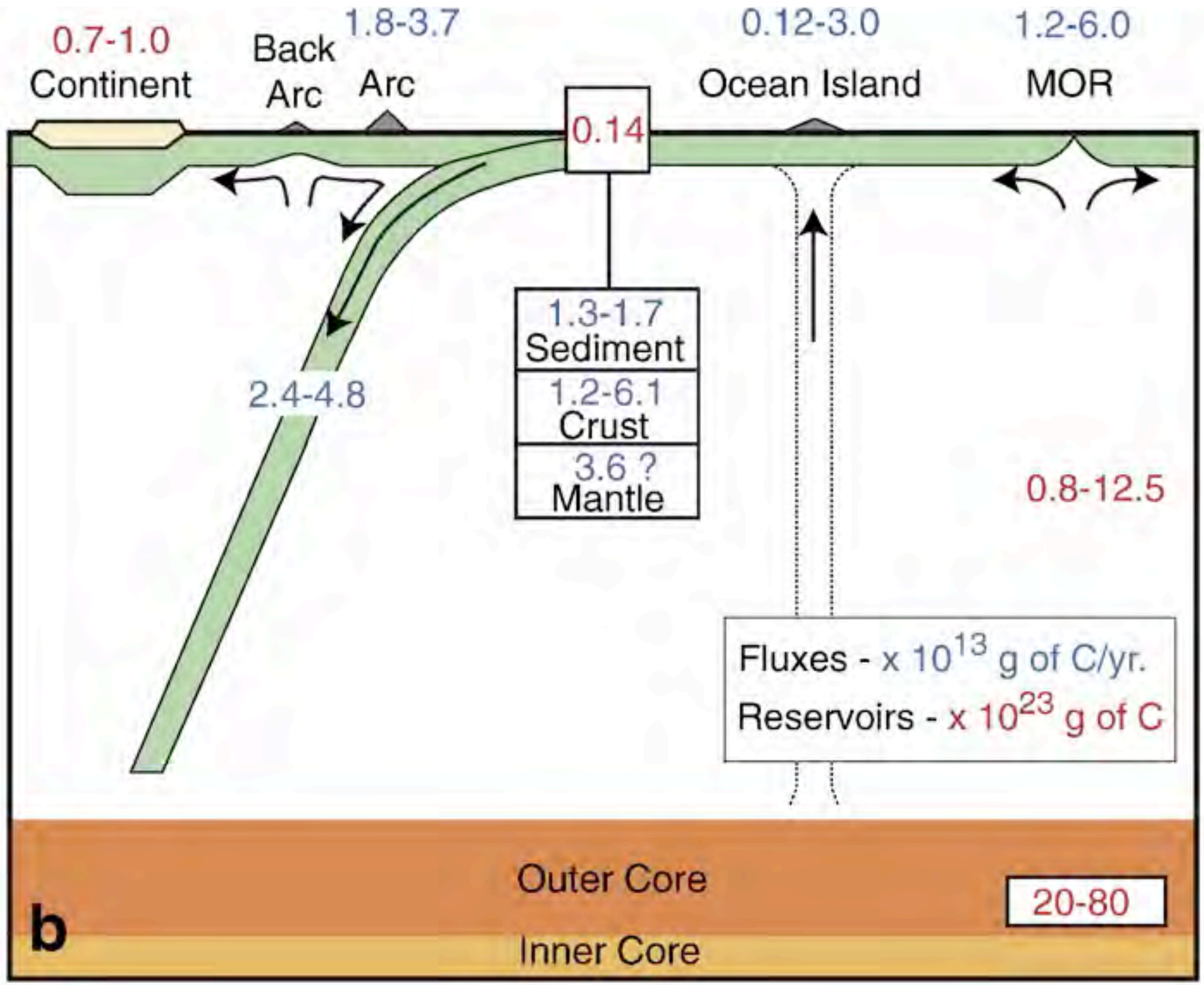
- Deep fluids: solubility and solute structure
- Deep fluids and Earth's deep volatile cycles

