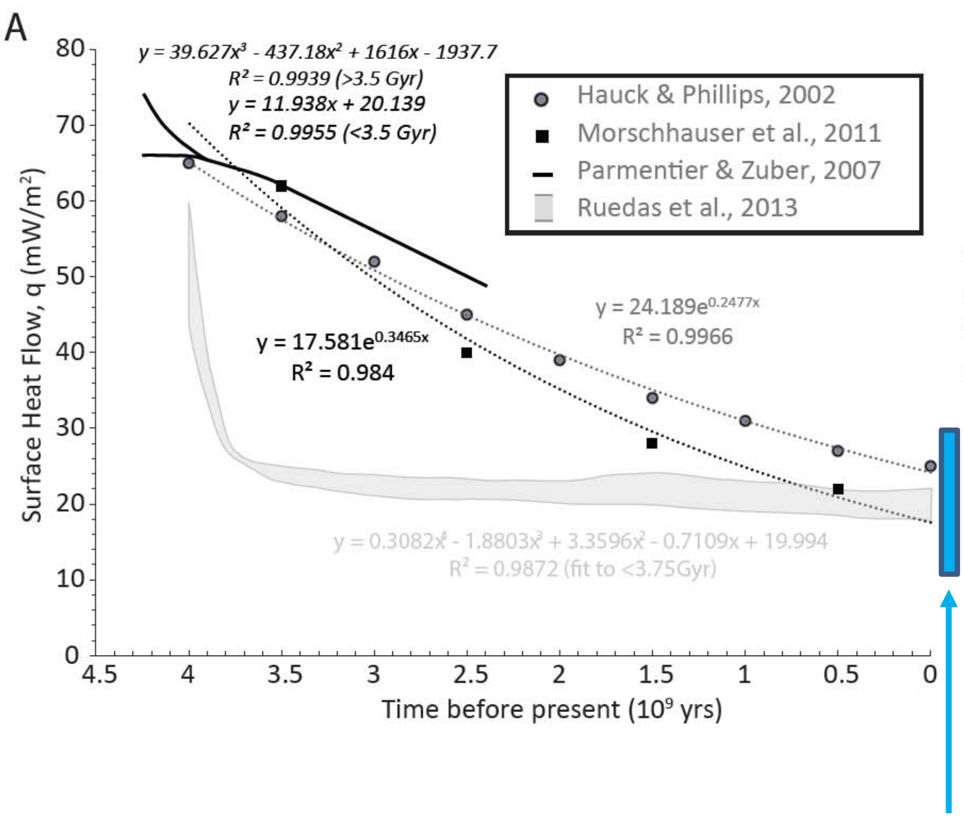
Some background on (1) Martian heatflow, (2) water and physical properties of the Mars subsurface, (3) water-rock reactions, (4) places of escape of methane

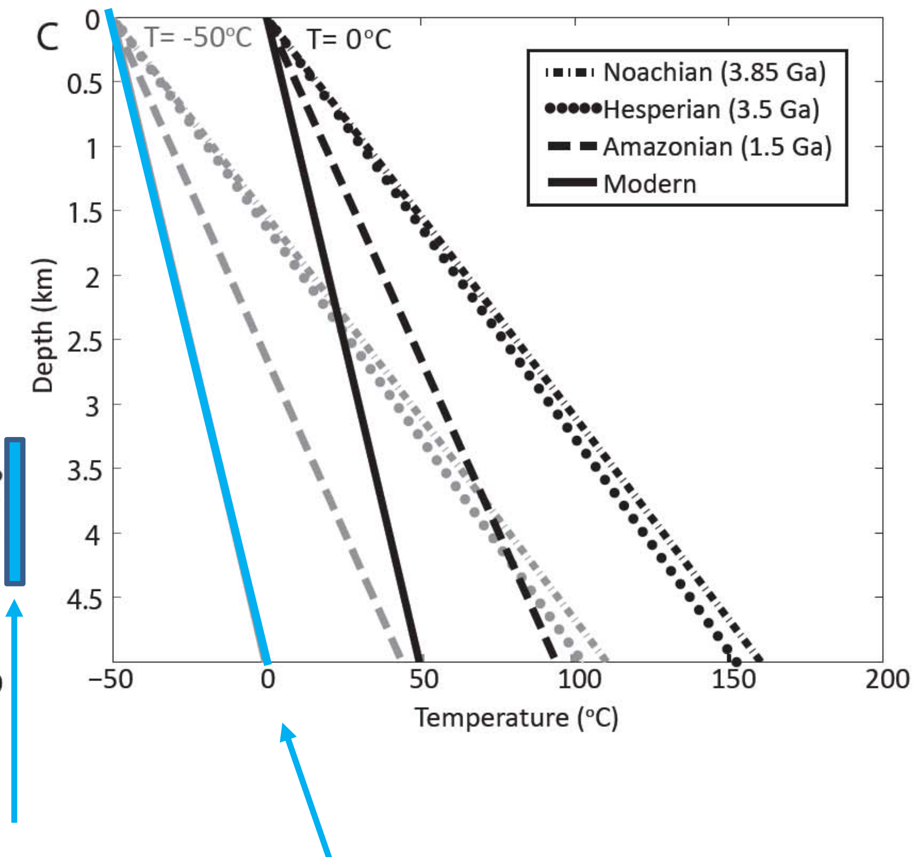
Bethany Ehlmann

8 Dec 2015

Heat flow and thermal gradient on Mars

compilation/calculation from Borlina, Ehlmann, Kite, JGR, 2015 (paper on Gale diagnesis)





Modern heat flow range of 10-30 mW/m2 most likely
Insight mission will determine in 2016/2017

gradient likely ~10 K/km, assuming
no local heat flux source

Possible depths with (pure) liquid water

upper boundary set by thermal gradient (~5km; but lower depths for a brine or in area with enhanced heat flow)

lower boundary set by assumed self sealing of fractures due to pressure (~10km)

