Chemical Environments During Mars' First Billion Years

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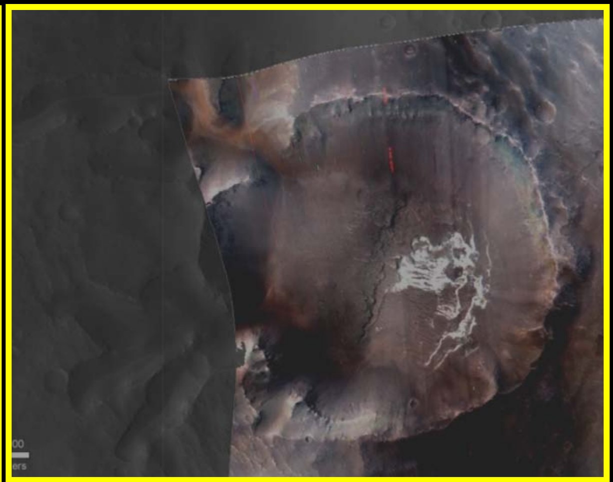
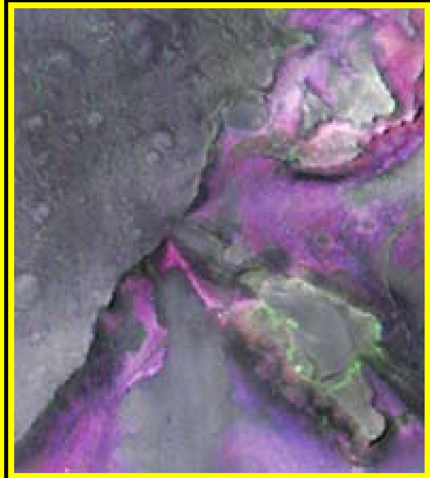
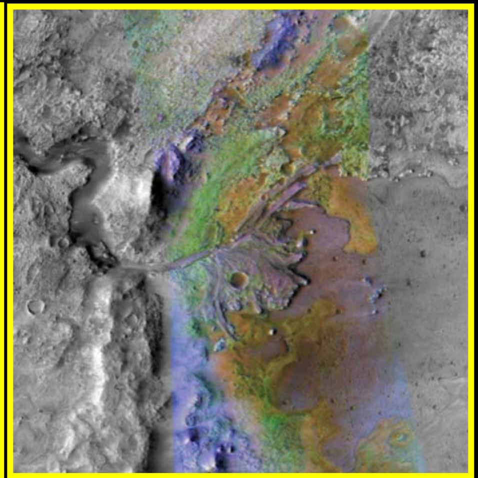
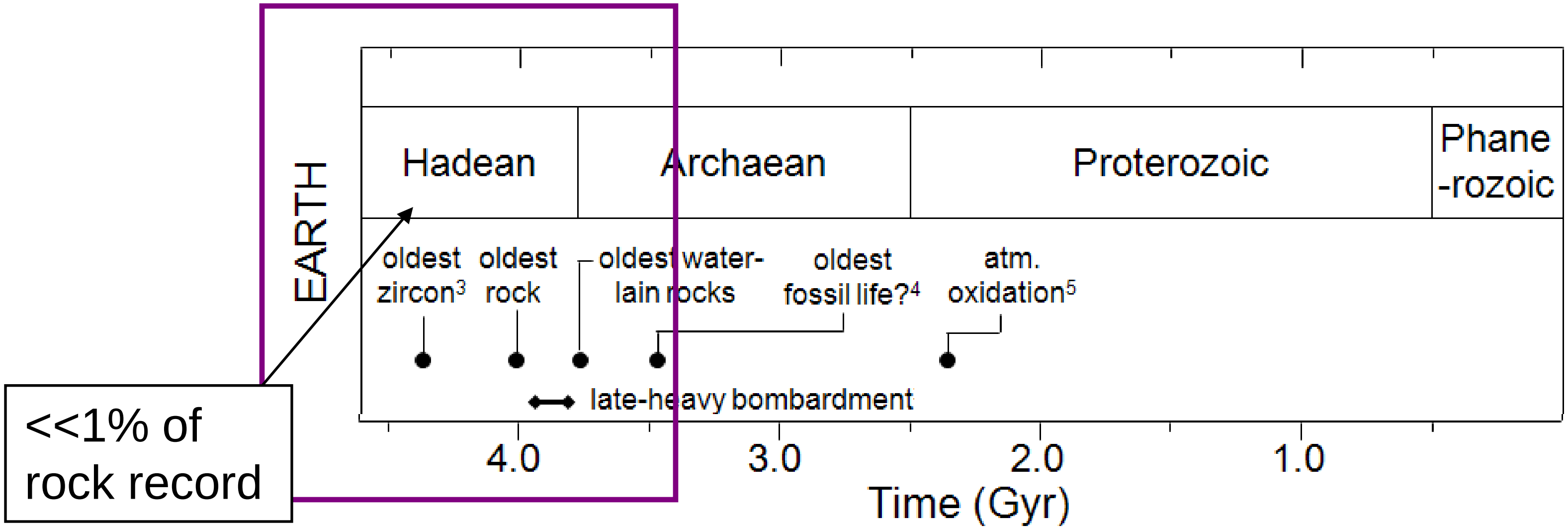
(from Sept. 2011 @ Caltech; ehlmann@caltech.edu)

June 27, 2011



~50% of rock record

KEY QUESTIONS:

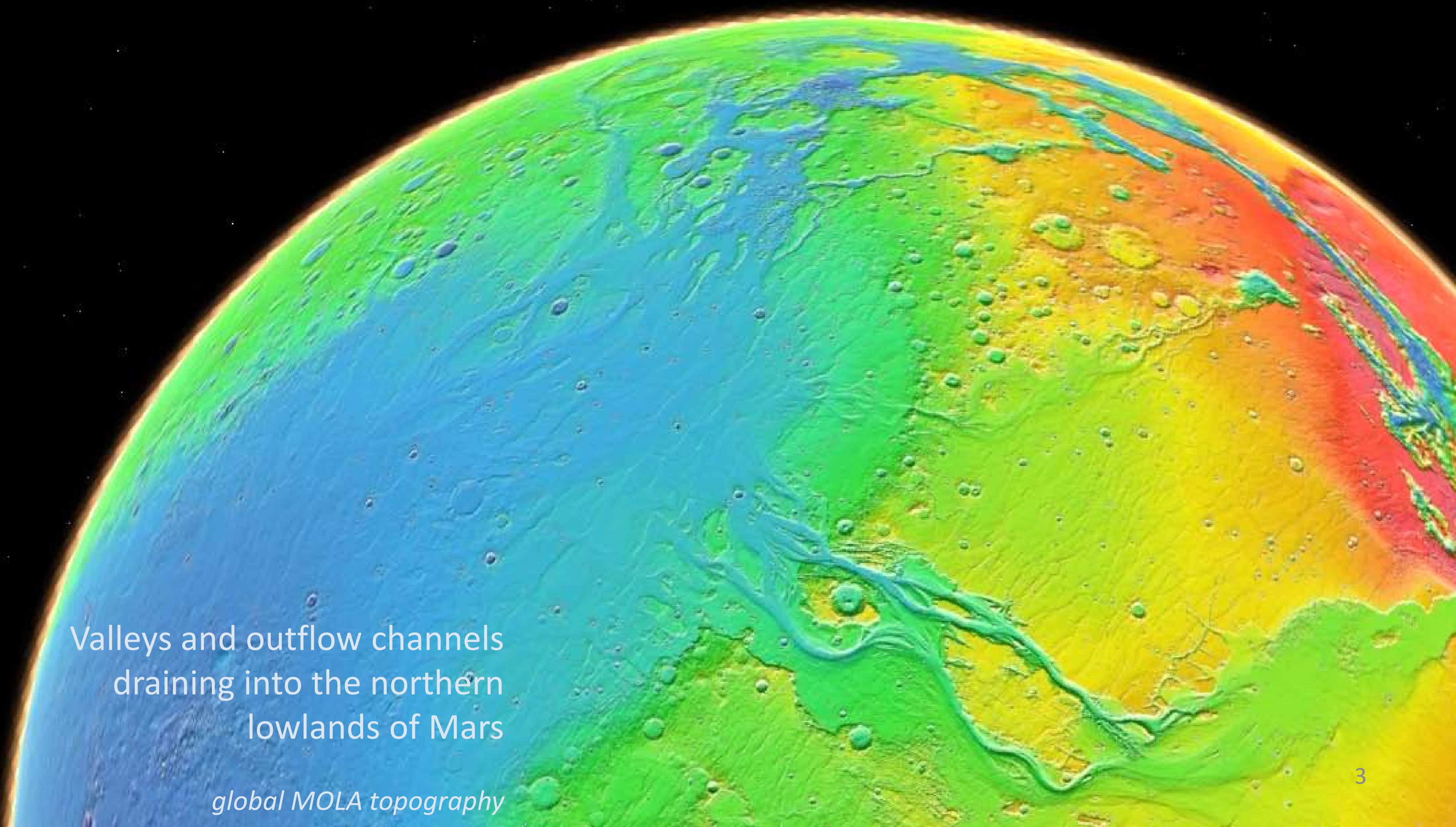
- When was liquid water first stable?
- When did Earth become habitable/inhabited?
- What was the nature of the first habitat(s)?

Mars provides a window into the early history of terrestrial planets

(1) Nyquist et al., 2001 (2) Borg et al., 1999 (3) e.g. Valley et al., 2005 (4) Schopf, 2006 (5) e.g. Farquhar et al., 2000

Morphologic evidence for water is abundant

Mineralogic evidence provides critical information for determining the nature of aqueous environments



Valleys and outflow channels draining into the northern lowlands of Mars

global MOLA topography

Key Environmental Parameters

- pH
- Redox (Eh)
- Activity (of water, other ions)
- Water:rock ratio
- Open- and closed-system
- Geologic Setting

APPROACH TO DETERMINING CHEMICAL ENVIRONMENTS:

consider
(1) mineral assemblages,
(2) deposit morphology, and
(3) stratigraphy

→

characteristic
“chemical environments”

Starting materials: basaltic rock and mafic minerals

Basalt is the most common igneous rock, made of

Feldspar = $(Ca,Na,K)Al(Al_XSi_{3-X})O_6$

and two major Fe, Mg-containing minerals

Pyroxene = $(Fe,Mg,Ca)\ SiO_3$
Olivine= $(Fe,Mg)_2SiO_4$

Sampling lavas near Kilauea, Hawaii

The Residues from Reaction with Water

- **Iron oxides** remain when Si+O dissolve, or they precipitate from acidic water.

- **Nontronite** (Fe-containing **smectite** clay) forms when water combines with Fe-bearing rock

- **Montmorillonite & Kaolinite** (Al-containing clay) forms where water dissolves Fe and Mg out of rocks.

- **Chlorite and serpentine** (Fe-Mg silicate) form where warm or hot water combines with rocks

Phyllosilicate – metal cations Si+O, OH, H_2O in sheets

Precipitates from the Saline Water

- **Silica** forms by evaporation or cooling of water that dissolved rock

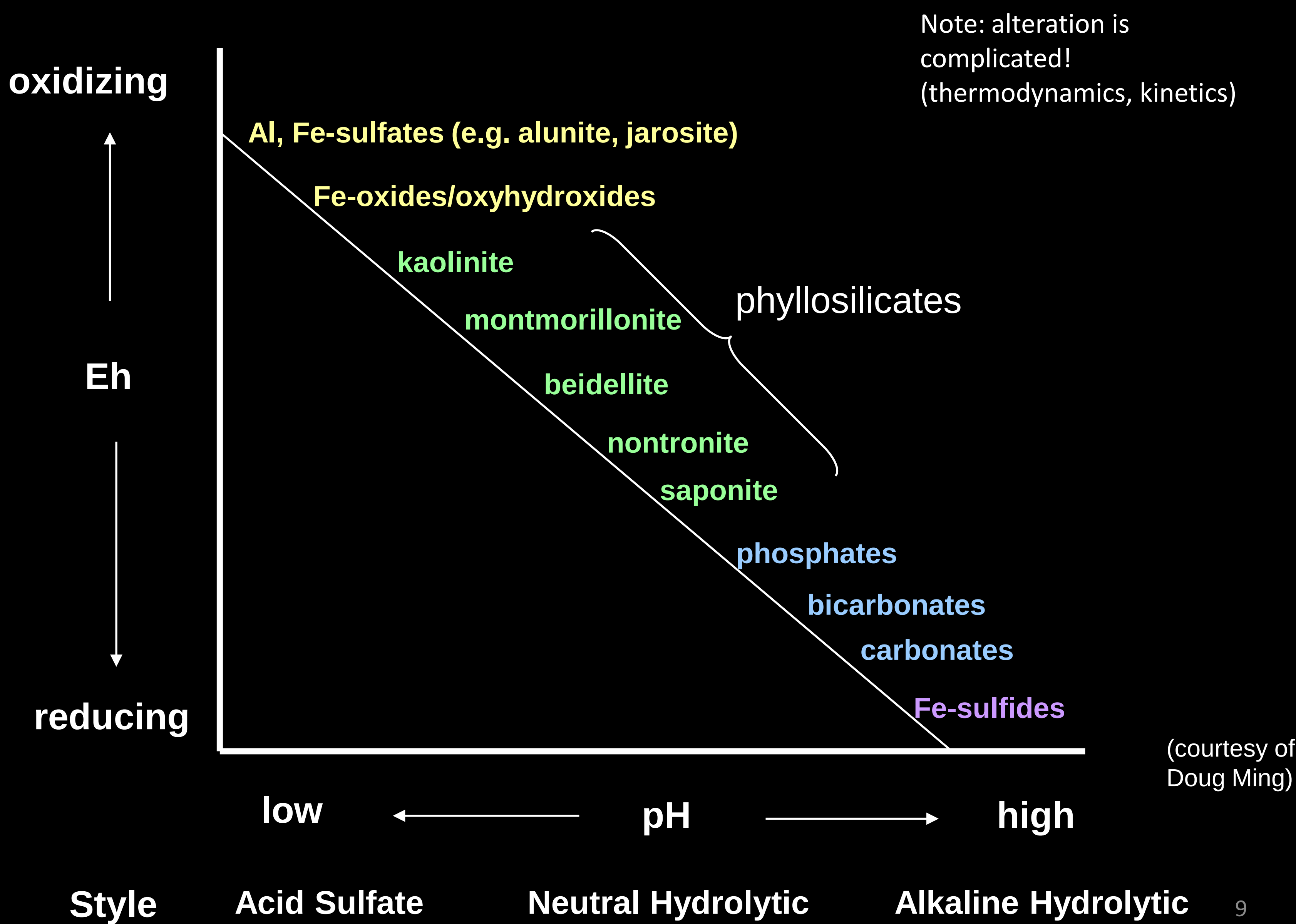
- **Carbonates** form where water weathers igneous rock. Traps ancient CO_2

- **Sulfates** form around springs, or where lake or ground water evaporates.

- **Chlorides** precipitate from the concentrated brine after most water has evaporated.

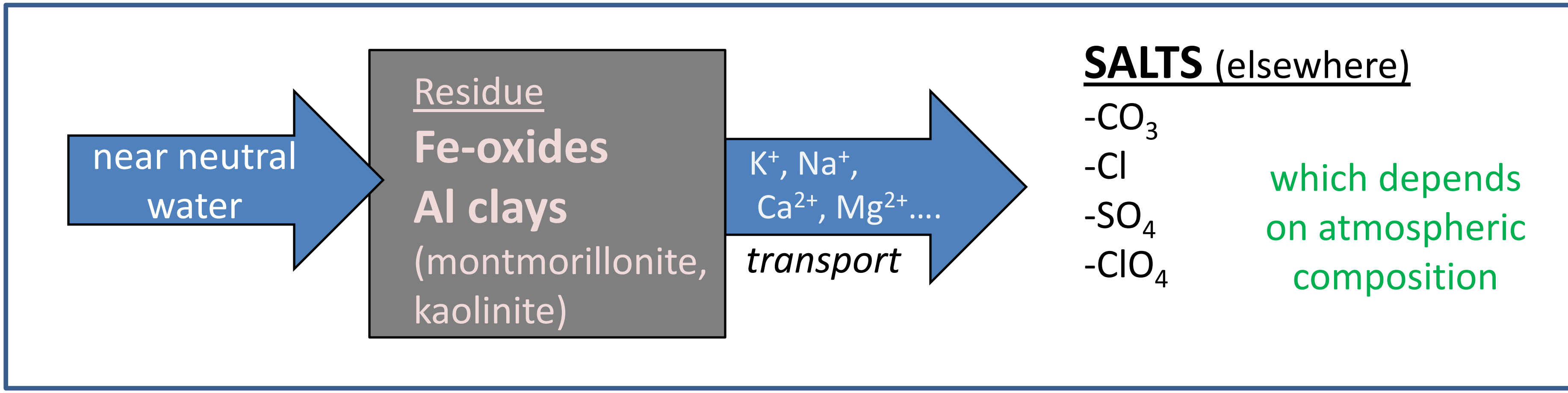
Increasing salinity

Example: Potential **Indicator Minerals**

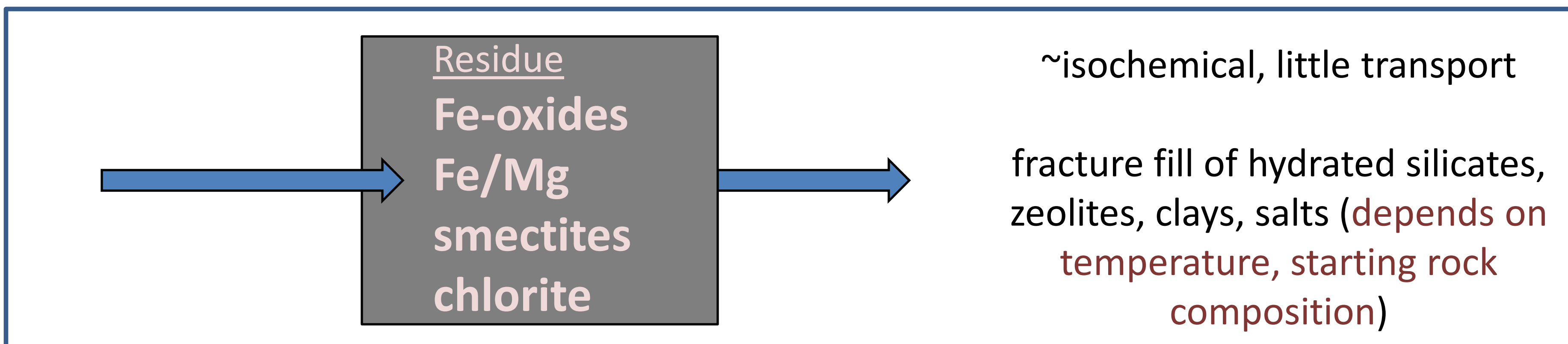


Example: Mineral Assemblages for Water-Rock Interactions With Basalt

e.g. High water:rock ratio (open system)



e.g. Low water:rock ratio (closed system)



Example: <u>Mineral Assemblages</u> for Water-Rock Interactions With Basalt

e.g. High water:rock ratio (open system)

e.g. Low water:rock ratio (closed system)

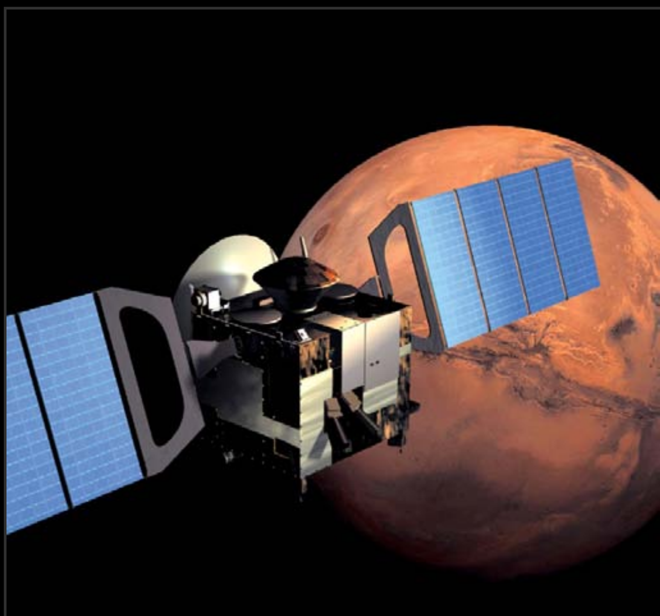
Data sets

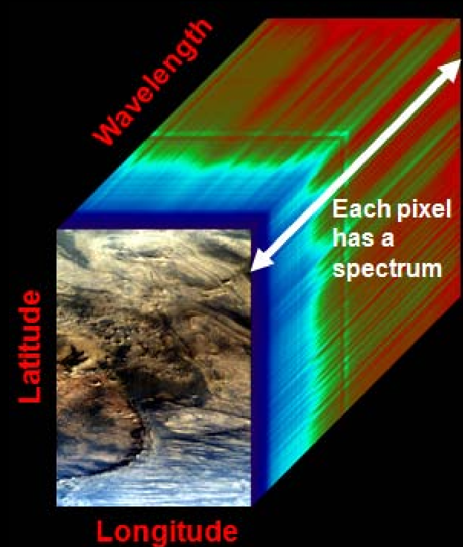
- Landed, in-situ data
  - Elemental chemistry (APXS, ChemCam)
  - Mineralogy (MB for Fe-mineralogy, CheMin XRD/XRF, MiniTES)
  - GC/TLS (isotopic composition of light elements)
  - PROS: Small spatial-scale relationships, precise chemistry/mineralogy
  - CONS: small sample size, still not same analysis level as possible in lab

- Orbital
  - GRS: chemistry K, Th, Fe, Si, Ca, Cl, H_2O (30km x 30km bins)
  - TES: mineralogy, especially Si-bearing phases (3x5 km pixels)
  - OMEGA, CRISM: mineralogy, especially Fe, H_2O, OH, CO_3 bearing phases (18m-2km/pixel)
  - PROS: Planet-wide investigation, multiple sites
  - CONS: some minerals/elements are hard to detect remotely, low spatial resolution means many things are undetectable

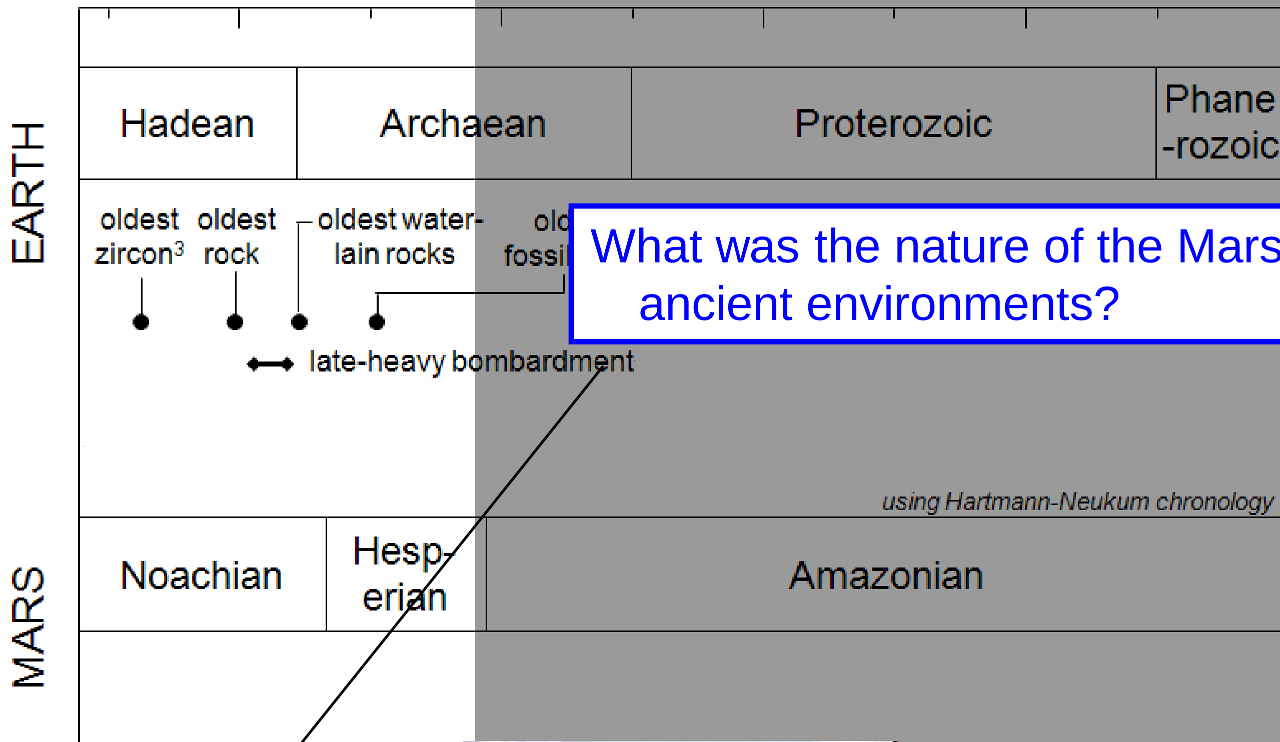
Two missions, two visible near-infrared imaging spectrometers

December 2003 OMEGA ESA Mars Express		October 2006 CRISM NASA Mars Reconnaissance Orbiter

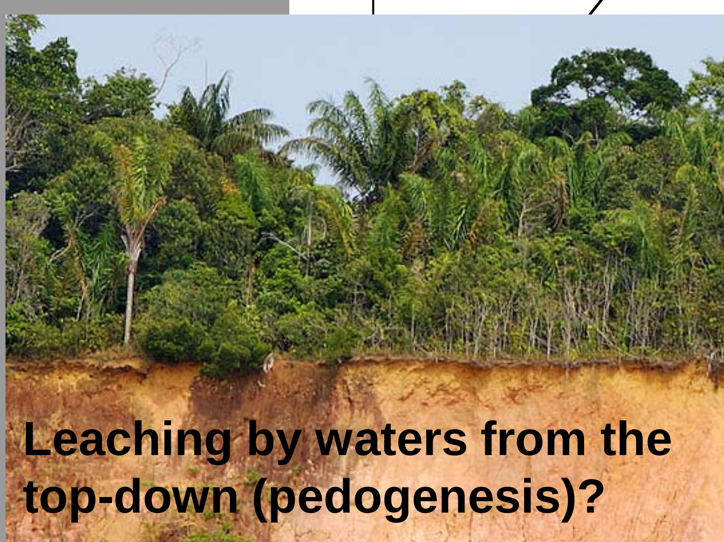


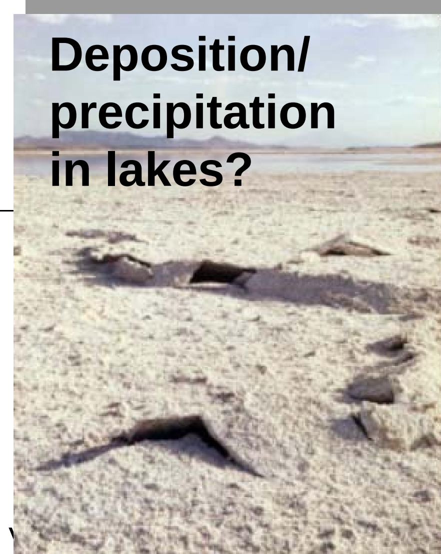


300-5,000 m/pixel	spatial resolution	18-200 m/pixel
0.4-5.0 µm	spectral range	0.4-4.0 µm
352	number of wavelengths	544

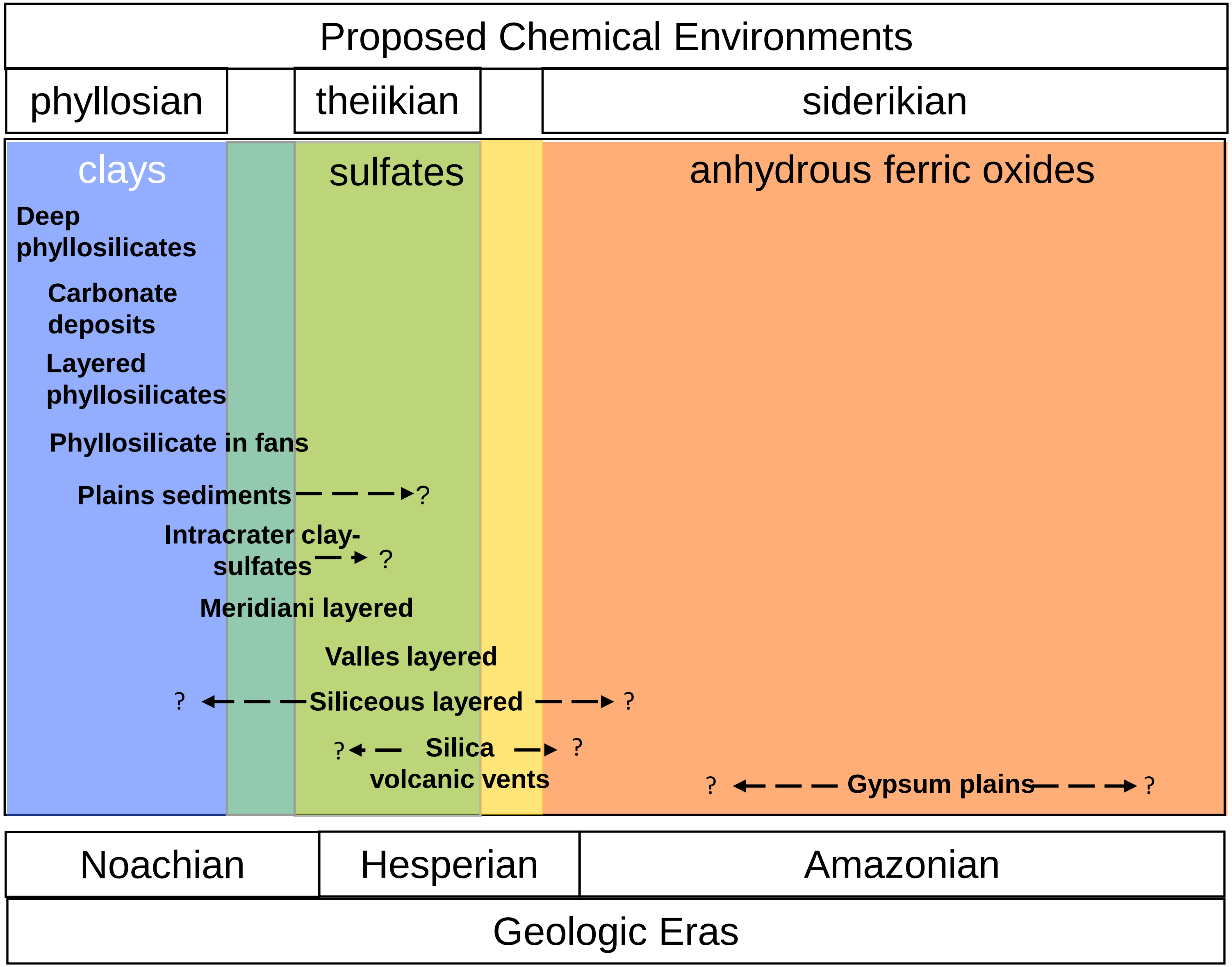


What was the nature of the Mars' most ancient environments?