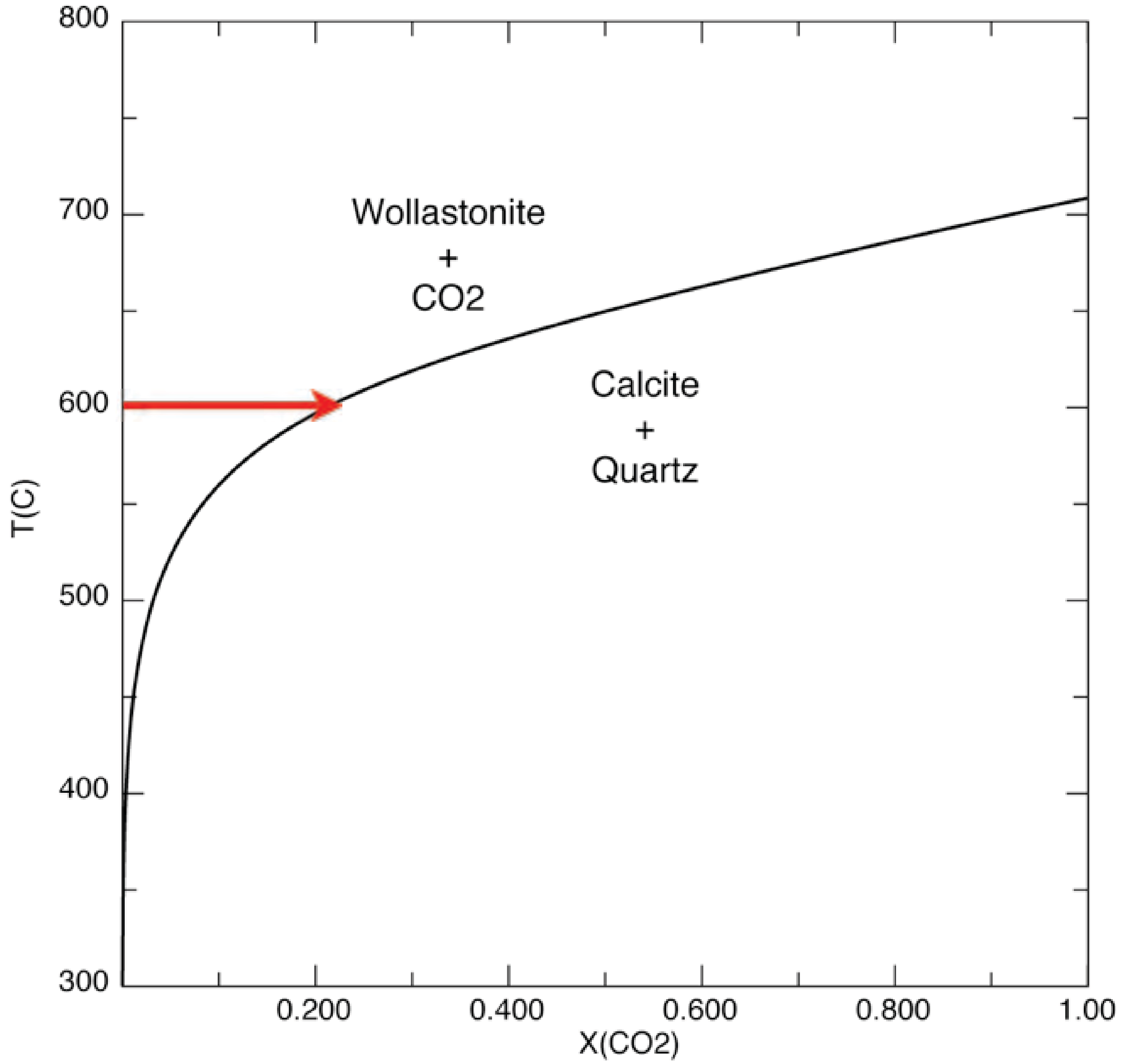
Volatile cycling - CO_2



Dasgupta & Hirschmann (2010)

Volatile cycling - CO_2

CO_2 in slab fluids low if derived internally or by H_2O infiltration



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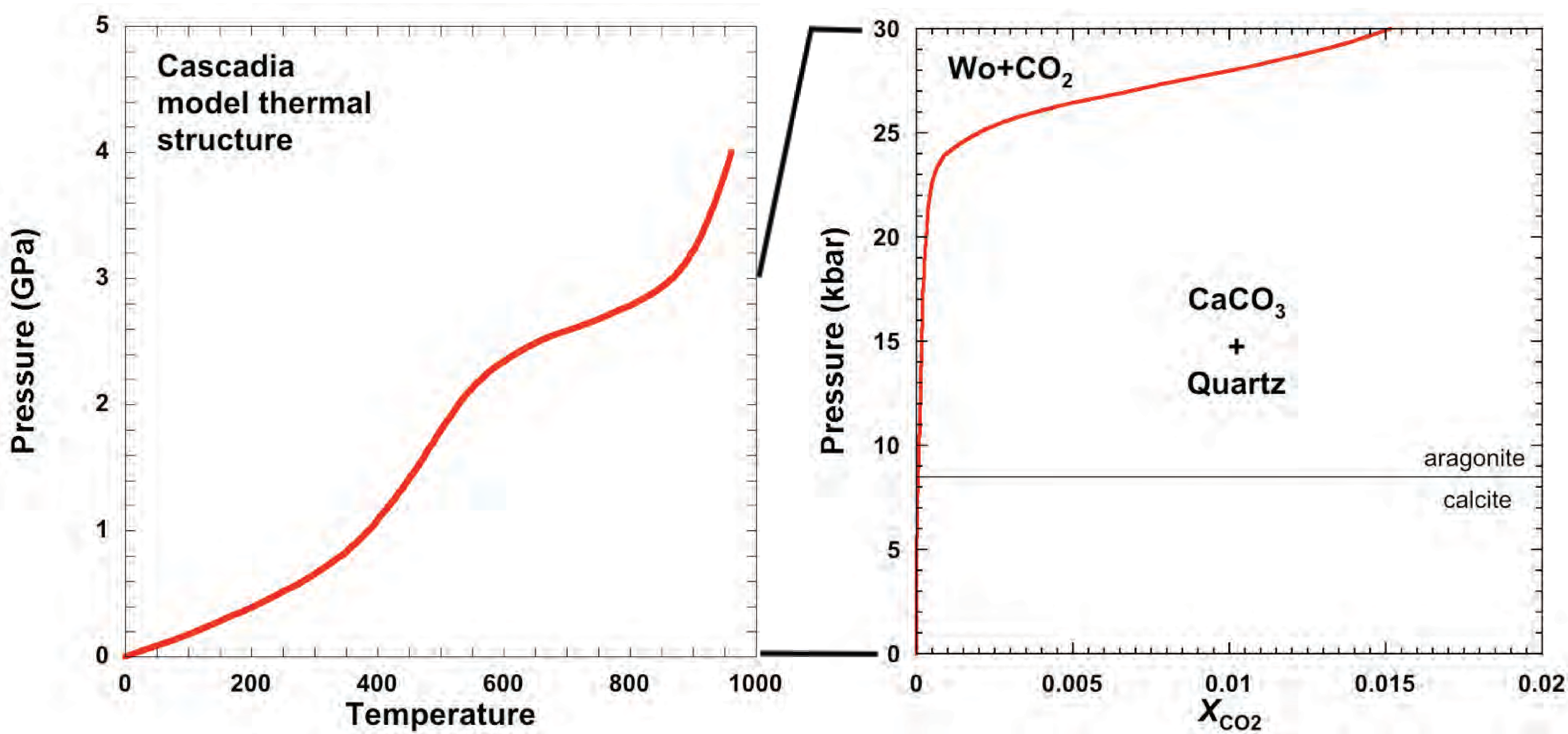
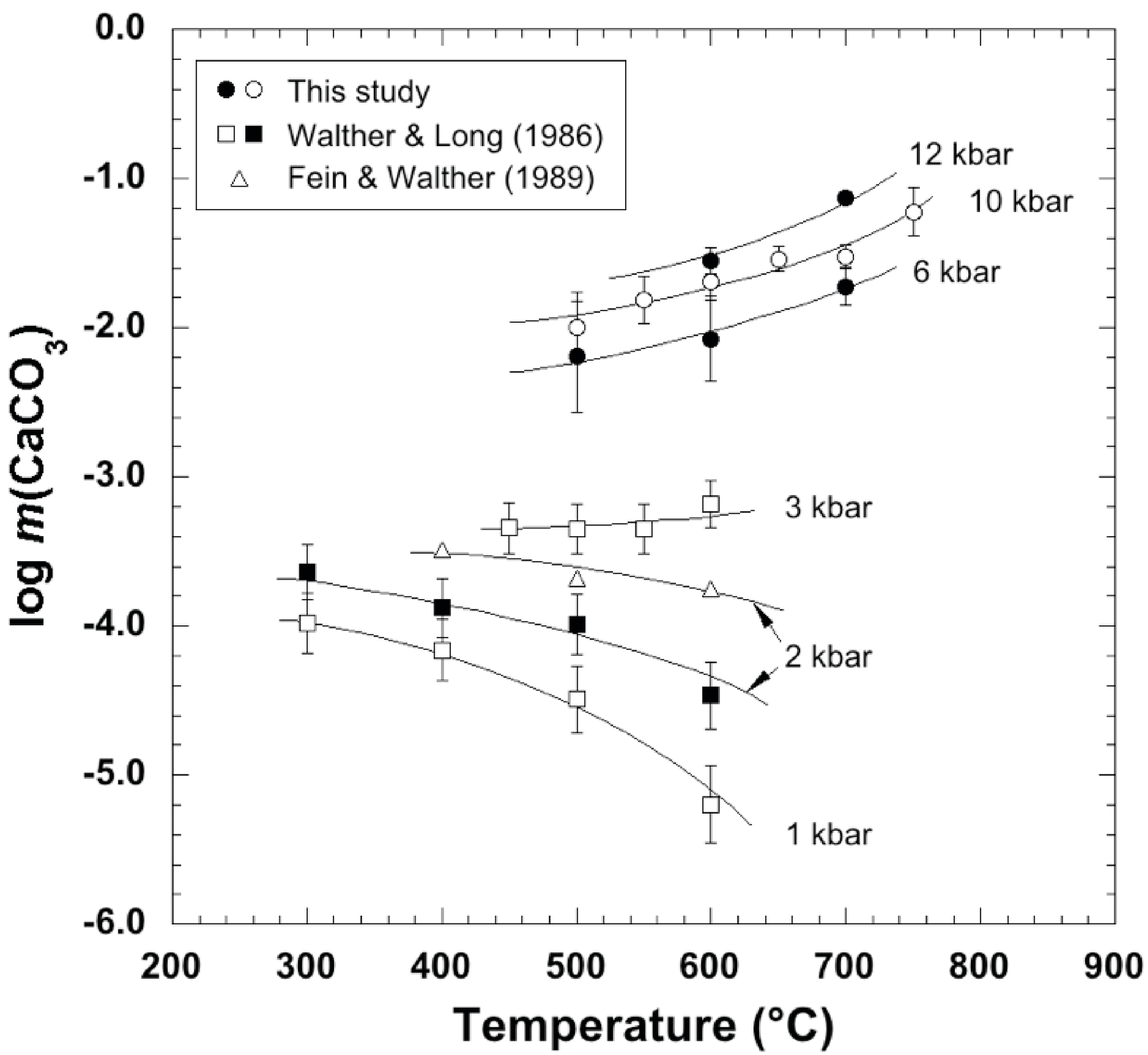


