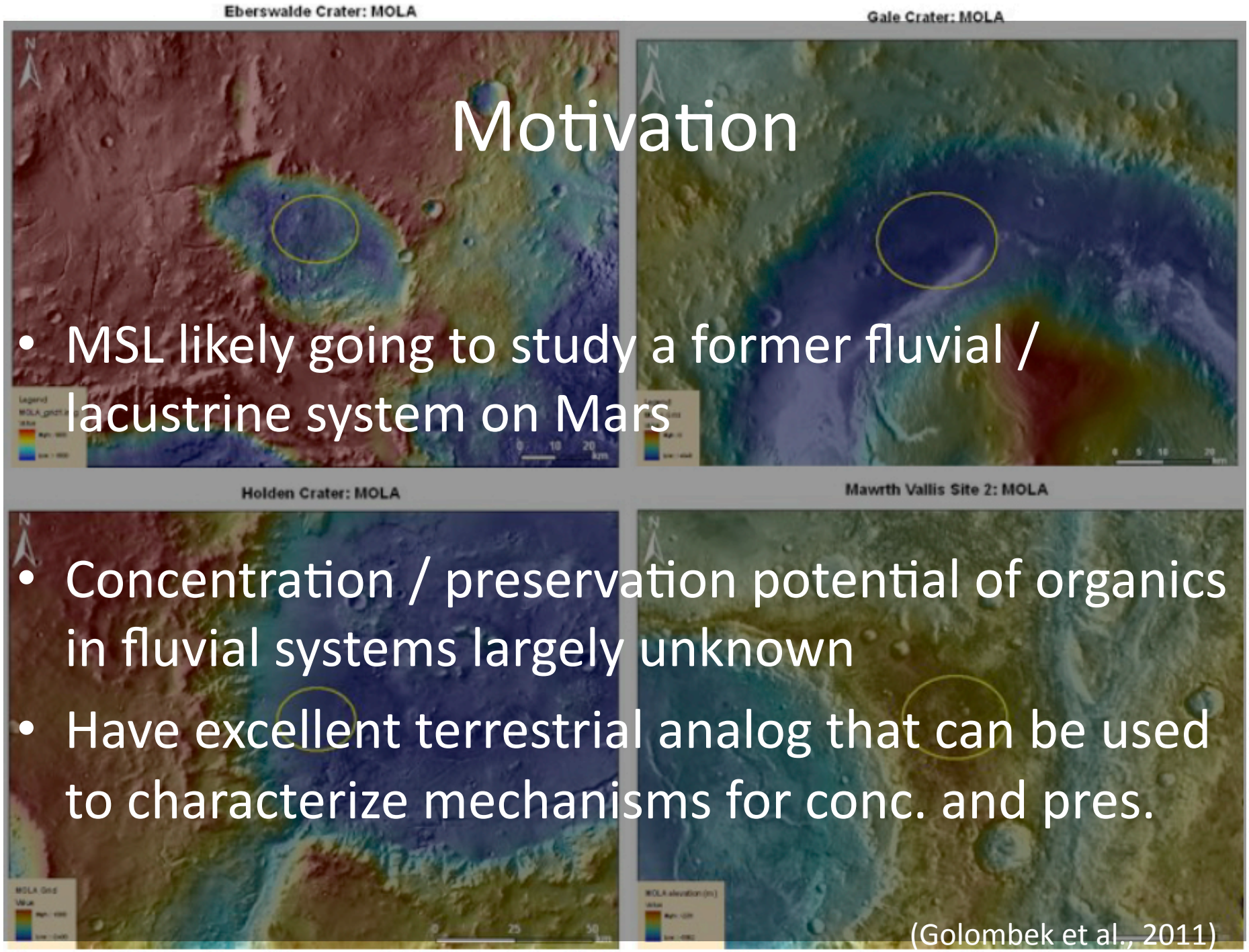
Concentration and preservation of organics in fluvio-lacustrine systems

E.Z. Noe Dobrea, A.D. Aubrey, F., D.P. Glavin, F. Calef, M.R. Hamersley, A.C. McAdam, C. Freissinet, H. Franz, B. Parker, D. Blake, P. Sarrazin

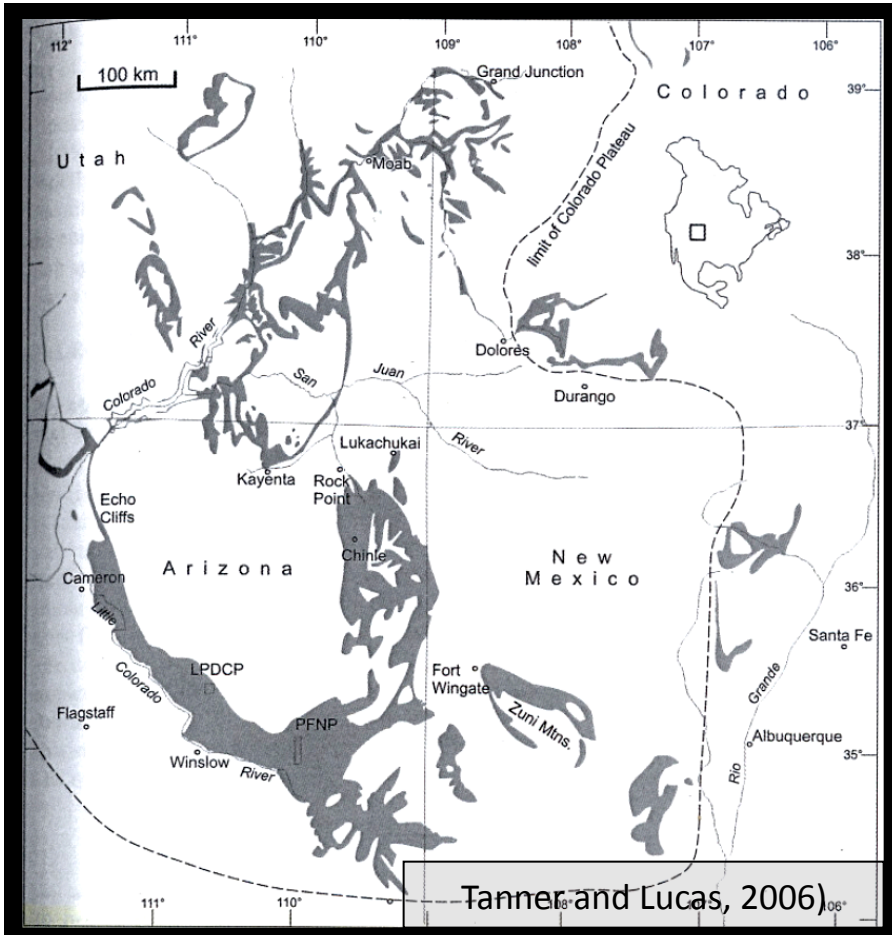
Motivation

- MSL likely going to study a former fluvial / lacustrine system on Mars
- Concentration / preservation potential of organics in fluvial systems largely unknown
- Have excellent terrestrial analog that can be used to characterize mechanisms for conc. and pres.



(Golombek et al., 2011)

The Painted Desert

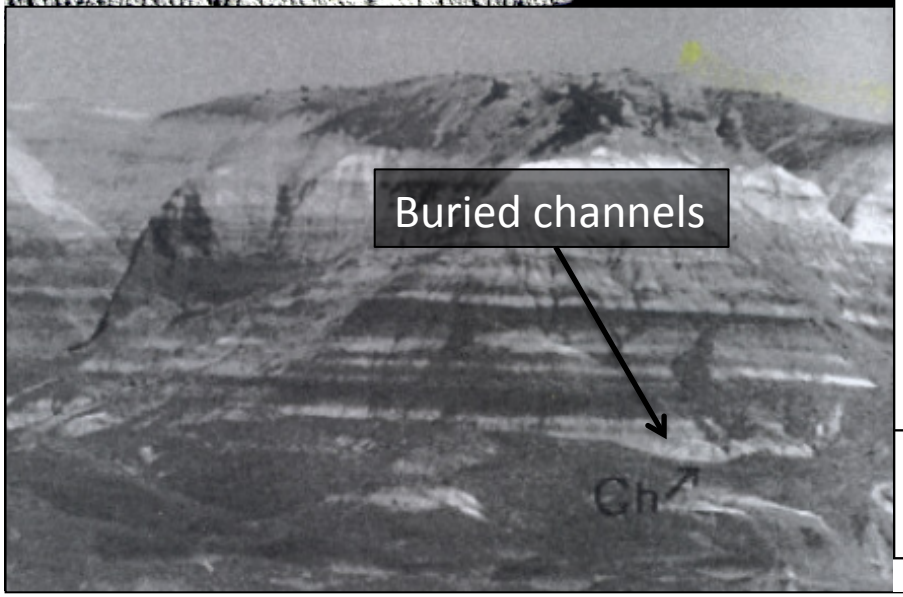


Tanner and Lucas, 2006)

- Desert region in northern Arizona characterized by badland morphology and colorful layering.
- Comprises the Triassic Chinle Group
- Late Triassic: 200-230 million years old

- Consists of thick (~100 m) layers of bentonitic mudstones interbedded with sandstones and limestones (Allen, 1930).
- Many layers were formed by deposition in **lacustrine and fluvial environments,** and are **incised by channels** with a fine-grained fill, (Tanner and Lucas, 2006).