Depth of Gale relative to its surroundings

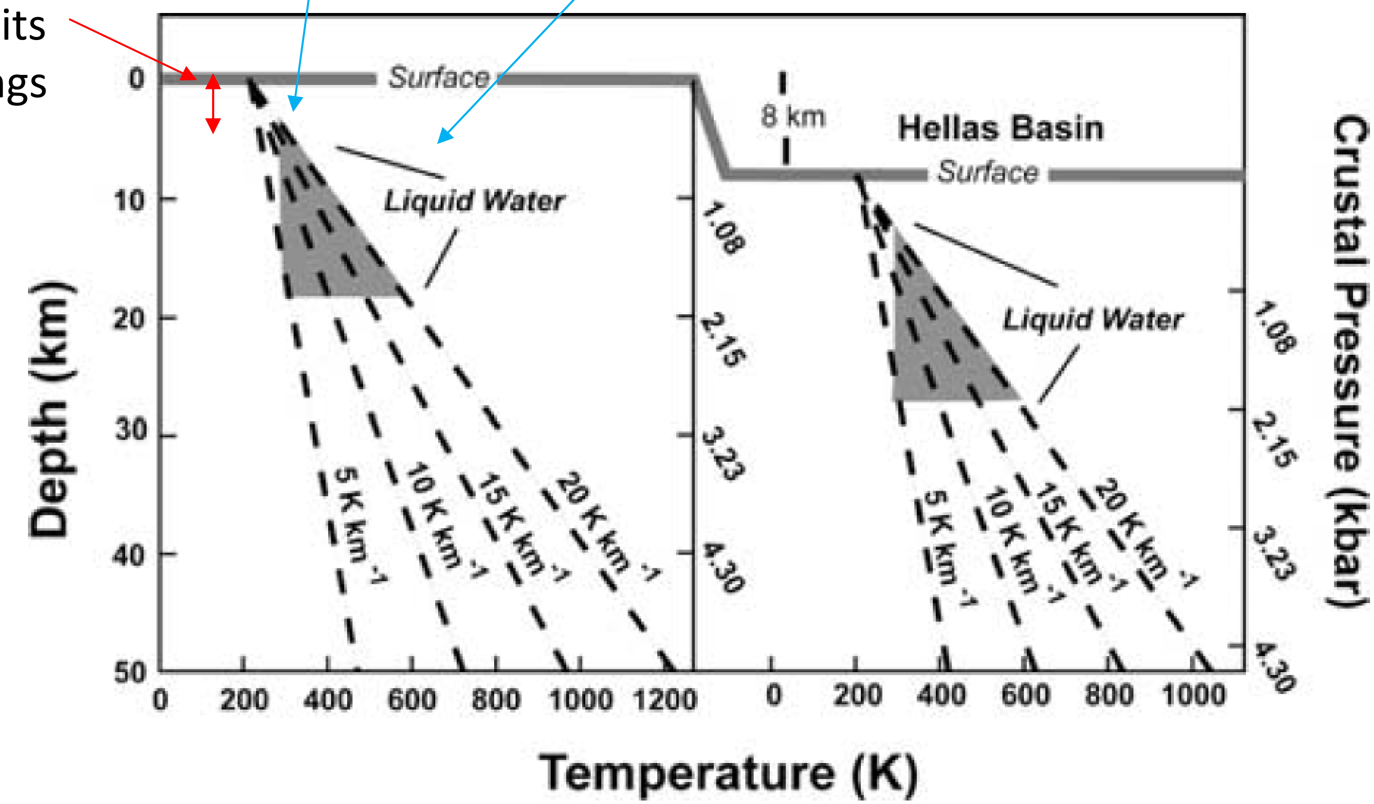
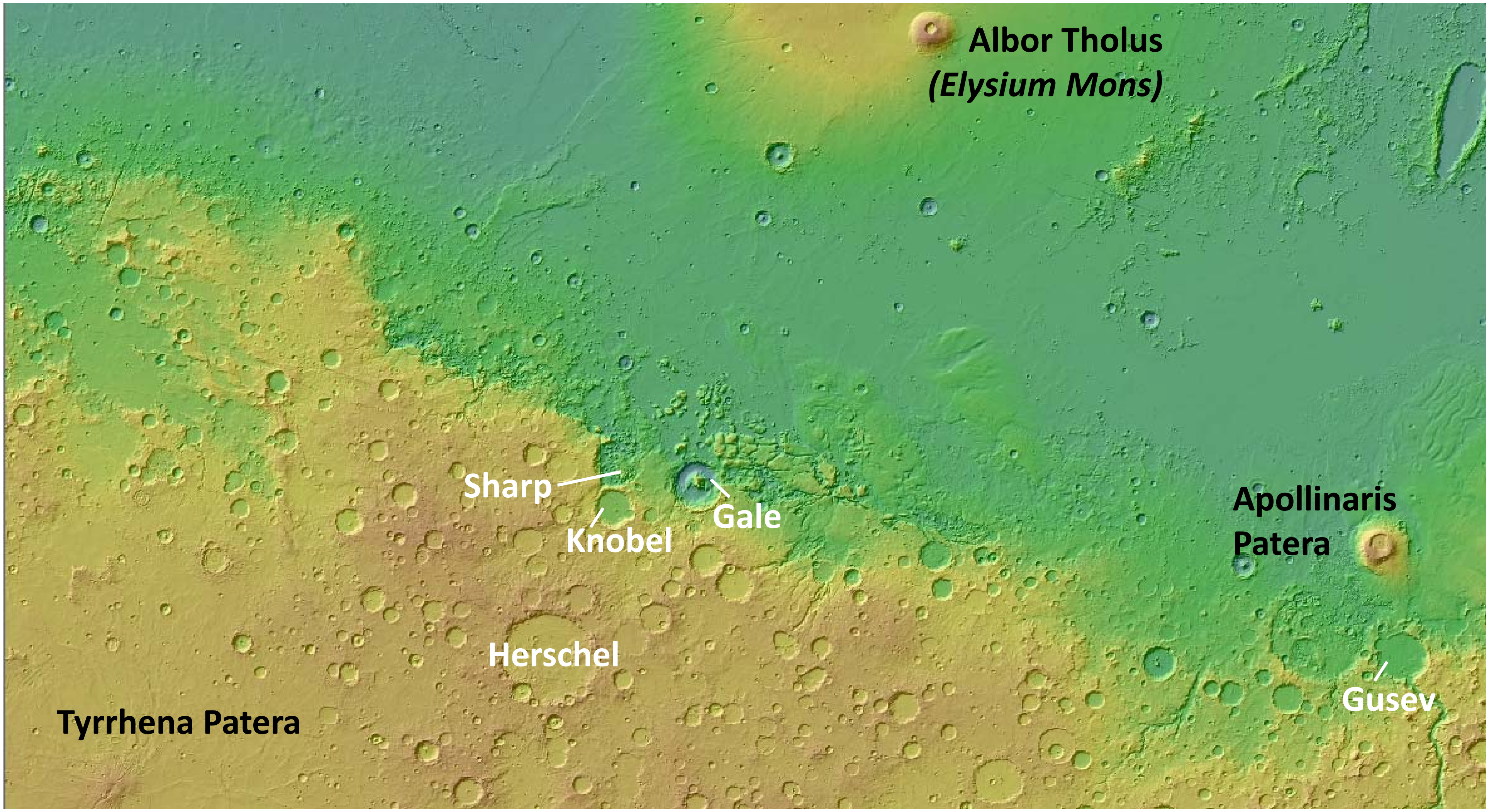