Kimura et al (2009)

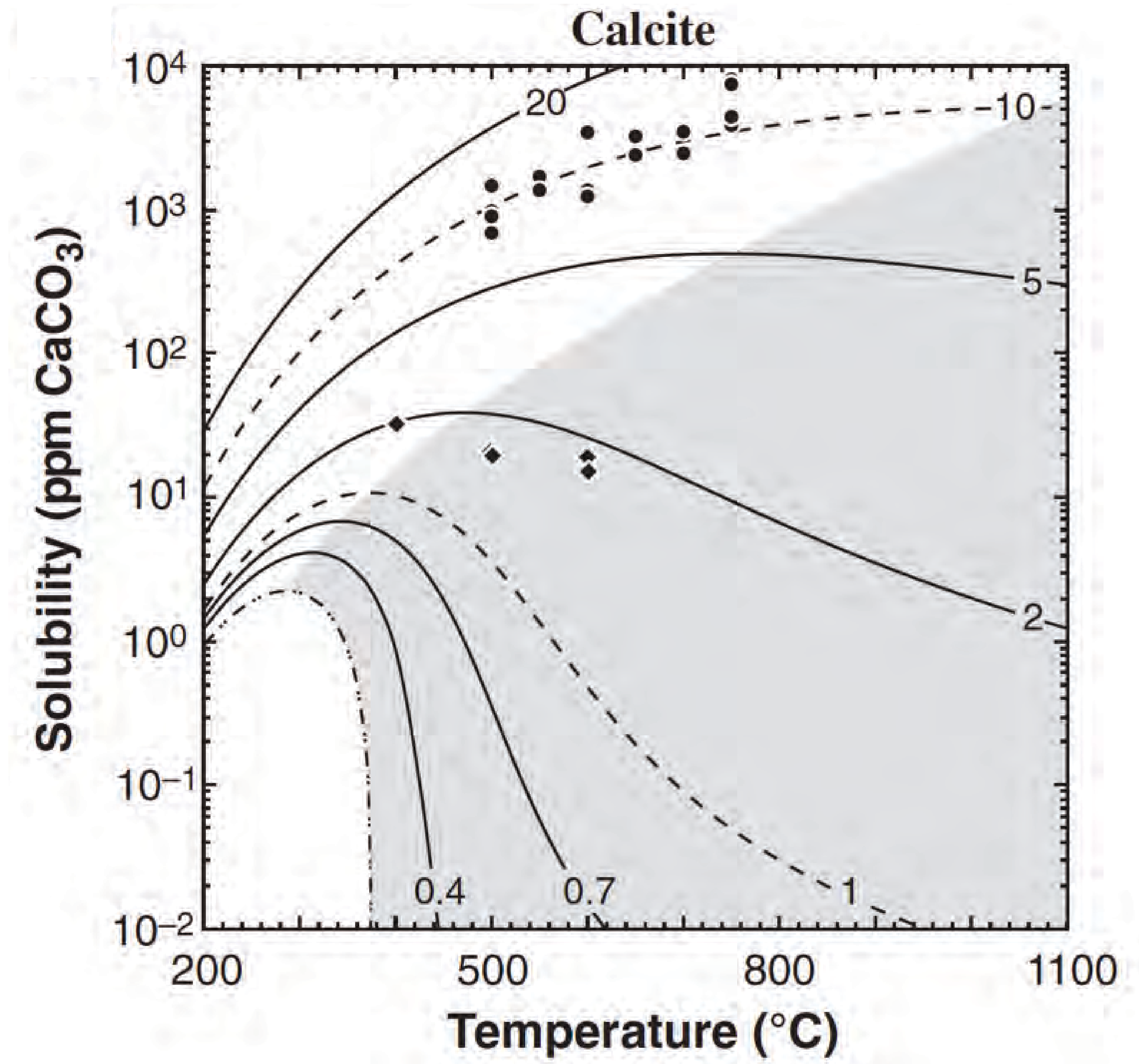
PERPLEX (J. Connolly)

