

The Long-Term Preservation Potential of Organics in Martian Halite

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ARES

ASTROMATERIALS RESEARCH & EXPLORATION SCIENCE



Discussion Topics

- A preferred sampling goal is to collect material preserved from a “warmer, wetter Mars”
 - Assuming up through the end of the Hesperian, ~ 3 Ga
- Halite can preserve ancient indigenous carbon for this length of time
- What can we expect to find in Hesperian-age halite with a carbonaceous component?

Some Background:

Organics are Rare on Mars But
Important for Life Detection Efforts

Carbon on the Martian Surface

I: The Literature

- Previous work predicts ~ppb or less organics at the martian near-surface due to ambient radiation flux, oxidation

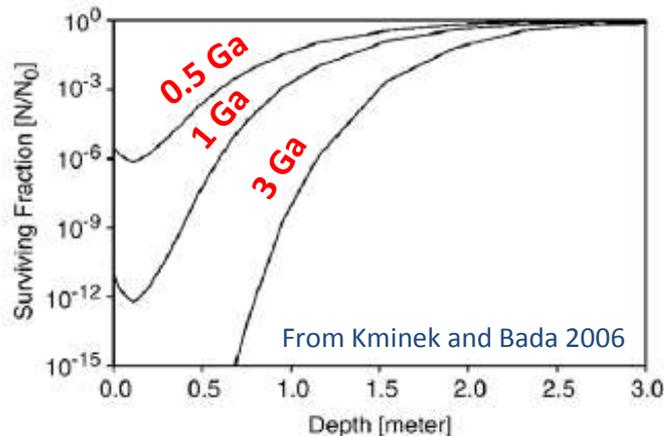


Fig. 2. Depth dependent surviving fraction of amino acids after being exposed half (top), one (middle), and three billion years (lower curve) to the ionizing radiation in the Martian subsurface. The current detection limit of 0.01 ppb per amino acid would allow a 2 to 6-log reduction until any amino acid signature of life became undetectable.

The Photolytic Degradation and Oxidation of Organic Compounds Under Simulated Martian Conditions

J. Oro and G. Holzer

The effect of ionizing radiation on the preservation of amino acids on Mars

Gerhard Kminek *, Jeffrey L. Bada

The effects of Martian near surface conditions on the photochemistry of amino acids

Inge Loes ten Kate^{a, b, c, d}, James R.C. Garry^a, Zan Peeters^a, Bernard Foing^e, Pascale Ehrenfreund^a

Amino acid photostability on the Martian surface

Inge Loes TEN KATE^{1, 2*}, James R. C. GARRY², Zan PEETERS², Richard QUINN^{2, 3}, Bernard FOING⁴, and Pascale EHRENFREUND²

Carbon on the Martian Surface

II: The Missions

- Viking I and II detected \sim ppb levels of chlorinated organics
- Mars Phoenix did not detect organics, but was not as sensitive
- Mars Science Laboratory (MSL) has detected high \sim ppb levels of chlorinated organics in the Cumberland mudstone [Freissinet et al 2014], none in other samples
- Light organics on Mars' surface are **rare** even with $5\text{E}^{-9} \text{ g m}^{-2} \text{ sol}^{-1}$ of IDP and carbonaceous chondrite infall [Flynn 1996]

Halite on Mars:

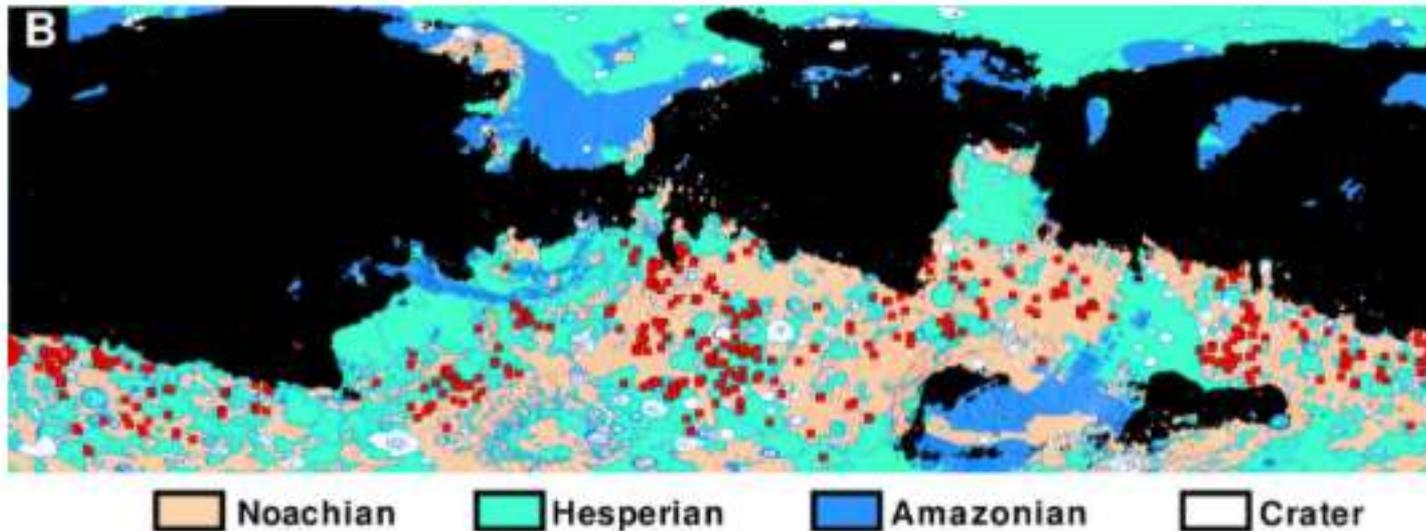
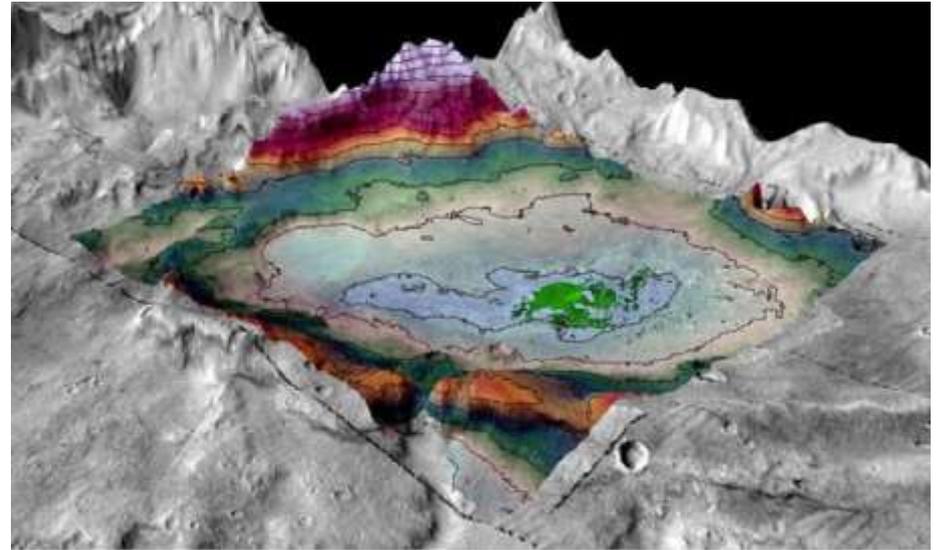
A Good Place to Look For Ancient,
Surface-Accessible Organics