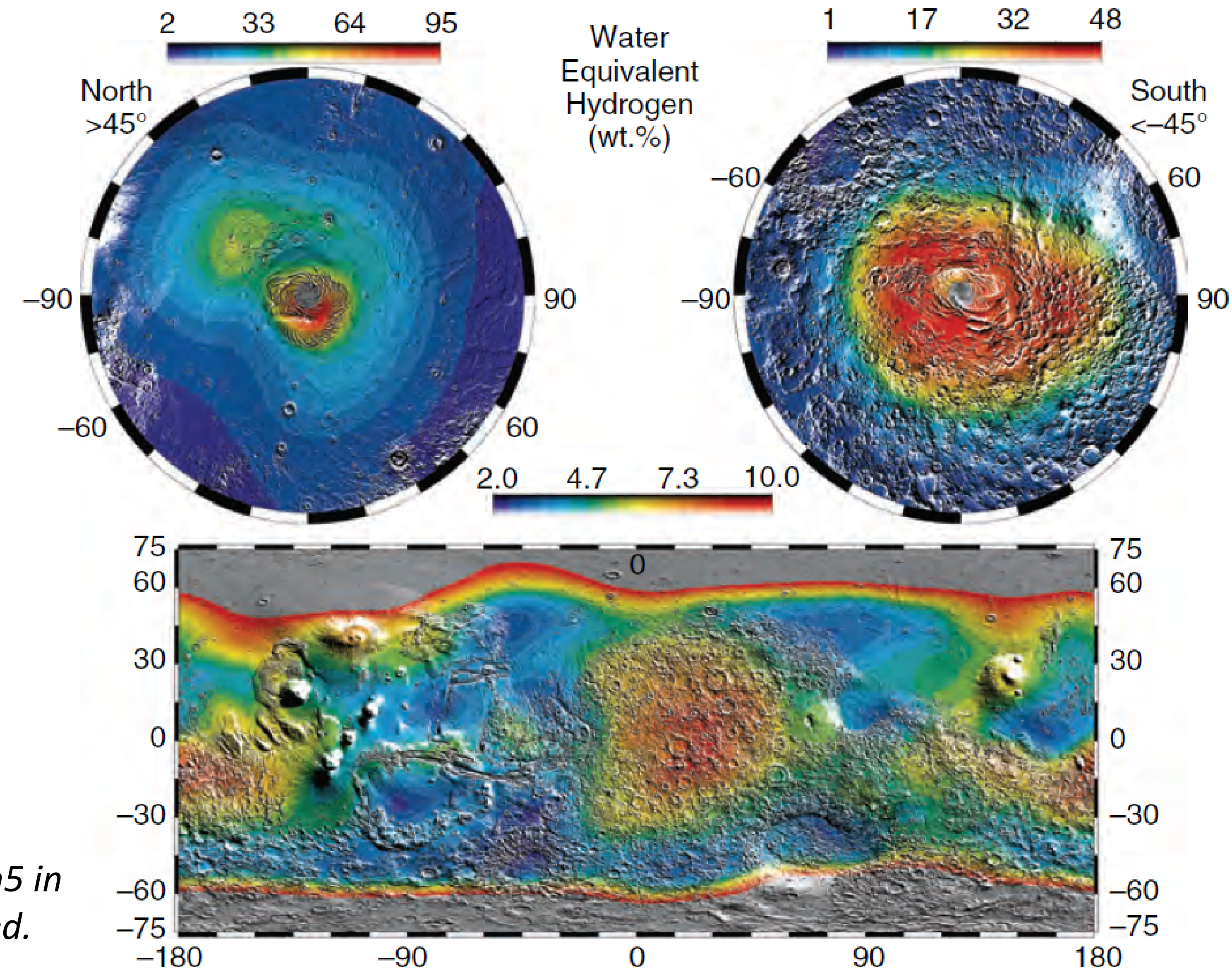
figure from Oze & Sharma, 2005



MOLA Topography

300 km

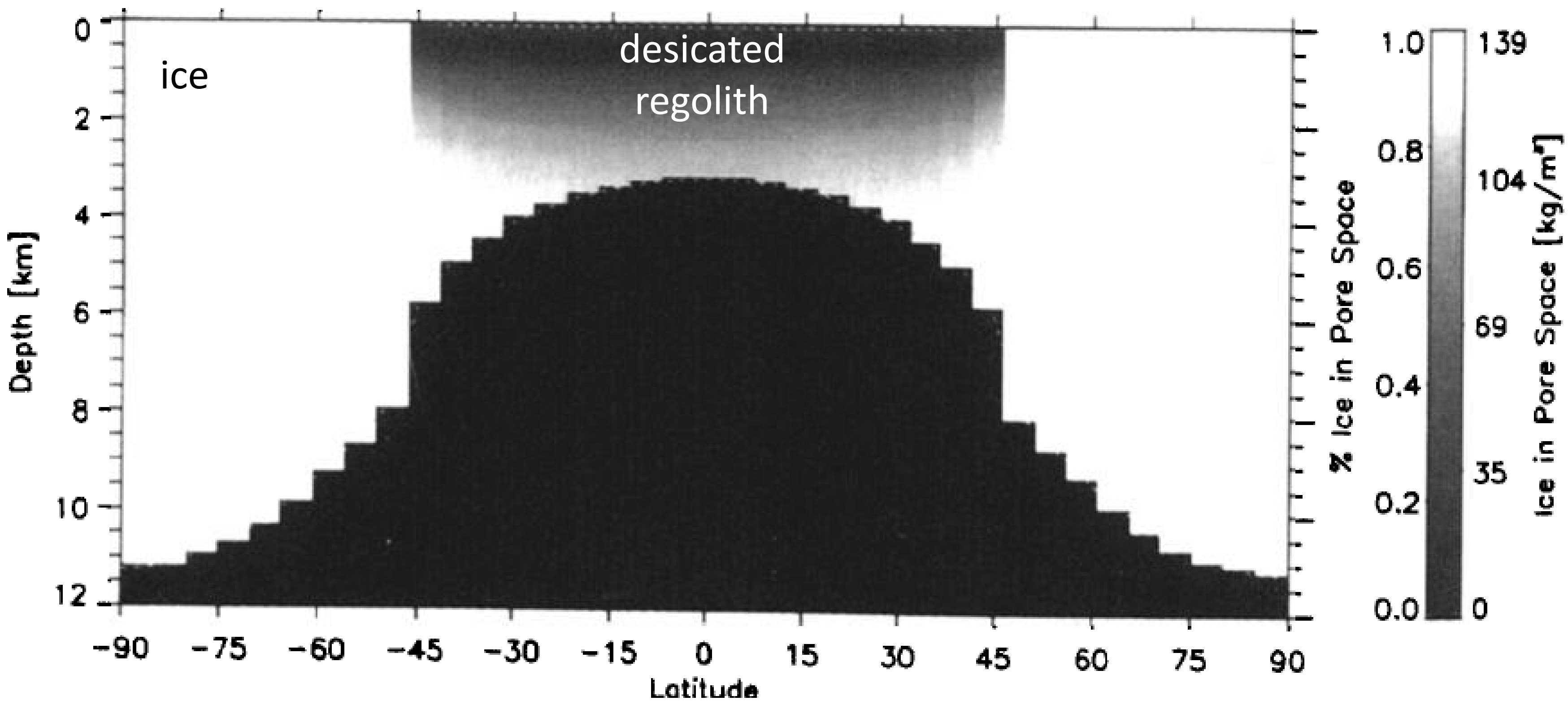
Hydrogen (water) on Mars



Feldman, Ch5 in Bell, 2008, ed.

Highly generalized ice stability profile

Mellon et al., 1997, JGR



*note: many papers reporting ices nearer to the surface in some places due to topography

Why doesn’t radar see an aquifer?

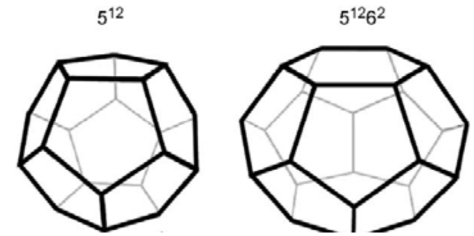
Clifford et al., 2010, JGR

3-5km

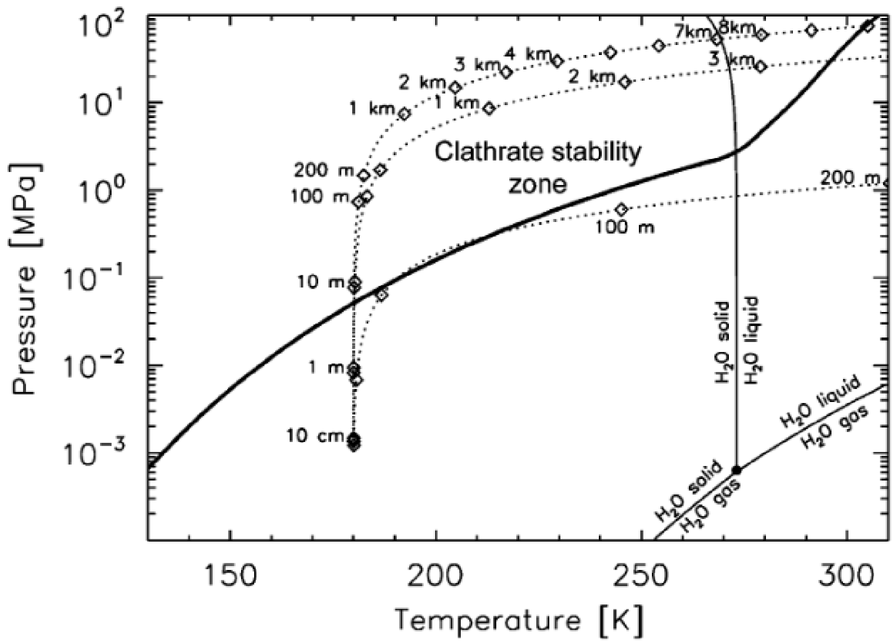
Contrast sharp over <25-50m; pore filled with water at >10%

[75] The absence of more widespread evidence of deep reflectors, potentially indicative of the presence of subpermafrost groundwater, has at least four possible explanations: (1) Subpermafrost groundwater may no longer survive on Mars, a once large inventory having been cold trapped into the growing pore volume of the thickening cryosphere or lost by other processes (e.g., chemical weathering or exospheric escape). (2) Groundwater is present but the cryosphere is deeper than previously expected, placing groundwater beyond the maximum sounding depth of MARSIS. (3) The presence of thin films of liquid water in the lower cryosphere, or within the vadose zone above a subpermafrost groundwater table, has reduced the dielectric contrast necessary to produce a detectable reflection [*Beaty et al.*, 2001; *LeGall et al.*, 2007]. (4) The dielectric loss and scattering properties of the subsurface are more attenuating than previously believed, resulting in a shallower than expected MARSIS sounding performance [*Heggy et al.*, 2006; *Grimm et al.*, 2006; *Boisson et al.*, 2009].

Clathrates



- Google Scholar "clathrate methane Mars" and you will have numerous publications
- In oversimplified terms, a gas clathrate hydrate is a lattice of hydrogen bonded H2O molecules forming cage-like cavities that contain gas molecules (*Chastain & Chevrier, 2007, Planetary and Space Science*) – possibly part of polar deposits – see their review

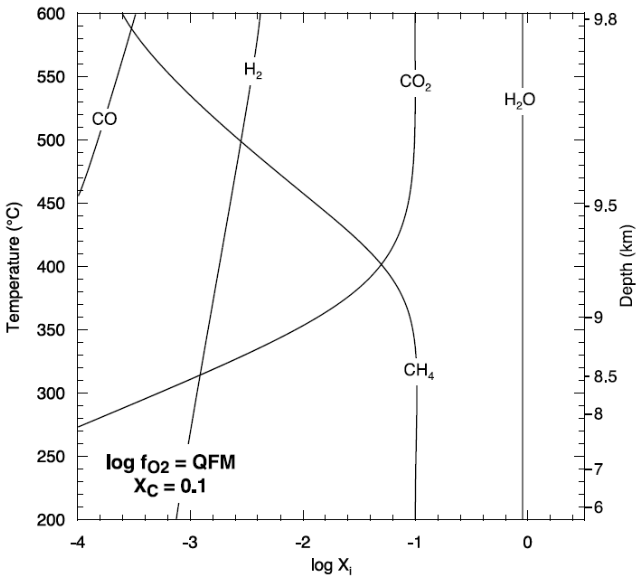


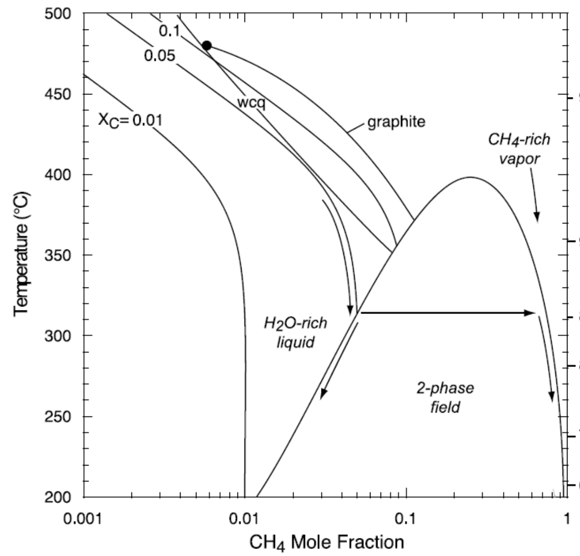
My opinion:

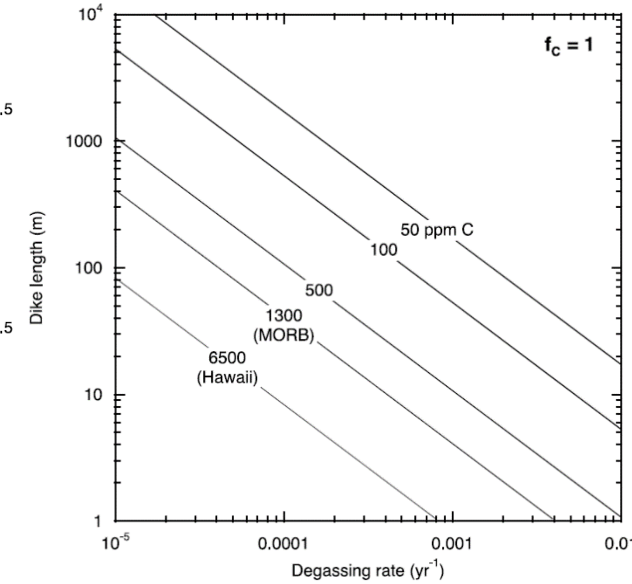
Doesn't solve generation problem

Might explain aspects of release timing

Carbon-bearing **magmatically sourced** hydrothermal fluid







- *Lyons et al., GRL, 2005: Formation of methane on Mars by fluid-rock interaction in the crust*
  - "Sub-regolith basaltic crust substantially lower fO2 of QFM to QFM - 4.5 based on studies of shergottite meteorites (auxiliary materials1). Because CH4 is a reduced C species, a conservative estimate of abiogenic CH4 production can be made by assuming that fO2 is the highest value permissible (QFM). We demonstrate that CH4 is the dominant C species in the fluid phase along the upflow path from a depth of 9.5 km (430C) to the surface by calculating the equilibrium distribution of molecular C-O-H species at a fixed carbon mole fraction of XC = 0.1 and at QFM (Figure 2)…Lower fO2 leads to CH4 predominance at greater depth.
  - If the source of carbon is a magmatic vapor phase, then the fluid is probably undersaturated with graphite or carbonate. In this case it will have lower total C and will intersect the two-phase field at lower temperatures (Figure 3). [10] Phase equilibrium considerations illustrate two features that strongly favor abiogenic hydrothermal methane production on Mars. **First, for expected fO2, C is present in a Martian crustal fluid almost exclusively as CH4 at T < 430C, and such fluids are essentially binary H2O-CH4 mixtures. Second, H2O-CH4 phase separation (Figure 3) will cause segregation of a CH4-rich vapor phase in the crust. Once formed, this low-density phase will rise rapidly through the crust and become more methane rich as it approaches the surface. Rapid rise through permeable crust will yield minimal capacity for reaction with host rock, minimizing C loss by precipitation of graphite**.

Family of **serpentinization-style water-rock reactions**

- Involve olivine **$(Mg,Fe)_2SiO_4$** and low-Ca pyroxene **$(Mg,Fe,Ca)_2Si_2O_6$**
- Formation of serpentine dominates volumetrically and involves the Mg – self-sustaining hydration reaction with 30% volume expansion

$$\underset{\text{Mg-olivine}}{2Mg_2SiO_4} + \underset{\text{Mg-pyroxene}}{Mg_2Si_2O_6} + 4H_2O = \underset{\text{serpentine}}{2Mg_3Si_2O_5(OH)_4} \quad [1]$$

$$\underset{\text{Mg-olivine}}{Mg_2SiO_4} + 2CO_2 = \underset{\text{magnesite}}{2MgCO_3} + \underset{\text{quartz}}{SiO_2} \quad [2a]$$

$$\underset{\text{Mg-olivine}}{Mg_2SiO_4} + \underset{\text{CaMg-pyroxene}}{CaMgSi_2O_6} + 2CO_2 + 2H_2O = \underset{\text{serpentine}}{Mg_3Si_2O_5(OH)_4} + \underset{\text{calcite}}{CaCO_3} + \underset{\text{magnesite}}{MgCO_3} \quad [2b]$$

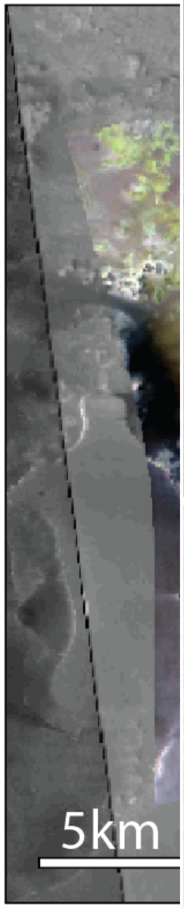
from Kelemen & Mater, 2008

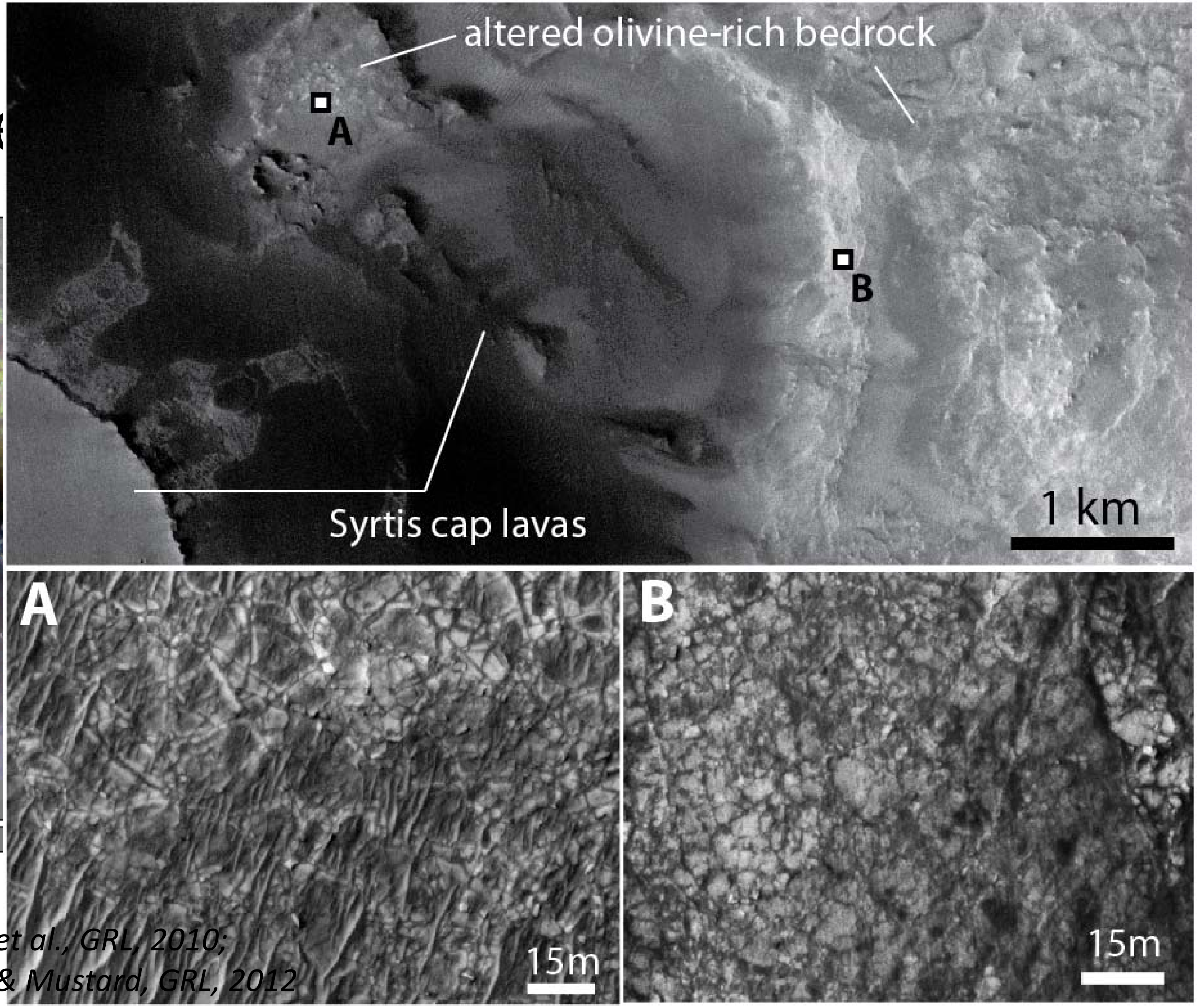
- However, it is the **oxidation of iron that is responsible for the quantity and magnitude of H2 and/or CH4 produced**. Key variables are Eh, pCO2, T, aSiO2, pH