Volatile cycling - CO_2

Calcite solubility in H_2O



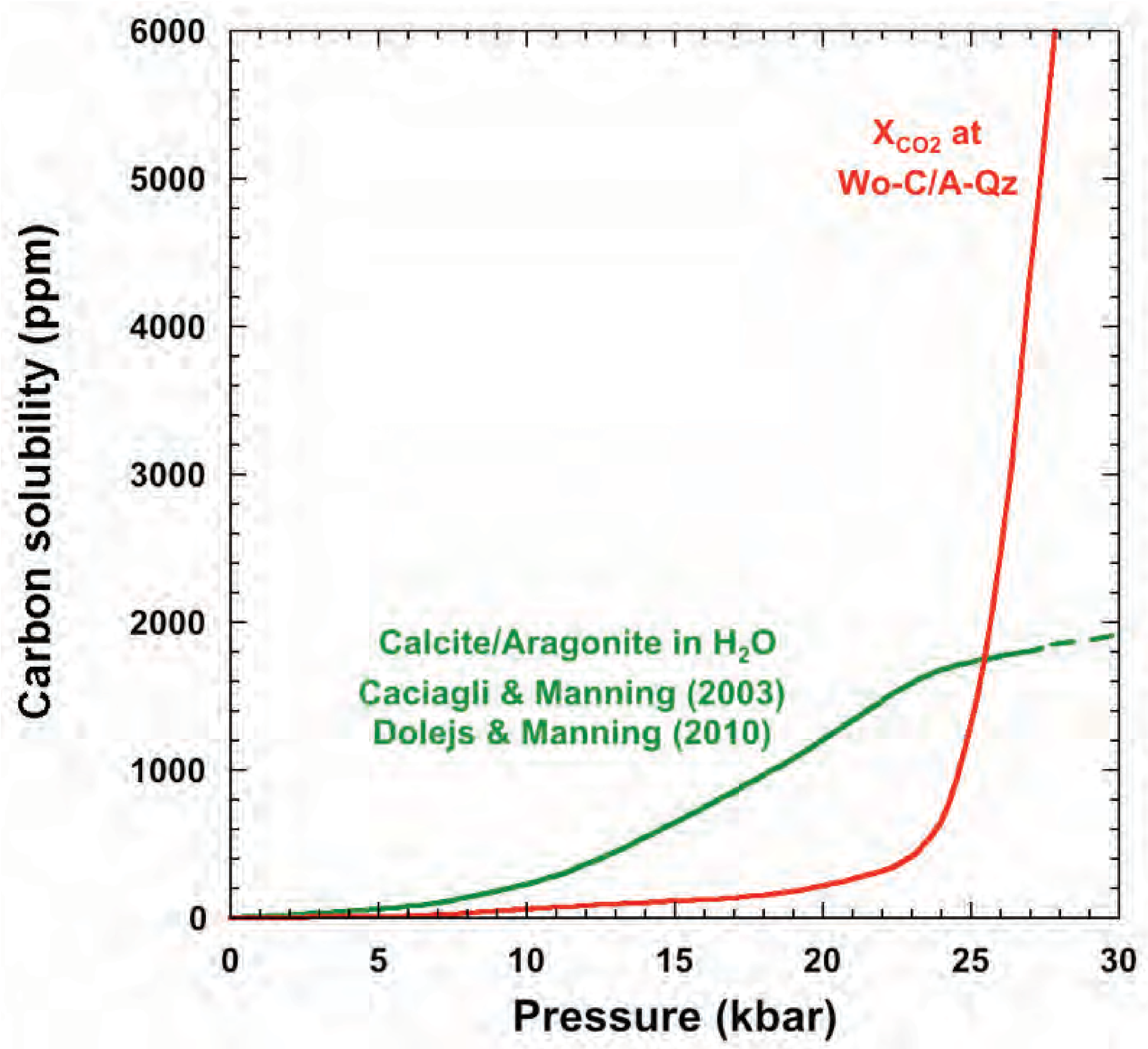
Caciagli & Manning (2003)



Dolejs & Manning (2010)