First Off: The Halite Sequestration Mechanism is Amenable to Biosignature Preservation

- Halite traps and protects carbon by evaporation
- If microbes lived in late Hesperian surface water, the microbes or their remains could be entrained in halite

Halite Deposits on Mars

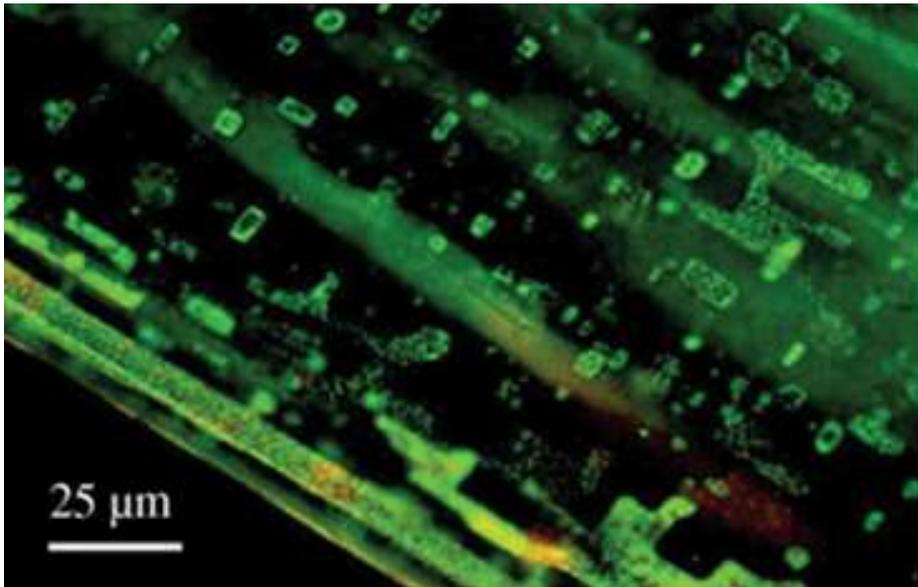
- Over 600 halite sites have been identified to date (Osterloo et al 2010 and references therein)
- Date from Noachian to late Hesperian



Halite and Biosignatures I:

Preservation of Extant Life

- In terrestrial examples, modern literature has reported resuscitating entrained archea from halite as old as $\sim 10^4$ years (34,000 y) [Shubert et al 2009]
- Some literature claims $\sim 10^5$ years (Mormile et al 2003)
- Disputed claims extend to $\sim 10^8$ yr (Permian halite, ~ 250 -300 Ma)
 - Shubert *et al* 2010 for discussion and references



- *Halobacterium salinarum* entrained in halite and stained with a fluorescent dye to study morphological response to entrainment. From: Schubert et al, *Env. Micro.* 2010.

Halite and Biosignatures II:

Preservation of Extinct Life

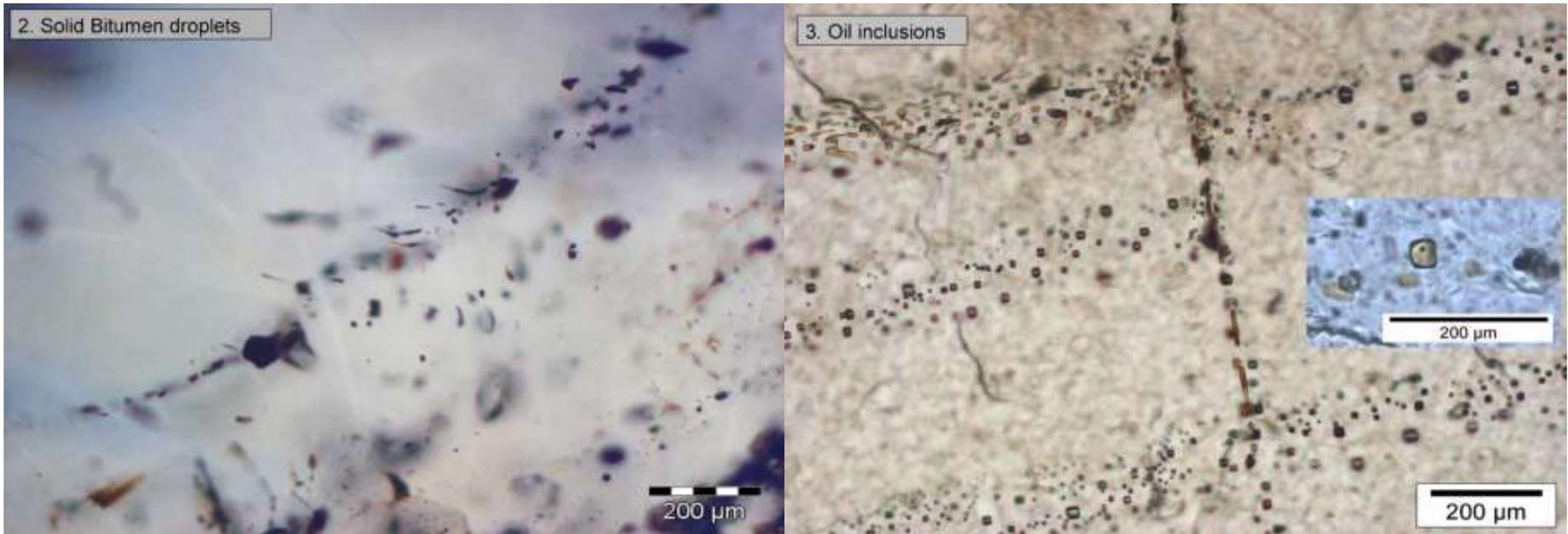
- Identified as the preferred avenue for Mars life detection efforts
- On Earth, halite deposits are plentiful, but they stay “young”:
- **Paradox Member halite**, Pennsylvanian (**298-323 Ma**), SE Utah: up to 0.28wt% total organic carbon (TOC)
- **Thai halites of Cretaceous age (66 to 145 Ma)**: “similar” to Paradox Member TOC, to include “macerated woody plant remains” (from Melvin 1991)
- **Michigan Basin halite**, Silurian age (**419 to 443 Ma**) 0.44 to 2.14wt.% TOC.
- **Pugwash salt mine, New Brunswick, Canada**, late Mississippian (**325-365 Ma**) with oil seeps
- **Zechstein halite deposit**, Poland (**251-260 Ma**)
- **Etc..., etc...**