Adapted from Murchie et al., JGR, 2009 with mineralogic epochs from Bibring et al., 2006



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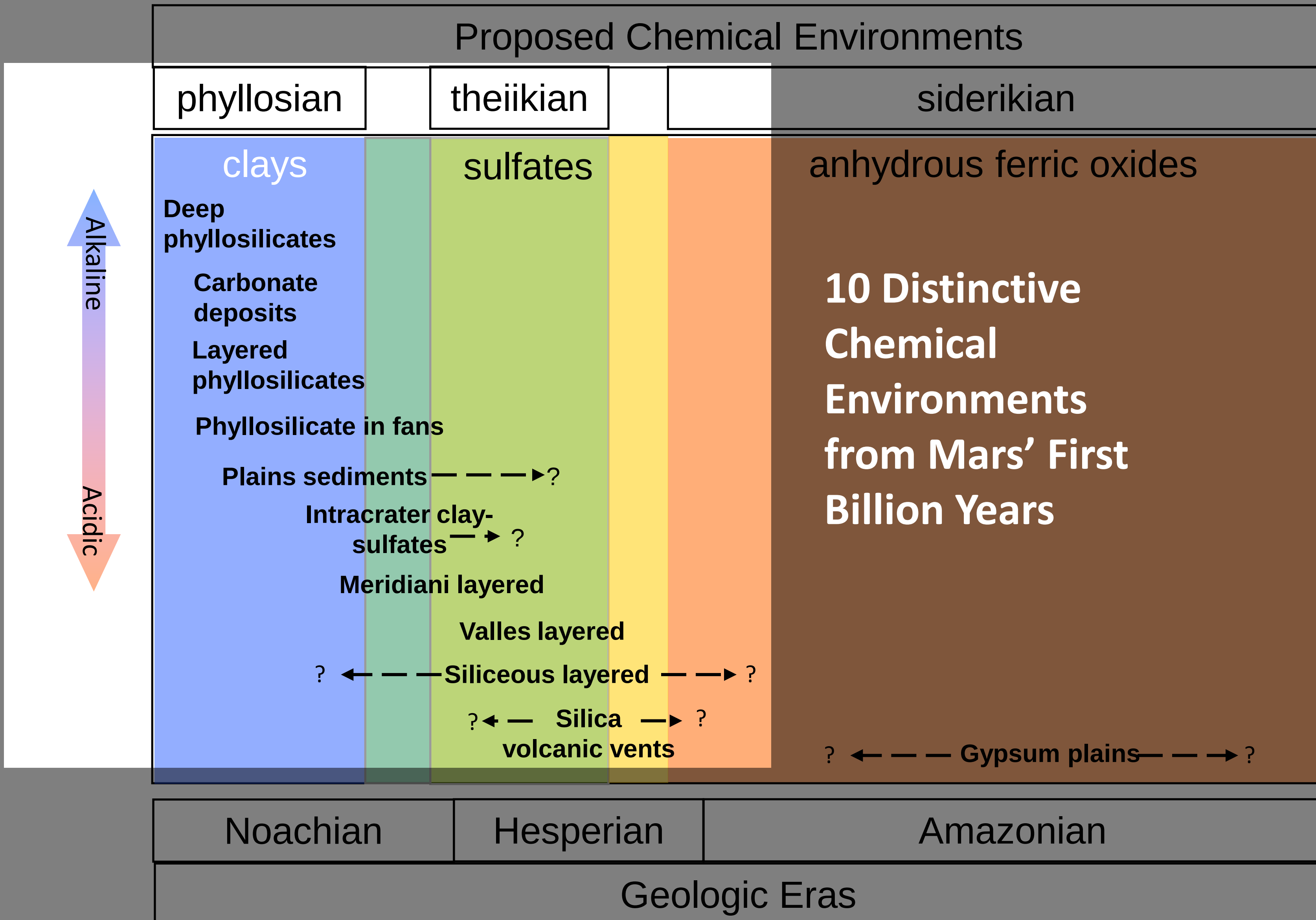

CHEMICAL ENVIRONMENTS

1. "Deep phyllosilicates"
2. Layered phyllosilicates
3. Carbonate deposits
4. Phyllosilicates in fans
5. Plains sediments (chloride+ phyllo.)
6. Intracrater clay-sulfate deposits

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7. Meridiani layered
8. Valles Marineris layered
9. Silica-rich layered
10. Silica volcanic vents

CHEMICAL ENVIRONMENTS

1. **"Deep phyllosilicates"** — craters / escarpments
2. Layered phyllosilicates
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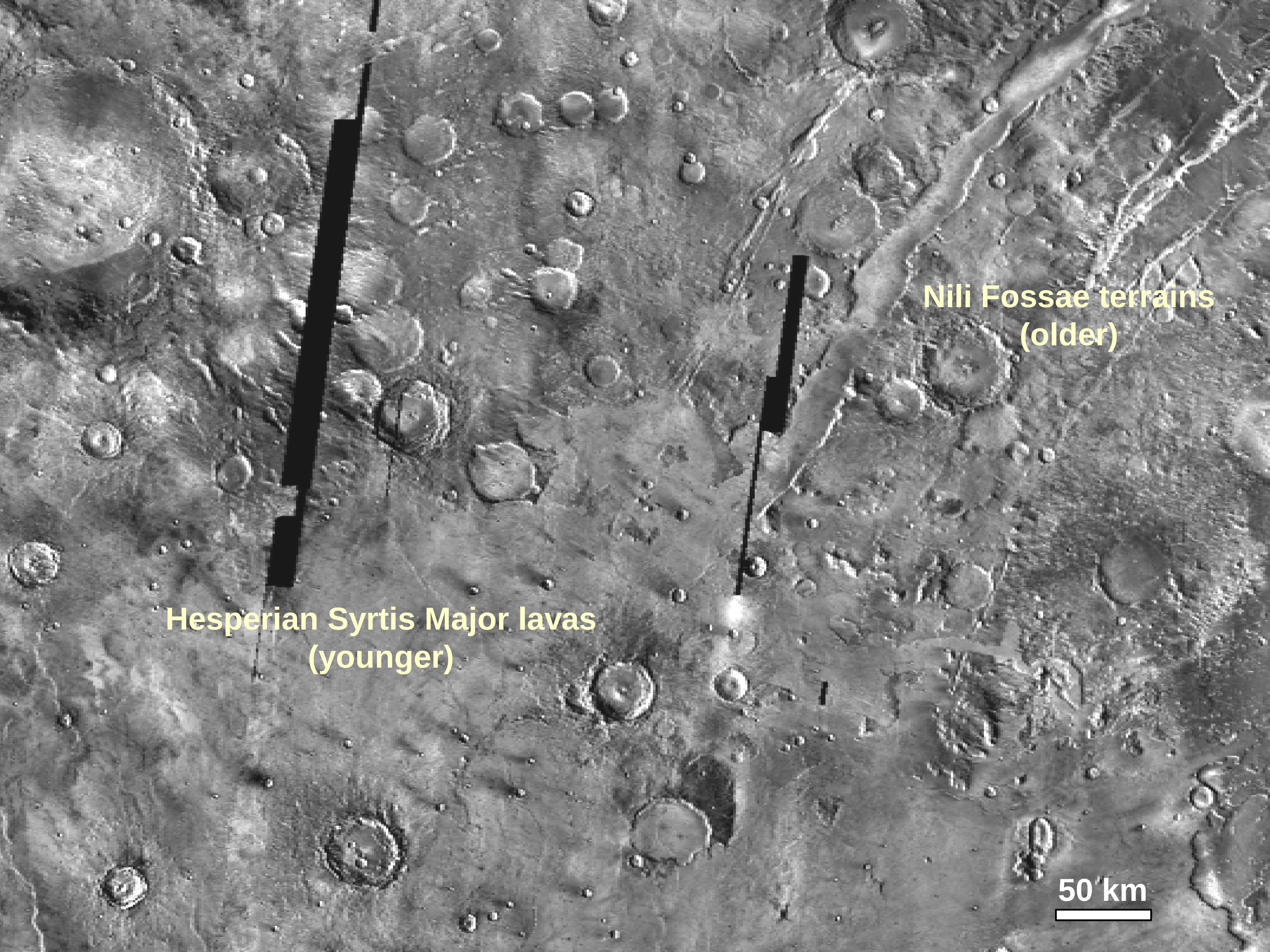
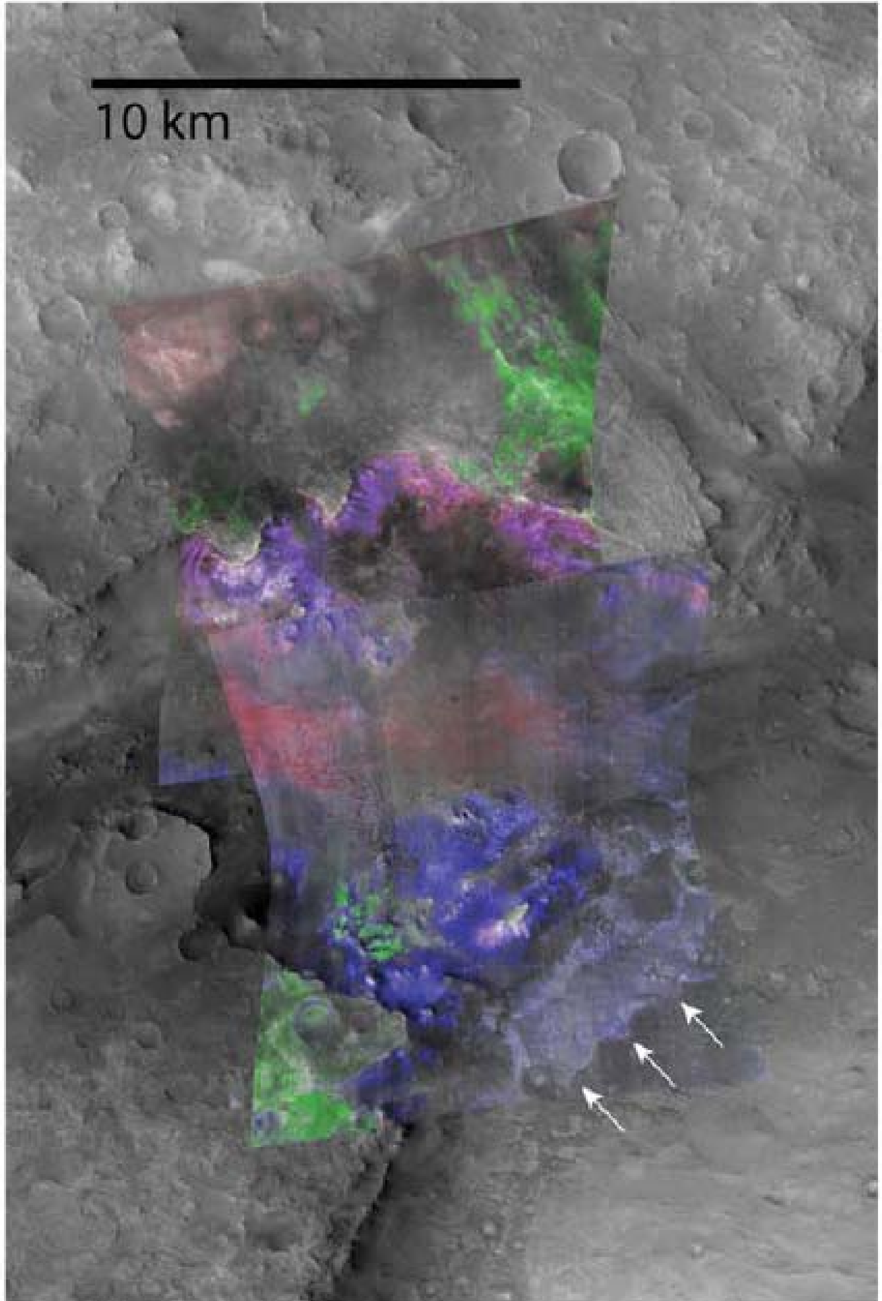
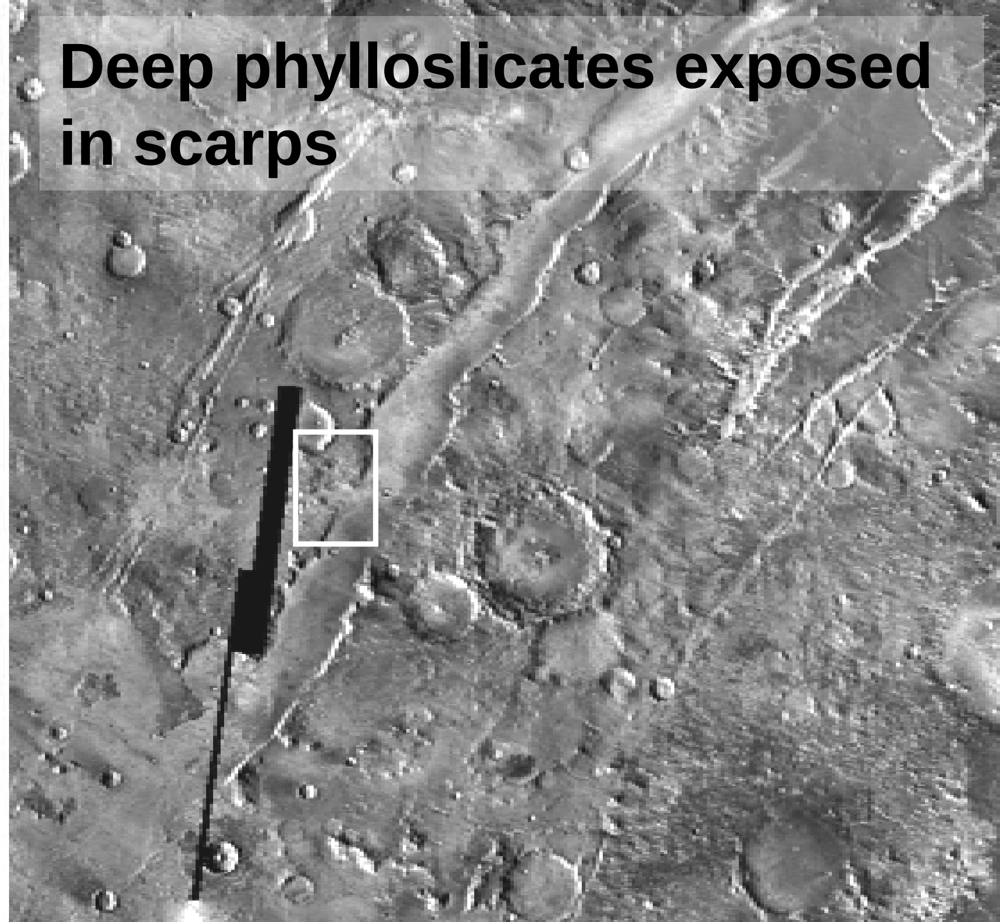

Nili Fossae terrains
(older)
Hesperian Syrtis Major lavas
(younger)
50 km

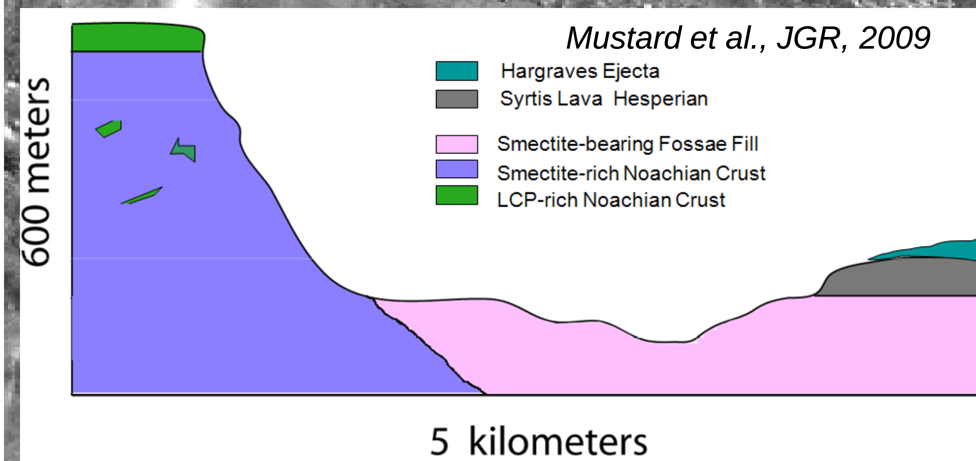
Deep phylloslicates exposed in scarps



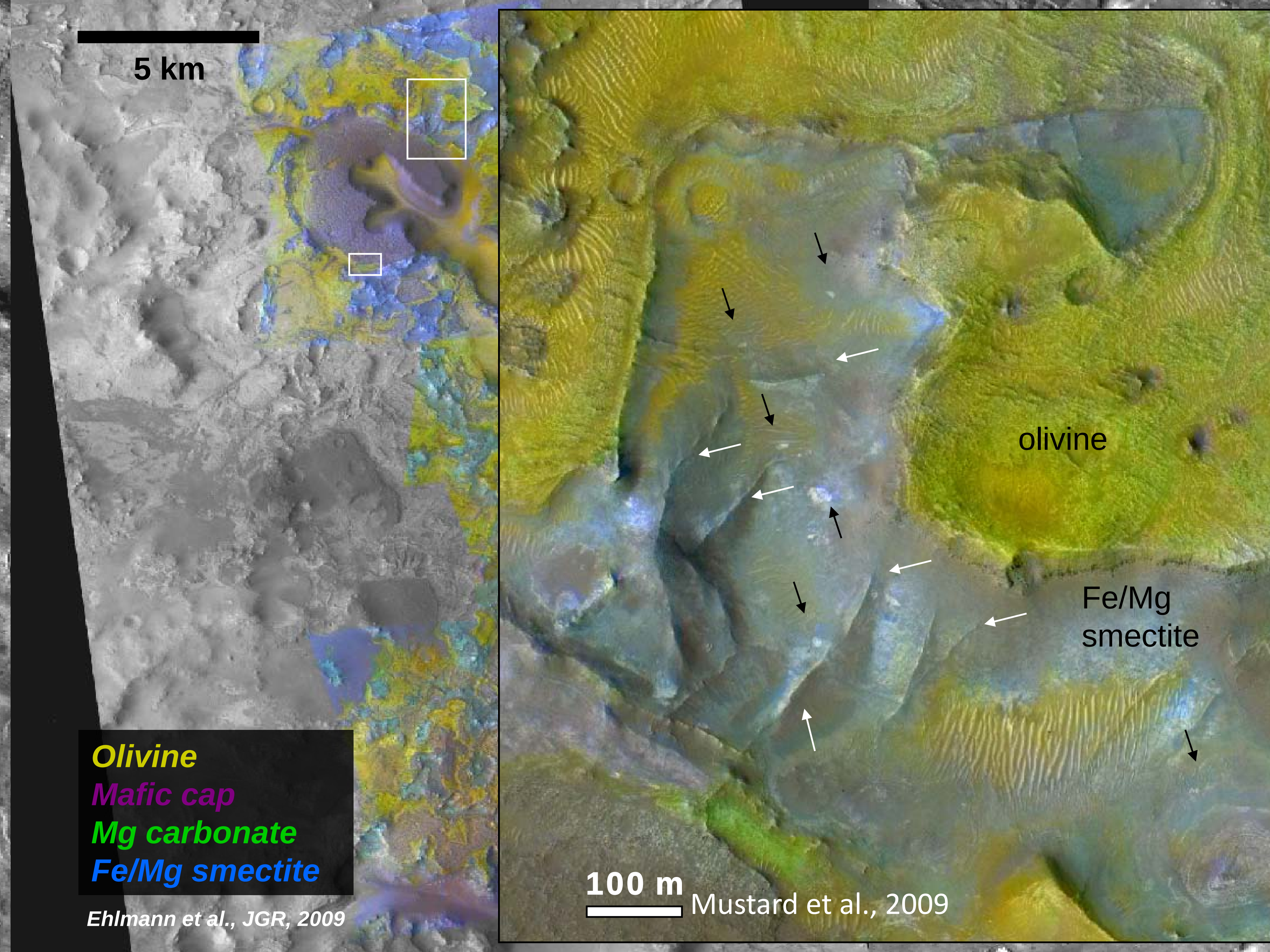
Phyllosilicate
Low-Ca pyroxene
Olivine

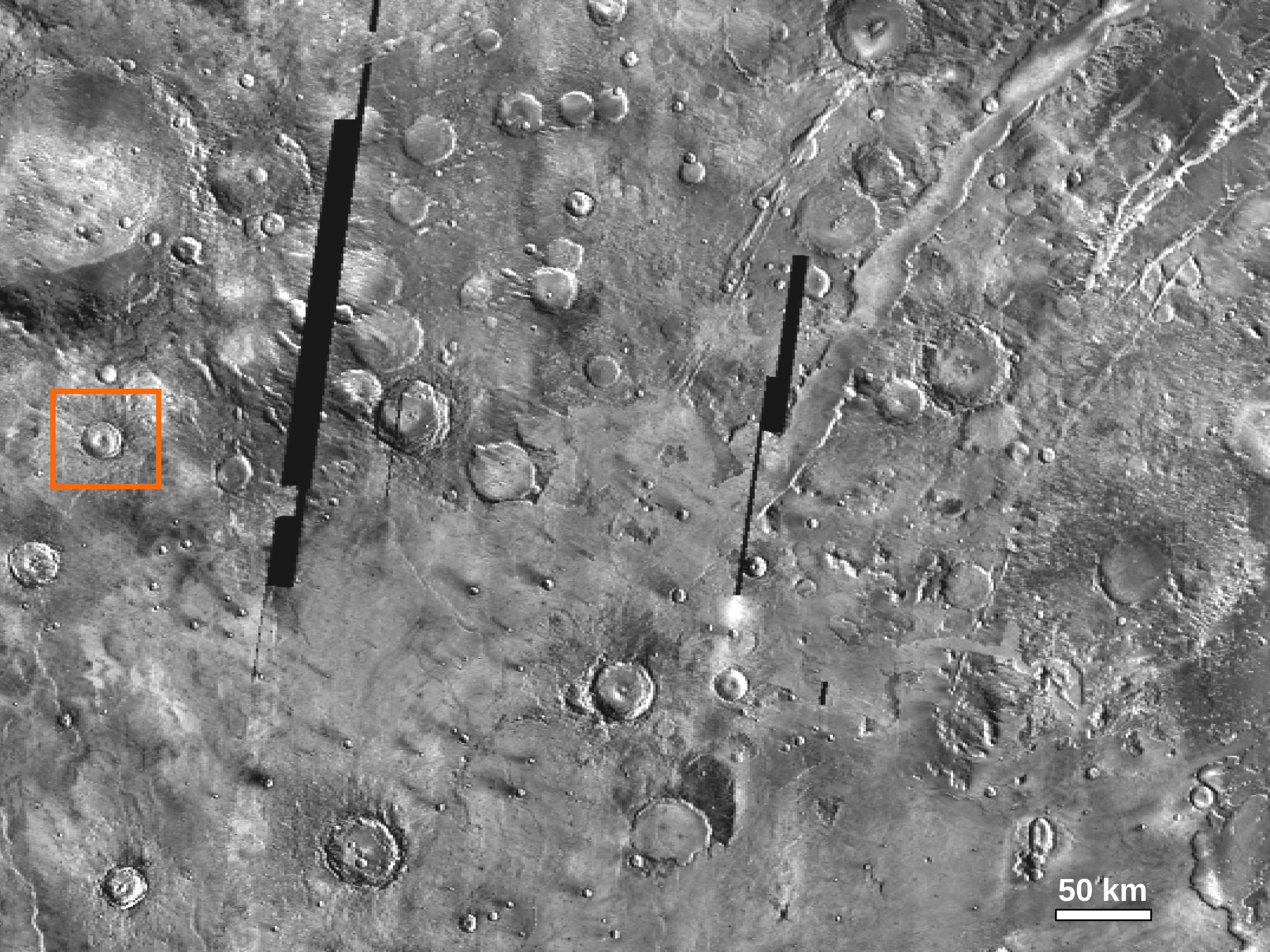
Mustard et al., Nature, 2008

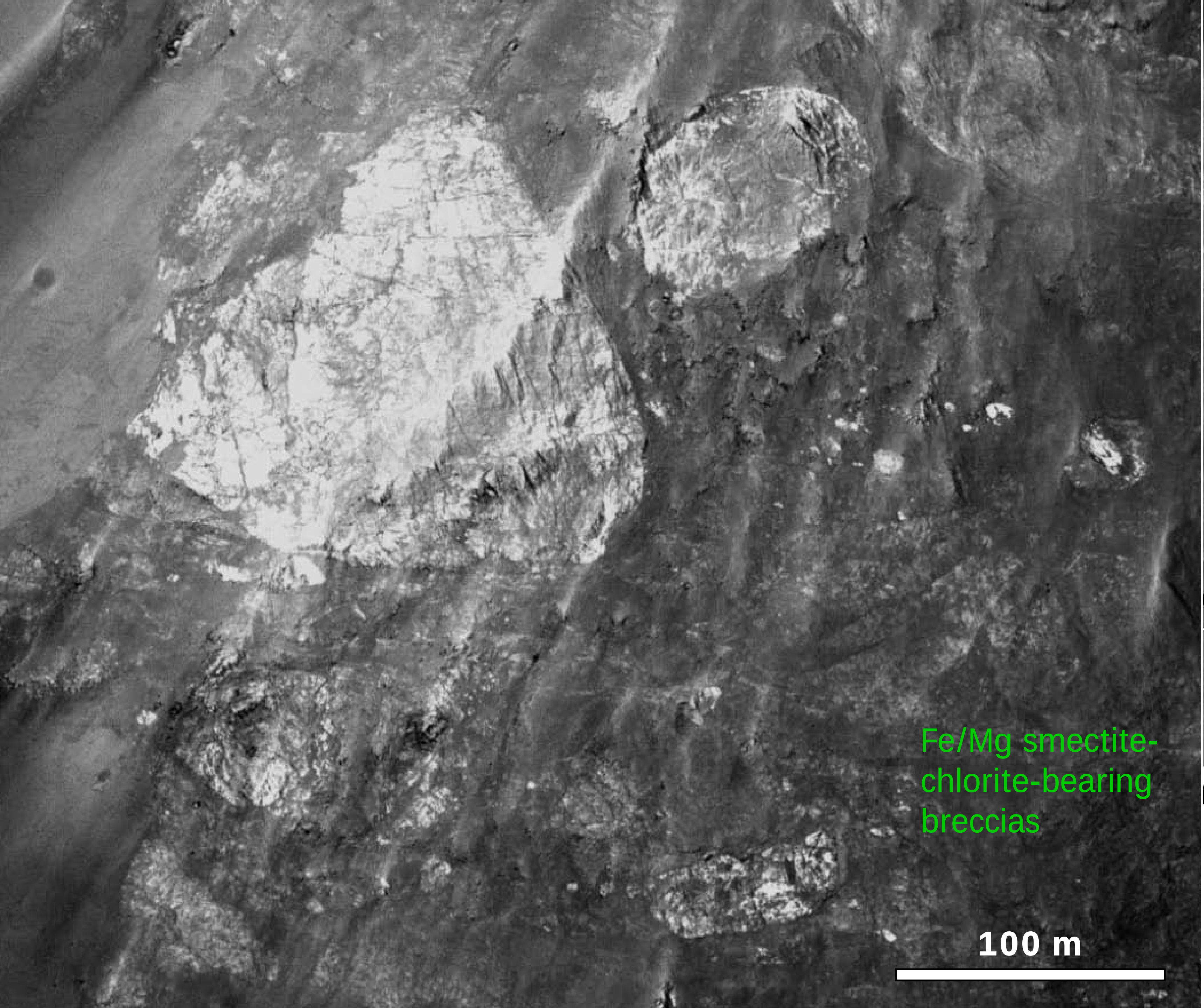


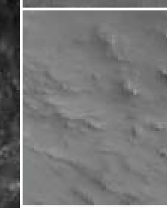


(Representative vertical and horizontal distances, not to scale)