Past fluvial activity at P.D.



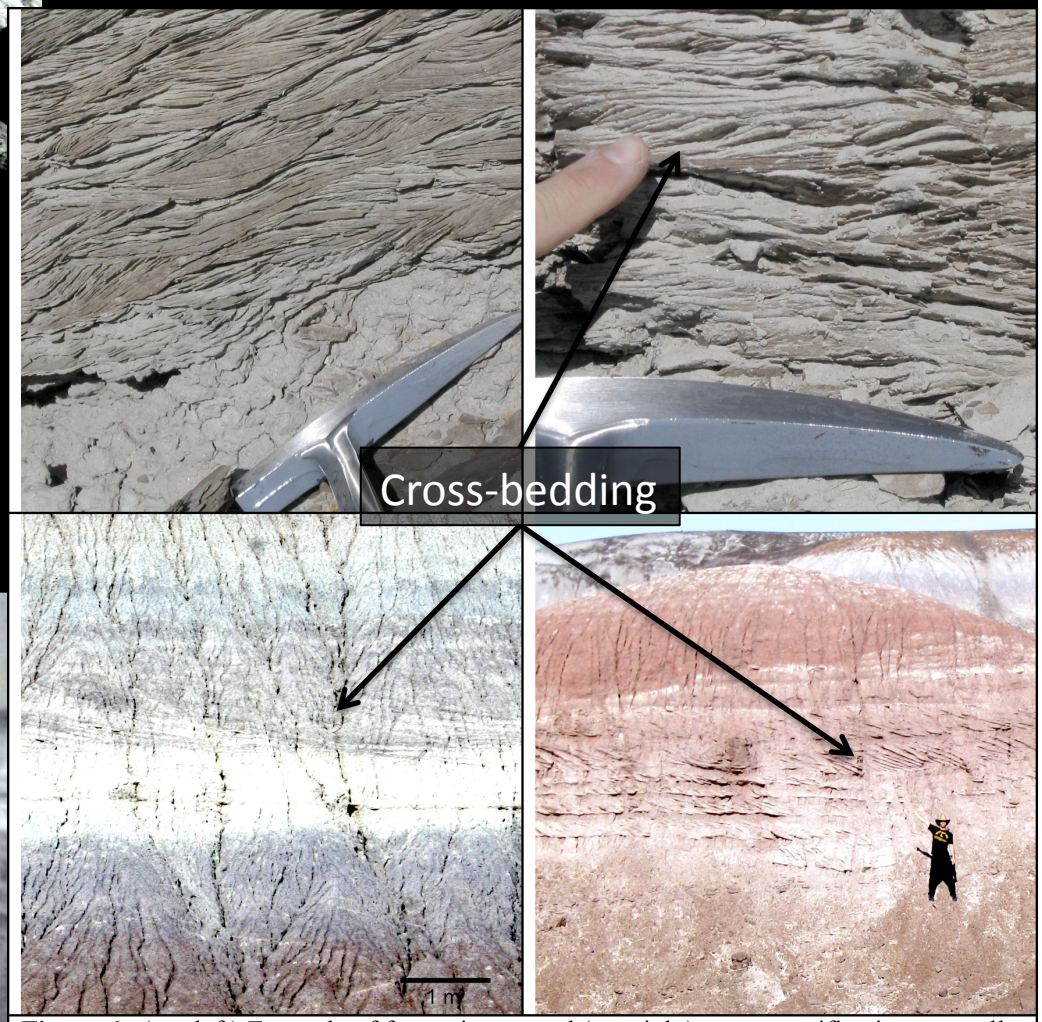
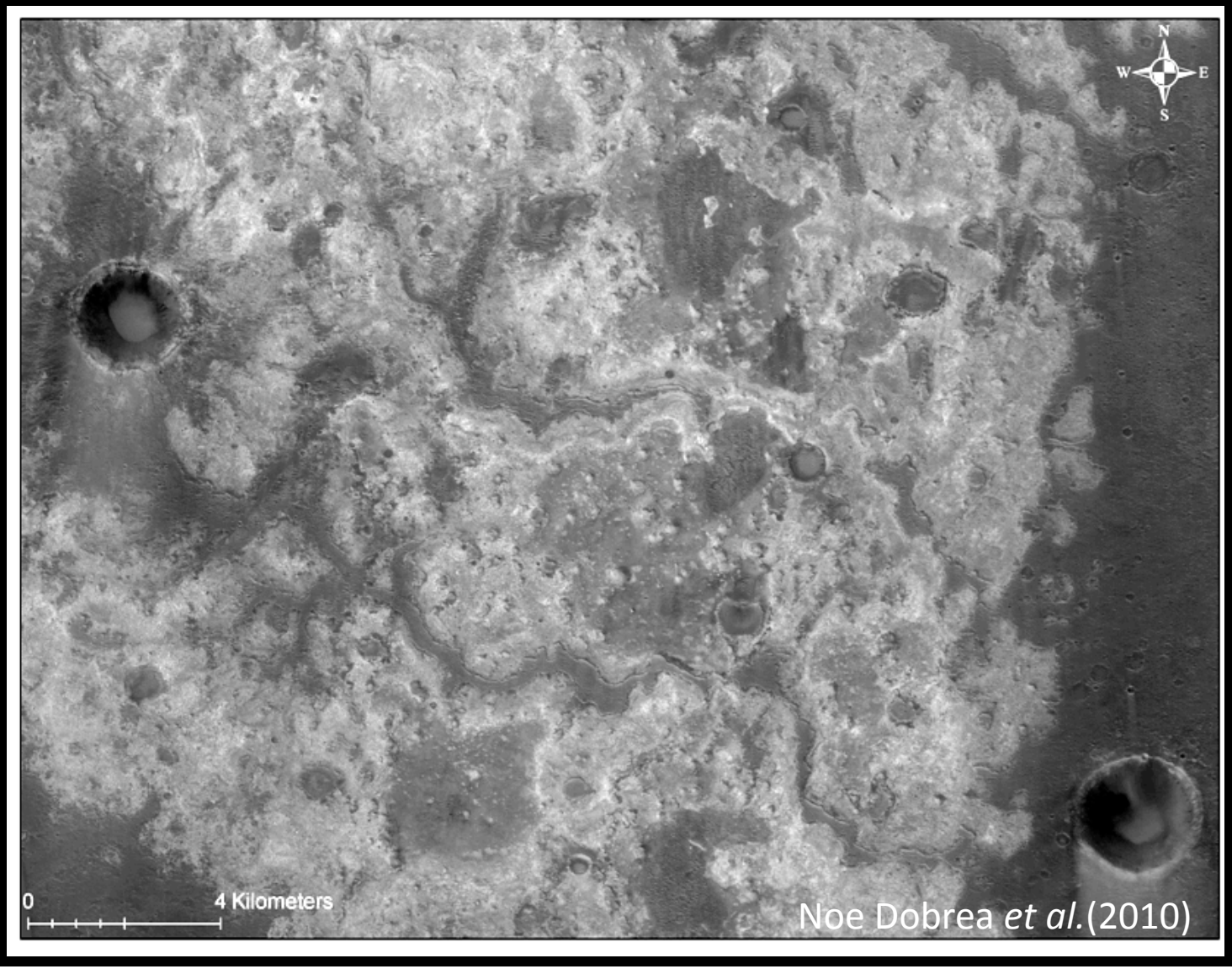