Liquid petroleum inclusion
Paradox Member. From
Evaporites, Petroleum and
Mineral Resources, J. Melvin,
ed. 1991



South Oman Salt Basin

- Late Cambrian (~530 to 550 Ma old)



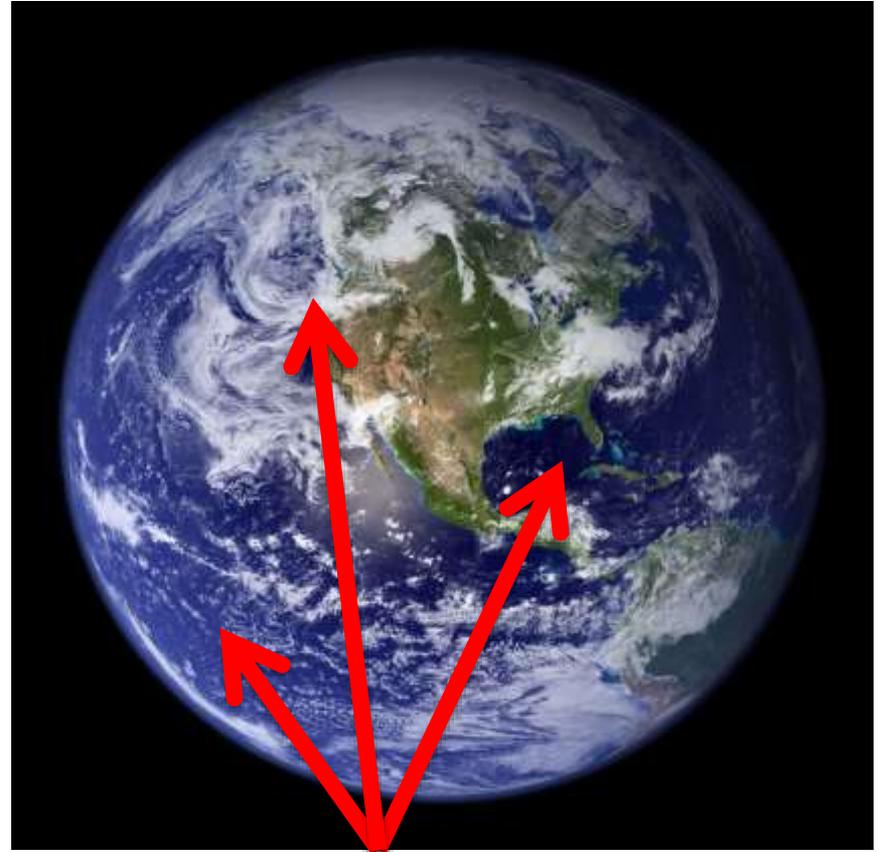
From: Schoenherr, Johannes, et al. "Hydrocarbon-bearing Halite in the Ara Group (South Oman Salt Basin)." *Geophysical Research Abstracts*. Vol. 7. 2005.

Preservation Summary

- In terrestrial examples:
 - Halite can preserve viable microbes for 10^4 years, possibly 10^5 , and disputed claims extend to 10^8 years
 - Organics-bearing halite deposits are found globally, with ages extending to 10^8 years
 - Limited by Earth's abundant water and tectonics
- The sequestration process is very gentle
 - Evaporation of a brine, to entrain suspended solids
 - Organics include solids, petroleum liquids, gases

Terrestrial Halites Differ Considerably from Martian Halites

- **Terrestrial halite** is disturbed by water, geological action so lifetimes are restricted to $< \approx 500$ Ma; may be altered *in situ*
- Mars halites are irradiated
- It would be better to examine halites from a dry, stable, irradiated locale