5 km
Olivine
Mafic cap
Mg carbonate
Fe/Mg smectite
Ehlmann et al., JGR, 2009
olivine
Fe/Mg
smectite
100 m
Mustard et al., 2009

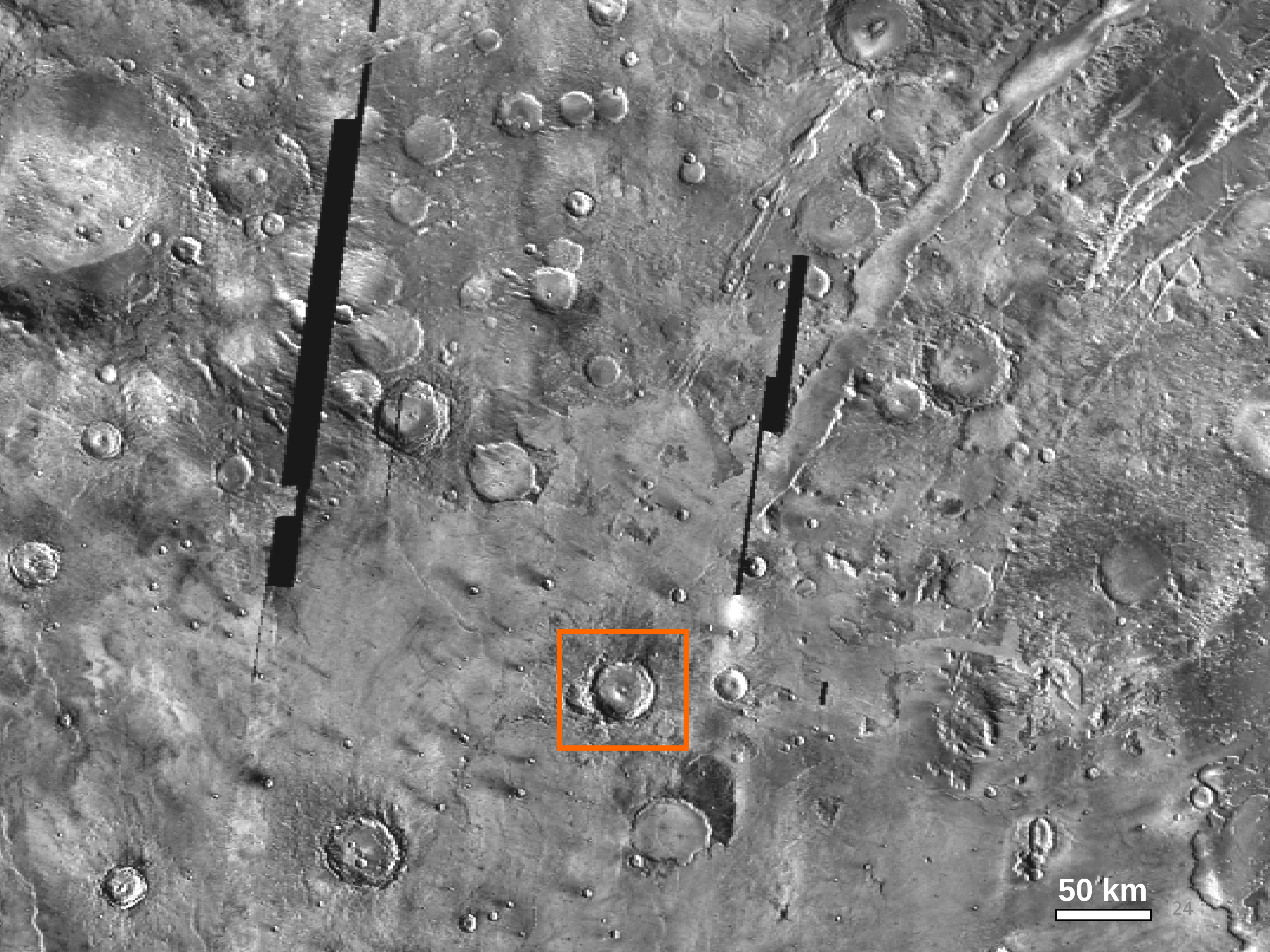

50 km



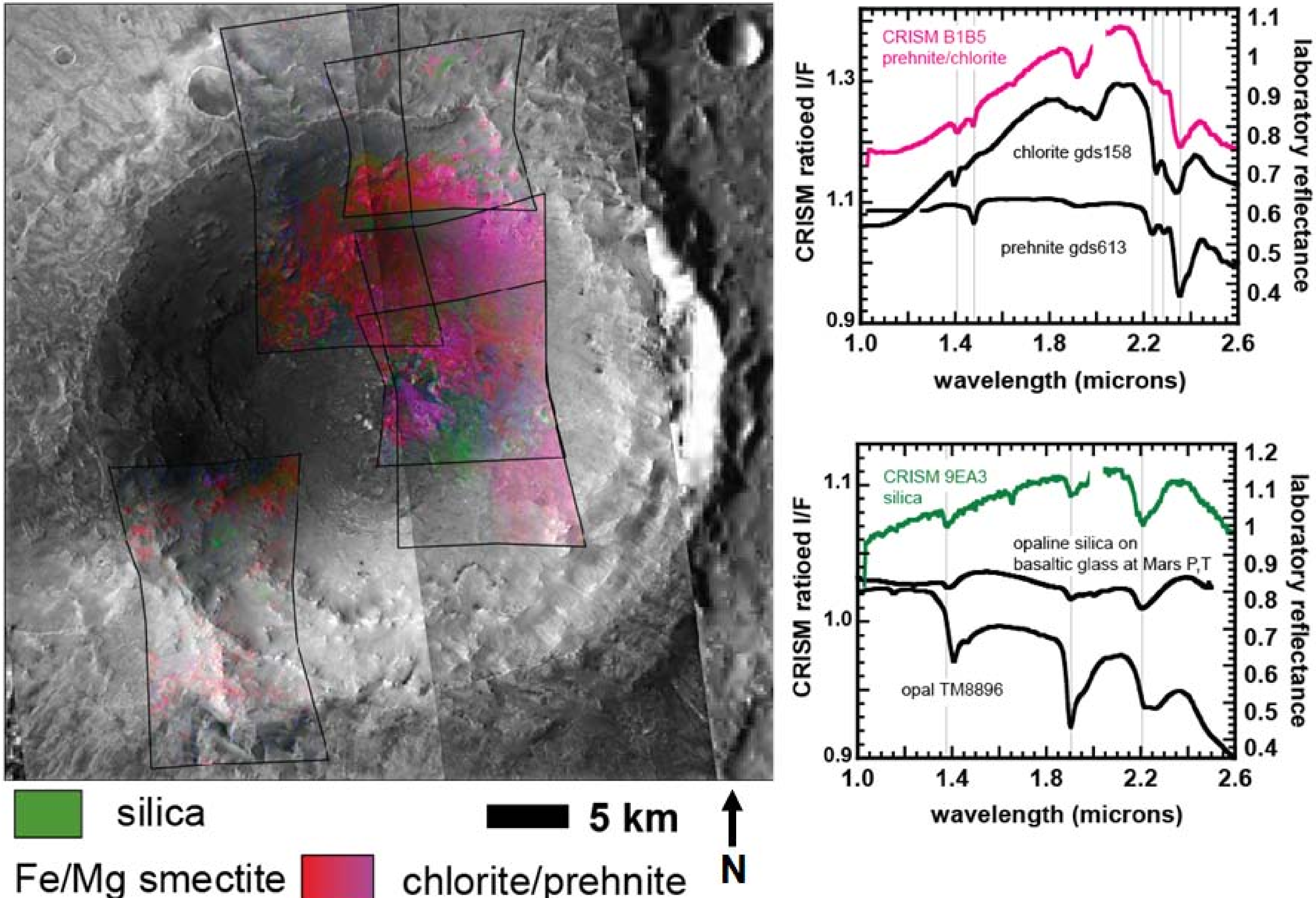


N

accepted

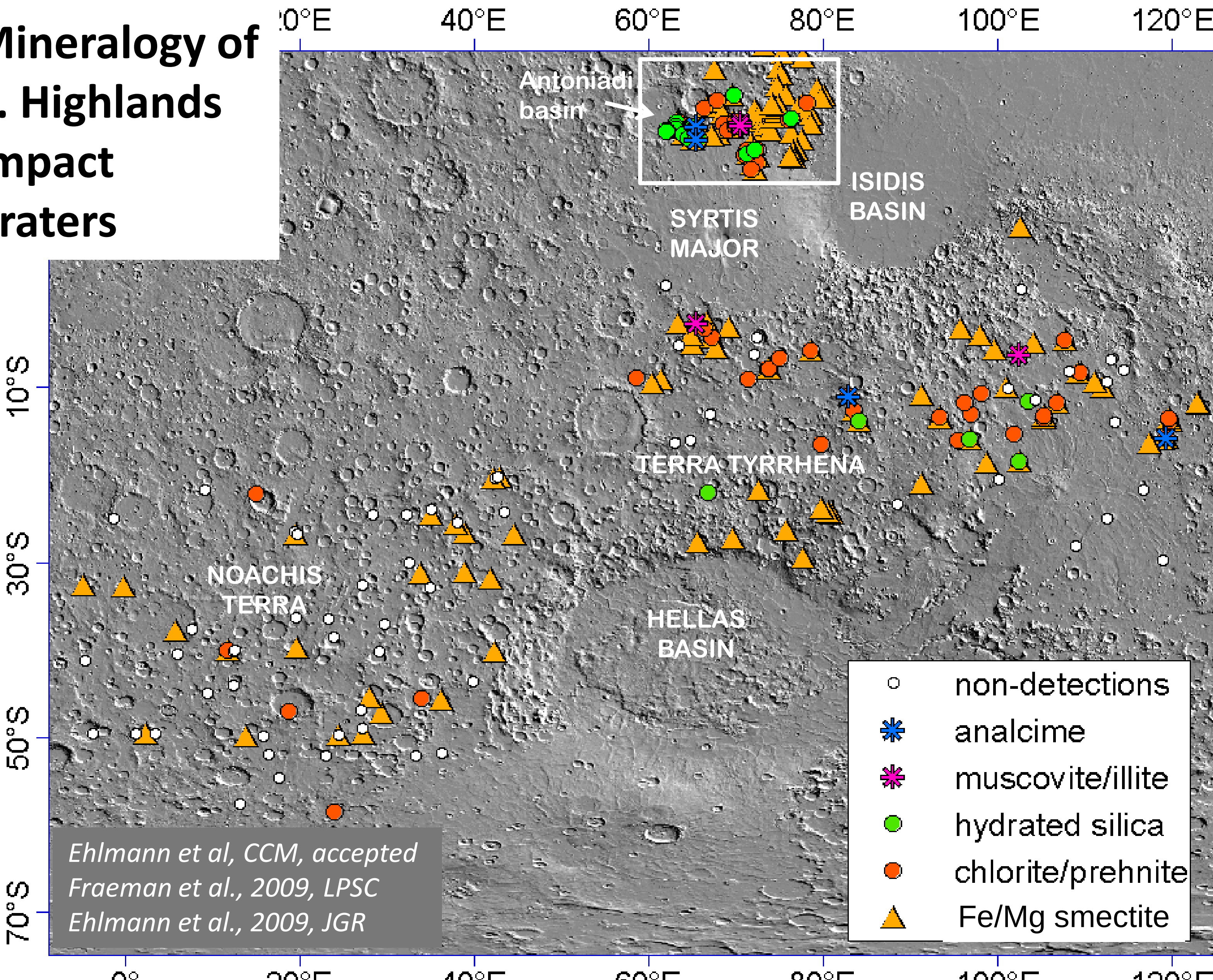

50 km

Prehnite-Chlorite-silica-Fe/Mg smectite



Ehlmann et al., JGR, 2009; CCM, accepted

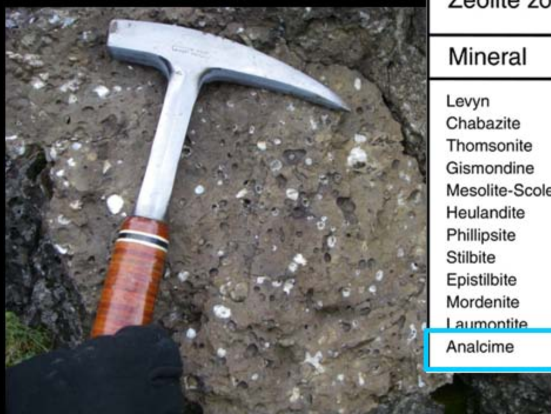
Mineralogy of S. Highlands Impact Craters

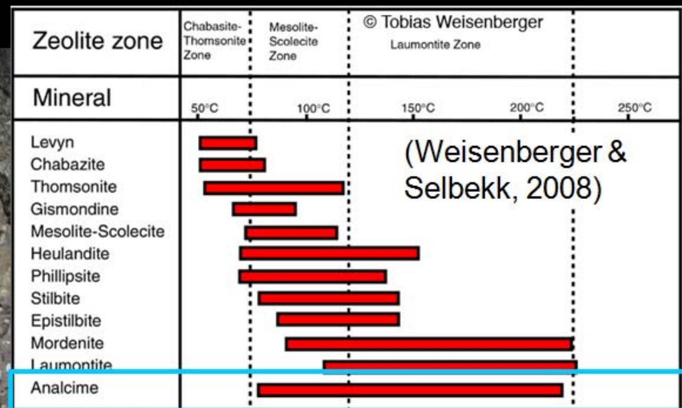


Ehlmann et al, CCM, accepted
Fraeman et al., 2009, LPSC
Ehlmann et al., 2009, JGR

Mineral Indicators

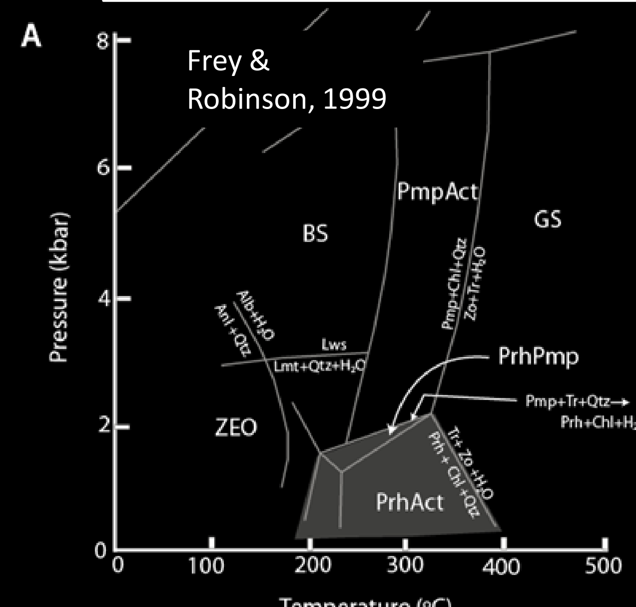
ANALCIME: 50-250ºC

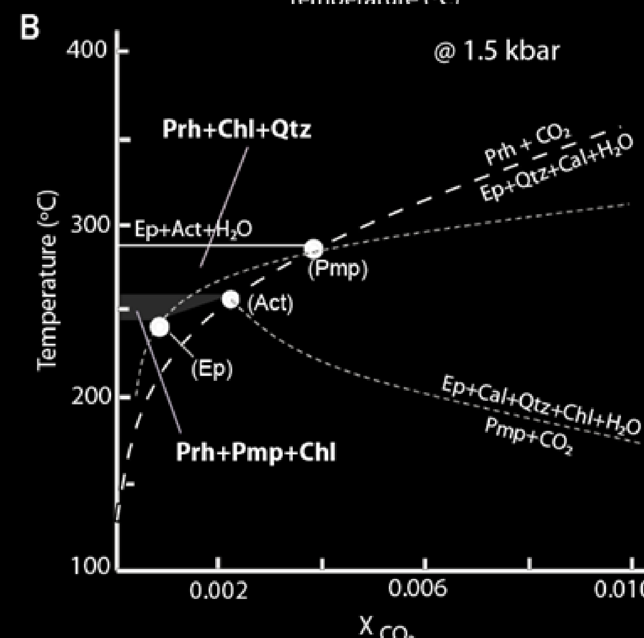




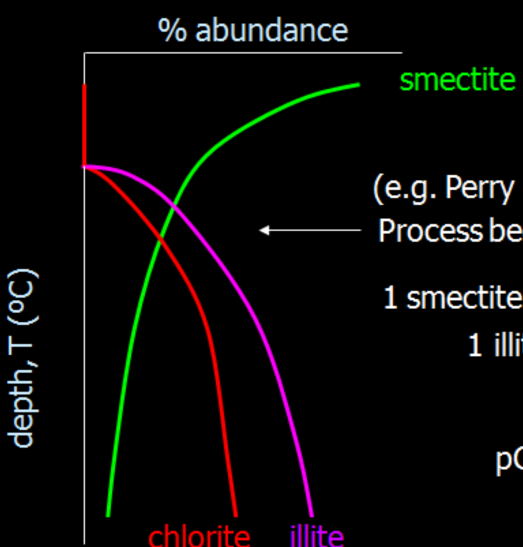
Zeolitized basalt, Iceland

PREHNITE: 200-400ºC





CHLORITE, ILLITE/MUSCOVITE: >40ºC



(e.g. Perry & Hower, 1970)

Process begins **T ~ 50-80ºC**

1 smectite + K^+ →

1 illite + Na^+ + Ca^{2+} + Si^{4+} + Fe^{2+} + Mg^{2+} + H_2O

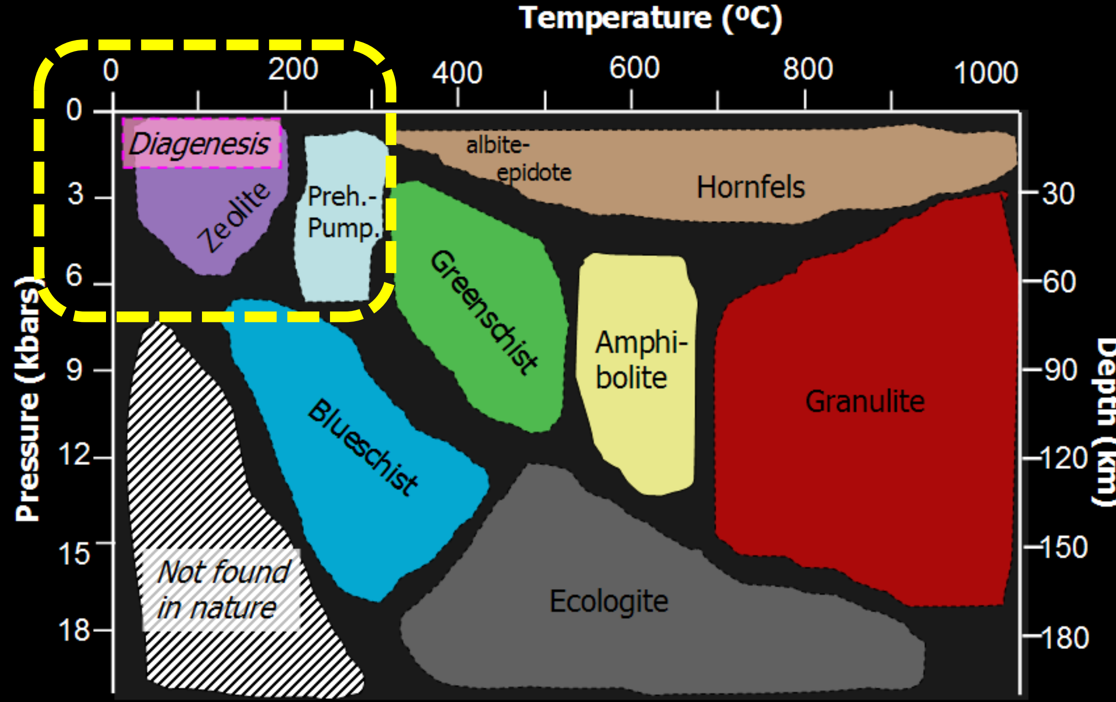
pCO_2
- high → carbonates (Ca, Mg, Fe)
- low → Fe-rich chlorites

Ehlmann et al., JGR, 2009; Clay & Clay Minerals, accepted

Nature of Mars' "Deep phyllosilicates"

- **Occupy (or sourced from) the deepest stratigraphic units**
- Ancient, formed in the Noachian
- >100s m thick, brecciated
  - related to impacts
- **Altered to Fe/Mg clay minerals**
  - in the matrix and blocks
  - Occasionally additional, diverse hydrated silicates
  - Al-clays rare

Analcime, Chlorite, Prehnite, (Serpentine)



Ehlmann et al., Clays & Clay Min., accepted

- Evidence for **effects of low-T hydrothermal alteration**
  - Mineralogy: indicator minerals, e.g prehnite, analcime
  - Morphology: Ridges when eroded—fluidized fractures?