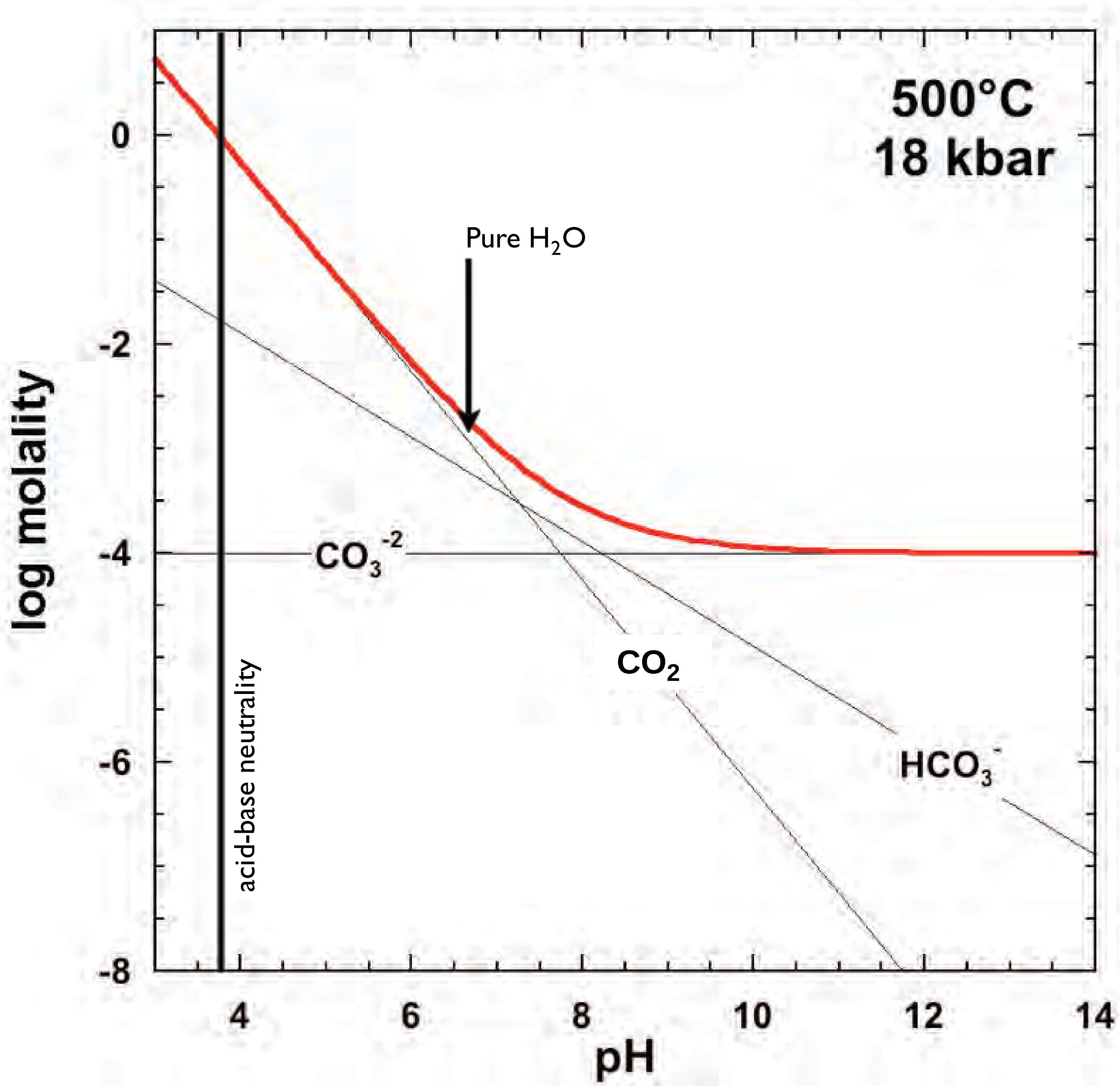
Volatile cycling - CO_2

Experiment and theory give totally different answer!!!