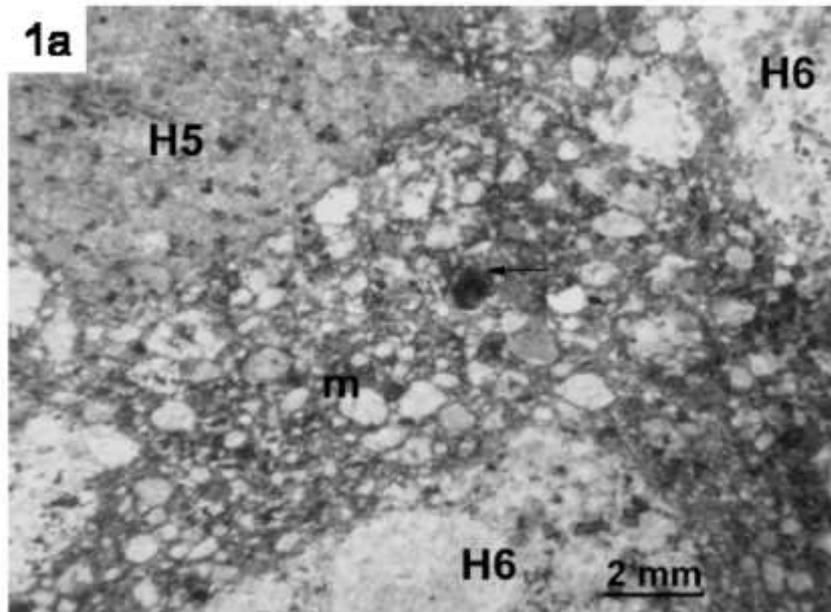
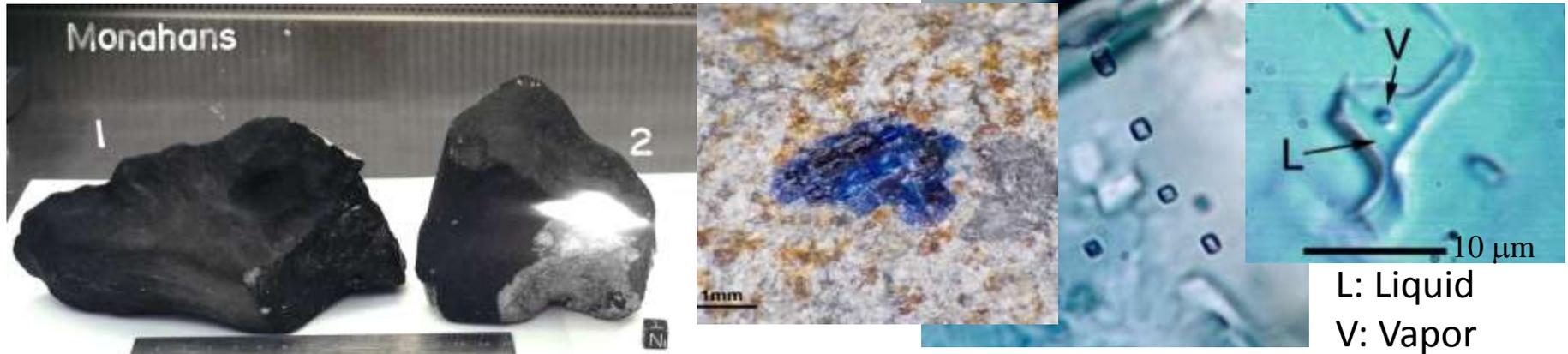
Lots of water!

This is bad for halite survival

Monahans and Zag Halite:

Mars-Analogue Halites from a Dry,
Irradiated, Tectonically Stable Locale

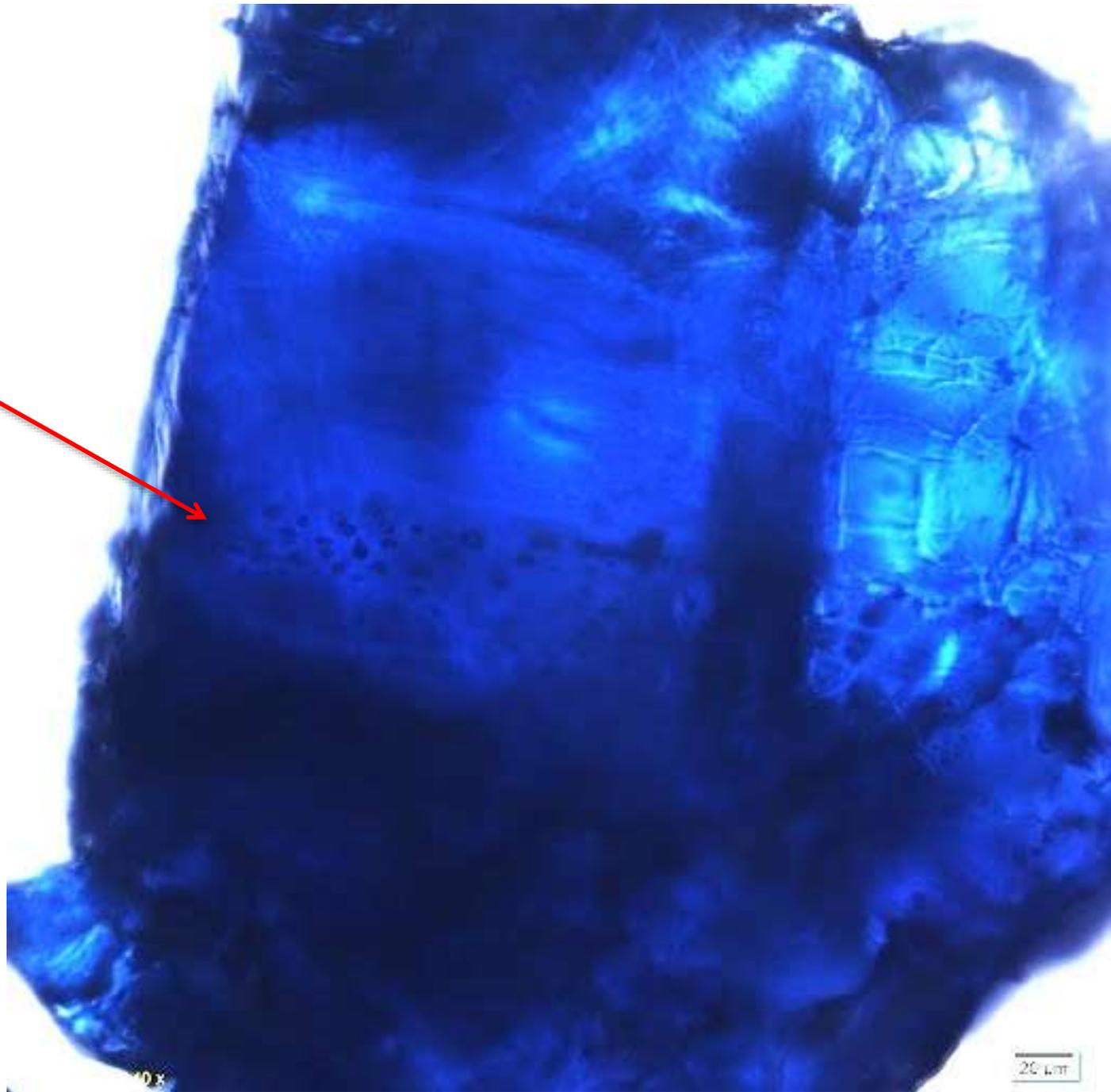
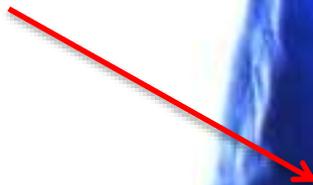
Mars-Analogue-ier Halite in the Zag and Monahans H-Chondrite Breccias