CHEMICAL ENVIRONMENTS

1. “Deep phyllosilicates”
2. **Layered phyllosilicates**
3. Carbonate deposits
4. Phyllosilicates in fans
5. Plains sediments (chloride+ phyllo.)
6. Intracrater clay-sulfate deposits

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7. Meridiani layered
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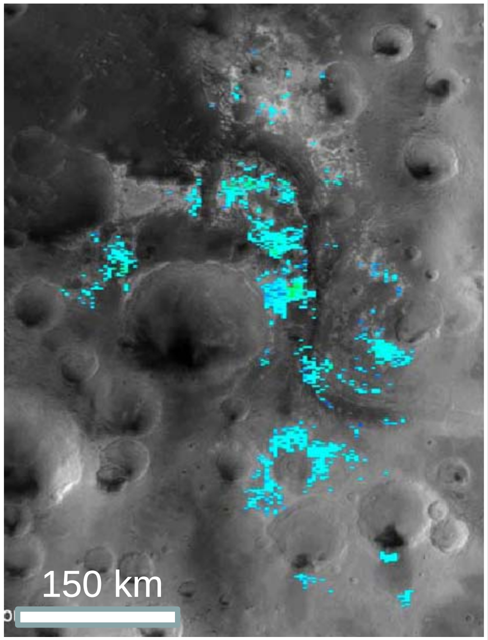
Layered phyllosilicates

- The largest exposures of clays on Mars show distinctive stratigraphic compositional variation: Al-clays above Fe/Mg-clays
- Al clays likely late Noachian or younger

Clays at Mawrth Vallis

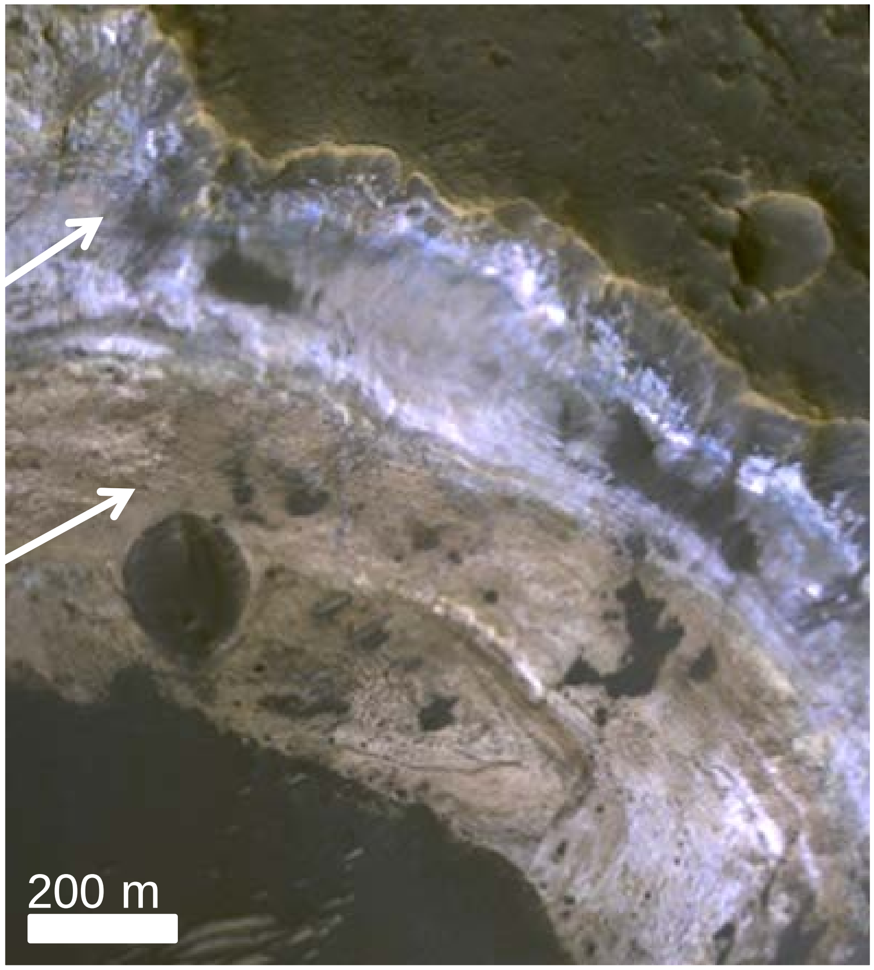


Poulet et al., 2005, Nature; Noe Dobrea et al., 2010, JGR

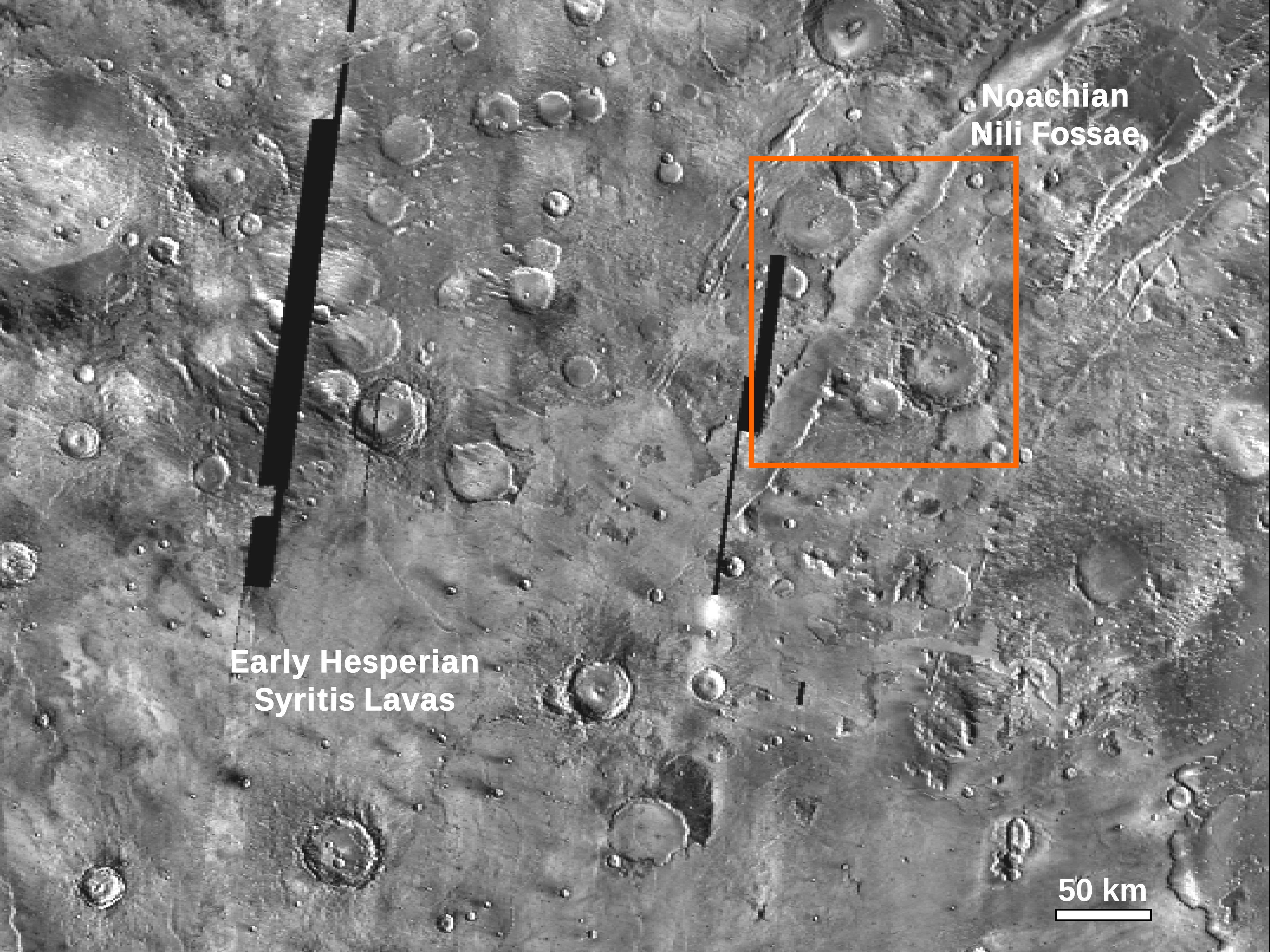
Type Locality: Mawrth Vallis

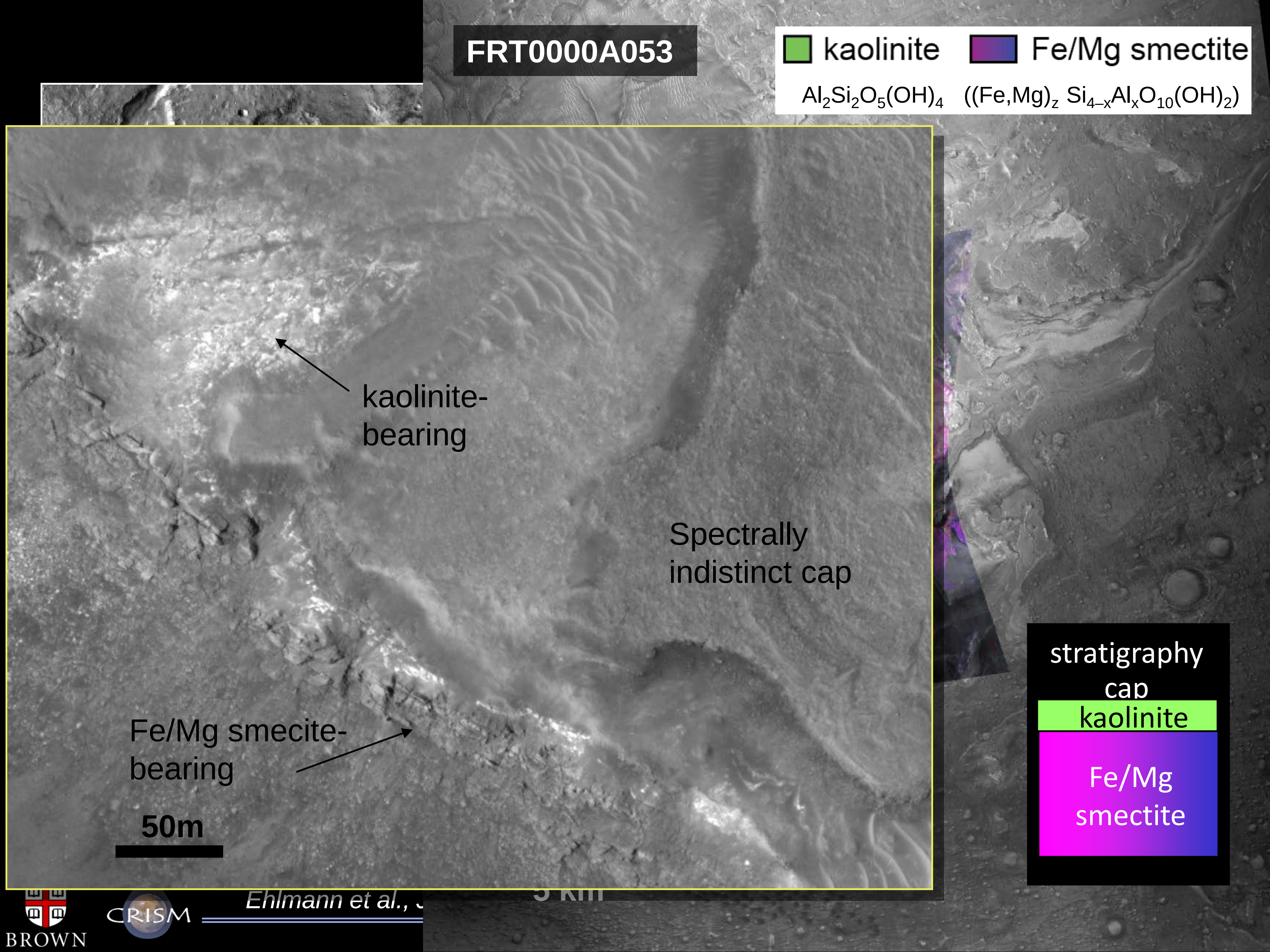
Al-clays
+ silica

nontronite
(Fe-clay)



Loizeau et al., 2011, Icarus


Noachian
Nili Fossae
Early Hesperian
Syritis Lavas
50 km


FRT0000A053
kaolinite
Fe/Mg smectite
$Al_2Si_2O_5(OH)_4$
$((Fe,Mg)_z Si_{4-x}Al_xO_{10}(OH)_2)$
kaolinite-bearing
Spectrally indistinct cap
Fe/Mg smecite-bearing
50m
stratigraphy
cap
kaolinite
Fe/Mg smectite
BROWN
CRISM


kaolinite overlying smectite
50km

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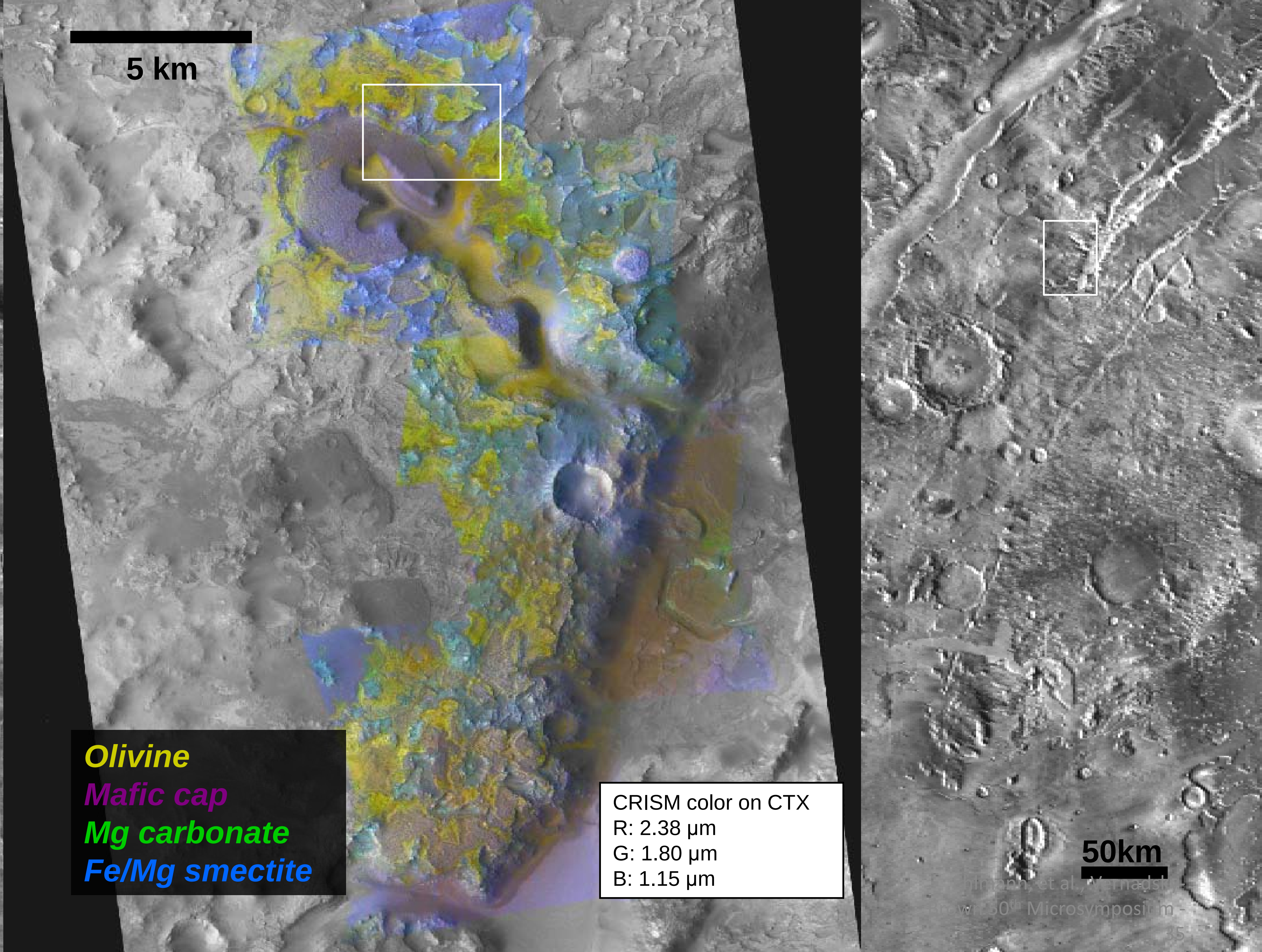
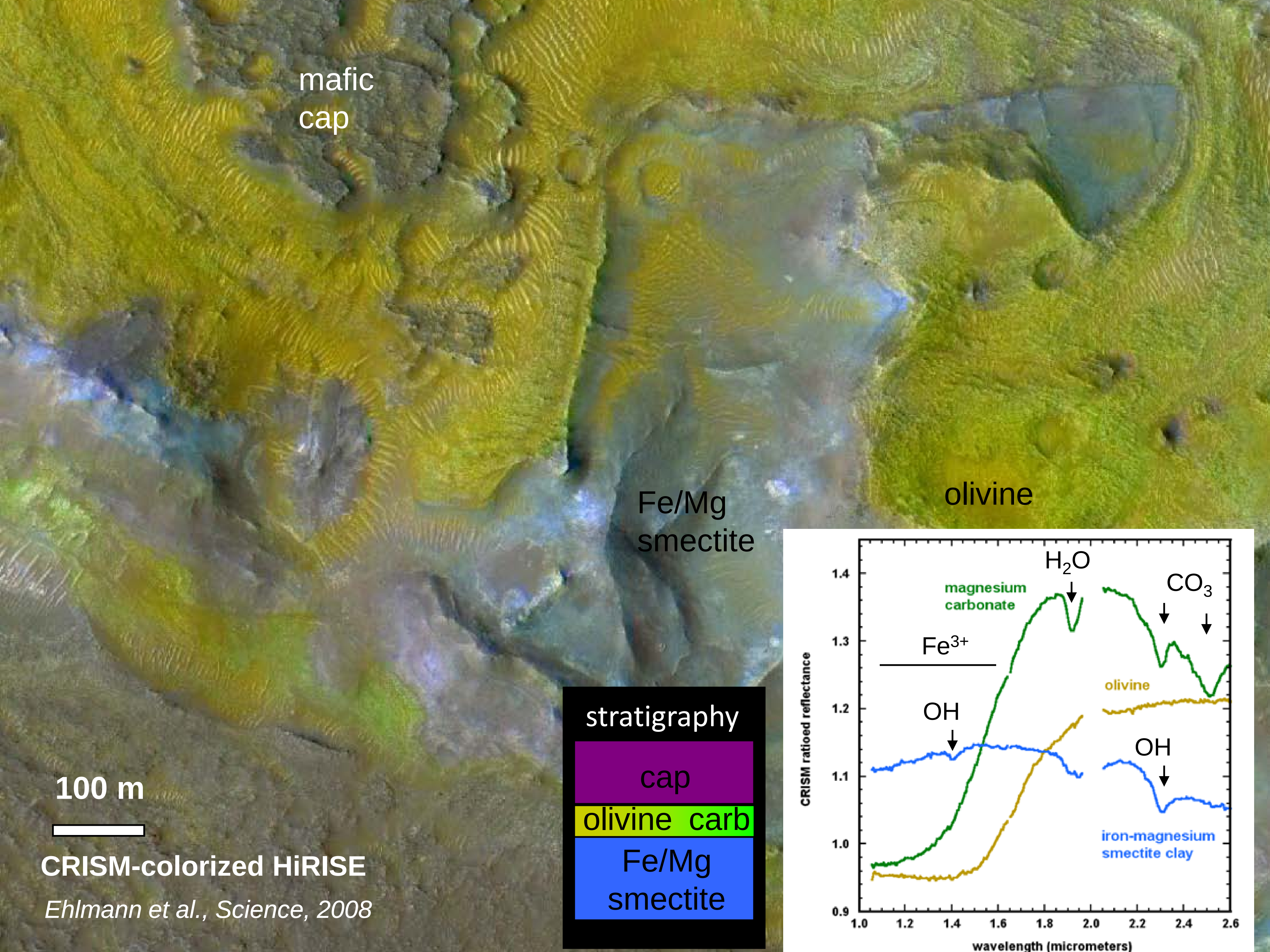
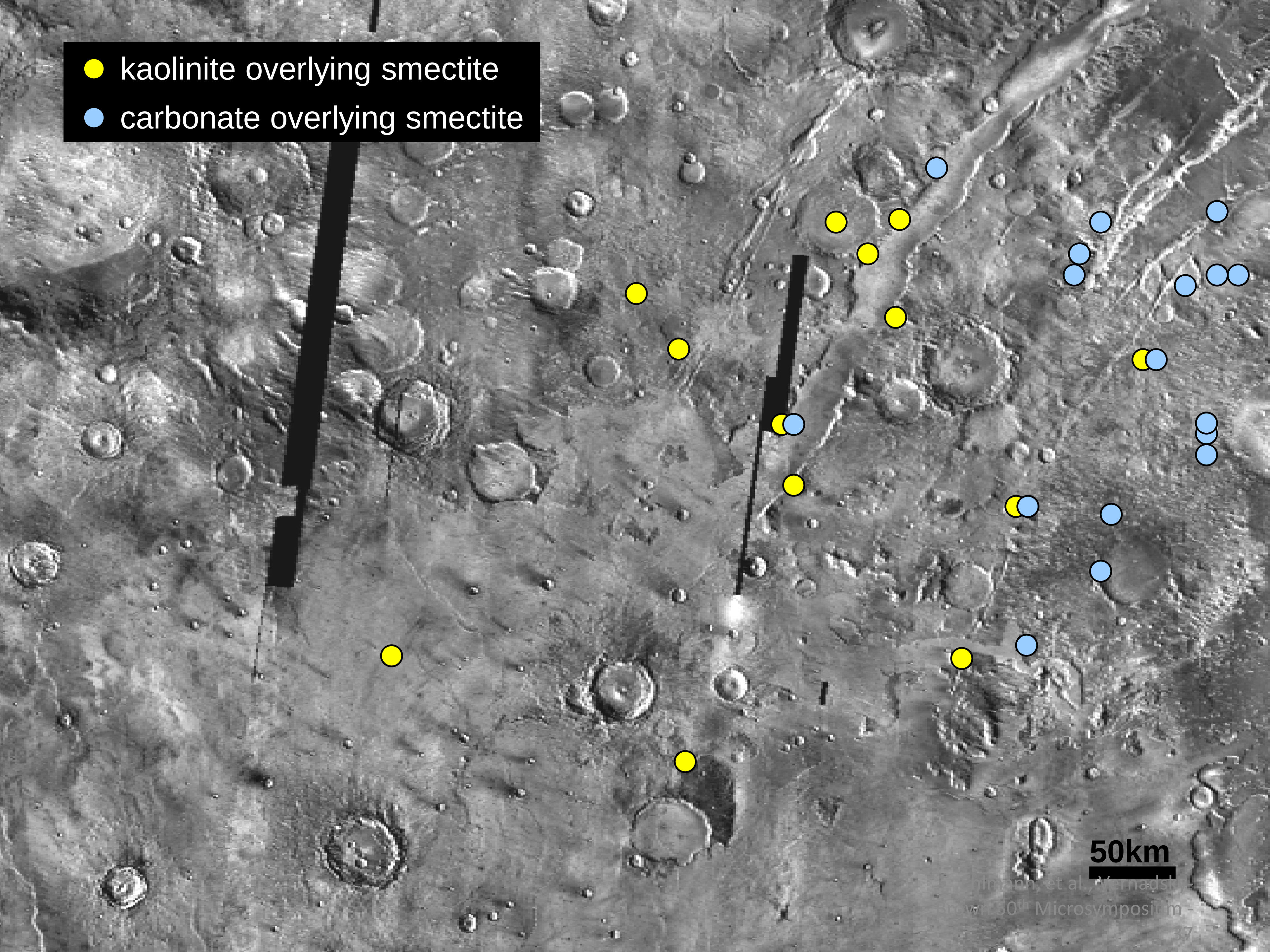
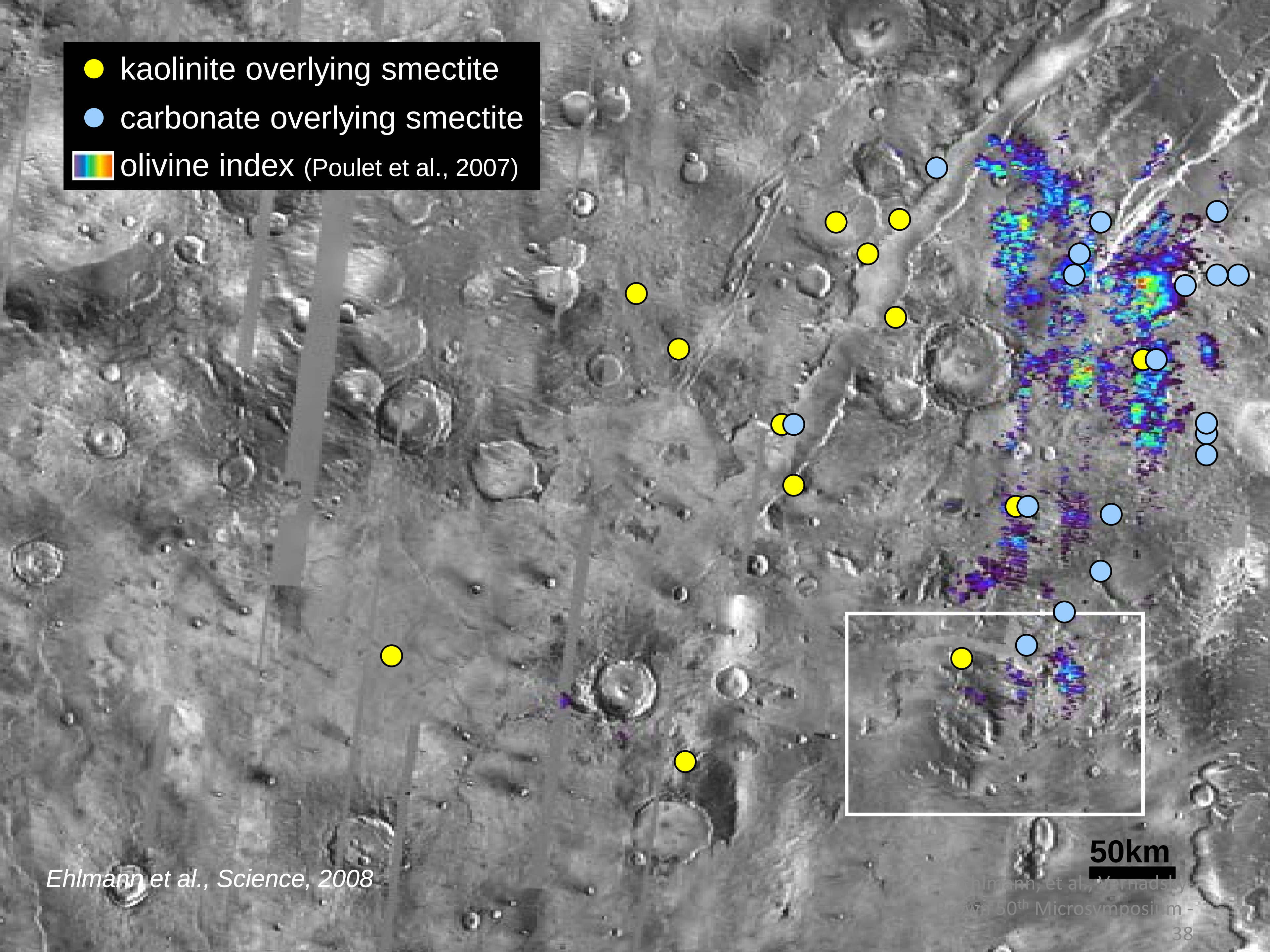
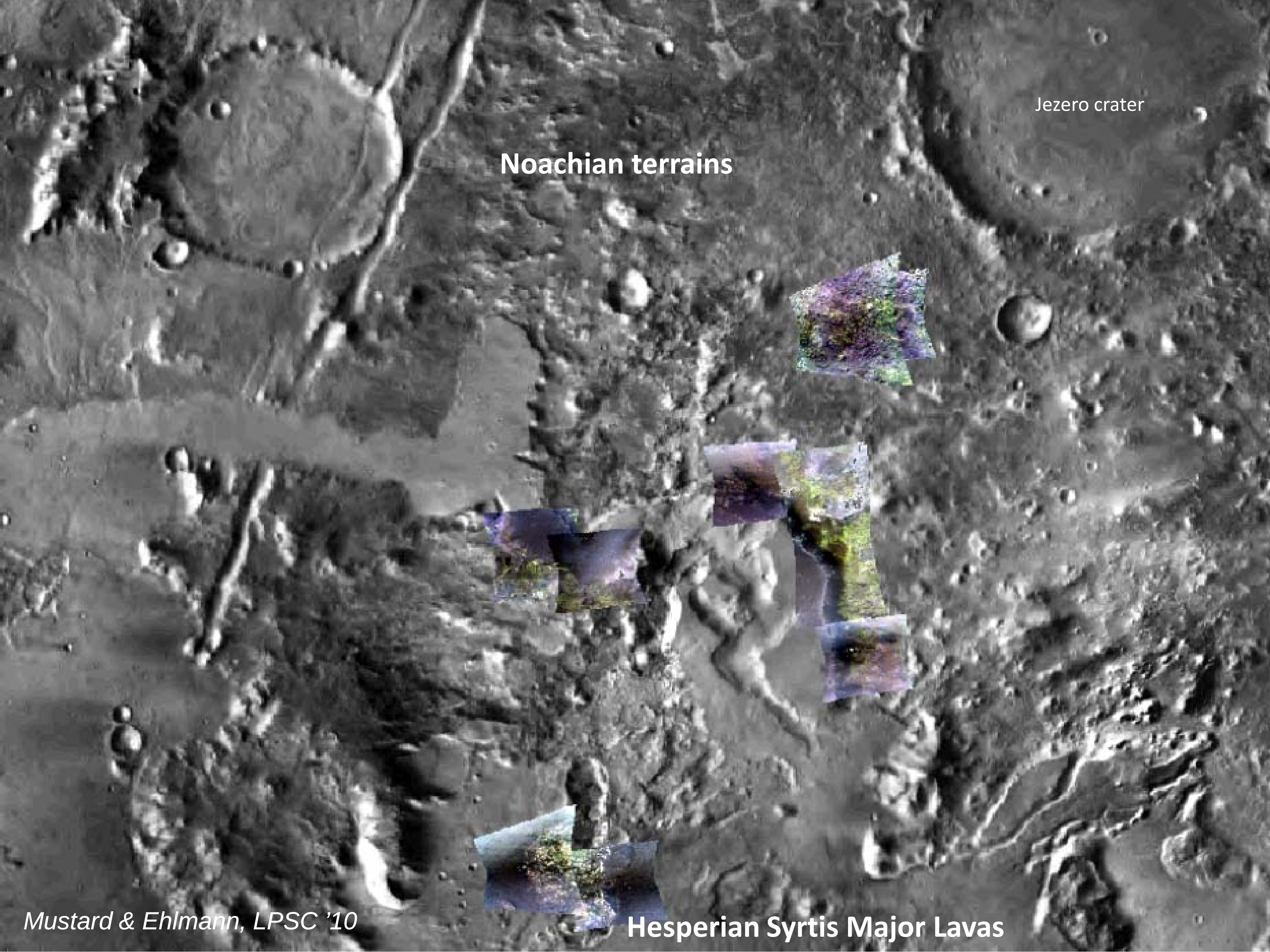