	Reactions
R1	$3Fe_2SiO_4 + 2H_2O = 3SiO_{2[quartz]} + 2Fe_3O_4 + 2H_{2(aq)}$
R2	$3Fe_2SiO_4 + 2H_2O = 3SiO_{2[Amorph\text{-}Silica]} + 2Fe_3O_4 + 2H_{2(aq)}$
R3	$3Fe_2SiO_4 + 2H_2O = 3SiO_{2(aq)} + 2Fe_3O_4 + 2H_{2(aq)}$
R4	$6Fe_2SiO_4 + 7H_2O = 3Fe_3Si_2O_5(OH)_4{}^{a} + Fe_3O_4 + H_{2(aq)}$
R5	$2Mg_2SiO_4 + 3H_2O = Mg(OH)_2 + Mg_3Si_2O_5(OH)_4$
R6	$6Fe_2SiO_4 + CO_{2(aq)} + 2H_2O = 6SiO_{2[Quartz]} + 4Fe_3O_4 + CH_4$
R7	$24Fe_2SiO_4 + 26H_2O + CO_{2(aq)} = 12Fe_3Si_2O_5(OH)_4{}^{a} + 4Fe_3O_4 + CH_4$
R8	$3FeSiO_3 + H_2O = Fe_3O_4 + H_{2(aq)} + 3SiO_{2(aq)}$
R9	$3FeSiO_3 + H_2O = Fe_3O_4 + H_{2(aq)} + 3SiO_{2[Amorph\text{-}Silica]}$
R10	$12FeSiO_3 + 2H_2O + CO_{2(aq)} = 4Fe_3O_4 + CH_4 + 12SiO_{2(aq)}$
R11	$12FeSiO_3 + 2H_2O + CO_{2(aq)} = 4Fe_3O_4 + CH_4 + 12SiO_{2[Amorph\text{-}Silica]}$
R12	$4H_2 + CO_2 = CH_4 + 2H_2O$
R13	$H_2 + SO_2 = H_2S + O_2$