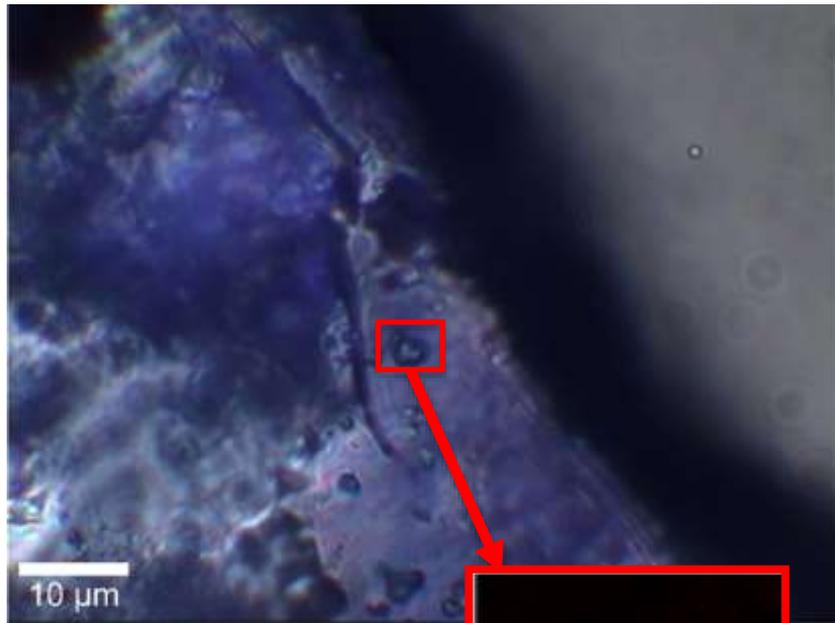
- Monahans and Zag are H chondrite breccias that contain blue halite grains within the fine-grained breccia matrix
- Halite contains ~4.5 Ga fluid inclusions
- Halite is blue/purple from irradiation

Figure from Bridges *et al* (2004) showing Zag halite (dark grain at center) in breccia matrix without alteration to surrounding matrix