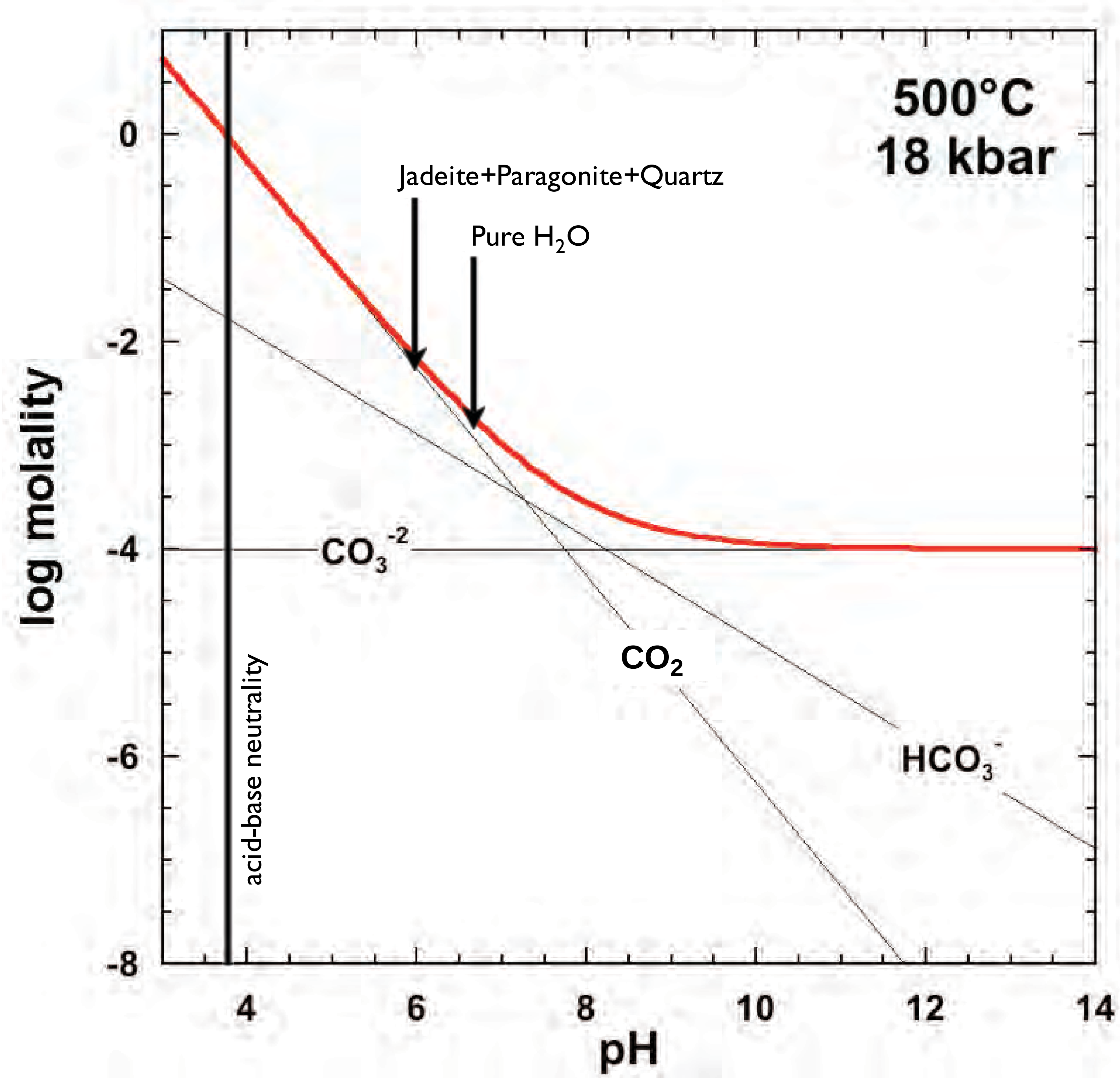
Volatile cycling - CO_2

pH control of carbon species



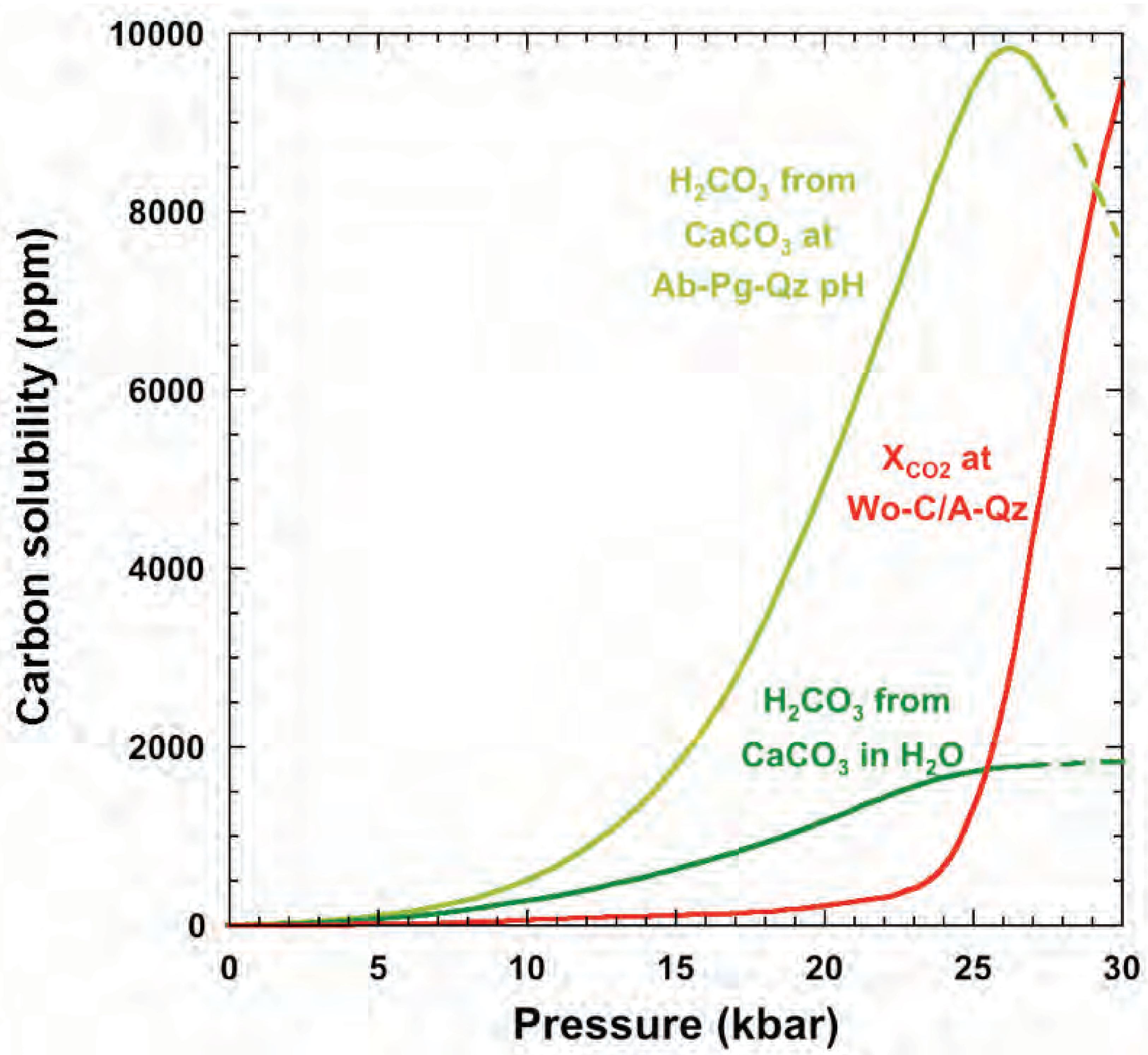
Volatile cycling - CO_2

pH control of carbon species



Volatile cycling - CO_2

pH control of carbon species

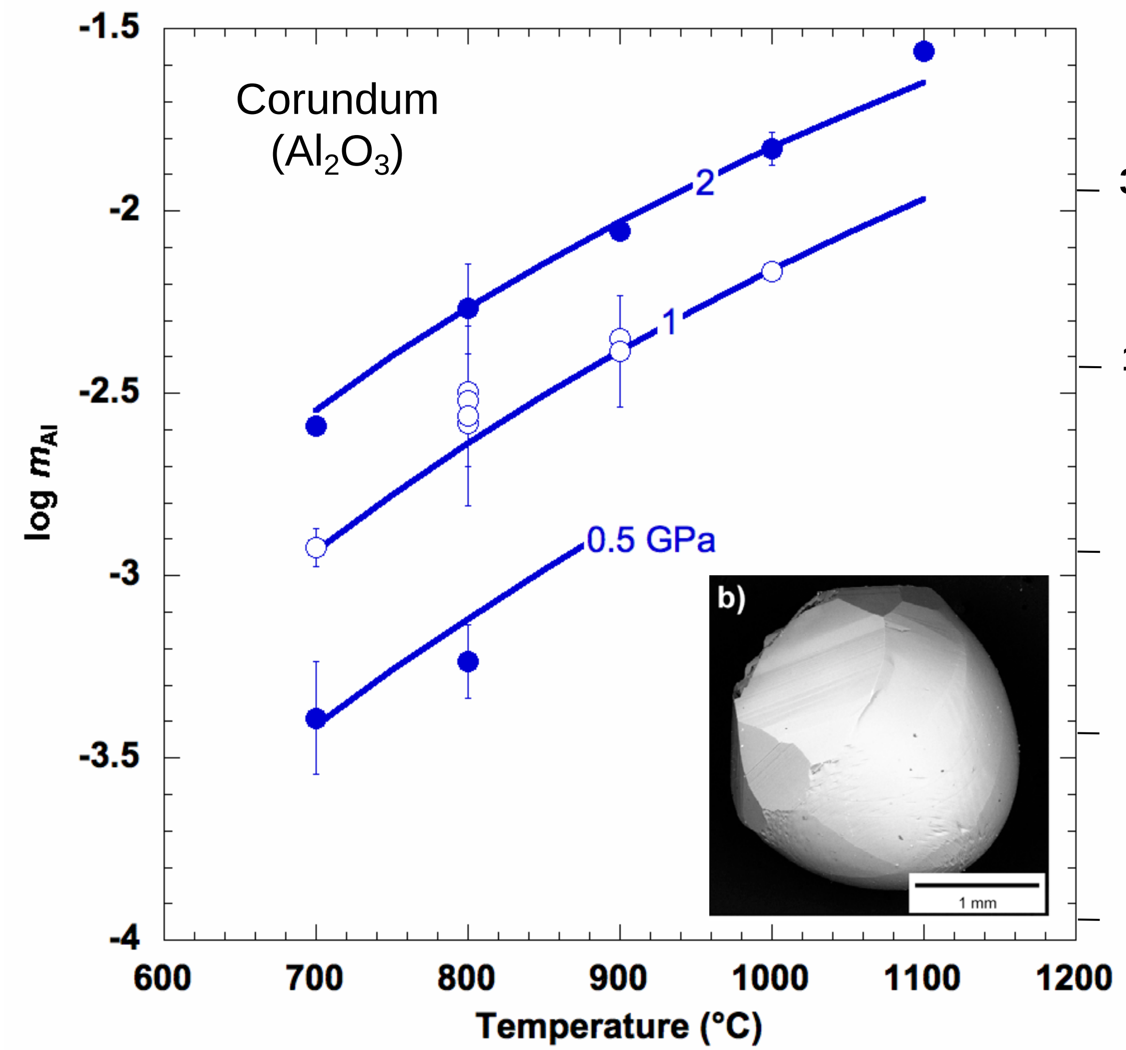


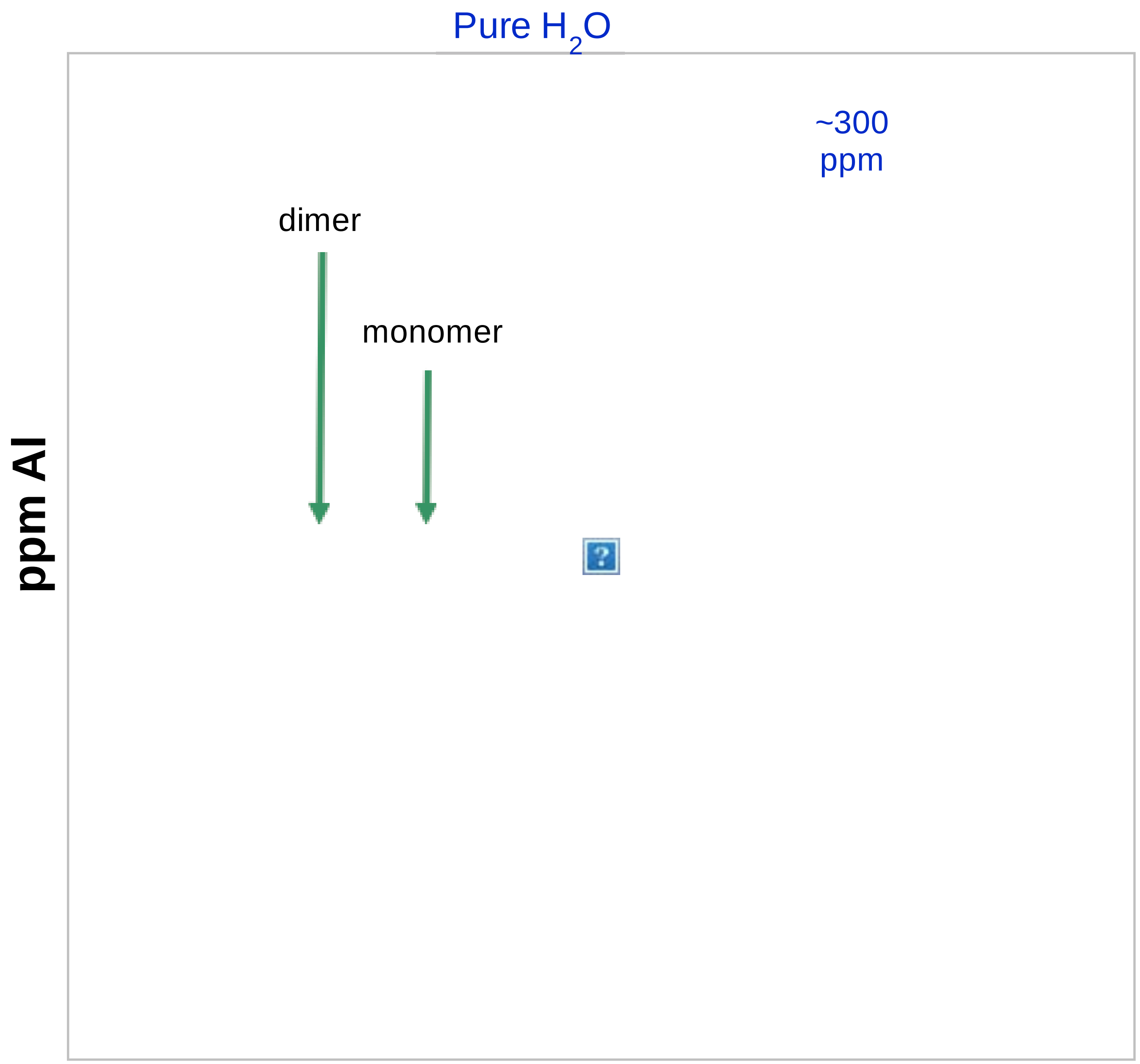
Conclusions

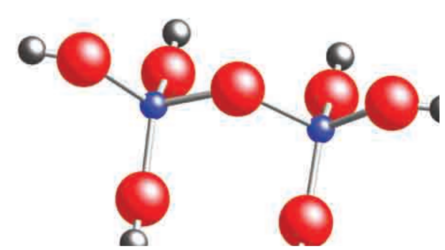
- Altyn Tagh springs sample mantle fluids and require connected permeability to at least 60 km depth