5 km
Olivine
Mafic cap
Mg carbonate
Fe/Mg smectite
CRISM color on CTX
R: 2.38 μm
G: 1.80 μm
B: 1.15 μm
50km


mafic
cap
Fe/Mg
smectite
olivine
100 m
CRISM-colorized HiRISE
Ehlmann et al., Science, 2008
stratigraphy
cap
olivine carb
Fe/Mg
smectite
CRISM ratioed reflectance
wavelength (micrometers)
magnesium
carbonate
H_2O
CO_3
Fe^{3+}
OH
olivine
OH
iron-magnesium
smectite clay
1.4
1.3
1.2
1.1
1.0
0.9
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6

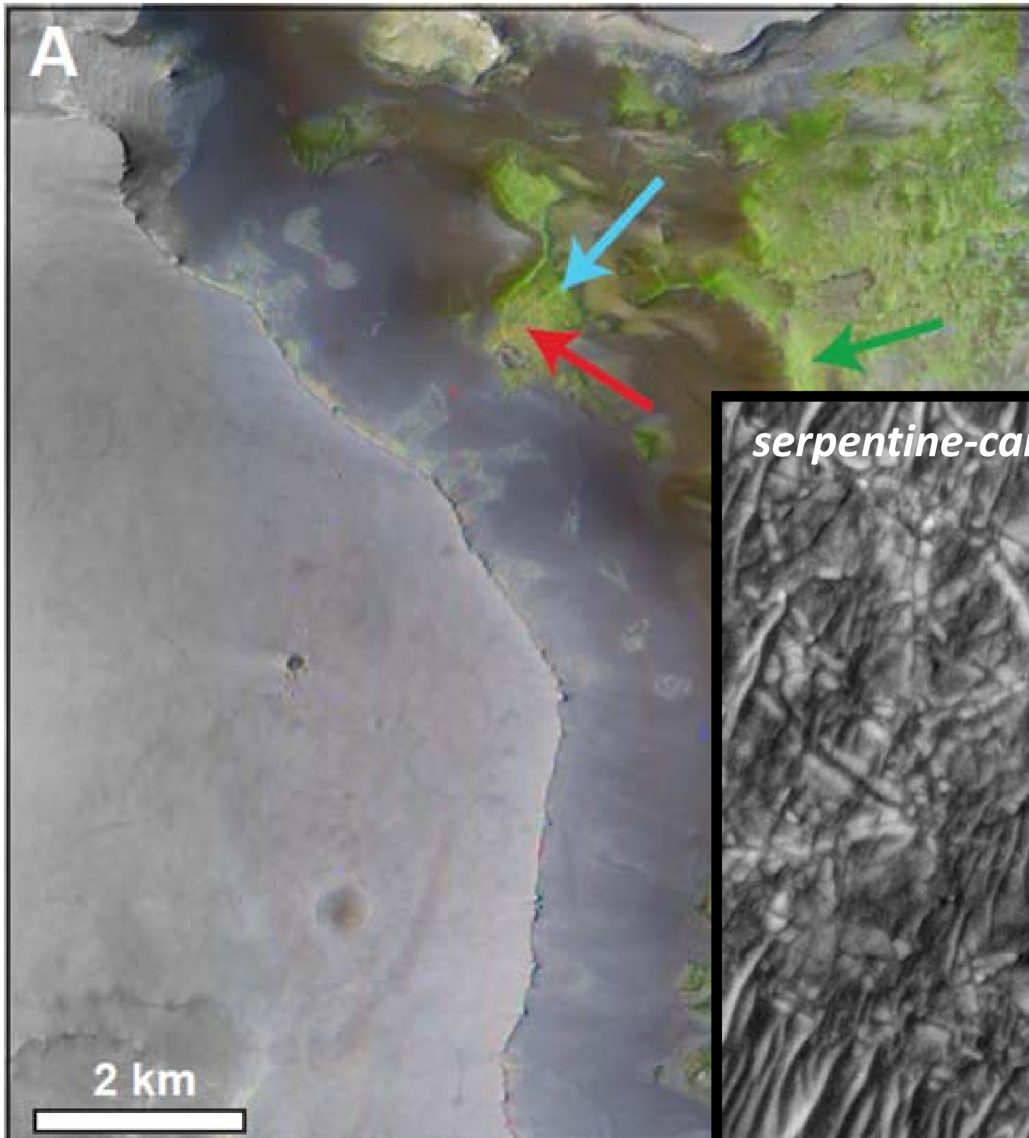

kaolinite overlying smectite
carbonate overlying smectite
50km

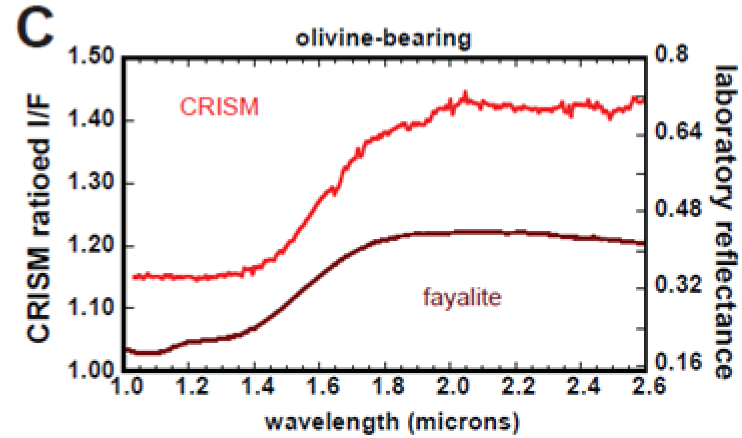


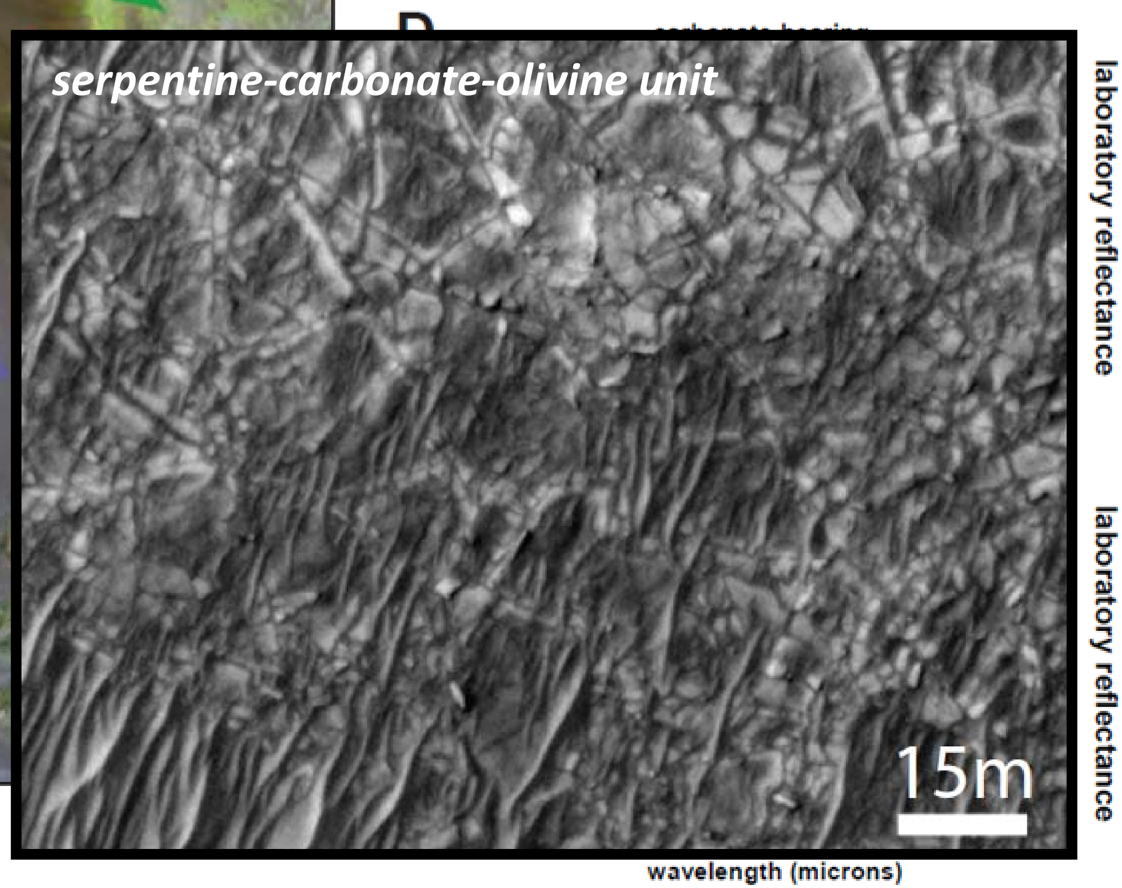
kaolinite overlying smectite
carbonate overlying smectite
olivine index (Poulet et al., 2007)
50km
Ehlmann et al., Science, 2008


Jezero crater
Noachian terrains
Hesperian Syrtis Major Lavas
Mustard & Ehlmann, LPSC '10

Northeast Syrtis: Serpentine/Carbonate







Formation of large-scale Mg carbonate deposits on Mars

Economic sources on Earth (Möller, 1989)

Ehlmann et al., *GRL* , 2010

- Hydrothermal fluids
- Serpentinization
- Diagenesis of marine beds

} SUBSURFACE

- Weathering of olivine and serpentine rich bodies
- Precipitate in playas fed by ultramafic catchments

} SURFACE

McLaughlin, CA (April 2009)

Serpentine and carbonate from Oman ophiolite (Keleman and Mater, 2008)

CRISM

CHEMICAL ENVIRONMENTS

1. "Deep phyllosilicates"
2. **Layered phyllosilicates**
3. **Carbonate deposits**

- Surface/near-surface weathering?
- Precursor lithology composition control of fluid chemistry & products

basalt —(partial alteration)→ Fe/Mg smectite —(enhanced leaching; loss of Ca^{2+}, Mg^{2+}, Fe^{2+} ions)→ Kaolin group mineral $Al_2Si_2O_5(OH)_4$

(Analog: soil formation under intermittantly wet conditions, Hawaii, Italy)

--or--

olivine $(Fe,Mg)_2SiO_4$ —(partial HT alteration; $H_2 \rightarrow CH_4$)→ serpentine $(Fe,Mg)_3Si_2O_5(OH)_2$ —(partial low-T alteration)→ carbonate $(Mg, Fe)CO_3$

(Analog: weathering serpentinites in Oman, N. California)

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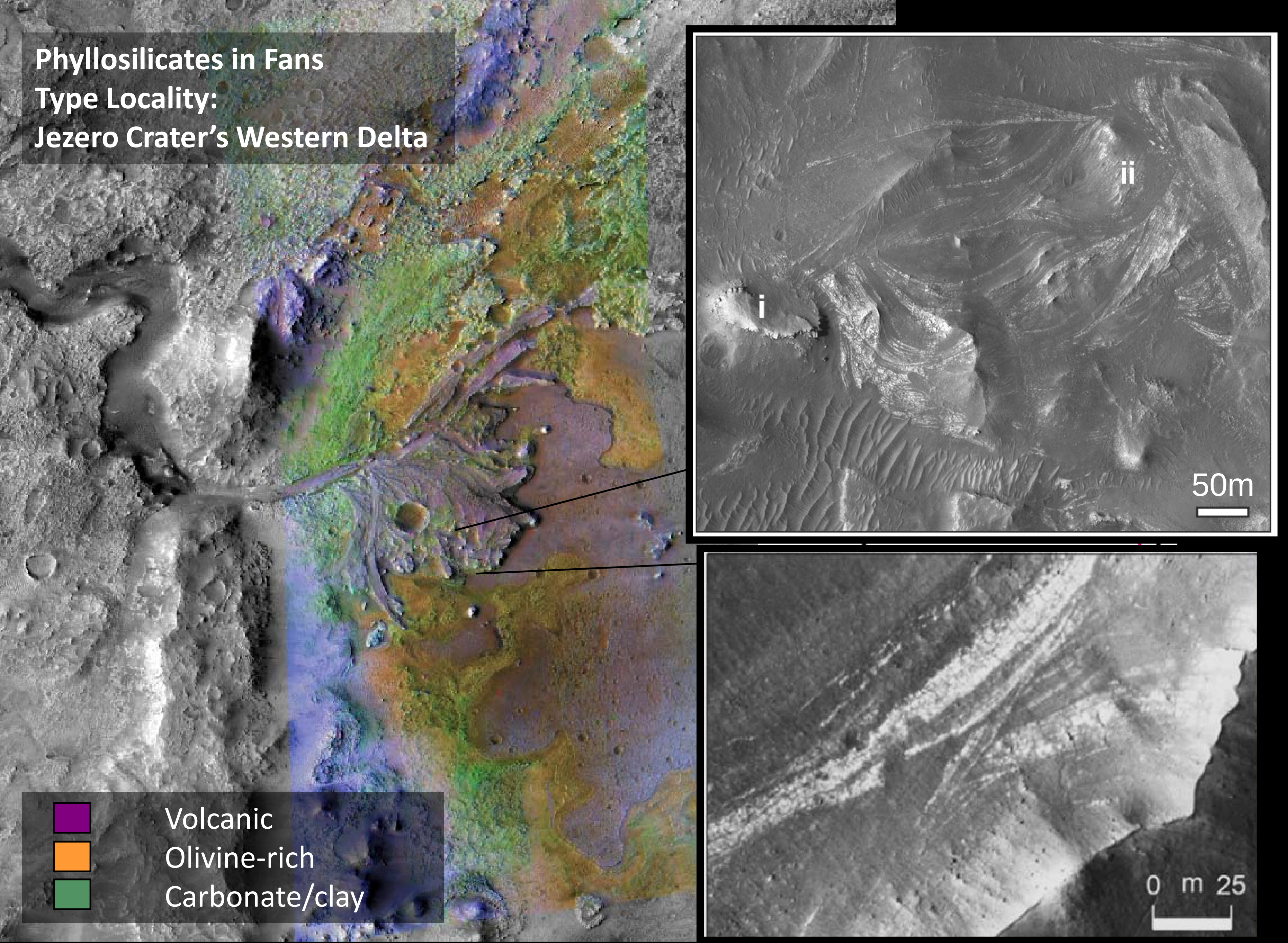
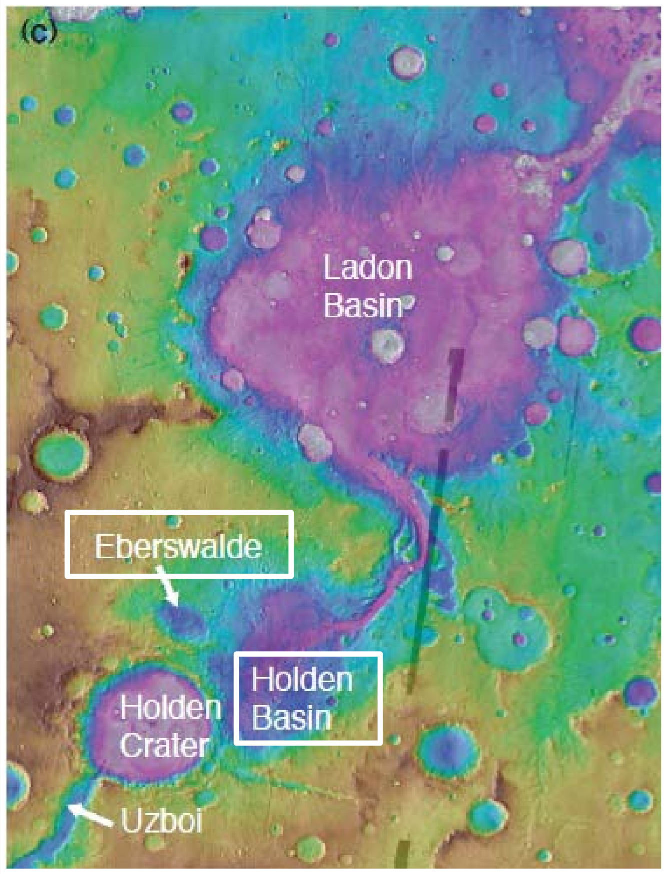


Ehlmann et al., Nat. Geosci. , 2008

Phyllosilicates in Fans and Deltas

- Jezero, Holden, and Eberswalde (and 6+ other locations) have clays in fans
- Each is part of a connected, largely open-basin, drainage system.
- Composition of clays (and carbonates in the case of Jezero) are spectrally identical to those in surroundings → Hypothesis: transported rather than formed in-situ.

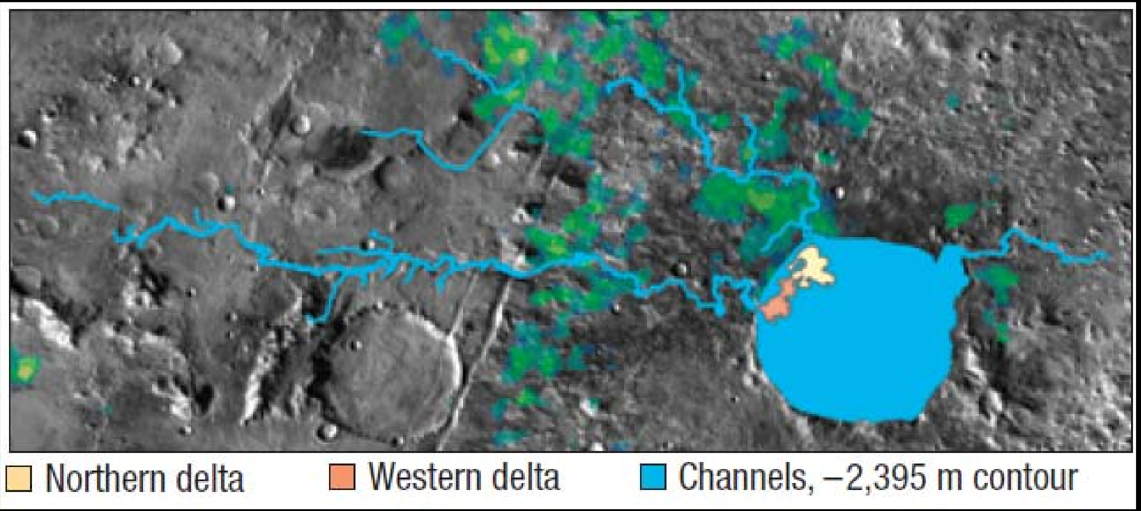
Milliken & Bish, 2010, Phil. Mag.

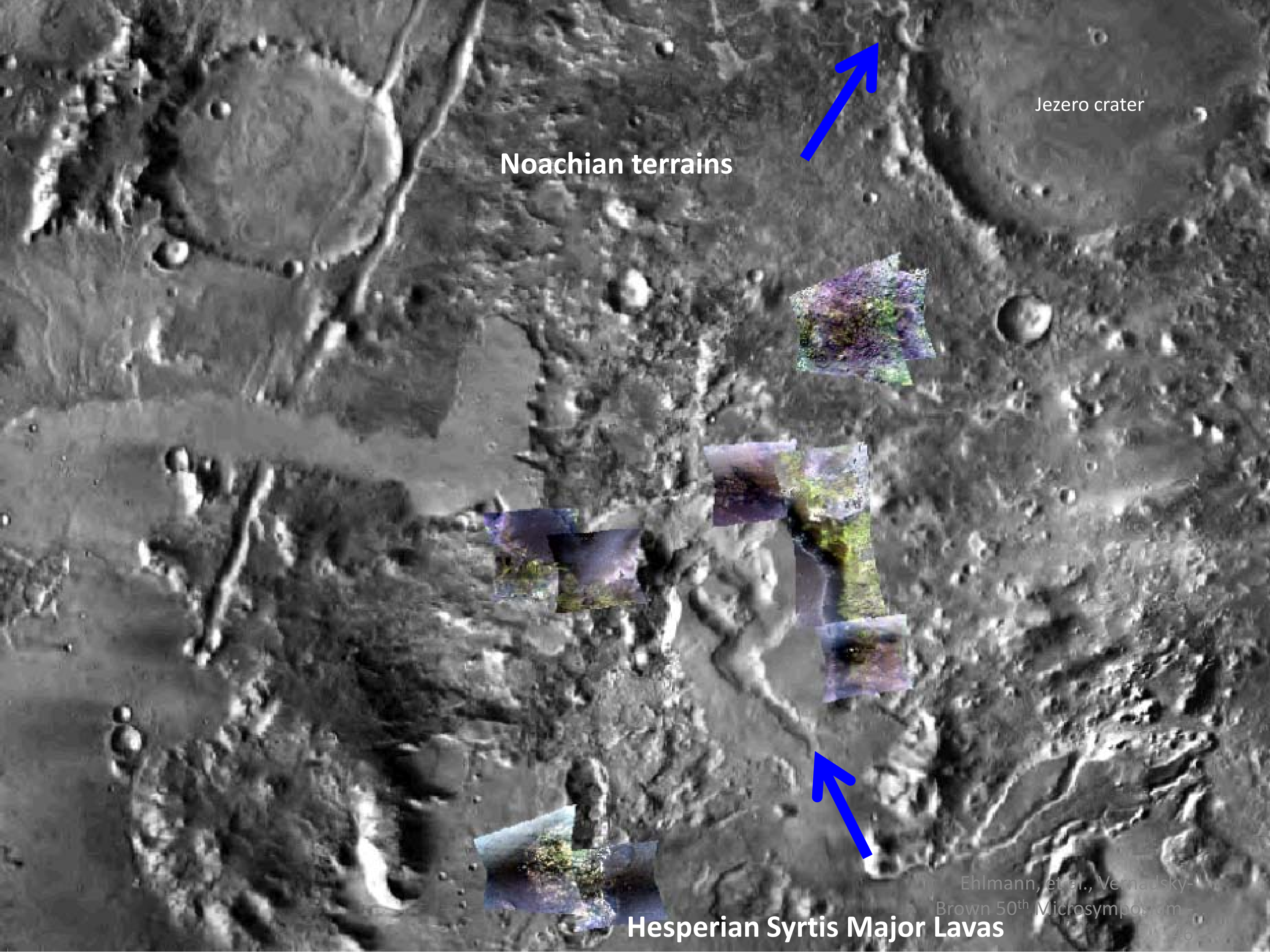


- Most activity in the late Noachian/early Hesperian

Clays & Carbonates in the Jezero watershed

(Fassett & Head, 2005, GRL; Ehlmann et al., 2008, Nat. Geosci.)