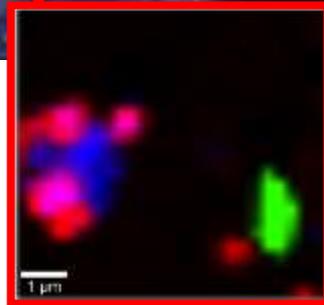
Fluid
inclusions



Materials Found in Zag & Monahans Halites



R: MMC
G: Pyroxene
B: Olivine

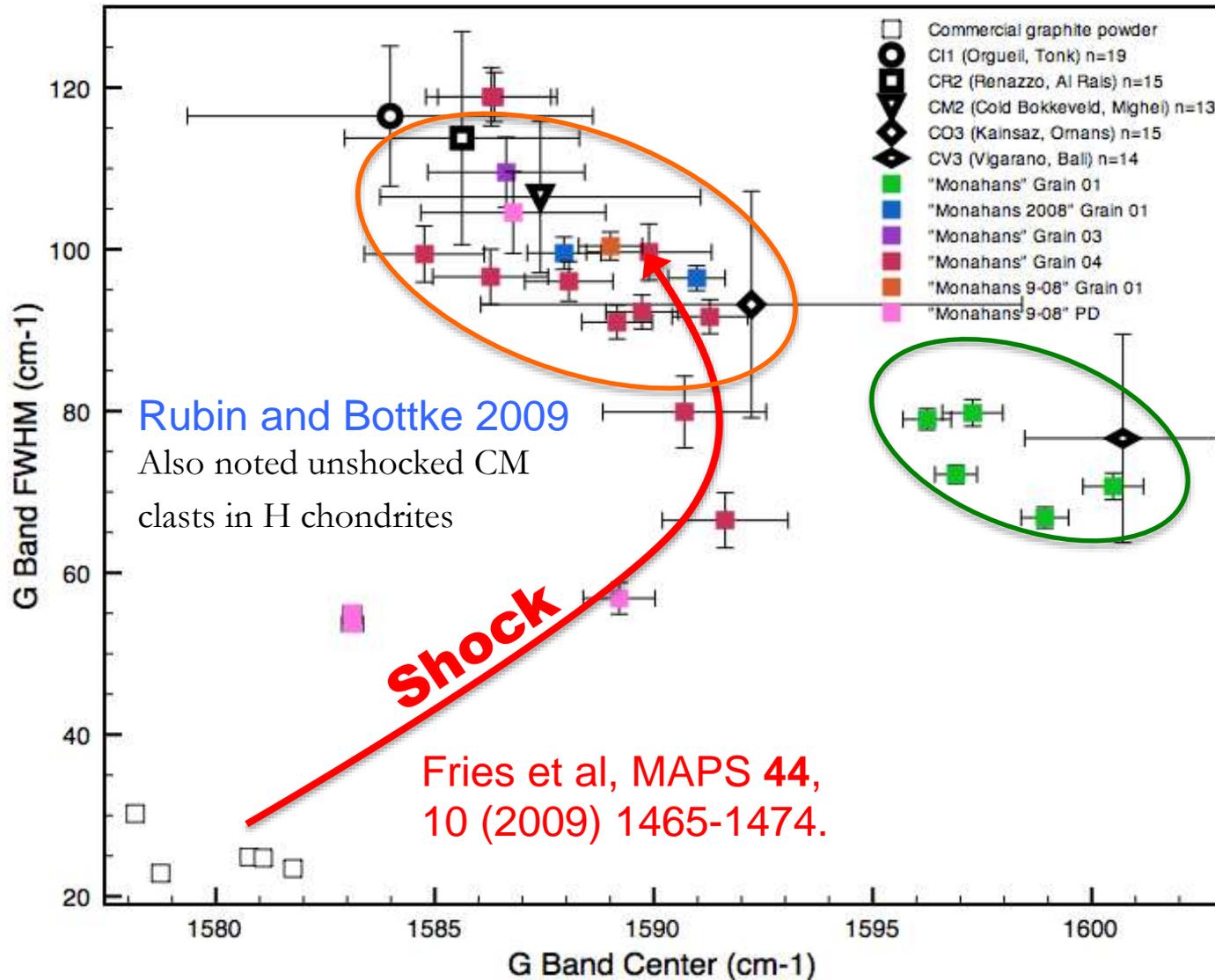


Our survey of halite grains from Monahans and Zag has yielded these inclusions so far:

- **Brine**
- Olivine, pyroxene, feldspars
- Saponite
- Zeolite? (1 discovery thus far)
- Apatite
- **Macromolecular carbon (MMC)**
- **Aliphatic hydrocarbons**
- **Halogen-substituted methane**
- Metal
- Magnetite
- Lepidocrocite (on metal?)
- Sulfides: troilite, pyrrhotite
- Nanodiamond+carbonate+graphite assemblages

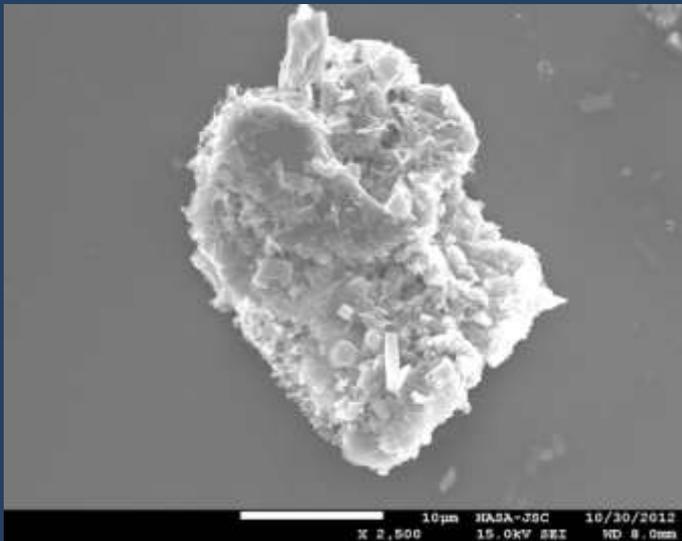
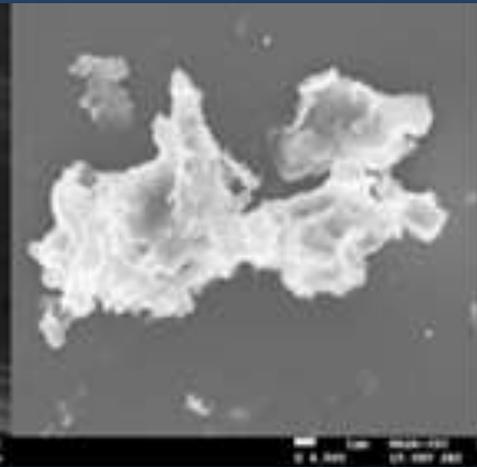
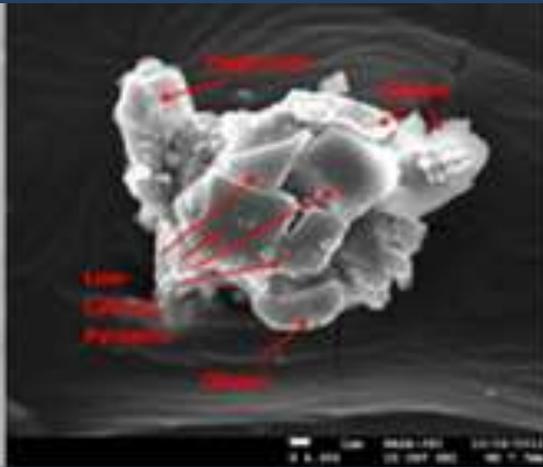
This is not consistent with H chondrite Mineralogy. **We have hypothesized that these halites originate from Ceres based on mineralogical, dynamical, and other factors [Fries et al 2013]**

Multiple Sources of Macromolecular Carbon (MMC)



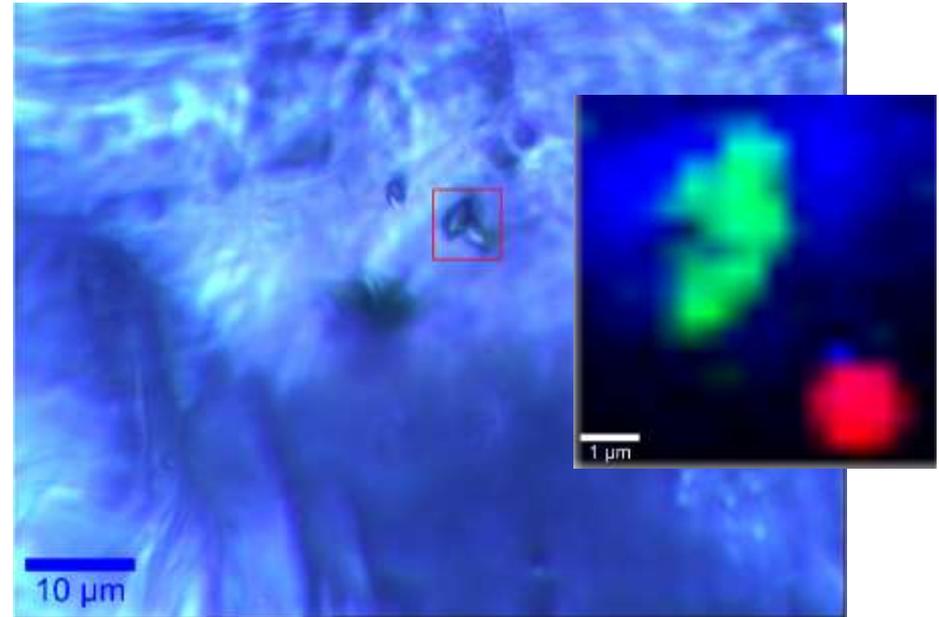
- There are at least **3 populations of MMC**:
- **One MMC material** is CV-chondrite-like (green oval)
- **Disordered material** includes aliphatic compounds and has not seen significant heating
- **Third material** is shocked graphitic component which formed at high temperature
 - Falls on a mixing line between graphite and disordered MMC
- Evidence of a large parent body?