- Solubilities of rock-forming minerals are very high in deep water. Polymerization of Si-Al-O, with other constituent cations, is responsible for elevating solubility
- Polymeric solutes likely control element transport
- Polymerization can be seen as a premelting effect, where species that will condense to melt are first formed in aqueous phase. Silicate polymer chemistry links fluids and melts
- The chemistry of deep fluids will impact transport of volatiles (eg, carbon). This must be taken into account in volatile cycle studies

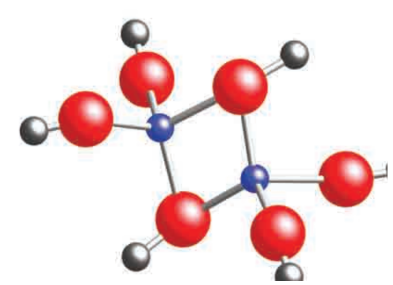
Experiment vs. theory

Al & polymerization: Corundum solubility in H_2O









Tropper & Manning (2007)

Mookherjee, Keppler & Manning (in review)

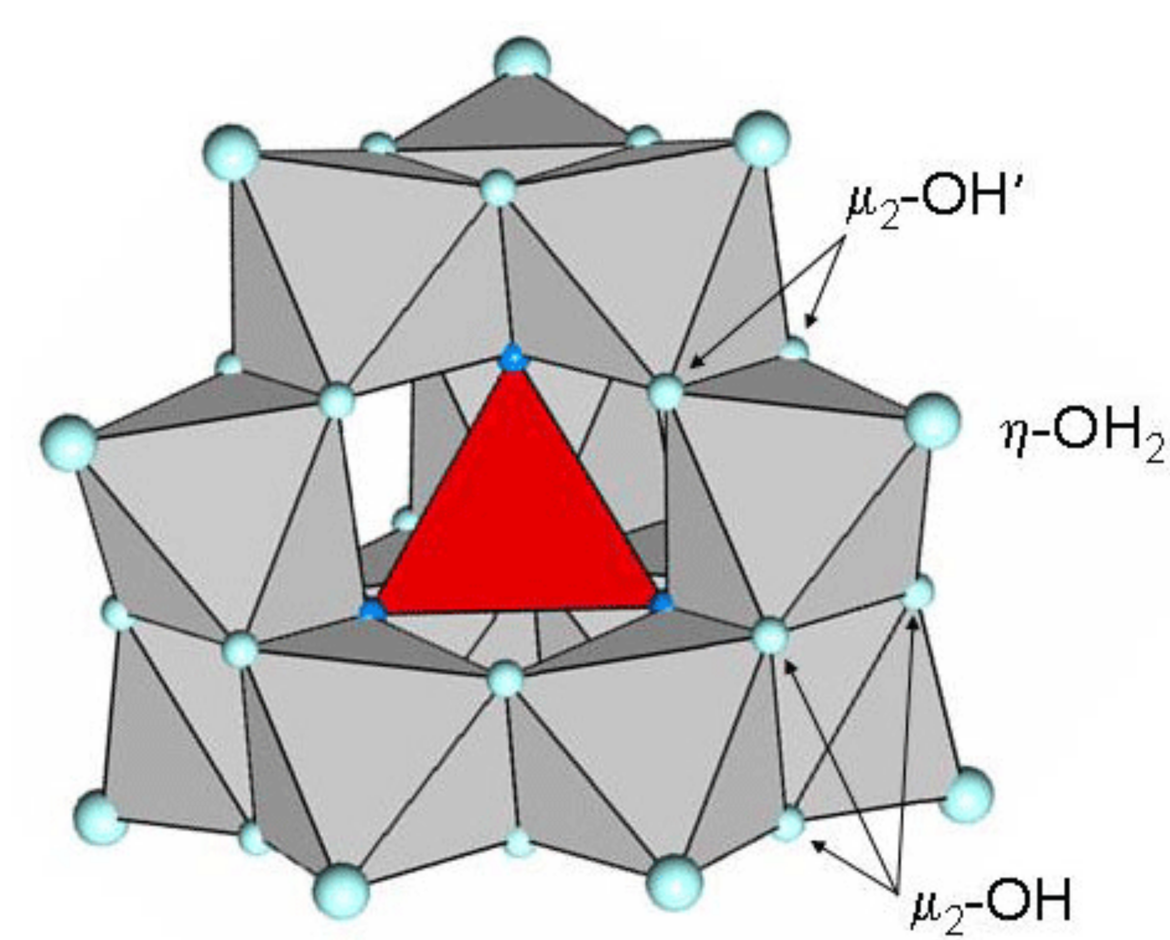
So what else is new?

Al clusters & environmental geochemistry

Fe & Al precipitates in acid mine drainage - Rio Tinto

Carol Stoker

Keggin-type clusters as precursors



Volatile cycling - CO_2

C as carbonate vs. molecular CO_2