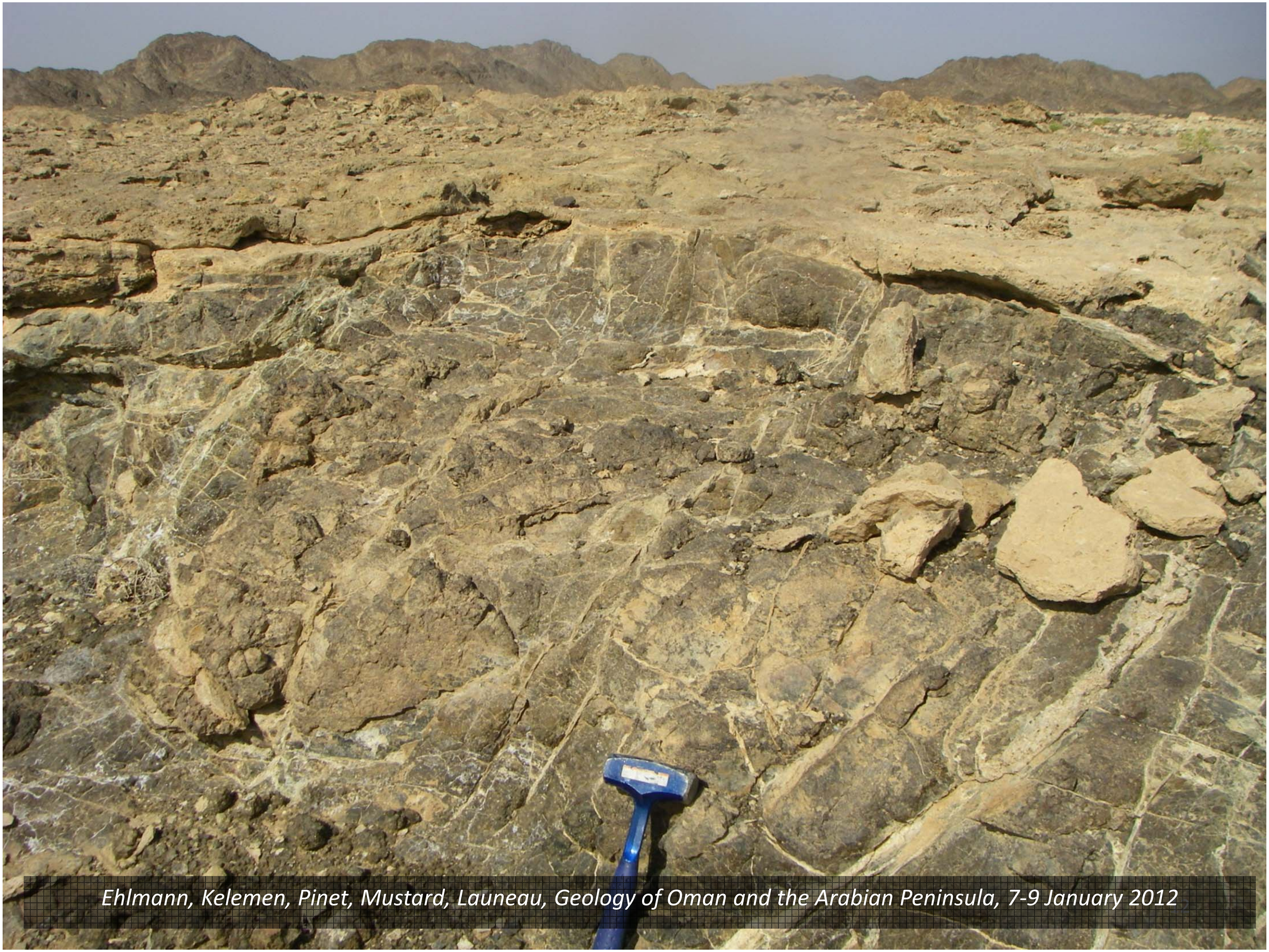
from Oze & Sharma, 2005

Se

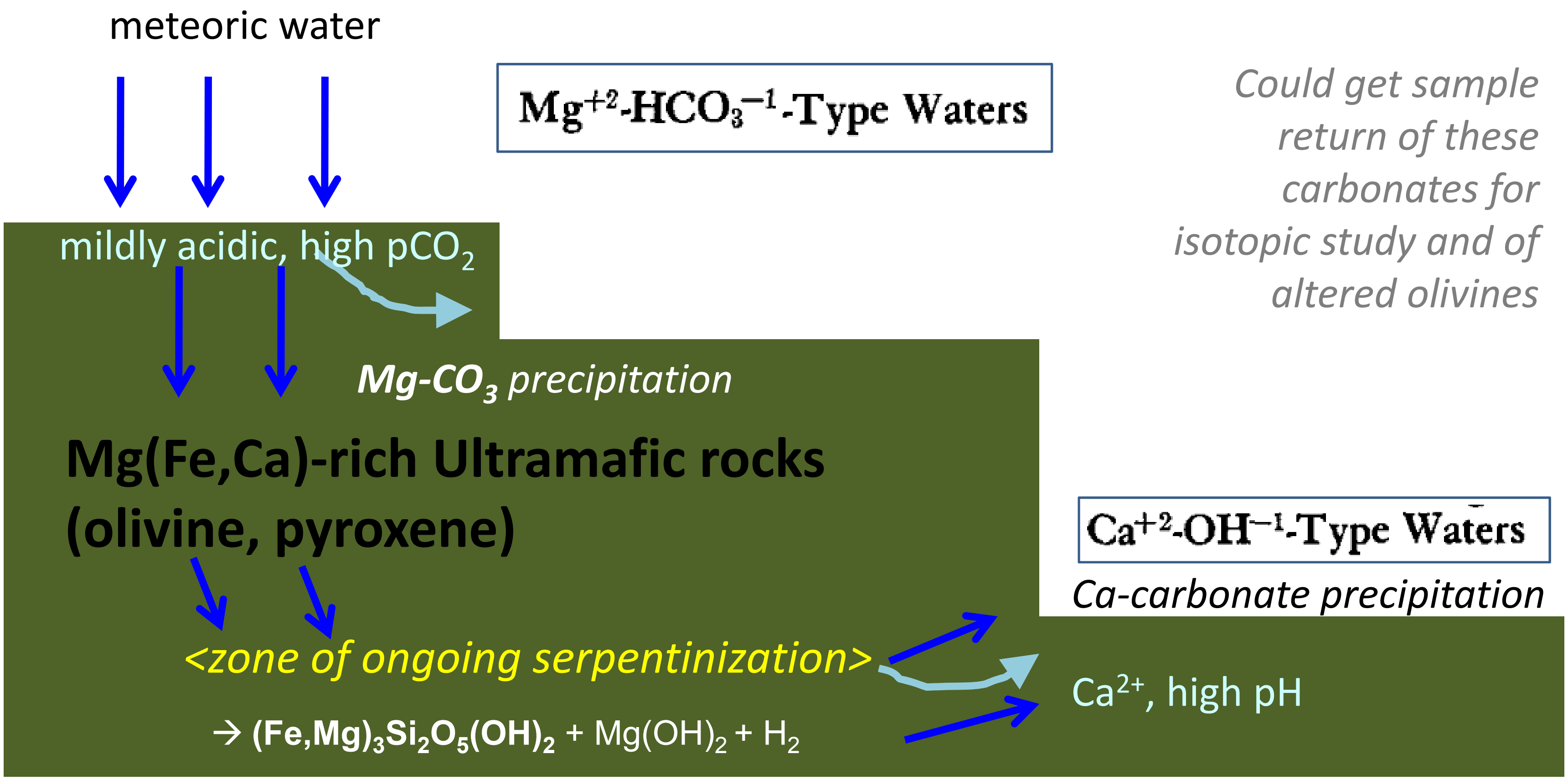




Ehlmann et al., GRL, 2010;
Ehlmann & Mustard, GRL, 2012


Ehlmann, Kelemen, Pinet, Mustard, Launeau, Geology of Oman and the Arabian Peninsula, 7-9 January 2012

Tracing the Serpenitinization Process through Carbonate Chemistry



Could get sample return of these carbonates for isotopic study and of altered olivines

process described in *Barnes & O'Neil, 1969*

Ehlmann et al., Geology of Oman & the Arabian Peninsula, 7-9 January 2012

Planetary and Space Science 59 (2011) 196–202

ELSEVIER

Contents lists available at ScienceDirect

Planetary and Space Science

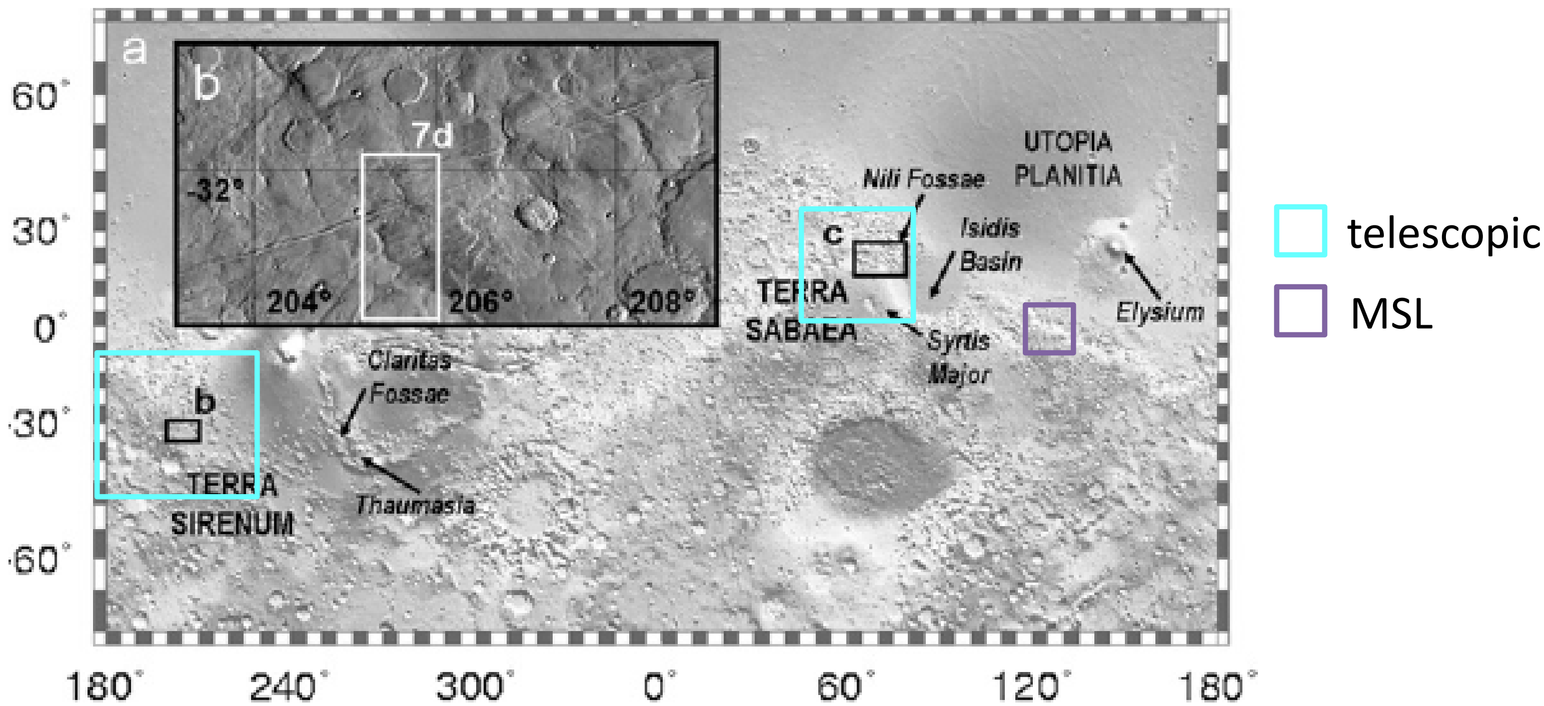
journal homepage: www.elsevier.com/locate/pss

Geology of possible Martian methane source regions

James J. Wray [a,*], Bethany L. Ehlmann [b]

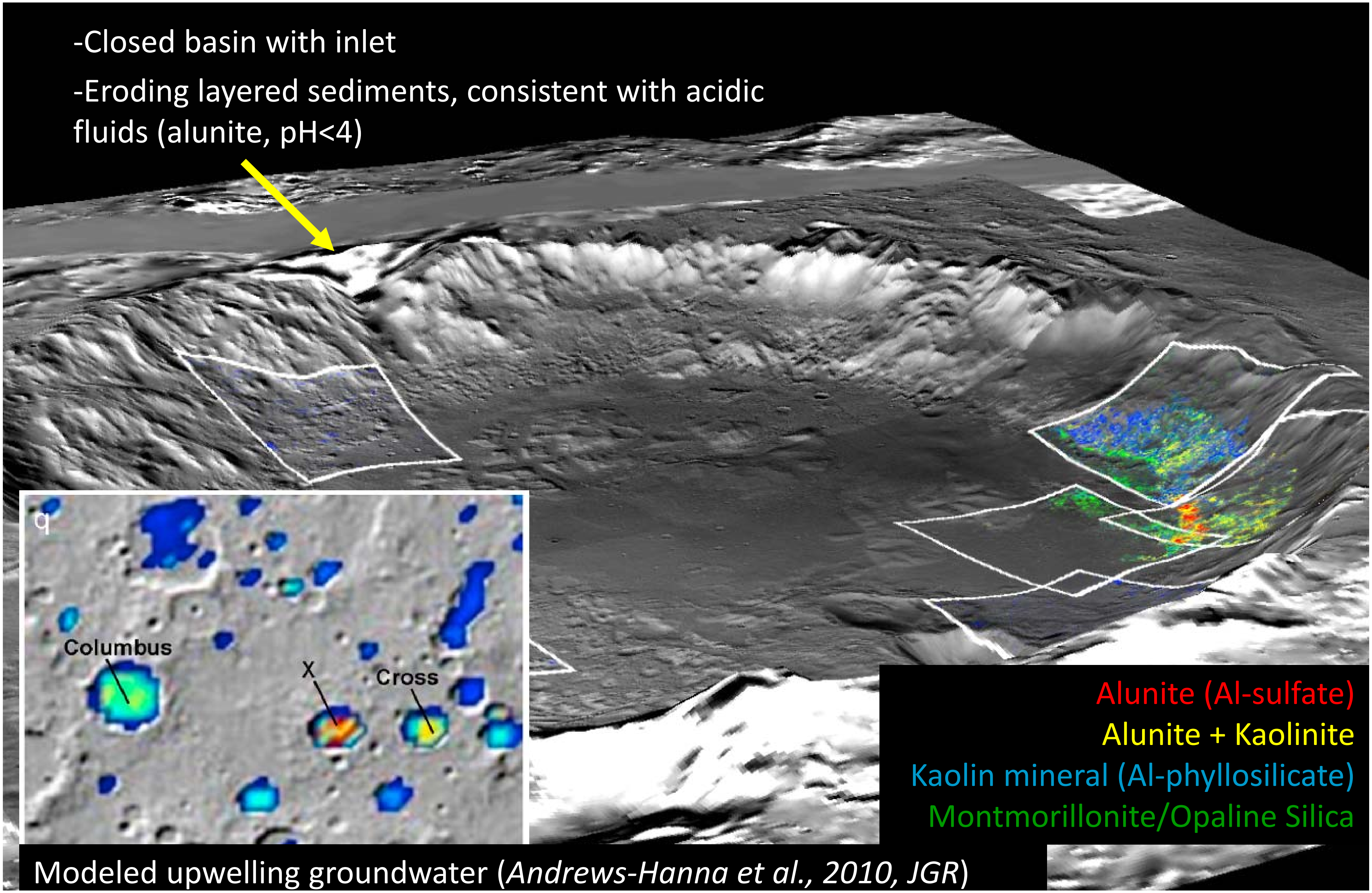
[a] Department of Astronomy, Cornell University, Ithaca, NY 14853, USA
[b] Department of Geological Sciences, Brown University, Providence, RI 02912, USA