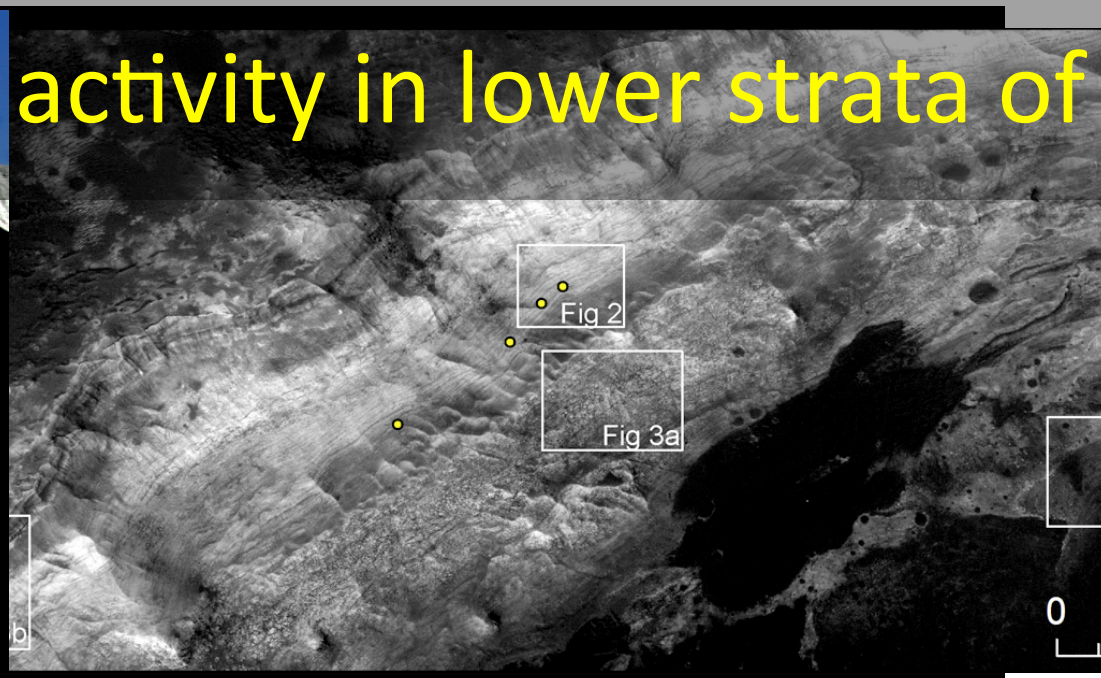
Figure 6. (top left) Example of festtoning sp and (top right) cross-stratification at small scales. (Bottom left and bottom right) cross-stratification from foreset beds at intermediate scales. All images taken at the Painted Desert. All of these features are too small to be resolved at HiRISE scales.