Ehlmann, et al., Vernadsky-Brown 50th Microsymposium

CHEMICAL ENVIRONMENTS

1. “Deep phyllosilicates”
2. Layered phyllosilicates
3. Carbonate deposits
4. Phyllosilicates in fans
5. **Plains sediments (chloride+ phyllo.)**
6. Intracrater clay-sulfate deposits

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7. Meridiani layered
8. Valles Marineris layered
9. Silica-rich layered
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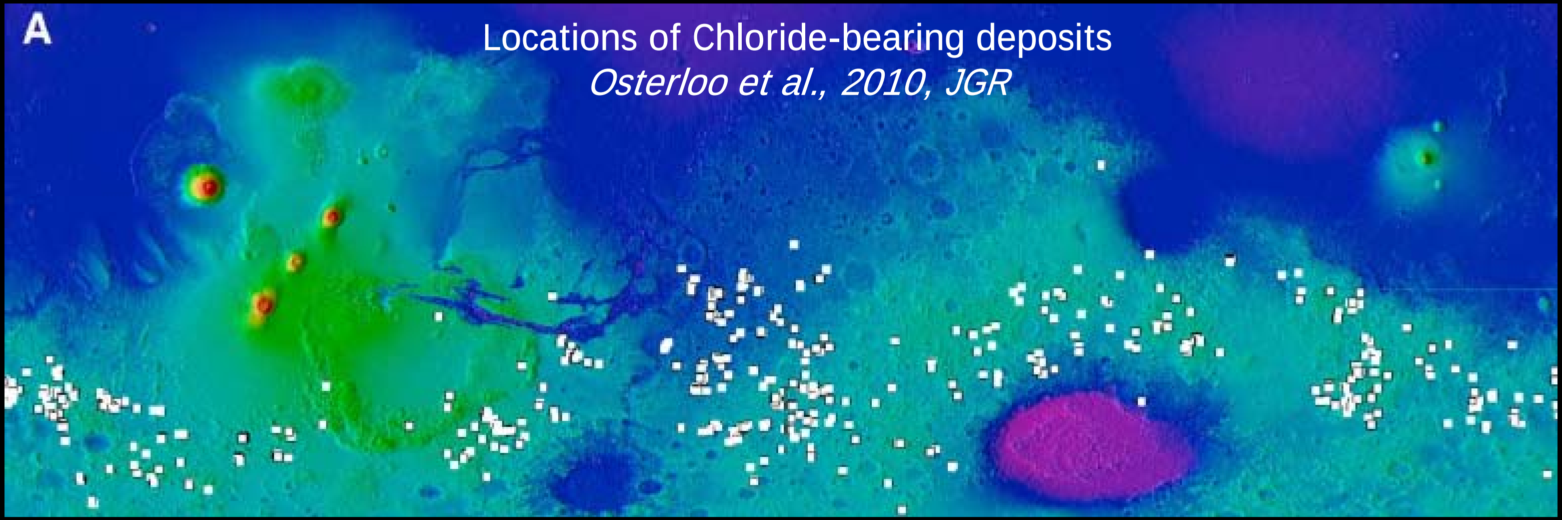
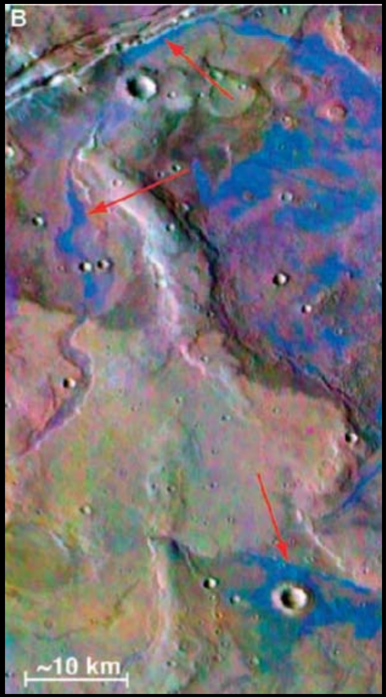
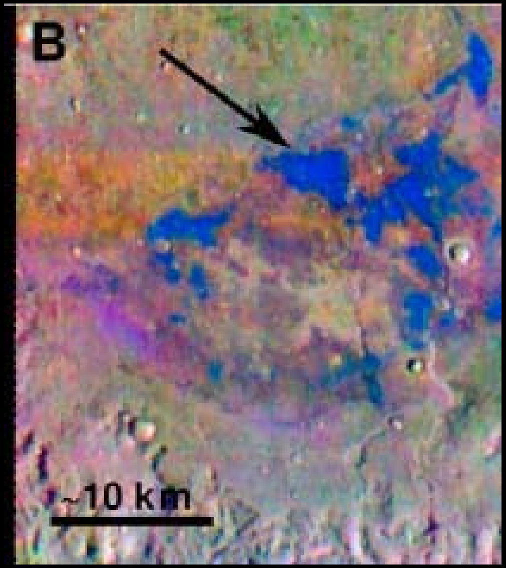
Phyllosilicate-Chloride Plains Sediments

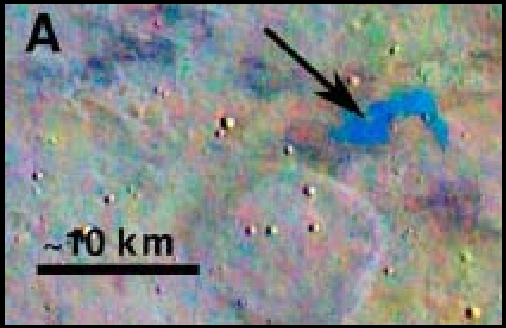






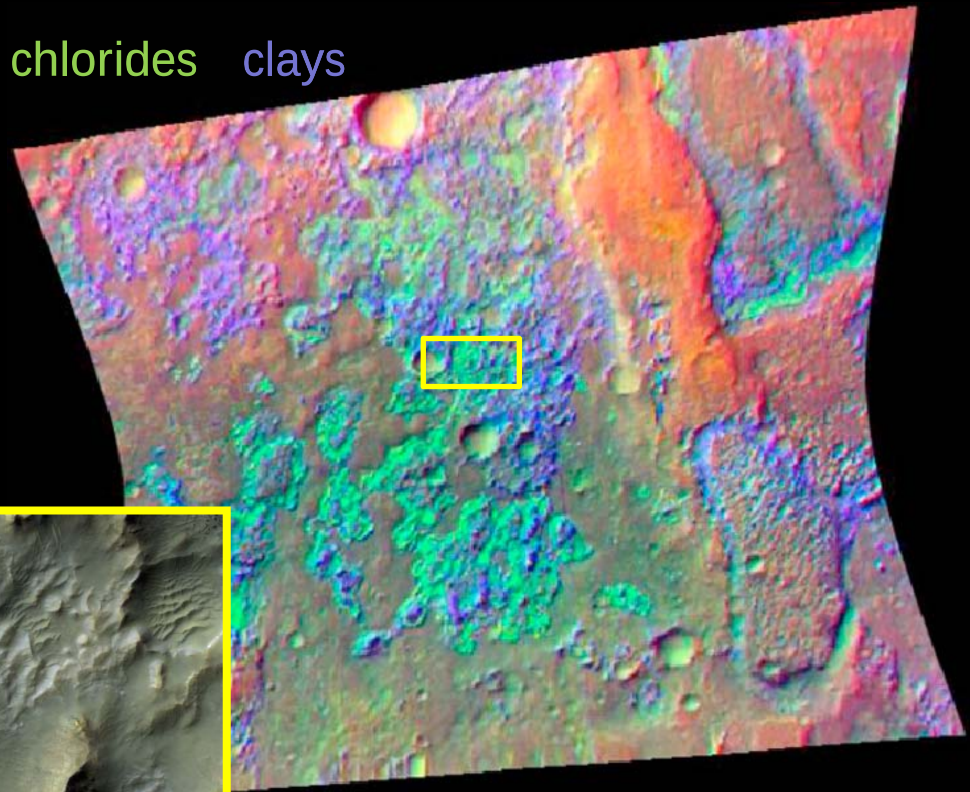
Osterloo et al., 2008, Science; 2010, JGR

- Chloride-bearing materials occupy irregularly-shaped topographic lows
- Hundreds of exposures across the southern highlands

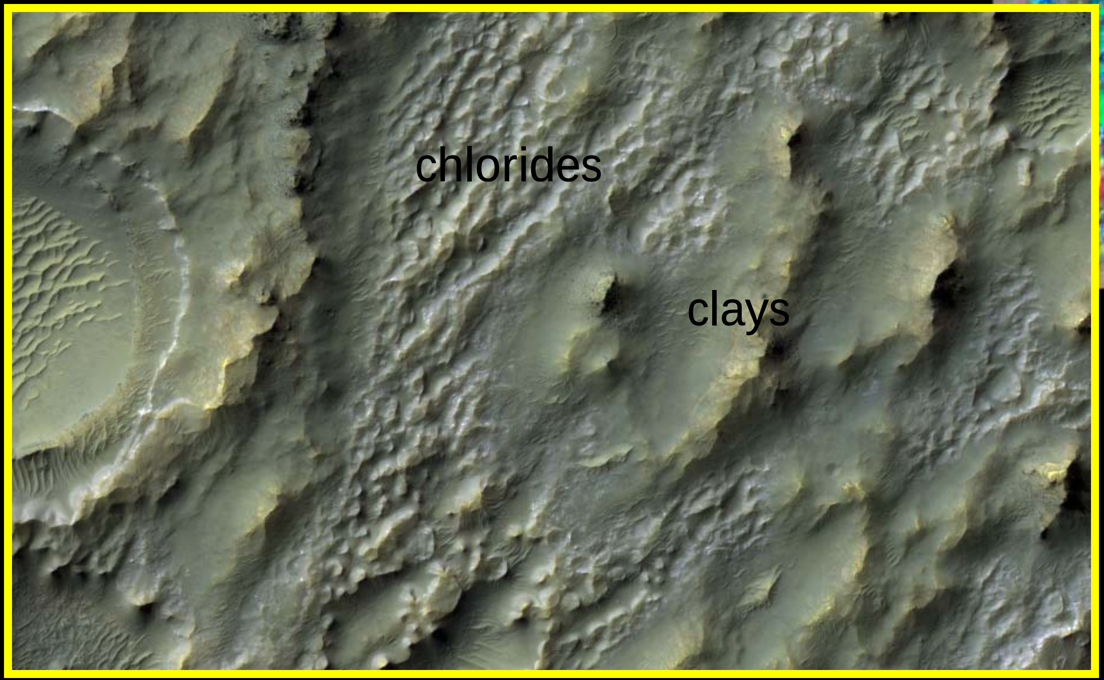


Phyllosilicate-Chloride Plains Sediments

- Sometimes, chlorides and clays are found together
- Phyllosilicates form the ancient, knobby crust. Salts formed later and surround



Glotch et al., 2010, GRL



- Most form in the late-Noachian early Hesperian, with some outliers

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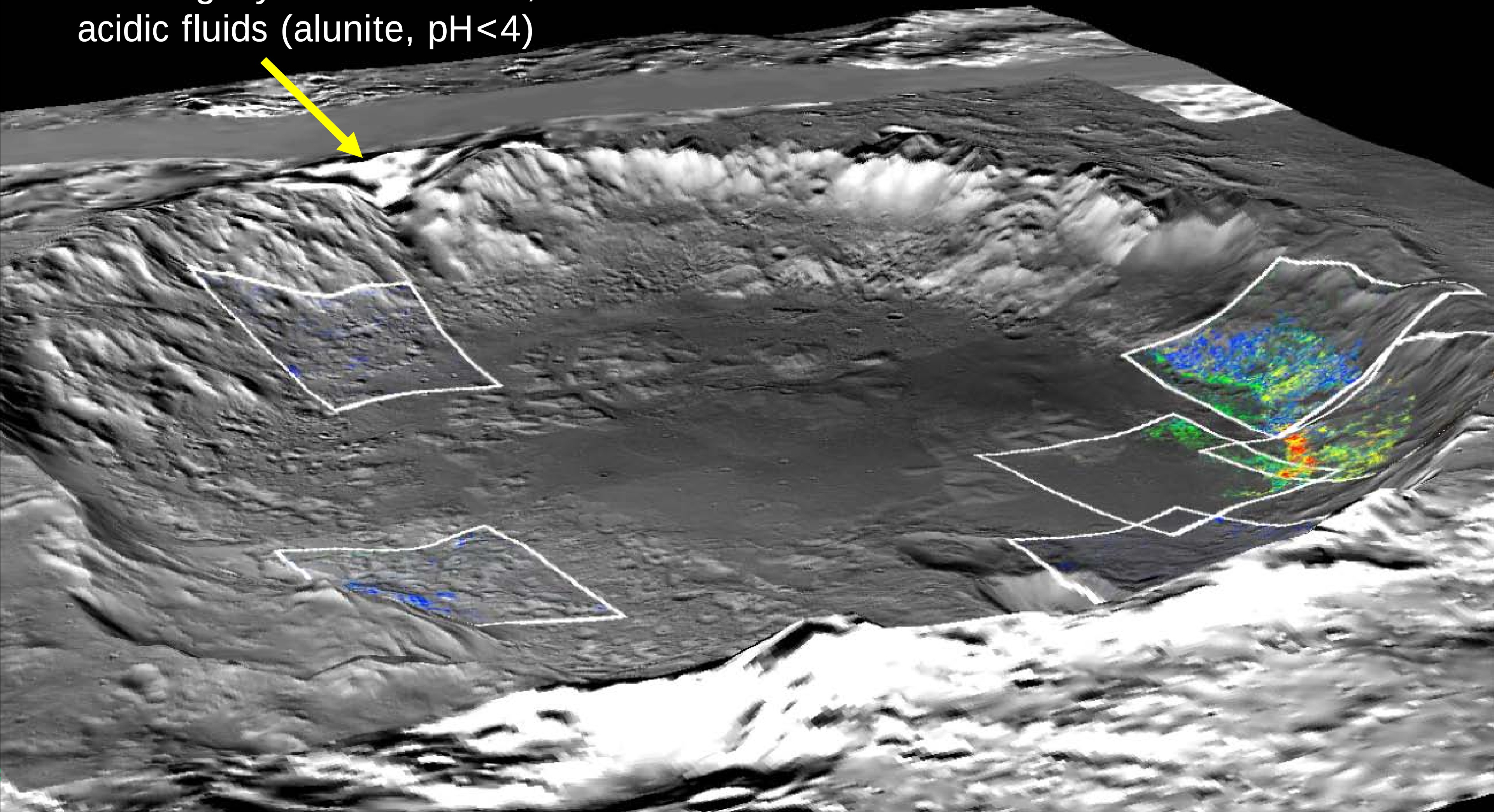
9. Silica-rich layered
10. S-rich alteration lavas

Intra-crater Clay-Sulfate: Cross Crater, Terra Sirenum (D~70km)

(Swayze, Ehlmann, Milliken et al., in prep., JGR)

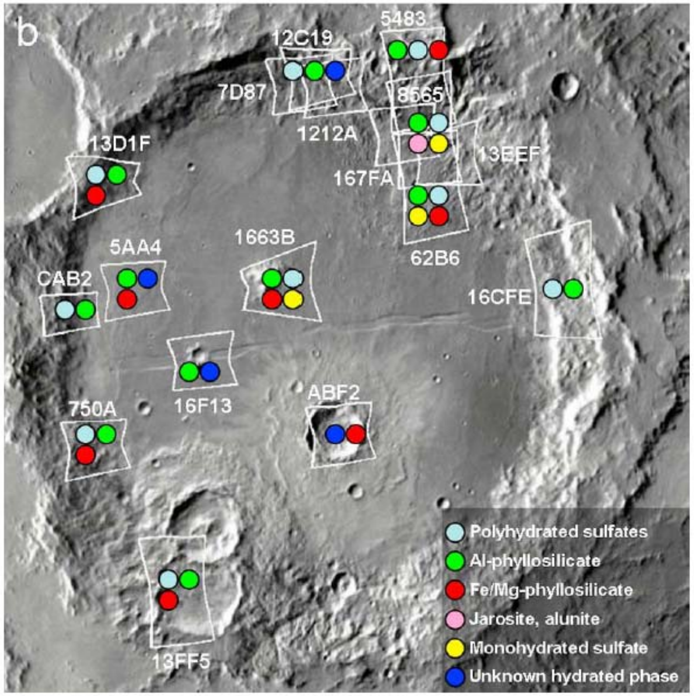
- -Closed basin with inlet
- -Eroding layered sediments, consistent with acidic fluids (alunite, pH<4)

Alunite (Al-sulfate)
Alunite + Kaolinite
Kaolin mineral (Al-phyllosilicate)
Montmorillonite/Opaline Silica

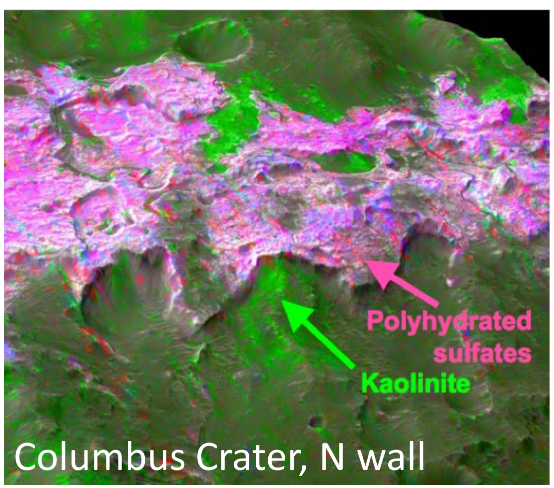


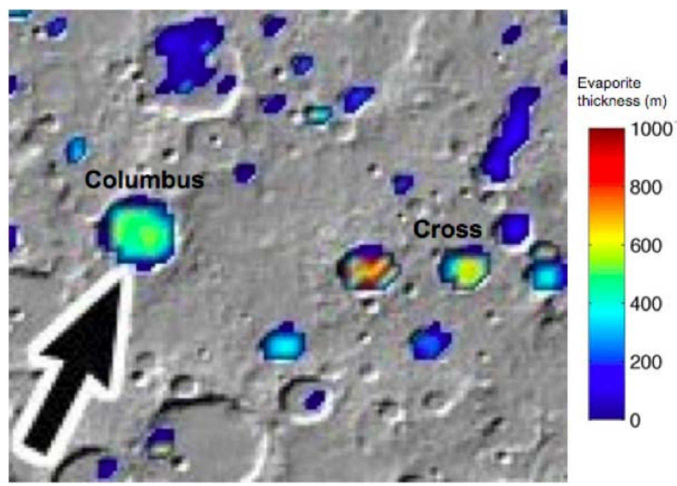
Intra-crater Clay-Sulfate: Coumbus Crater, Terra Sirenum (D~110km)

(Wray et al., 2011, JGR)



- Diverse sulfate mineralogy including the acid sulfate jarosite
- Mostly Al clays
- Some Fe/Mg phyllosilicates eroding from the walls and central mound
- Bathtub-ring deposits of sulfates and kaolinite occur in Columbus and Cross craters west of Tharsis





- These deposits likely formed from acidified groundwater-sourced fluids

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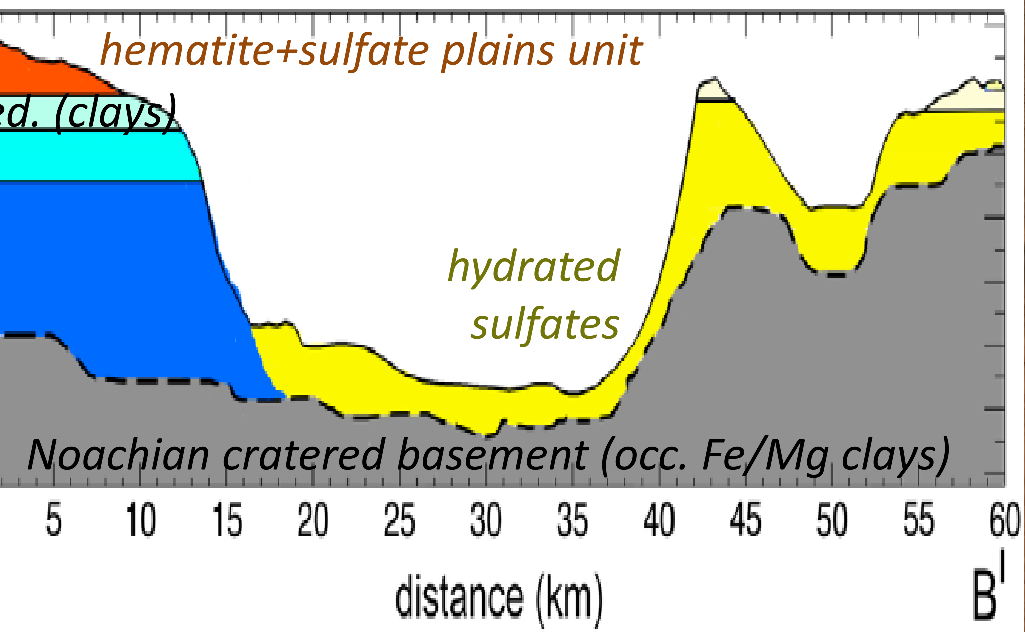
10. Silica volcanic vents

- Sedimentary rocks with sulfates, iron oxides, and silica alteration minerals
- Hesperian sedimentary plains and transported Fe/Mg smectite-bearing units above ancient cratered terrain

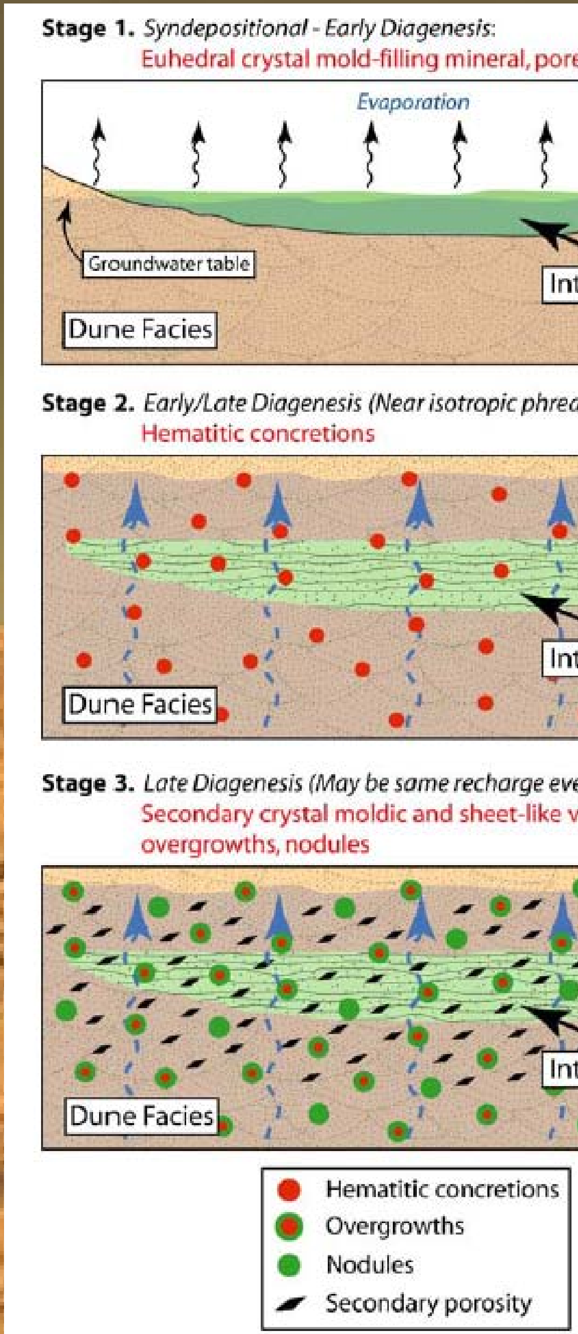
View from Meridiani Orbit
(Wiseman et al., *JGR*, 2010)



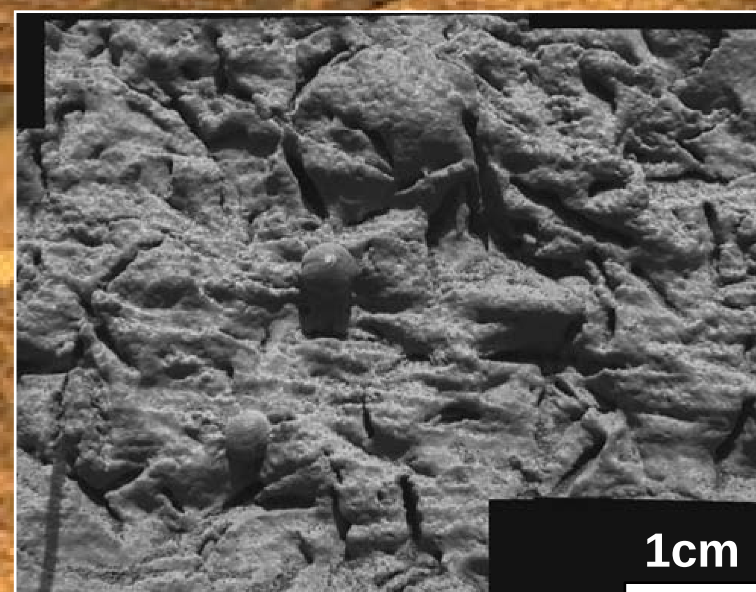
Bulk mineralogy estimate
(Clark et al., 2005, EPSL)
Mg, Ca sulfates 24%
Fe sulfate 10%
Allophane 7%
Hematite 6%
Silica 22%
Feldspar 17%

Opportunity’s Lion King Pan
(Pancam approximate true-color from MER-B sols 58-60)

- Likely an environment dominated by aeolian deposition of sediments
- Episodic groundwater upwelling leads to occasional shallow playa lakes
- Festoon cross-lamination indicates some subaerial deposition in a shallow, standing body of water
- Hematite concretions, vugs point to multiple episodes of subsurface diagenesis



McLennan et al., 2005, EPSL



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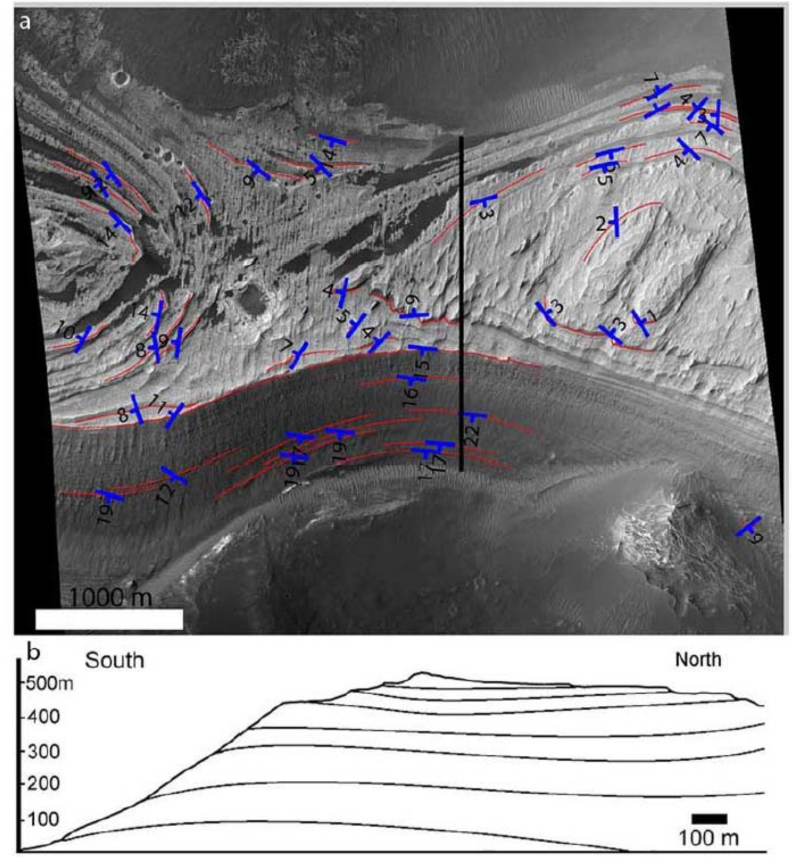
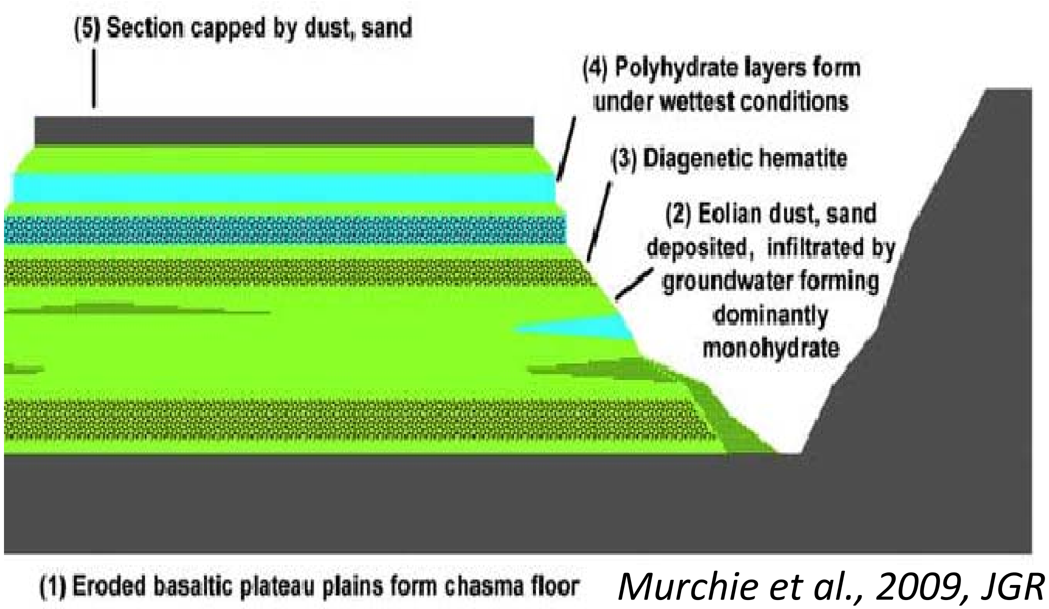
Valles Marineris Layered Sulfate Deposits

- Flat-lying or modestly sloped beds occupy mounds on the floor of chasma
- Alteration (non-regular) of polyhydrated salts and kieserite, a monohydrated sulfate
- Hydration generally increases up-section



