The Long-Term Preservation Potential of Organics in Martian Halite

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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.

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

J. Oró 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 Kate¹,², James R.C. Garry¹, Zan Peeters¹, Bernard Foing³, Pascale Ehrenfreund⁴

Amino acid photostability on the Martian surface

Inge Loes ten KATE¹,², James R. C. GARRY², Zan PEETERS², Richard QUINN²,³, Bernard FOING⁴, and Pascale EHRENFREUND²
Carbon on the Martian Surface

II: The Missions

• Viking I and II detected \( \sim \text{ppb} \) levels of chlorinated organics

• Mars Phoenix did not detect organics, but was not as sensitive

• Mars Science Laboratory (MSL) has detected high \( \sim \text{ppb} \) 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 \( 5 \times 10^{-9} \) g m\(^{-2}\) 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, $\sim 250$-300 Ma)
  – Shubert et al 2010 for discussion and references

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 Mississipian (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)."
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

Image Credits: Left: NASA ARES. Center: Serge de Faestraets, Right: Zolensky et al 1999
Fluid inclusions
Materials Found in Zag & Monahans Halites

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?

Fries et al, MAPS 44, 10 (2009) 1465-1474.

Rubin and Bottke 2009
Also noted unshocked CM clasts in H chondrites
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
• 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

• Producing the methane is straightforward
  — ~20wt.% 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

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

Oro and Holzer 1979, Stoker and Bullock 1997, Loes ten Kate 2005, Kminek and Bada 2006
A Hypothesis: Halite-Resident Organics in Cumberland?

- Chlorohydrocarbons may have formed in SAM oven via rxn with perchlorates
- Another possibility:
  - Cumberland is ~0.1 wt.% halite [Vaniman et al. 2014]
  - Assume 1 wt.% of the halite is entrained carbonaceous solids
  - Use Schuerger et al. 2012 20% yield of CH₄ via UV photolysis under martian conditions, complete conversion
  - Result: ~200 ppbw of chlorinated hydrocarbons possible in Cumberland sample

- MSL measured amount is "150-325 ppbw chlorobenzene [Freissenet 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