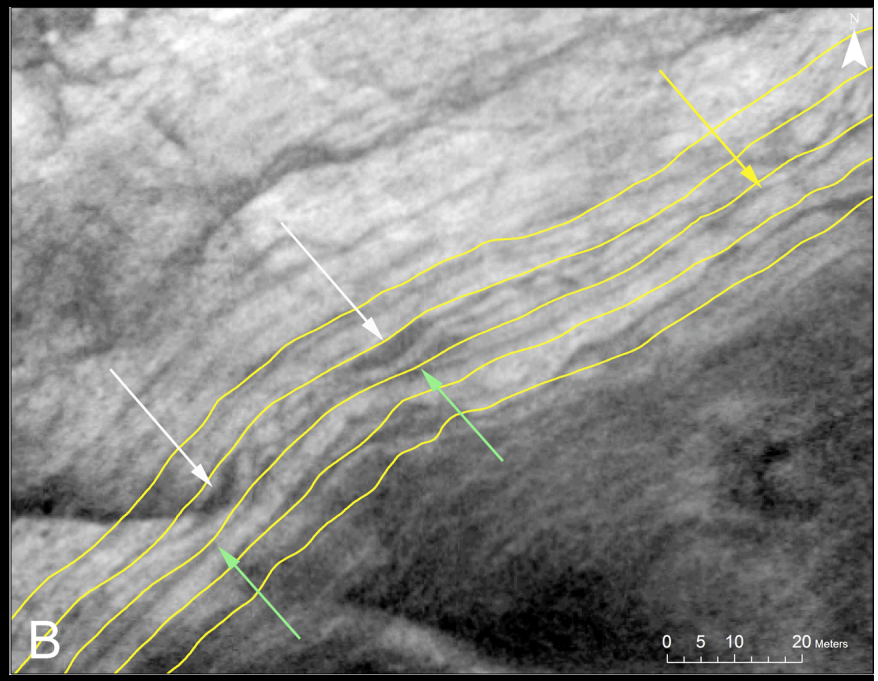
Past Fluvial Activity at Mawrth

Valleys at Mawrth show meander morphology → point bar deposition



Evidence for fluvial activity in lower strata of

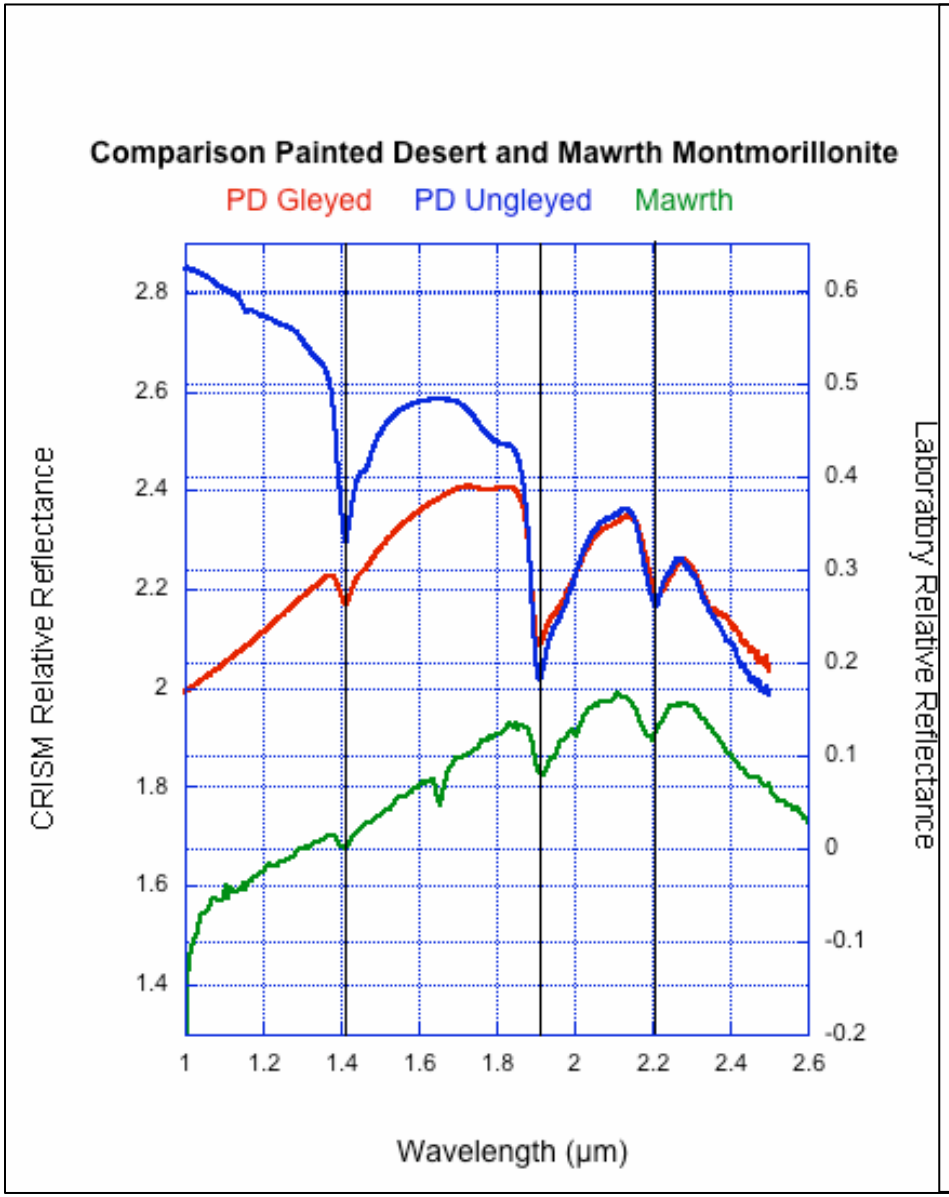


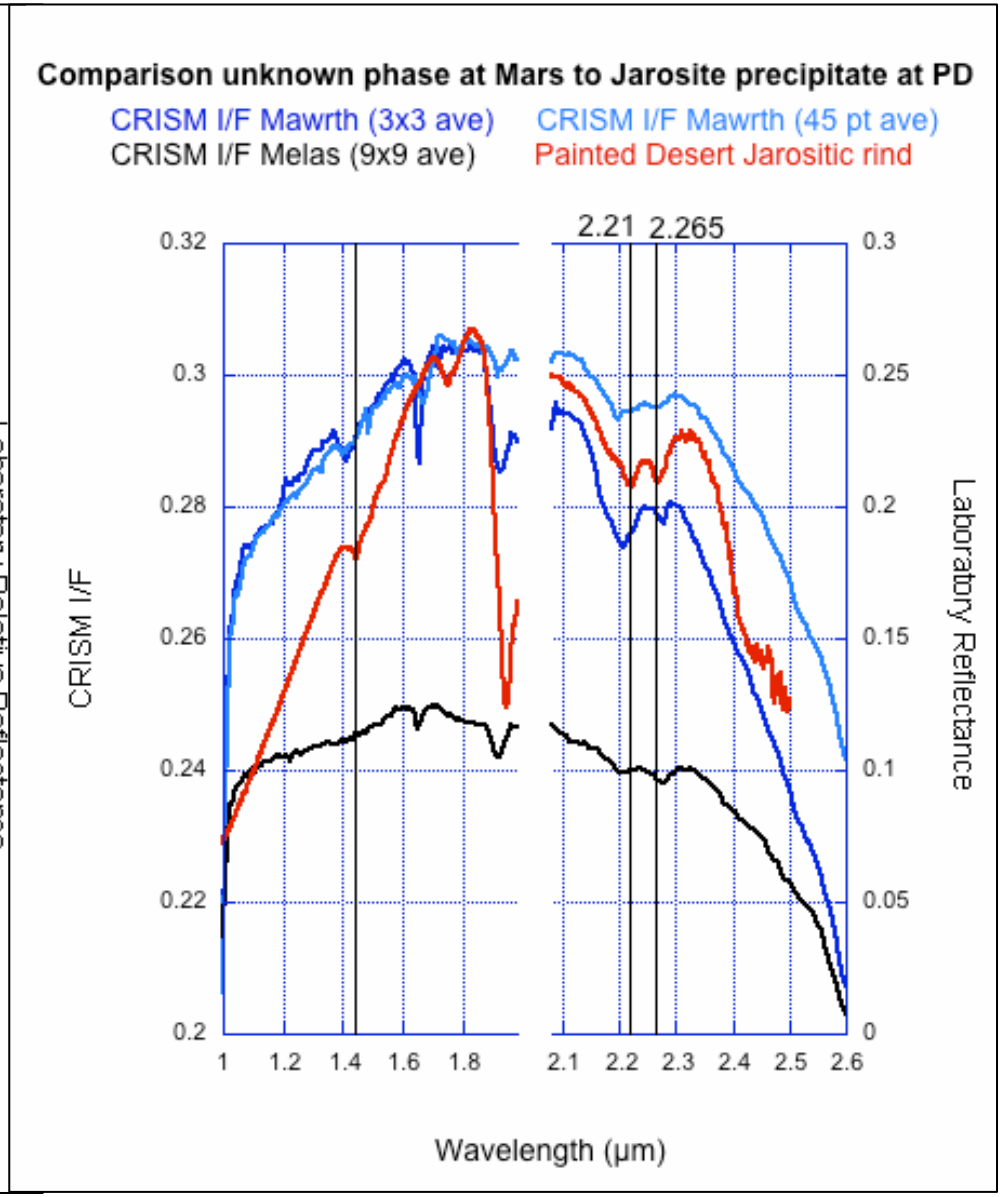


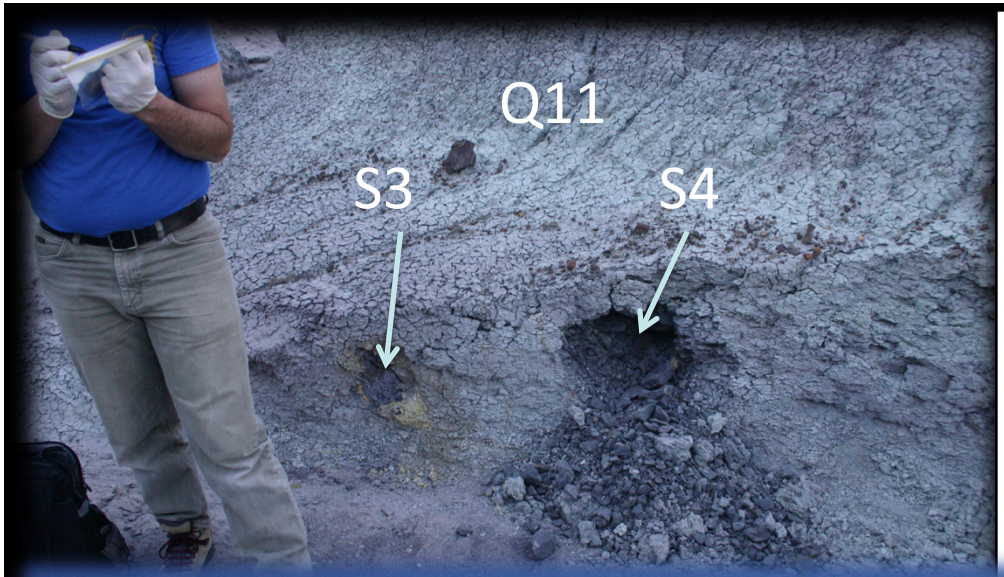
(Tanner and Lucas, 2006)

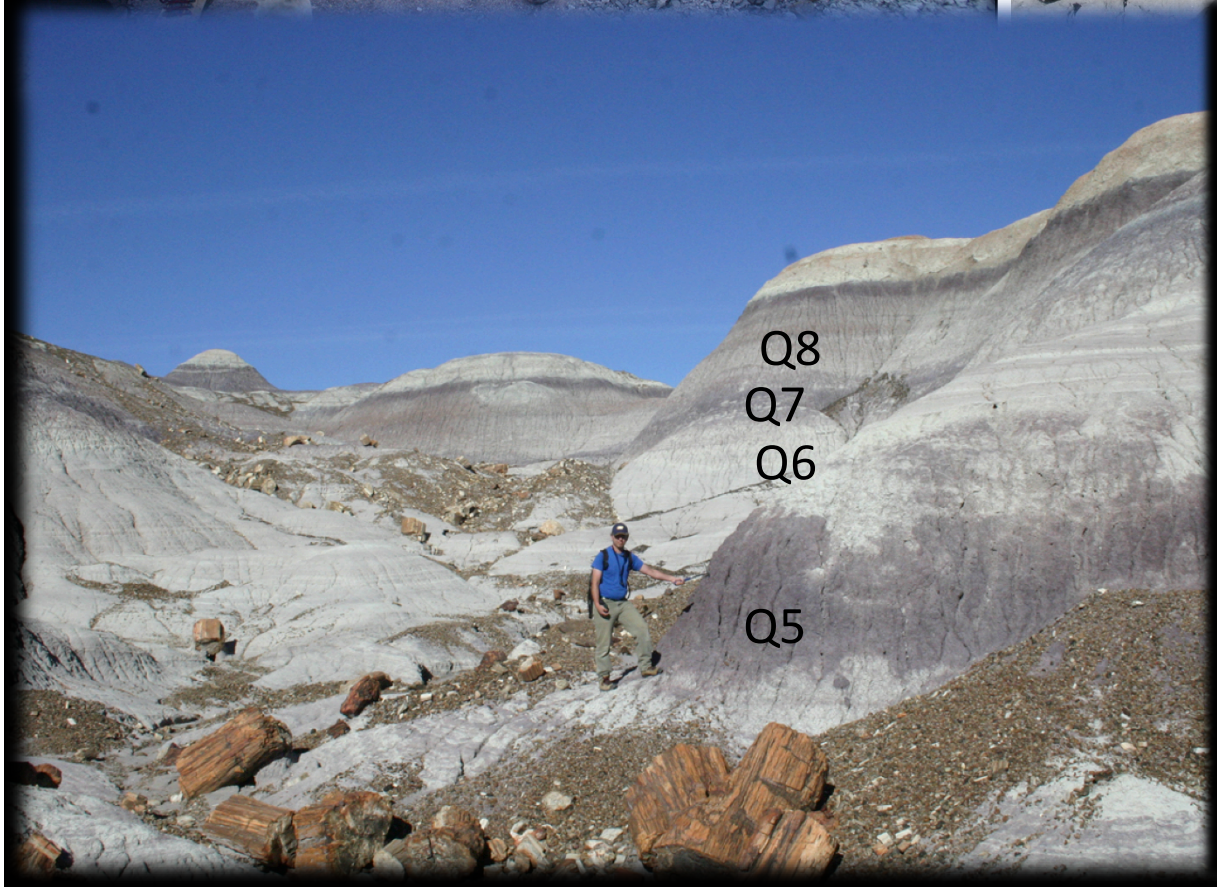
(Noe Dobrea *et al.*, 2011)

Spectral similarities









- Dark units thought to have organic C
- Field/laboratory studies
  - Terra XRD
  - Evolved Gas Analysis
    - SAM Breadboard
  - Pyrolysis GCMS
  - VNIR spectra
  - Total Organic Carbon

Total organic carbon:

- Carbonates removed before analysis by acidification and vacuum desiccation.
- Carbon and nitrogen content analyzed by automated combustion, GC separation and thermal conductivity detection (SerCon ANCA-GSL elemental analyzer, UC Davis Stable Isotope Facility).
- Background C contamination <5%.