Solid Residue Grains



Halite Preserves Ancient Light Organics

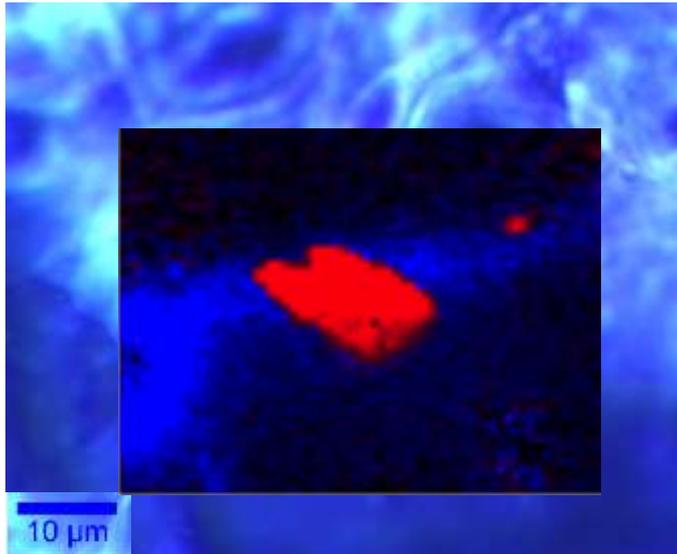
- Monahans and Zag H-breccia meteorites are samples of an H chondrite asteroid regolith
 - Dry, geologically stable
- Halite dated to ~ 4.5 Ga [Zolensky 1999, Whitby 2000, Bogard 2001] via multiple systematics
- These halite grains retain original fluid inclusions as well as solid inclusions from their parent body



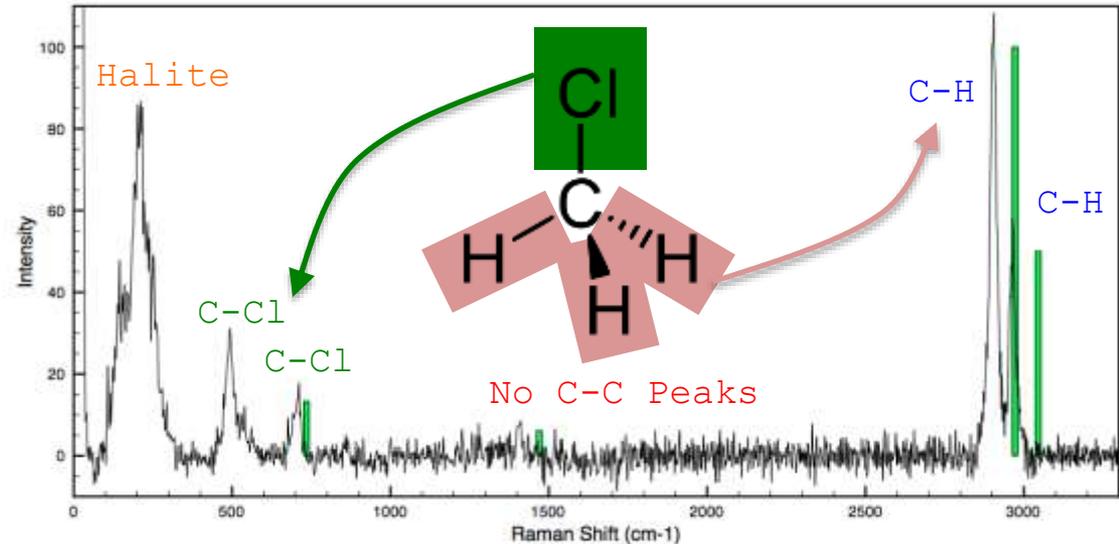
~ 4.5 Ga halite in the Monahans meteorite.

Raman image of macromolecular carbon (Red), apatite (Green) and chloromethane (Blue). Chloromethane is dissolved in the halite matrix.

Halites Contain Methane/Chloromethane



Raman image of the same field of view.
Red: MMC
Blue: Methane dissolved in halite



Raman spectrum of chlorine-substituted methane from Monahans halite (CH_3Cl). Spectrum shows C-Cl peaks, C-H peaks $\sim 3\times$ the C-Cl peak intensity, and no C-C peaks. Consistent peak shifts vs. standard spectrum (green bars) indicate it is dissolved in halite.

- Producing the methane is straightforward
 - $\sim 20\text{wt.}\%$ yield from UV irradiation of Murchison (Schueler et al 2014)
- Methane evolves from carbonaceous inclusions, dissolves in halite to form chloromethane
 - Radiolytic generation of methyl radicals that dissolve in halite matrix
- **Dry halite can preserve light organics for an extraordinarily long time, longer than Hesperian age**

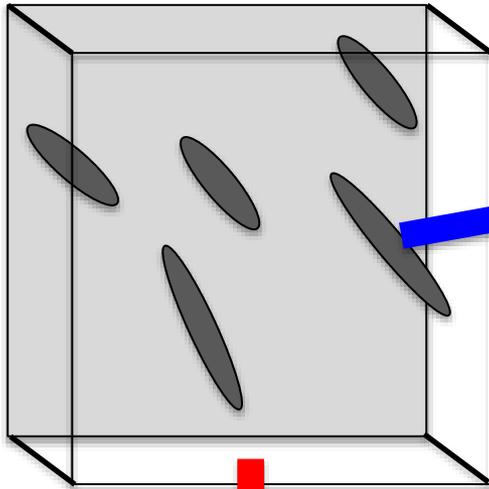
Halite on Mars:

What Can We Expect of Martian Halite-
Hosted Organics?