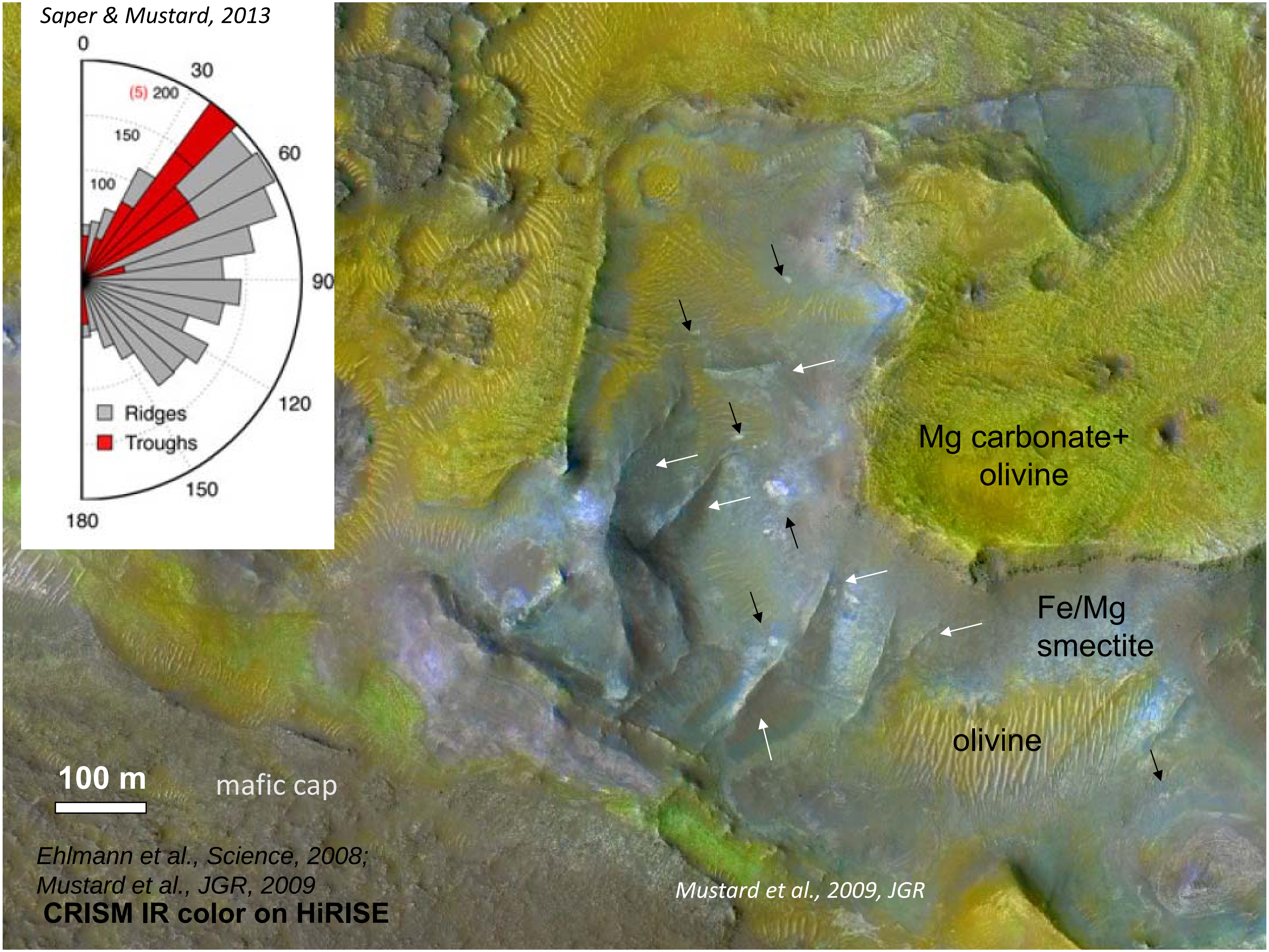
Bottomline: evidence of hydrated minerals, fractures, (ancient) grounwaters in the source regions but not unique to these regions



Late Noachian/Hesperian Mars: Diverse Aqueous Environments
Groundwater-fed acid lakes

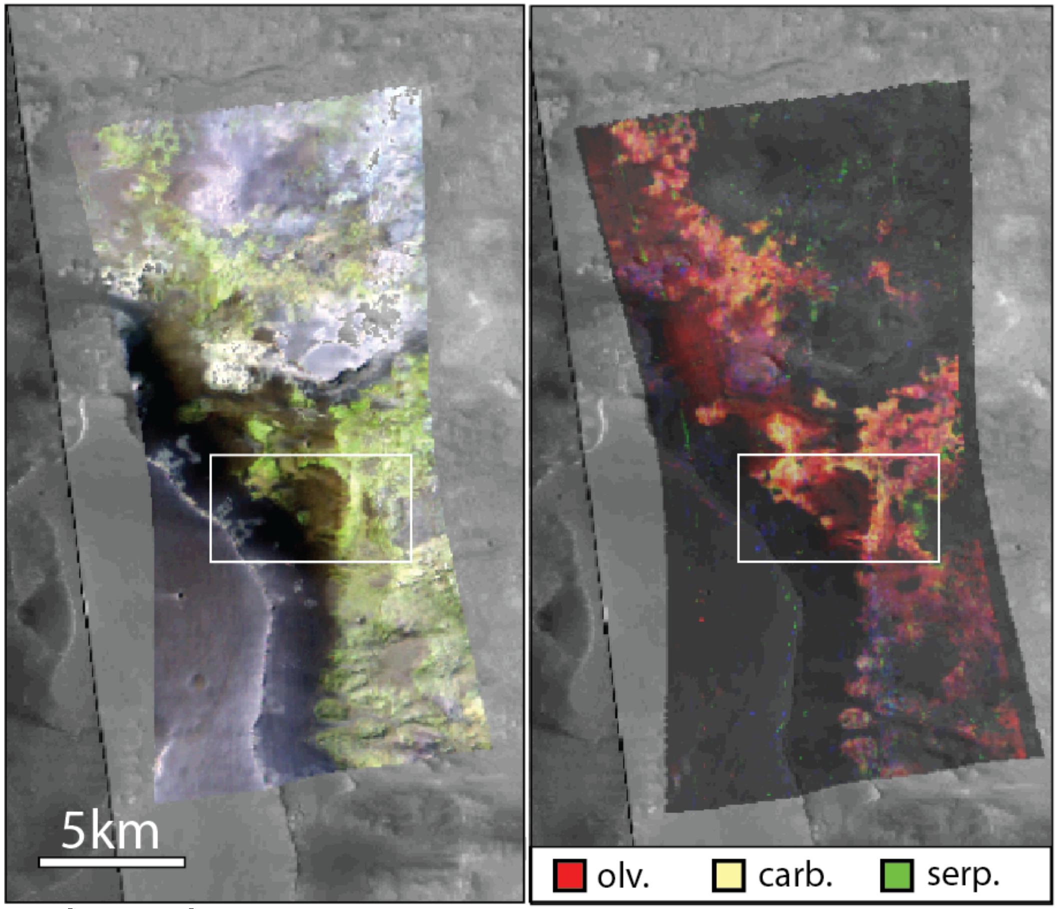
Wray et al., 2011, JGR; Ehlmann et al., submitted, AmMin