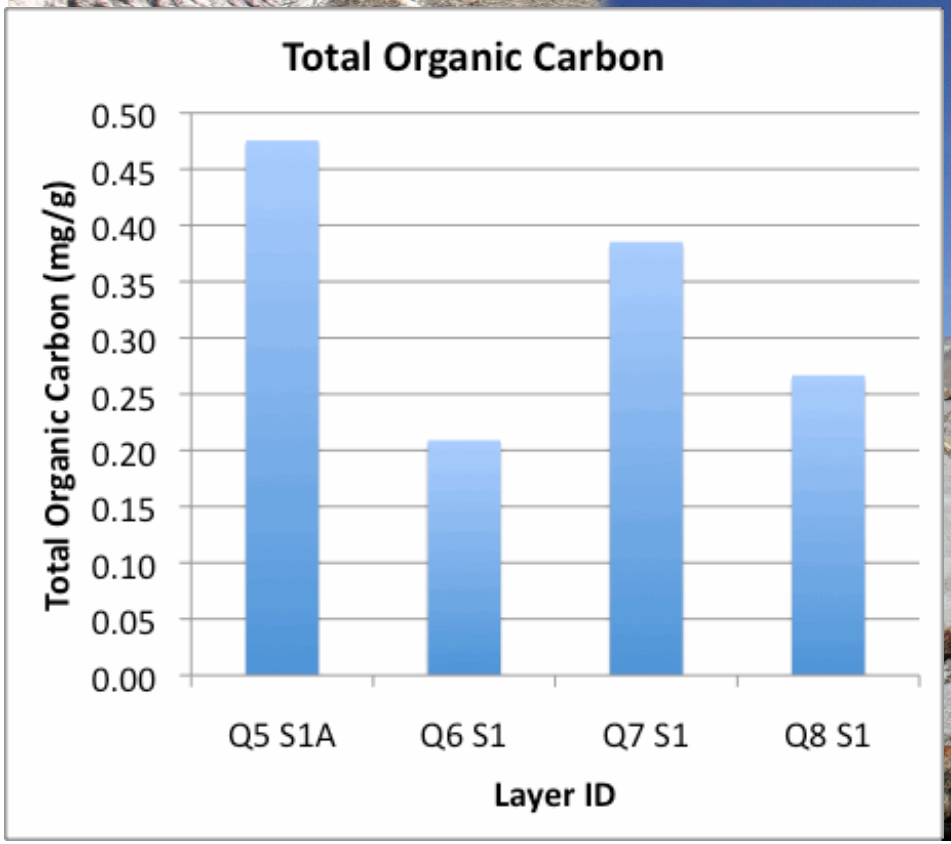
- Small quantities detected throughout. Large quantities detected at Q11 (and Q1 using GCMS).

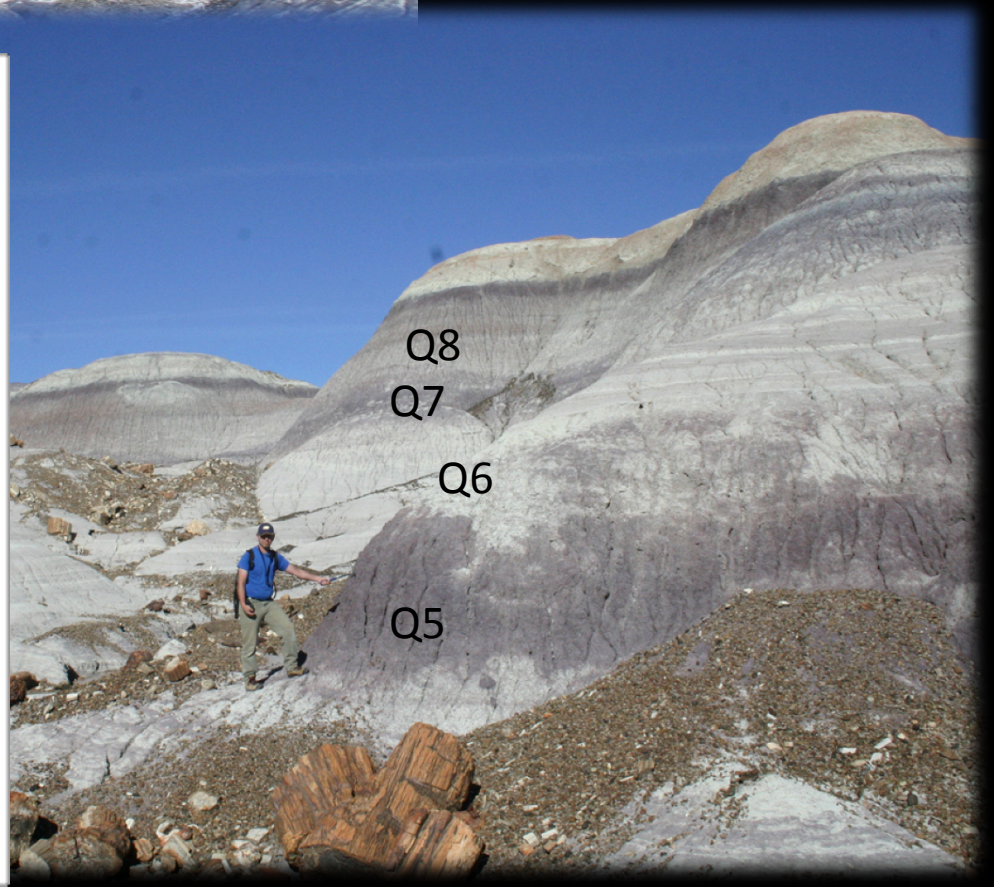
Site	Sample	Organic C mg g^{-1}	N mg g^{-1}	Molar C/N ratio
I1	S1	0.54	0.04	16.2
Q4	S1	0.35	0.24	1.7
Q5	S1A	0.48	0.11	5.1
Q6	S1	0.21	0.07	3.6
Q7	S1	0.39	0.06	6.9
Q8	S1	0.27	0.11	2.9
Q9	S1	0.20	0.08	2.9
Q10	S1	0.30	0.05	7.3
Q11	S1	328.16	3.22	118.8
Q11	Gyp2	1.32	0.19	8.3
Q4	S2	0.67	0.02	50.7
Q4	S3	0.32	0.05	7.0
Q11	S3	141.29	2.92	56.5
S11	S3b	3.21	0.20	18.6

XRD/VNIR:

Major component montmorillonite and quartz.