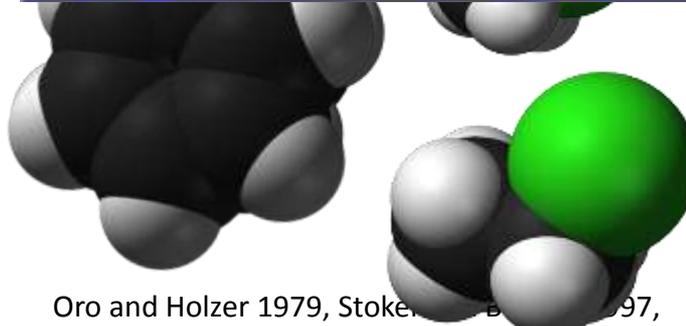
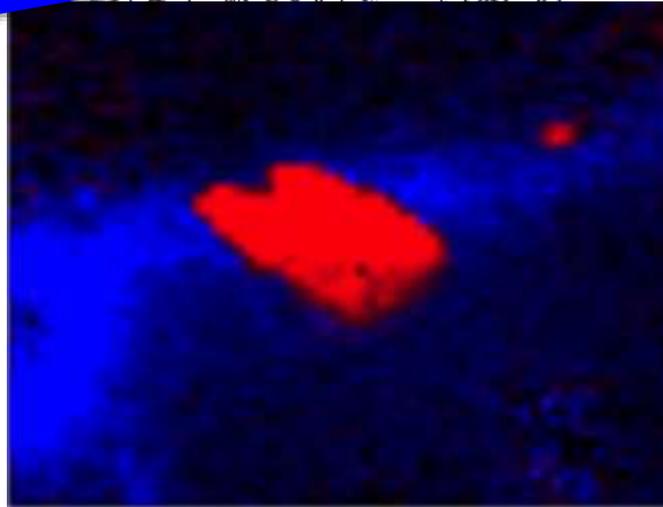
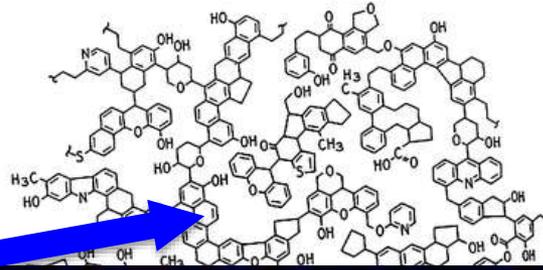
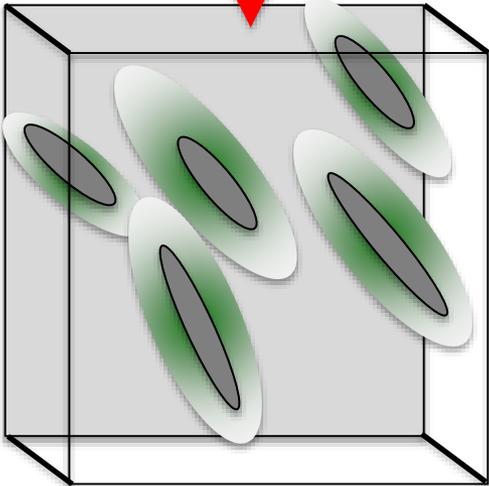
What Should We Expect on Mars?

Dry, Relatively Static Crust, but Irradiated

Martian Halite with
Inclusions



Irradiated for ~3 Ga



Oro and Holzer 1979, Stoker et al 1997,
Loes ten Kate 2005, Kminek and Bada 2006

If biosignatures are present,
They can be identified via:

- Morphological
- Contextual
- Chemical
- Isotopic



Biosignature features
retained:

- Morphological
- Contextual
- ~~Chemical~~
- Isotopic?

e.g. Eisenreich et al 1989,
Fernandez-Remolar et al 2013

A Hypothesis: Halite-Resident Organics in Cumberland?

- Chlorohydrocarbons may have formed in SAM oven via rxn with perchlorates
- Another possibility
- Cumberland is ~ 0.1 [Conrad 2014]
- Assume 1 wt.% of the carbonaceous solid
- Use Schuerger et al. UV photolysis under complete conversion
- Result: ~ 200 ppbw possible in Cumberland
- MSL measured amount of chlorobenzene [Frederickson et al. 2014]
- MSL chlorine isotope measurements may be consistent with preferential reaction with light Cl from dissolution in halite [Conrad 2014]



- Further work is required

Discussion

- The halite exercise illustrates just how rare light organics are at the martian surface
 - A single salt grain becomes significant
 - 200 ppbw chlorohydrocarbons is actually 10x more than the maximum amount the Mars 2020 Organic Contamination Panel suggested Mars 2020 should be designed to preserve in the cache: “single ppb to tens of ppb”
 - Cross-contamination between samples on the scale of a fraction of a salt grain is significant

Summary

- Halite sequesters carbonaceous material via a gentle process (brine evaporation)
- Ancient halite from Zag and Monahans demonstrate that halite can retain organics and carbonaceous solids for ~ 4.5 Ga timescale if kept dry
- Halite deposits exist on Mars at over 600 sites in massive deposits, and has been found in MSL samples in sub-wt.% amounts
- Halite should be considered an important mineral with a high preservation potential for biosignatures; Mars 2020 science goals
- Halite might extend the range of surfaces where organics may still be found, in terms of the surface ages.
 - Radiolytic alteration will still occur; Zag and Monahans halite retains identifiable carbonaceous chondrite-like MMC and light organics
 - Irradiated residue remains in inclusions, protected against perchlorates