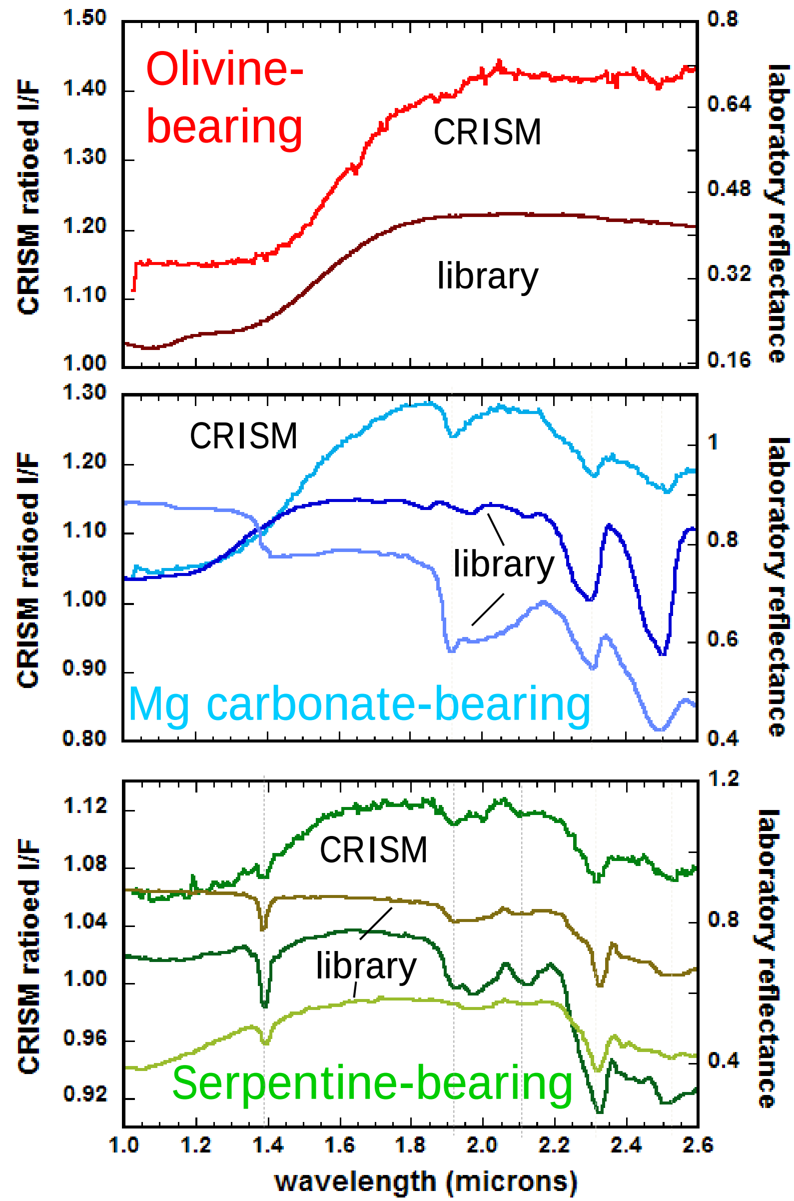


Saper & Mustard, 2013
0
30
(5) 200
150
100
60
90
120
150
180
Ridges
Troughs
Mg carbonate+
olivine
Fe/Mg
smectite
olivine
100 m
mafic cap
Ehlmann et al., Science, 2008;
Mustard et al., JGR, 2009
CRISM IR color on HiRISE
Mustard et al., 2009, JGR

Serpentine in olivine-rich bedrock

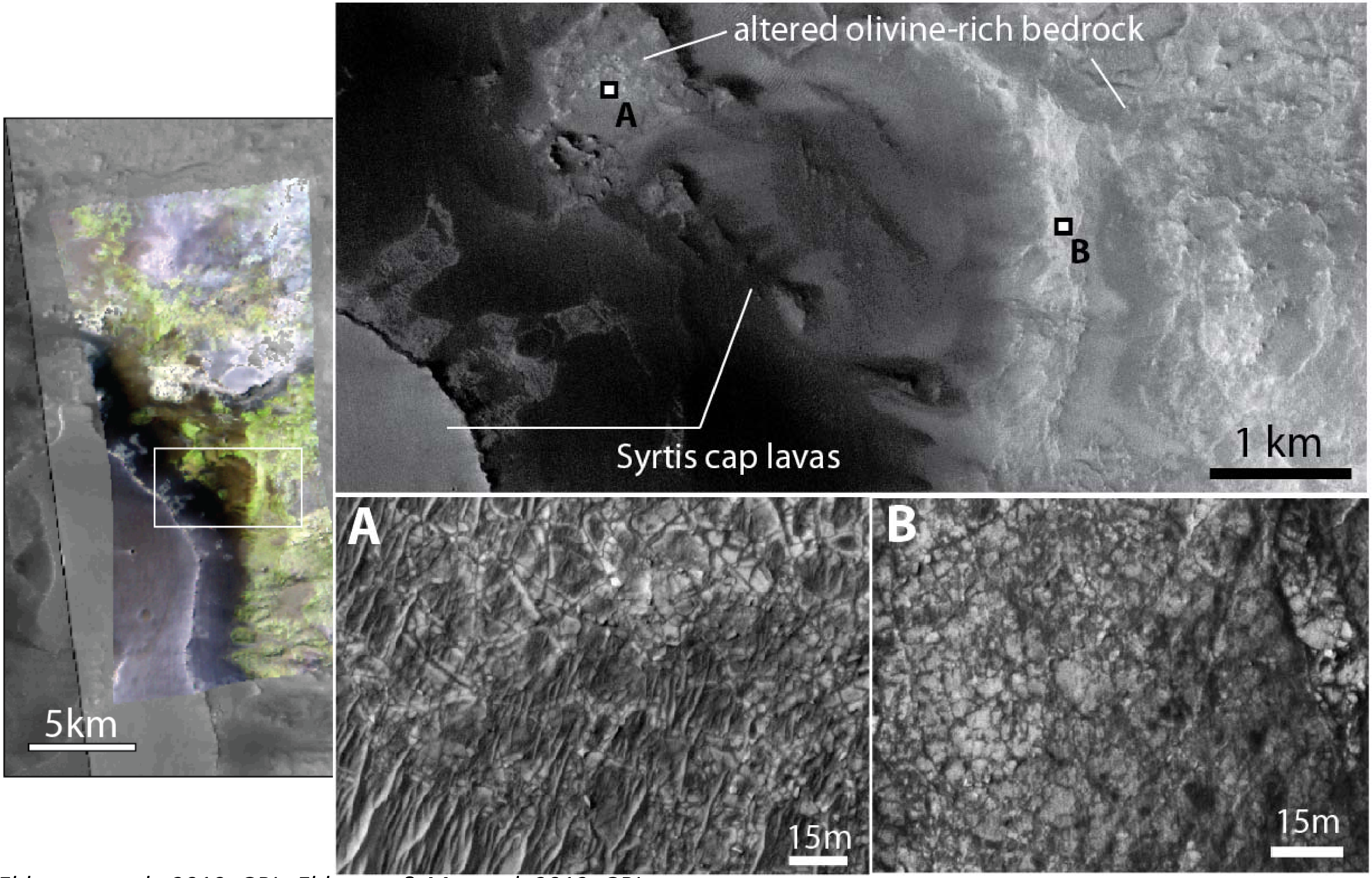


False color CRISM RGB



Ehlmann et al., 2010, GRL; Ehlmann & Mustard, 2012, GRL

Serpentine in olivine-rich bedrock



Ehlmann et al., 2010, GRL; Ehlmann & Mustard, 2012, GRL

Thoughts from Bethany's Mars Intuition

- Probably is (sometimes) small amounts of liquid water in the Martian near-surface and sub-surface
  - It is actually going to be really hard to prove this – esp. subsurface – one way or the other with instruments and not deep drills
  - How briny and what chemistry is likely highly spatially variable
  - Large holes in the ground (like Gale crater) and fracture systems may be enabling conduits for gases from chemical rxns to reach the surface
  - Multiple processes involving iron-oxidation might also create H2 – not clear to me "classic" serpentinization reactions are needed (this would imply more olivine-rich crust than commonly observed). Then reaction with CO2 produces methane
- Mars is likely not volcanically dead either
- Destruction by oxidants – many and significant surface area—in Mars dust and soils probably accelerates CH4 destructions
- I still think exogenous organic materials may have a role in the methane story – should discuss Fries paper further