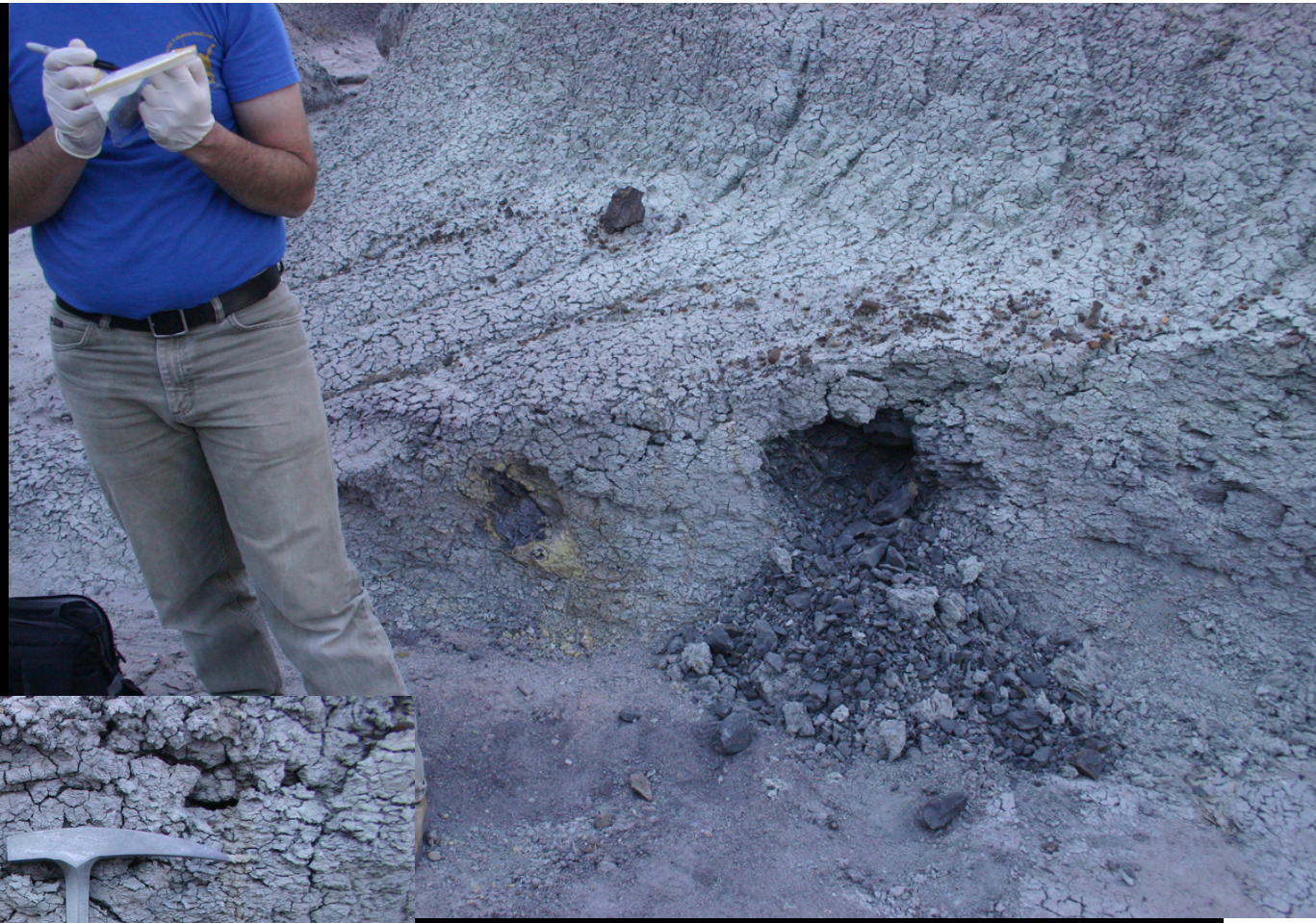
Some kaolinite + other minor species

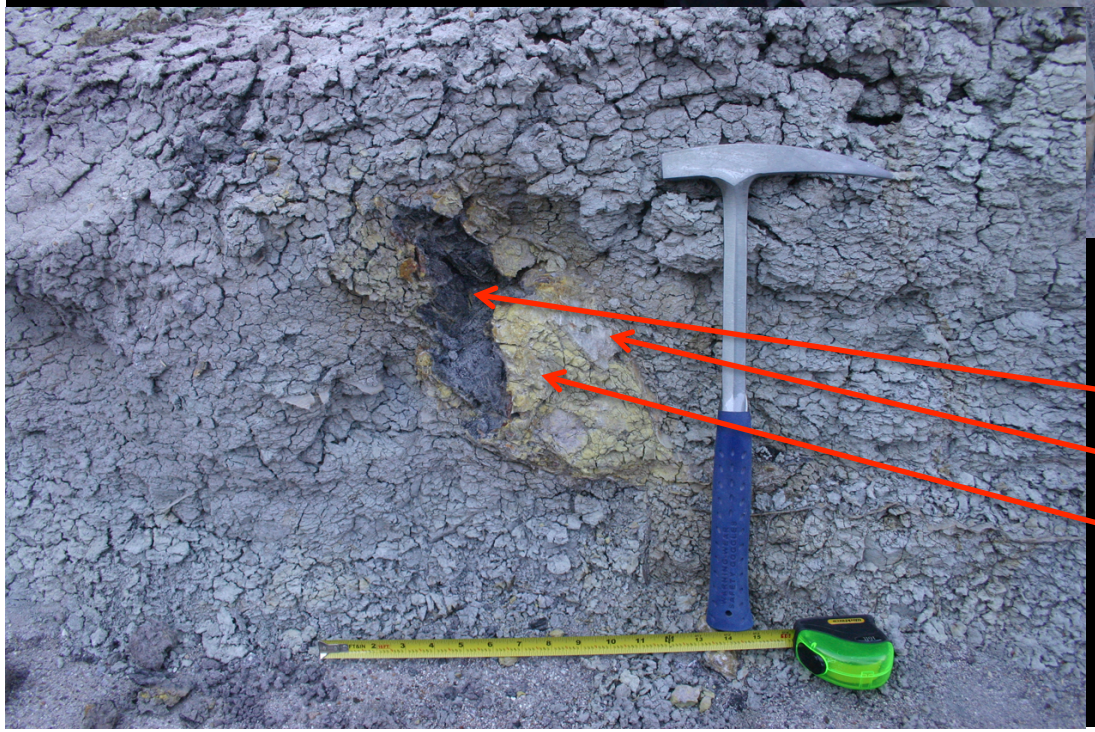




Site Q11:

- Dark material Encased in yellowish rind
- Embedded in bentonite approx 30 m below Petrified Forest Formation





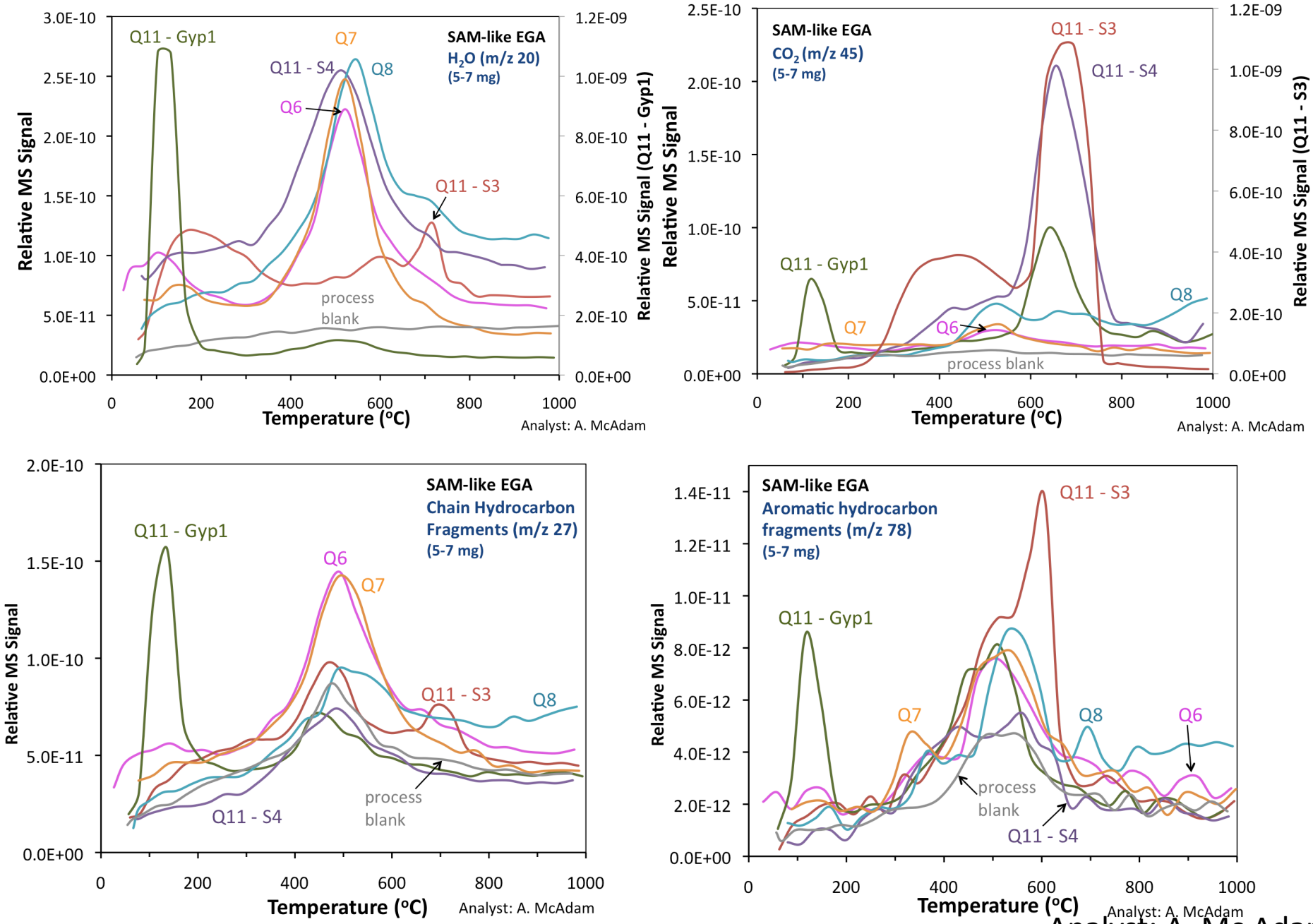
Terra XRD / VNIR results:

Q11-S3: Predominantly Calcite

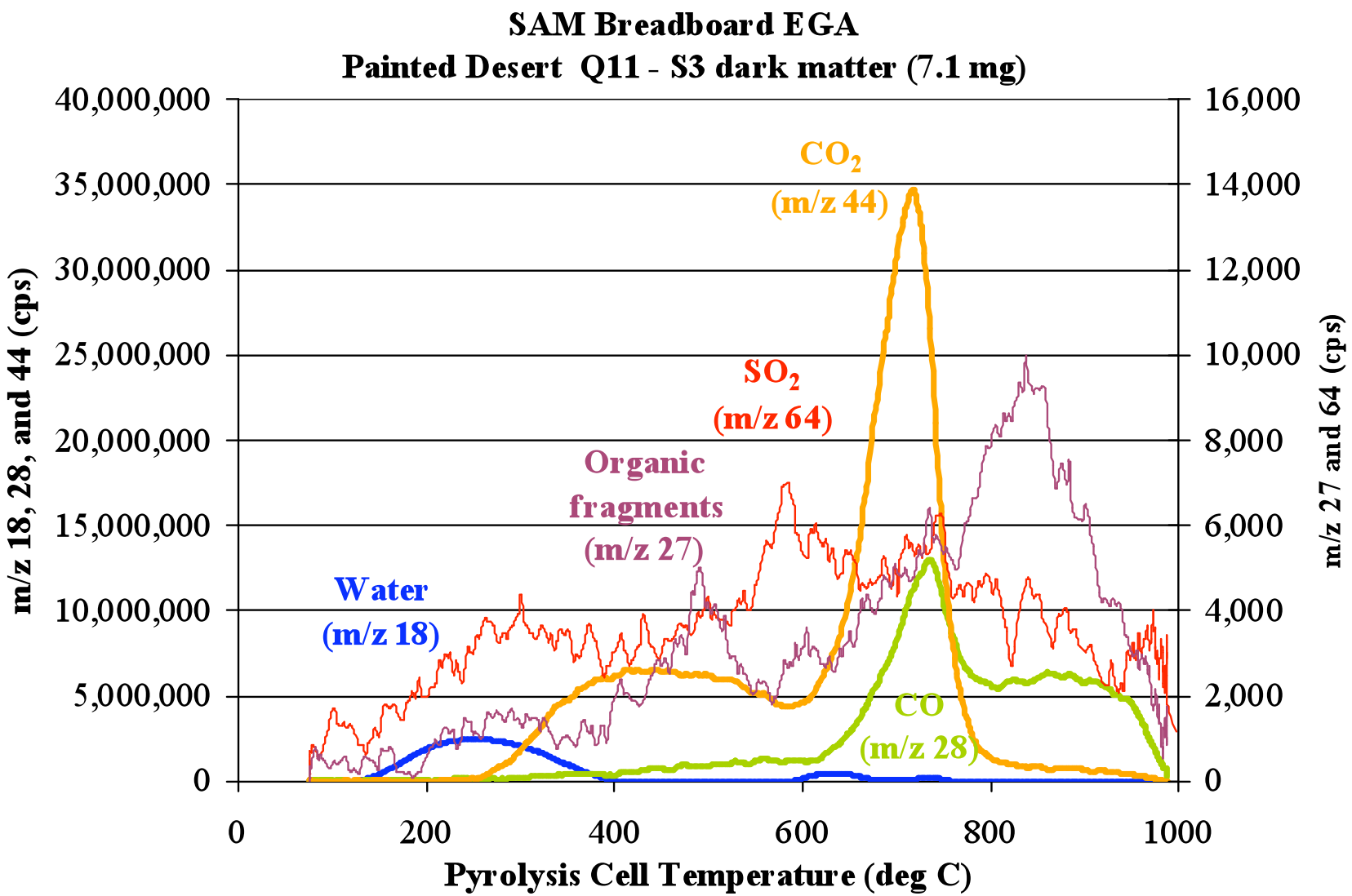
Q11-Gyp: Gyp + Qtz + Mont

Predominantly Jarosite

SAM-Like Evolved Gas Analysis



Analyst: A. Mc Adam

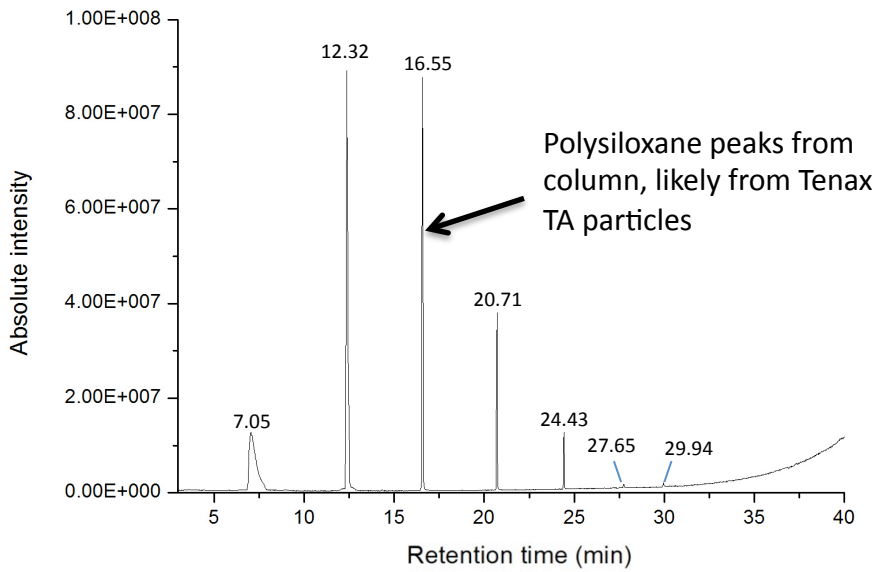


Analyst: H. Franz

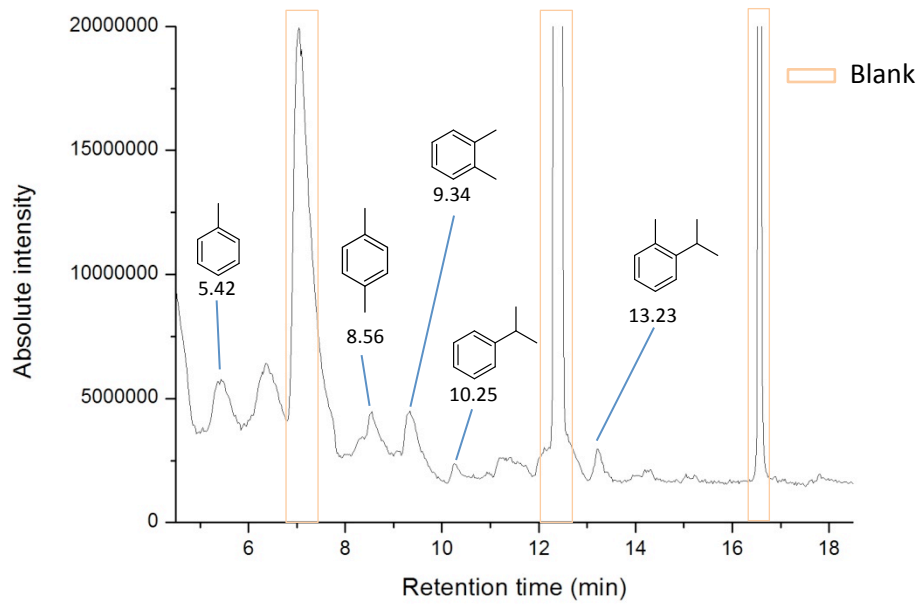
Pyrolysis Gas Chromatography Mass Spectrometry (GCMS) Data

Pyrolysis: 600°C - 1min under He carrier gas flow. Organics collected on hydrocarbon trap (Tenax TA). Trap desorb: 280°C - 3min. GC: 50°C -> 300°C, 6°C/min, He carrier flow 1.3 mL.min^{-1}