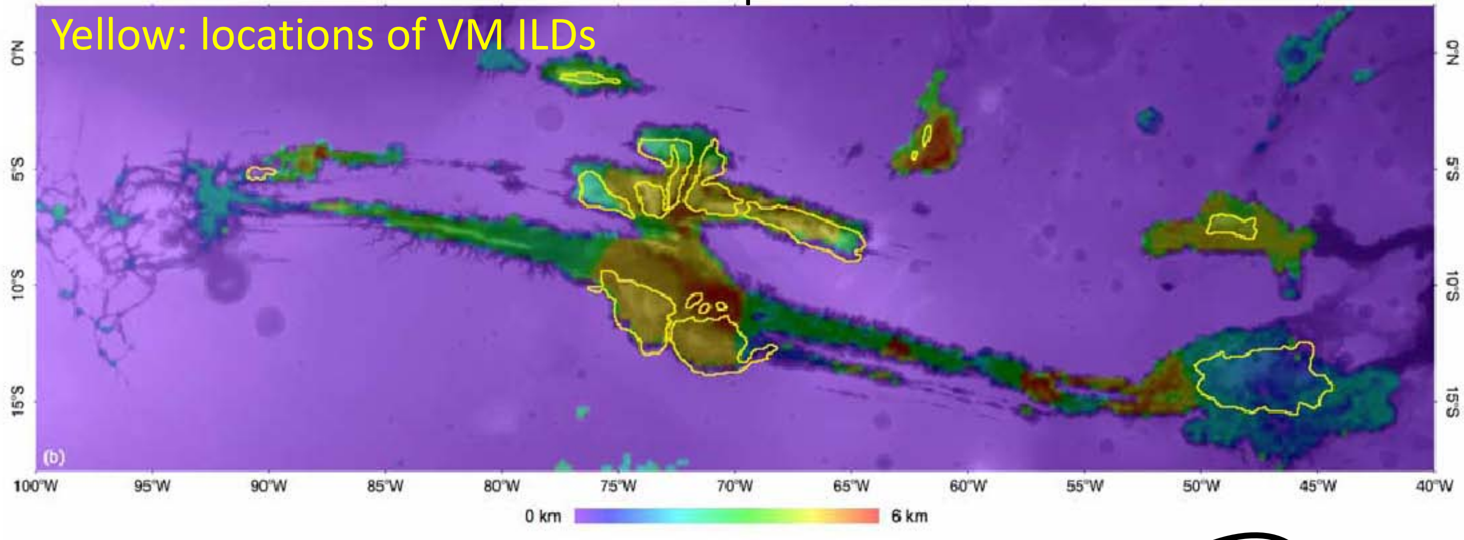
Roach et al., 2009, JGR



Murchie et al., 2009, JGR

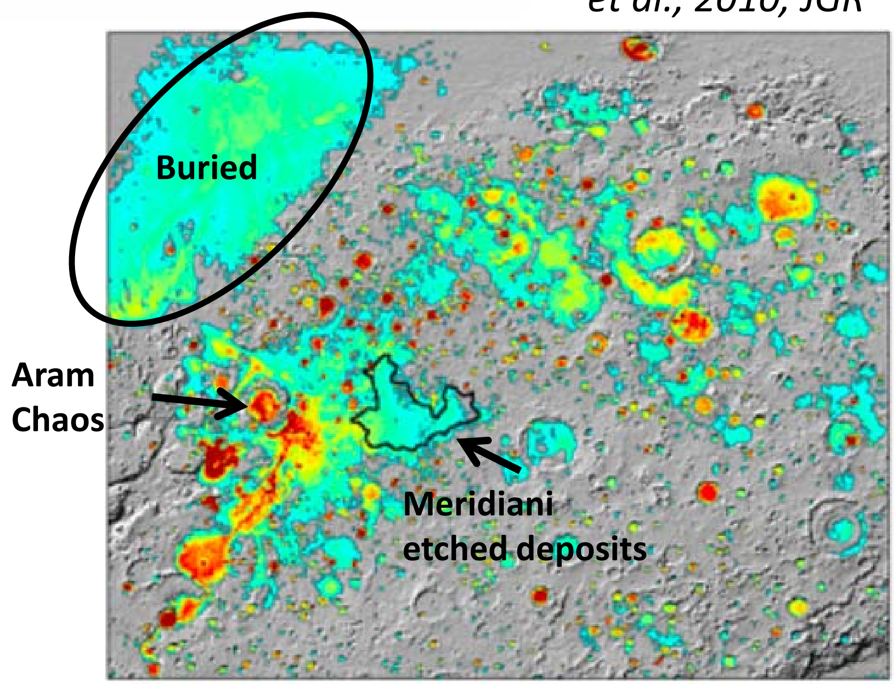
Valles Marineris Layered Sulfate Deposits

Color bar: thickness of modeled evaporites



Murchie et al., 2009, JGR

Andrews-Hanna et al., 2010, JGR



- Sulfate-bearing deposits also occur in etched terrain in Terra Meridiani, craters in Arabia, and in Aram Chaos, areas of predicted groundwater discharge

- Many of the predicted locations of groundwater discharge are buried by younger units or dust, so sulfates are hidden if they occur in those locations

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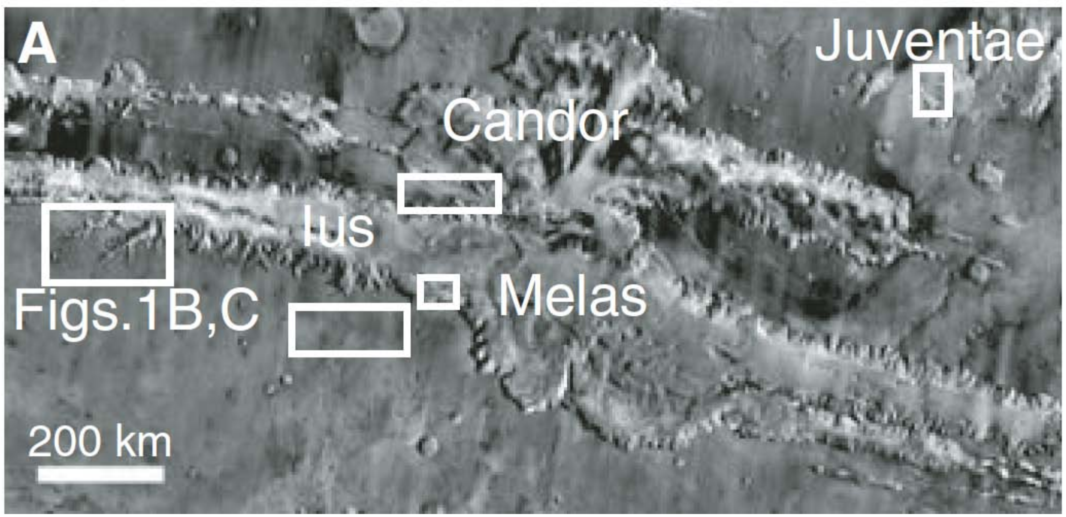
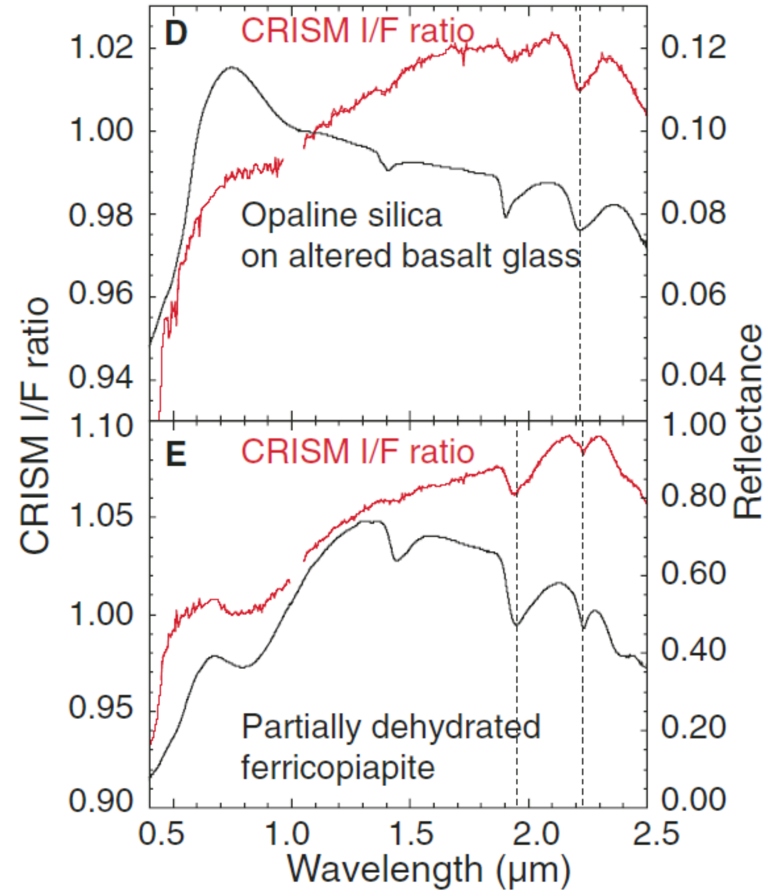
Opal & Fe Sulfates Surrounding Valles Marineris

- Fe sulfates + silica indicate acid (pH <4) conditions
- CRISM sees layered deposits around Vallis Marineris

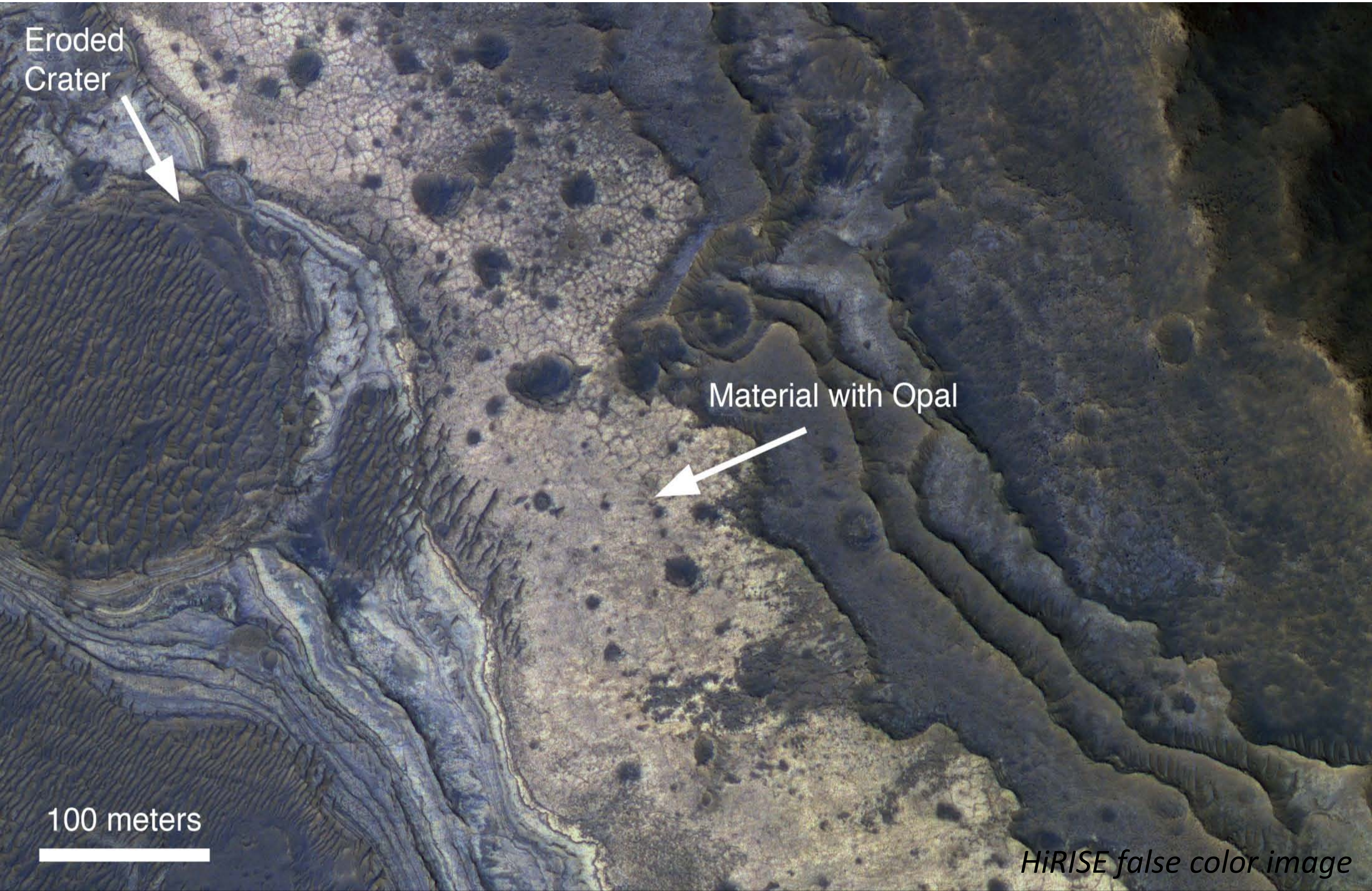




Milliken et al., 2008, Geology

- These outcrops were below the spatial resolution of previous investigations.

Opal & Fe Sulfates Surrounding Valles Marineris



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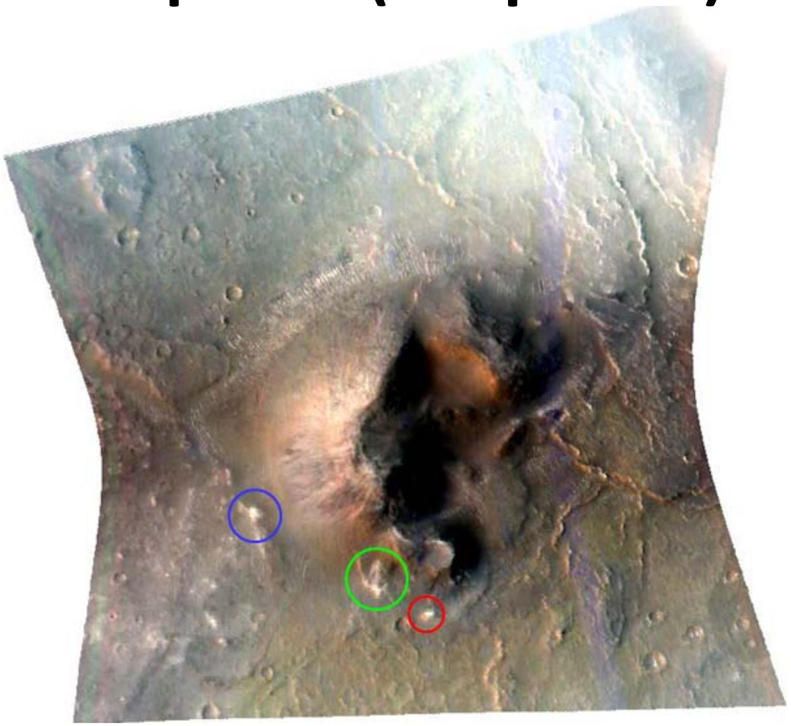
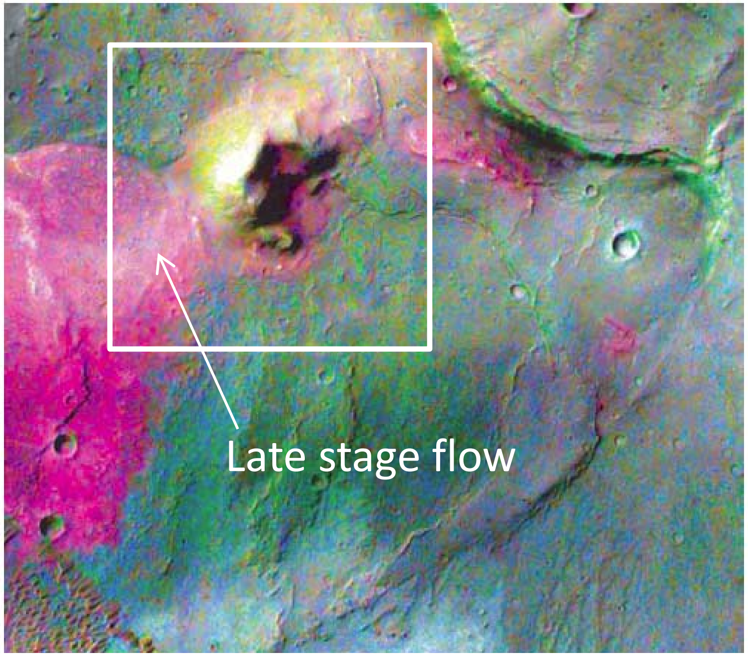
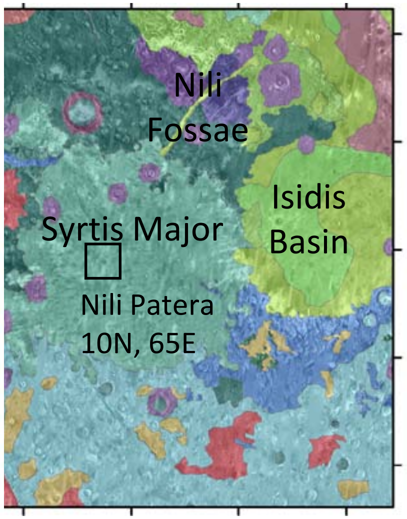
Volcanic Hydrothermal Silica Deposits (Hesperian)

- Younger probable volcanic hydrothermal deposits occur within Syrtis Major's Nili Patera caldera
- The late-stage volcanic cone is surrounded by mounds with absorption features due to hydrated silica

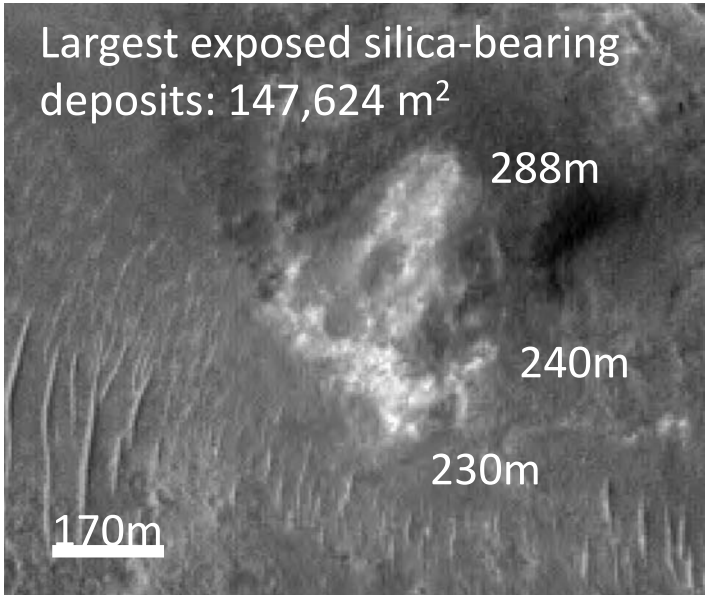






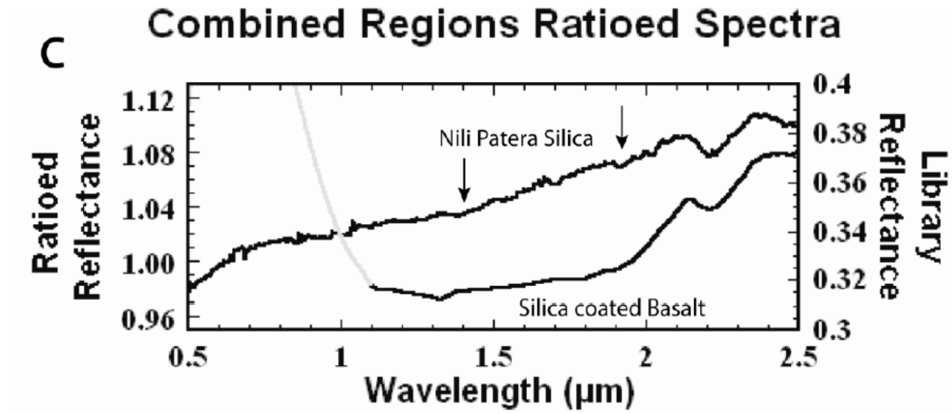
(Skok et al., *Nature Geosci*, 2010)

Volcanic Hydrothermal Silica Deposits (Hesperian)



(Skok et al., *Nature Geosci*, 2010)

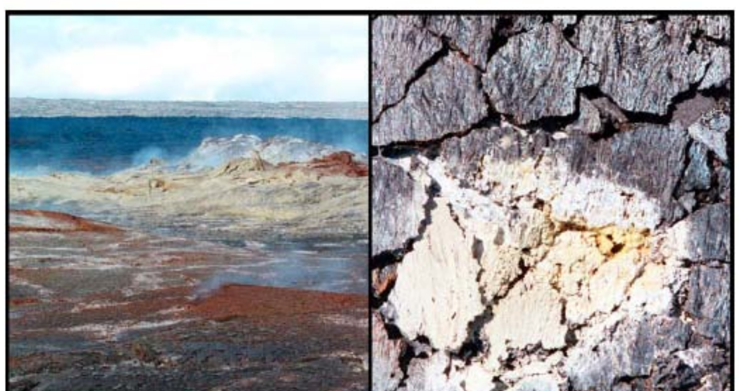
- Distinguishing feature: Silica-bearing materials in localized, discrete deposits on and near the volcanic cone summit



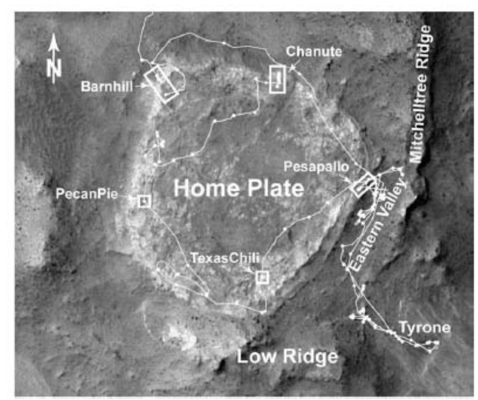
- Analogous environments? Yellowstone, Kilauea, Home Plate

Yellowstone sinter *(e.g. Walter & Des Marais, 1993, Icarus)*

Kilauea solfatara (*Seelos et al., 2010, JGR*)



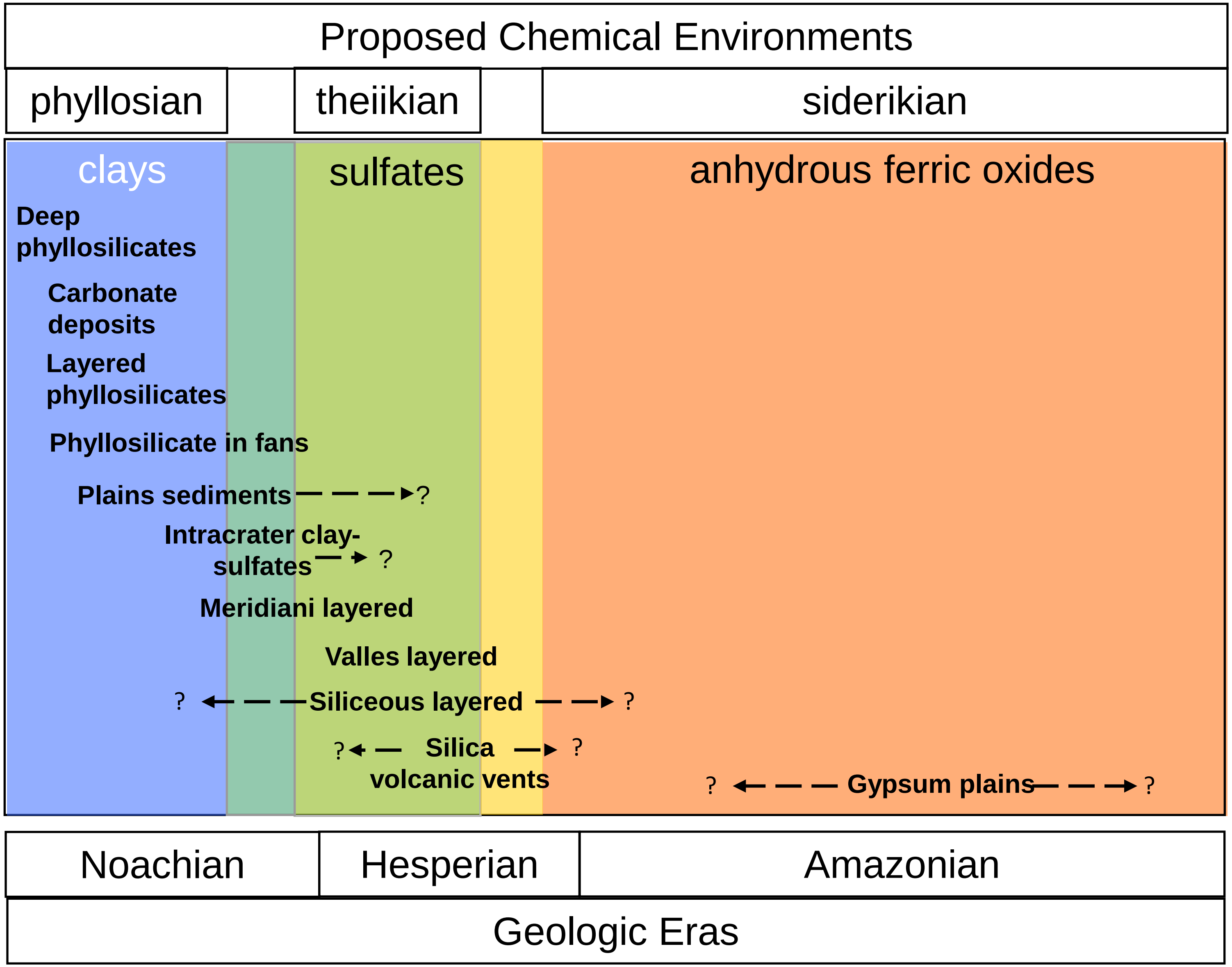
Acid-sulfate volcanic feature, Gusev Crater *(Schmidt et al., 2009, JGR)*



Chemical Environments During Mars' First Billion Years

- Key advance: mineralogy + morphology at high resolution
- **Think locally, not globally on ancient Mars** to understand the mineralogy
  - **But there are global trends**
- **Neutral to alkaline weathering** dominant **in earliest environments** (both sub- and near-surface), **transition to acidic**
- **Low-grade Metamorphic / Hydrothermal processes** in the deepest (oldest?) altered materials
- **Intact rock record on Mars pushes backward our ability to access early terrestrial planetary environments at the time of life's origins**
  - But complicates it? Multiple potentially habitable environments

Adapted from Murchie et al., JGR, 2009 with mineralogic epochs from Bibring et al., 2006