Fused silica (preheated 900°C 7 h) – 45 mg = procedural blank



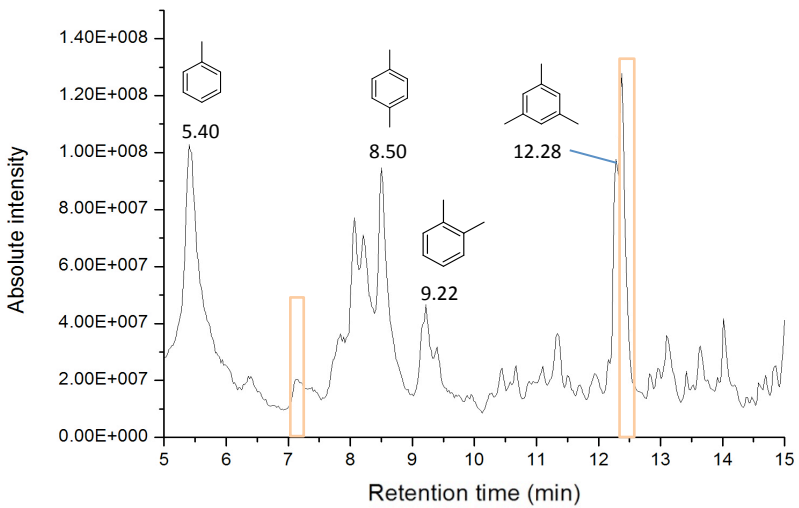
Sample Q1 (Shale) – 49.6 mg

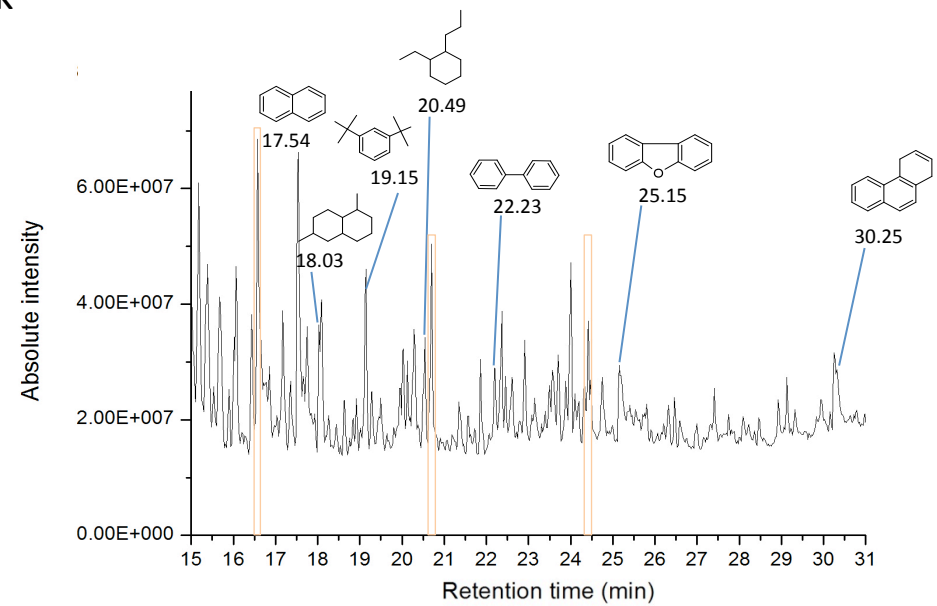


Analyst: C. Freissinet

Sample Q11-S3 (Black nodule) – 40.9 mg

Blank





•Several different aromatic compounds identified by mass fragmentation patterns in samples Q11 S3 and Q1 that were not present in the procedural blank or Whirl-pak bag blank.

•Many more organics are also present (as shown by several peaks) but they could not be identified by matching their respective mass fragmentation patterns to the NIST spectral library due to lower abundances and/or background peak interferences.

•The pyrolysis GCMS mode of SAM will enable us to make specific organic compound identifications that cannot be achieved in SAM direct EGA mode.

Conclusions

- Mineralogy: Aqueous chemistry at PD may have been similar to that at Mawrth:
  - Thick Al-phyllo sequence
  - Iron reduction
  - Acid sulfate precipitation in Al-phyllosilicate material
- Detection: Organic material has been identified trapped in 200-220 Million year-old fluvial clay and shale sediments *using techniques available to MSL*
  - Preservation due to restriction of water flow by clays, or encasement in insoluble rind
- MSL Analog instrumentation (EGA and GCMS):
  - The high temperature (*i.e.*, >600C) organics evolved in the EGA results are indigenous to samples
  - SAM EGA temp range (up to 1000C) exceeds Viking limit (500C) and clearly allows observation of additional organics in naturally-occurring samples
  - EGA also sensitive to release of trace quantities of sulfur undetectable by XRD
  - Ability to correlate mineral decomposition temperatures (*e.g.*, from CO_2 in calcite) with release temperatures of organics by SAM EGA will help us begin to understand the association between organics and minerals in the sample.
- XRD, EGA, and pyrolysis GCMS will all be needed by MSL to understand bulk chemical differences between layers.
  - mineralogy → association w/ organics → types of organics

Summary

- Variations in total OC may correlate to darkness of clay-unit, but neither SAM-like EGA nor GCMS can see them
- EGA and GCMS see organics in
  - ancient (approx 215 million years old) tree-trunk protected by clays and jarositic rind
  - Ancient shale interbeded with the clays

Backups

Buried channel at P.D.

Discontinuous Layering

“Lensing” a end of pinch-out

Site	Layer	^{13}C	Organic C mg g^{-1}	^{15}N	Organic N mg g^{-1}	Molar C/N ratio
S1	I1	-27.7	0.54	-6.60	0.04	16.2
S1	Q4	-27.4	0.35	0.86	0.24	1.7
S1A	Q5	-26.1	0.48	5.74	0.11	5.1
S1	Q6	-28.2	0.21	0.23	0.07	3.6
S1	Q7	-28.0	0.39	3.83	0.06	6.9
S1	Q8	-27.4	0.27	1.41	0.11	2.9
S1	Q9	-26.9	0.20	0.79	0.08	2.9
S1	Q10	-26.6	0.30	1.61	0.05	7.3
S1	Q11	-20.8	328.16	2.78	3.22	118.8
Gyp2	Q11	-25.3	1.32	1.88	0.19	8.3
S2	Q4	-25.8	0.67	30.89	0.02	50.7
S3	Q4	-25.9	0.32	11.05	0.05	7.0
S3	Q11	-20.6	141.29	3.34	2.92	56.5
S3b	S11	-23.3	3.21	3.88	0.20	18.6

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S1	Q7	-28.0	3.83
S1	Q8	-27.4	1.41
S1	Q9	-26.9	0.79
S1	Q10	-26.6	1.61
S1	Q11	-20.8	2.78
Gyp2	Q11	-25.3	1.88
S2	Q4	-25.8	30.89
S3	Q4	-25.9	11.05
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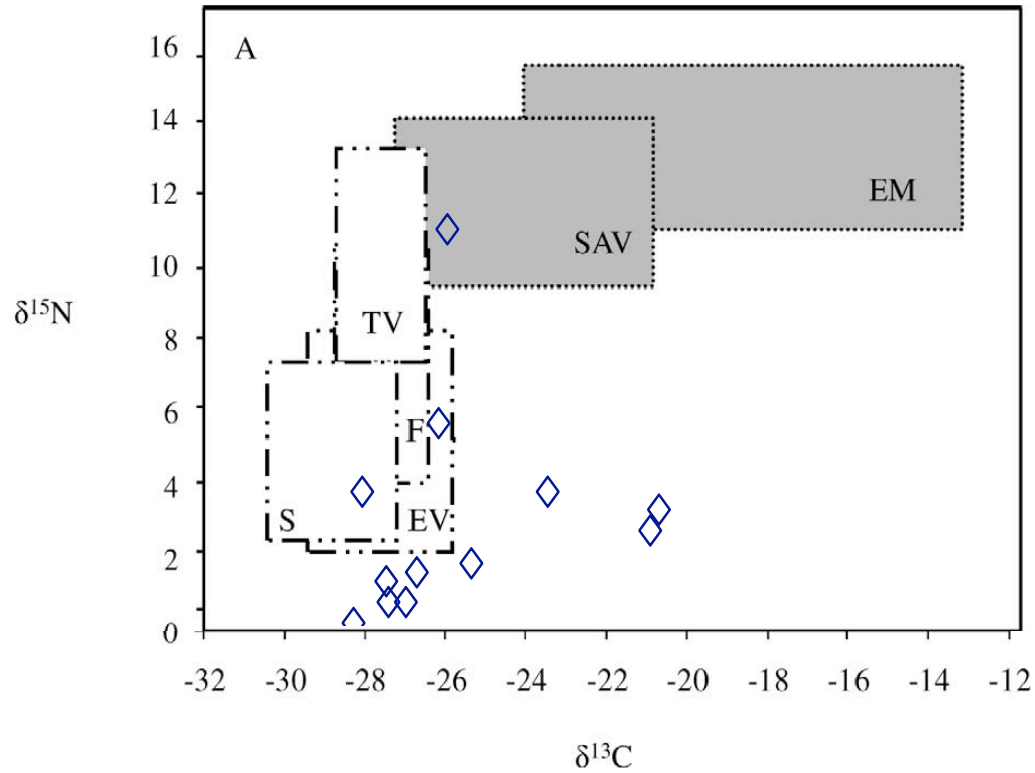

EM: epiphytic microalgae,
EV: emergent vegetation
S: seston (phytoplankton),
SAV: submerged aquatic vegetation,
TV: terrestrial vegetation
(Grimaldo et al. 2009)