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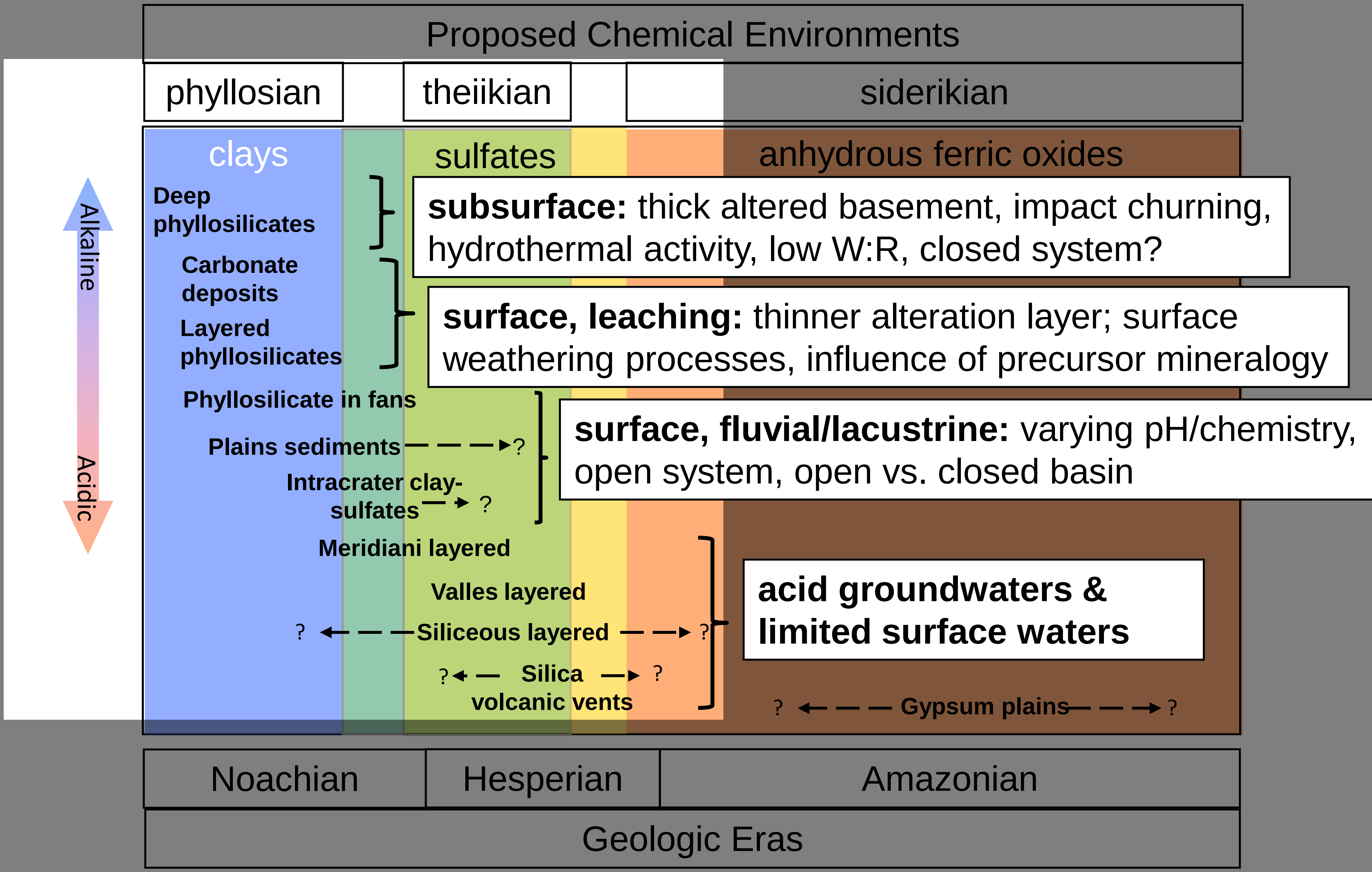
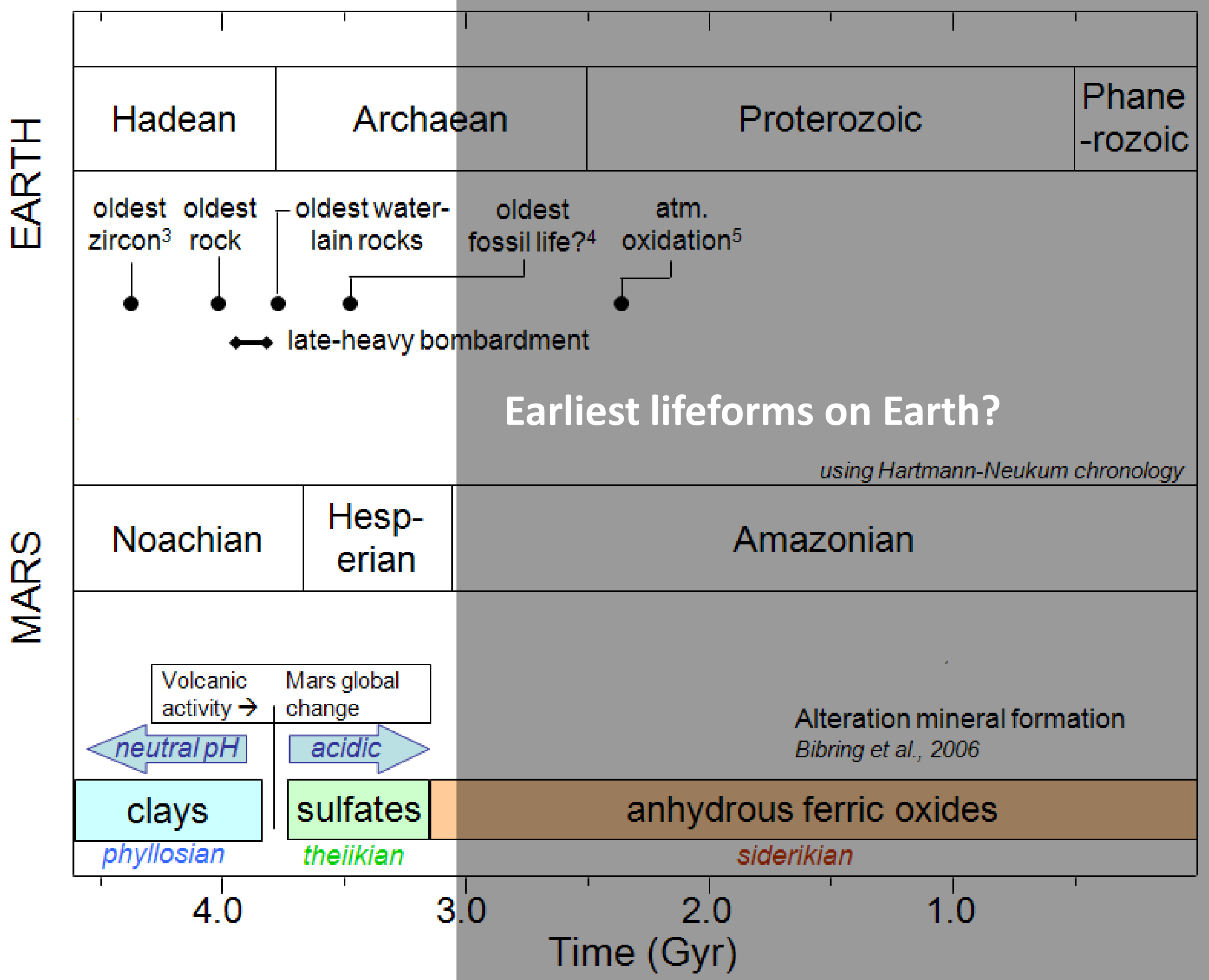




Earliest lifeforms on Earth?

Ten distinctive habitable environments from this time period on Mars!

EXTRAS

Styles of Alteration

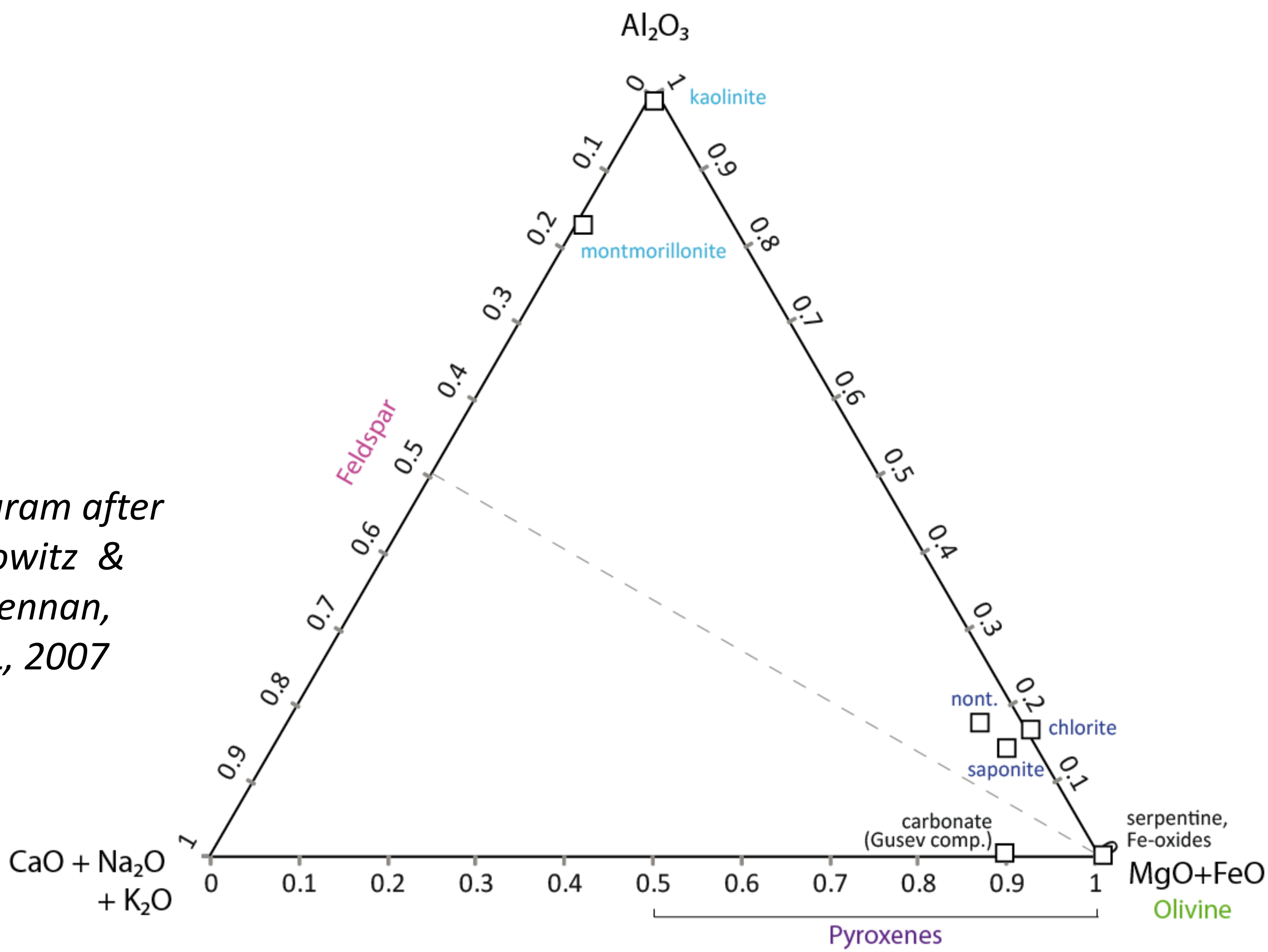
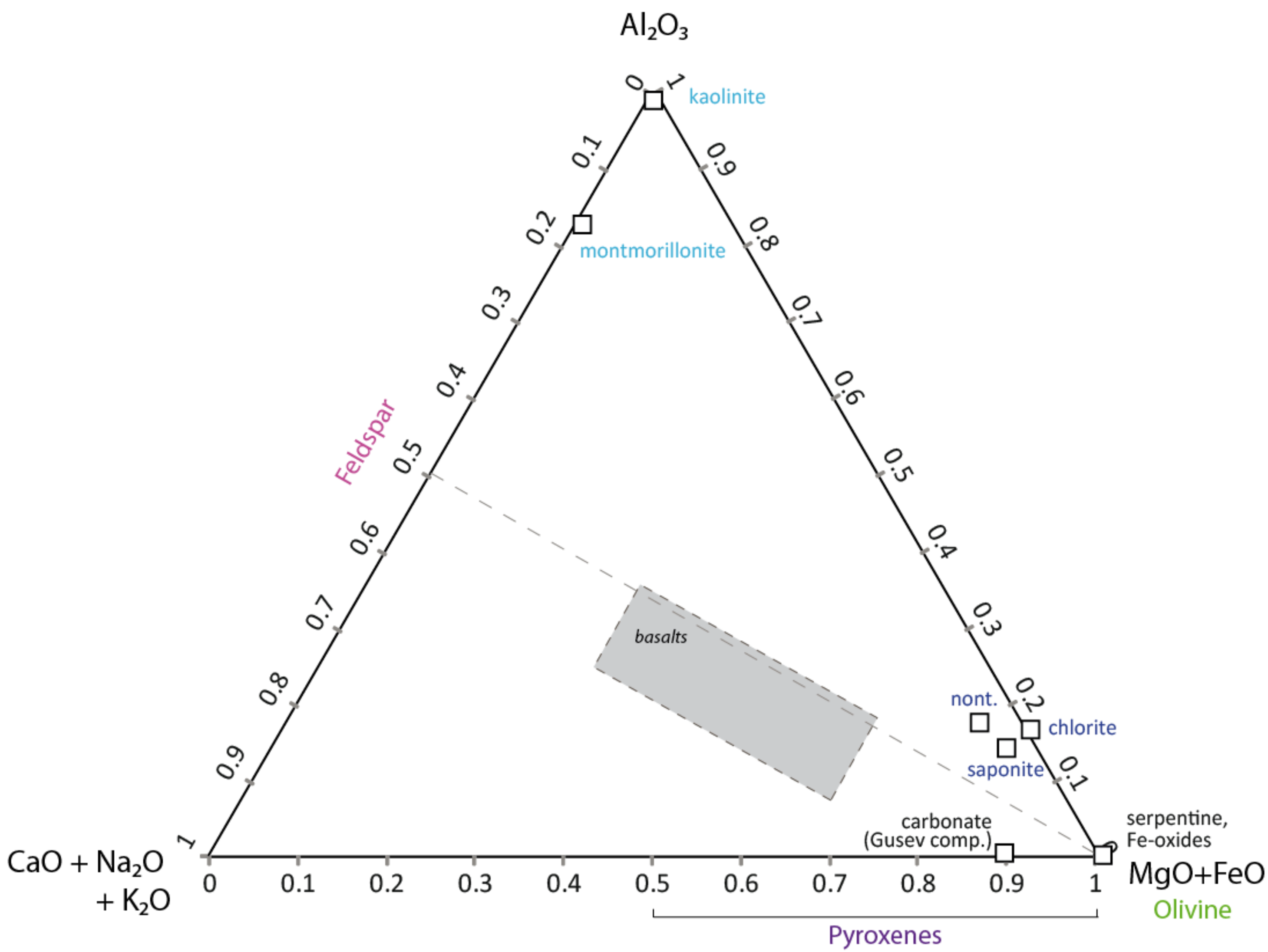


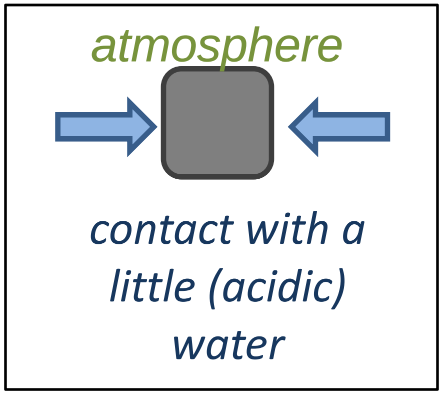
Diagram after Hurowitz & McLennan, EPSL, 2007

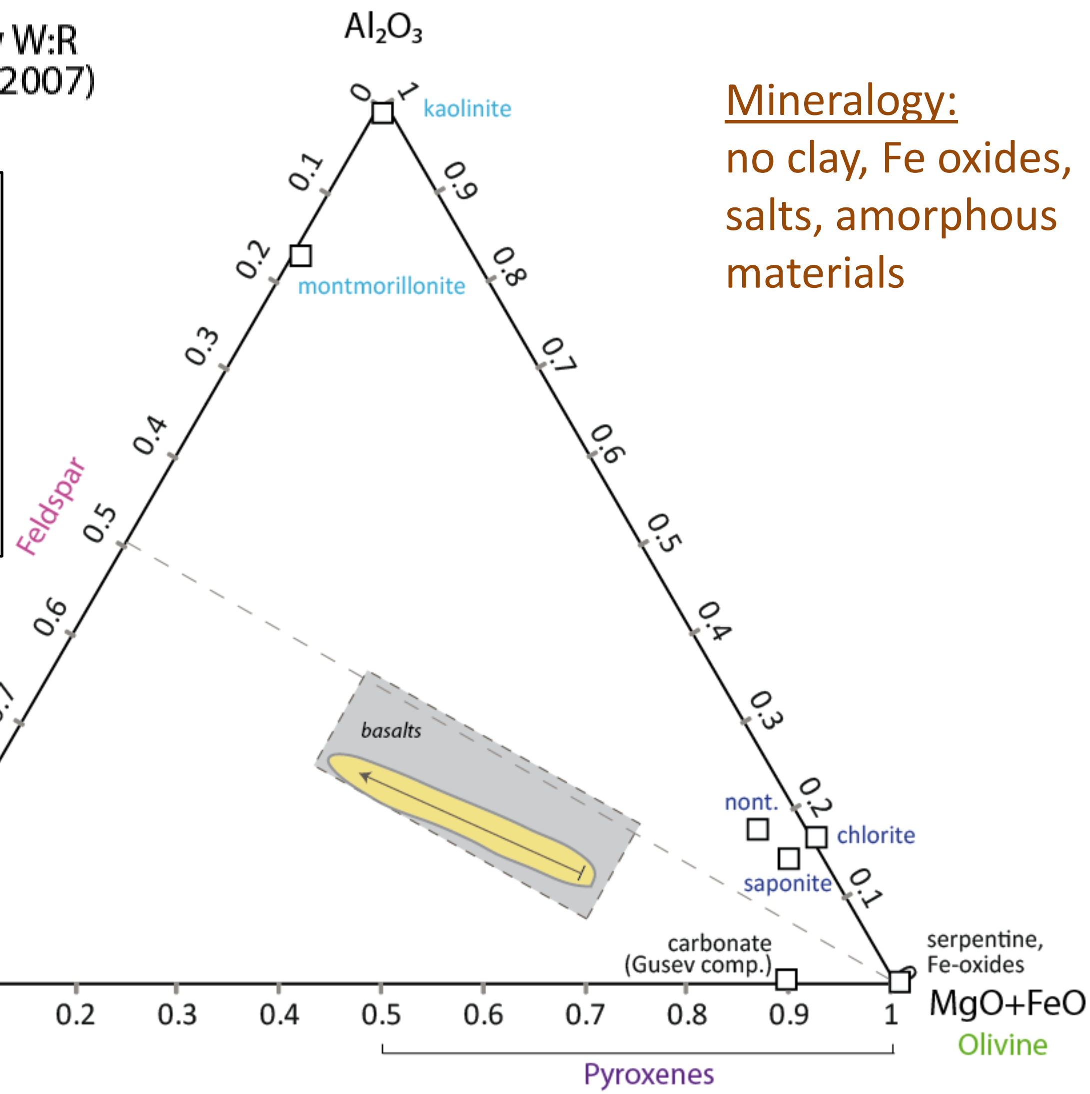
Styles of Alteration



Styles of Alteration to form <not clay>

- Near-surface, acidic, low W:R (Hurowitz & McLennan, 2007)



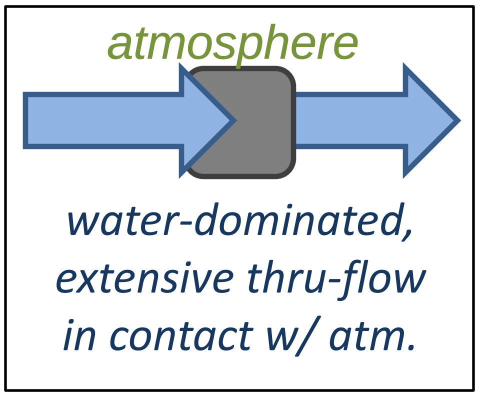


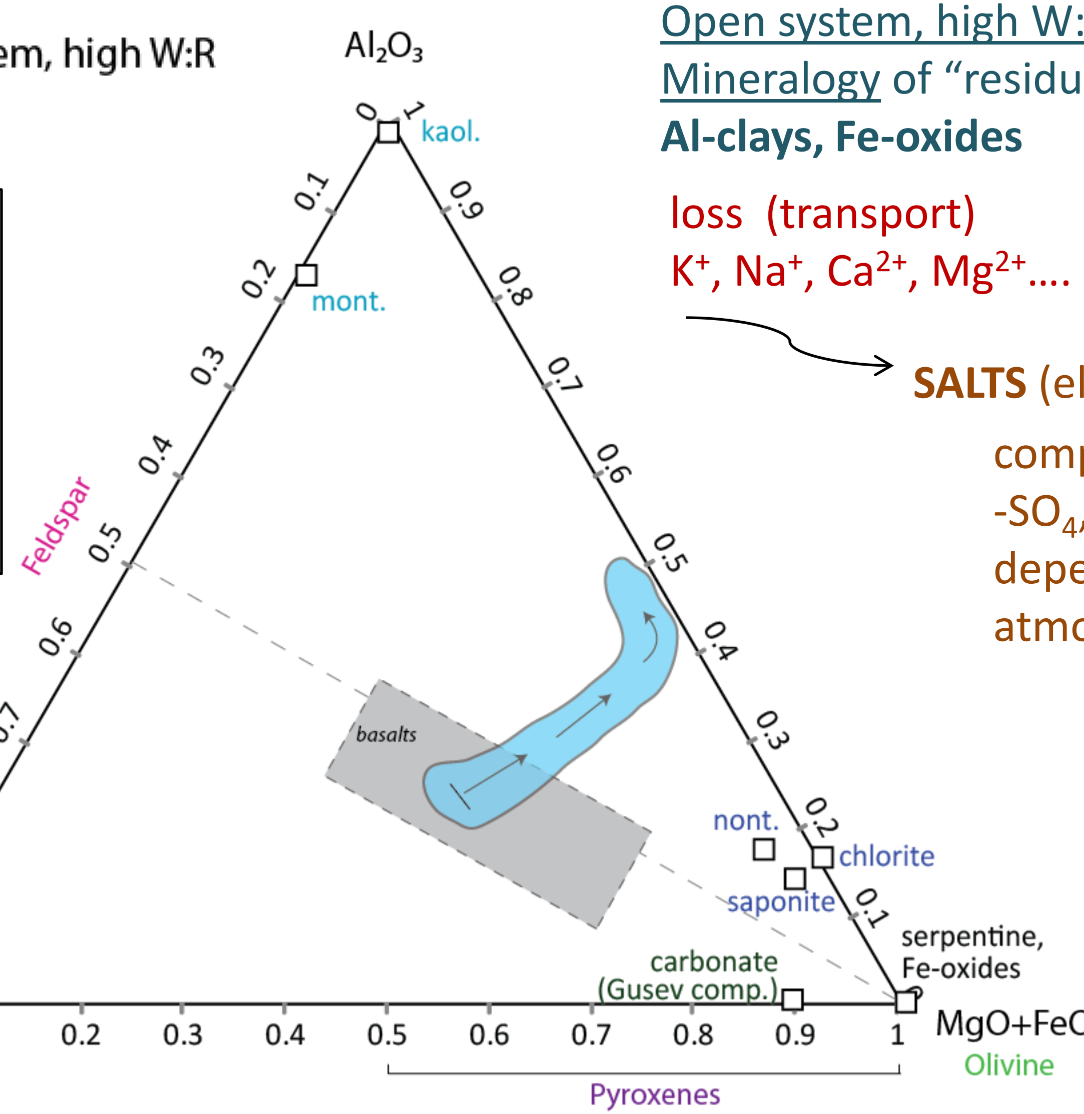
Mineralogy:

no clay, Fe oxides, salts, amorphous materials

Styles of Alteration to form Clays

Near-surface, open system, high W:R
(Nesbitt & Wilson, 1992)





Open system, high W:R

Mineralogy of "residue":

Al-clays, Fe-oxides

loss (transport)

K^+, Na^+, Ca^{2+}, Mg^{2+}….

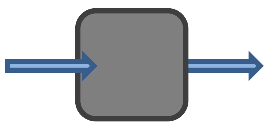
SALTS (elsewhere)

composition…
$-SO_4$, -Cl, $-CO_3$,
depends on
atmosphere

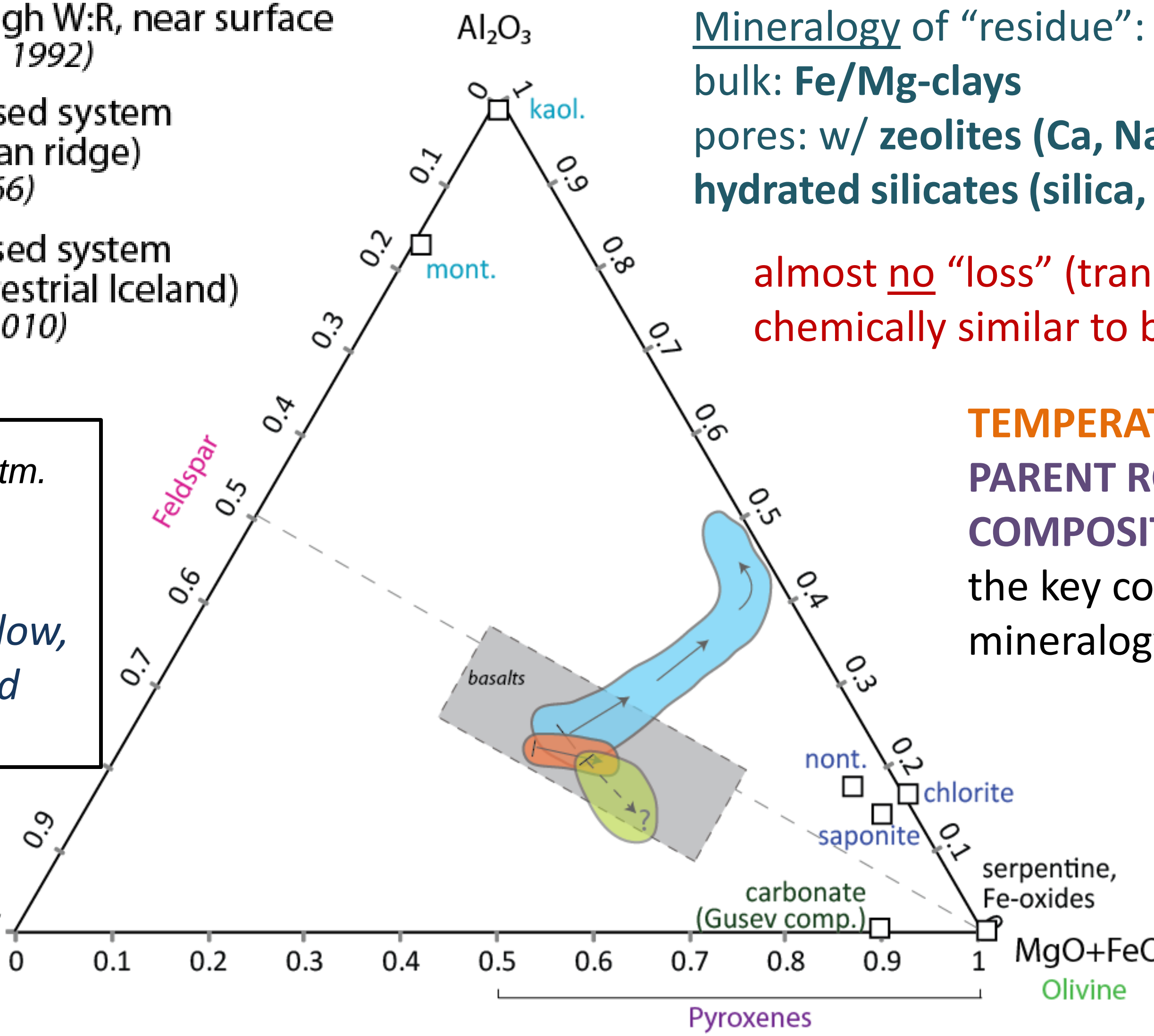
Styles of Alteration to form Clays

- Open system, high W:R, near surface *(Nesbitt & Wilson, 1992)*
- Subsurface, closed system (hydroT alt. ocean ridge) *(Cann & Vine, 1966)*
- Subsurface, closed system (hydroT alt., terrestrial Iceland) *(Ehlmann et al., 2010)*

not in contact w/ atm.



little water thru-flow, rock-dominated



Low W:R, closed system

Mineralogy of "residue":

bulk: **Fe/Mg-clays**

pores: w/ **zeolites (Ca, Na),** other **hydrated silicates (silica, prehnite)**

almost no "loss" (transport), chemically similar to basalt

TEMPERATURE, PARENT ROCK COMPOSITION are the key controls on mineralogy