Methane on Mars

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Possible origins of methane

- **External sources:** meteorites, comets, IDP? → small
- **Biological sources?**
- **Geochemical sources:**
  - Volcanism
  - Hydrothermalism (serpeninization, thermodynamical equilibration?)

Atreya et al., 2006
Thermodynamical equilibration of C dissolved in hydrothermafluids at depth

- Model of hydrothermal system (Lyons et al, 2005)
Transport and release of CH$_4$ to the atmosphere

- Assuming a C molar fraction of 0.05, exsolution occurs at 8.5 km depth.
- Above 8.5 km depth, progressive enrichment of the gas phase in CH$_4$.
- Ultimate release to the atmosphere.
- No H$_2$ produced together CH$_4$. 
Convection and enrichment of the cryosphere in CH$_4$

- Water convection in Martian crust (Travis et al, 2003)

Progressive enrichment of water ice in methane clathrates at the interface?
**CH$_4$ Clathrates**

- Clathrates: molecules of CH$_4$ trapped in cages of H$_2$O: CH$_4$-5.85 H$_2$O.
- Formed at high pressure (oceanic groundfloor on Earth), but NOT in Martian atmospheric conditions.
- May be formed in the subsurface at $p>\approx 1$ bar.

Chastain and Chevrier, 2007
Possible formation of mixed CO$_2$-CH$_4$ clathrates on the south polar cap
Calculation/lab. measurements

- « Van der Waals » approach.
- $T < 150 \text{ K} :$ formation of CO$_2$ clathrates.
- $T(\text{south cap}) \approx 145 \text{ K}.$

Herri et al., 2011
Abundance fraction of component in clathrate versus component in gas

Herri et al., 2011

<table>
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<th>T (K)</th>
<th>P (kPa)</th>
<th>CO₂</th>
<th>N₂</th>
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</table>

Equilibrium condition
Gas = 97,4% CO₂, 2,7% N₂, 2% Ar, 15 ppb CH₄

Abundance ration = xᵢ/fᵢ
xᵢ : composition of i in the hydrate
fᵢ : composition of i in the gas

Herri et al., 2011
Path of a CH$_4$-rich fluid parcel in the phase diagram

Chassefière et Leblanc, PSS, 2011
Physical states of the fluid
Release of water and methane to the surface and atmosphere

From Gulick, 1998
Another possible abiotic source of CH$_4$ : serpentinization

- Generic serpentinization reaction at Mars, with Mg/(Mg + Fe)=0.75 (Oze and Sharma, 2005)

\[
\text{Mg}_{1.5}\text{Fe}_{0.5}\text{SiO}_4 + 1.17\text{H}_2\text{O} \rightarrow 0.5\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 0.17\text{Fe}_3\text{O}_4 + 0.17\text{H}_2
\]

- Further oxidation of H$_2$ through hydrocarbon formation processes (McCollom and Bach, 2009) :

\[
\text{CO}_2 + \text{H}_2 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_6 + \ldots + \text{C}_n\text{H}_m + \ldots + \text{H}_2\text{O}
\]

- CH$_4$ released to the atmosphere, then oxidized (in the subsurface?), through the net redox reaction :

\[
\text{CH}_4 + 2\ \text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\ \text{H}_2
\]
Possibility of a cycling of carbon through atmosphere and crust

- Released to the atmosphere oxidized to CO$_2$
- CO$_2$ recycled to the crust (basal melting at the south polar cap?)
- CO$_2$ precipitation to carbonates in the crust
- Decomposition of carbonates and reduction by H$_2$
Crustal carbonates on Mars ($\approx$ 1 bar equivalent or more?)

**Atmosphere**
- Carbonate deposits
- Water table
- Cold water sheet

**Subsurface hydrosphere**
- Hot hydrothermal fluid

**Crust**
- Magma
Detection of carbonates at the surface of Mars

- Carbonates observed by CRISM/MRO in the Nili Fossae region (green circle).
- Fe-Mg phyllosilicates (zones outlined in yellow).

Ehlmann et al., 2009
Detection of serpentine

Ehlmann et al., 2009
Carbon hydrothermal cycle from a redox point of view

Chassefière and Leblanc, 2011
Present imbalance between H and O escape fluxes

- Imbalance between H and O escape fluxes ($\Phi_O \neq 1/2 \Phi_H$) → variation of $H_2$ to restore the balance (Mc Elroy and Donahue, 1972, Liu and Donahue, 1976).
- Typical damping time of imbalance = $\tau(H_2) \approx 1000$ years.
- Present escape O and H fluxes:
  - H thermal escape flux close to the limited-diffusion flux (Chaufray, 2007; Zahnle et al., 2008) : $4 \times 10^8$ cm$^{-2}$ s$^{-1}$
  - O non-thermal escape : $2-8 \times 10^7$ cm$^{-2}$ s$^{-1}$ (Valeille et al, 2009; Chassefière and Leblanc, 2010)
  
  - $\Phi_O \approx 0.05-0.2 \quad \Phi_H < 0.5 \Phi_H$ : small O escape/ H escape → strong redox imbalance.
- Two possibilities (Nair et al., 1994):
  - Flux of reduced gases from the interior ($CH_4, H_2...$)
  - Continuous oxidation of surface rocks.
CH₄ : a potential sink for atmospheric O₂?

- A CH₄ mixing ratio of 15 ppbv and a CH₄ lifetime of ≈200 days results in a CH₄ flux compatible with the global redox balance of H and O fluxes ($\Phi_H = 2 (\Phi_O + \Phi_{ox})$).
- The present CH₄ release flux could have been at a comparable level for at least ≈1000 yr (H₂ lifetime).
- At the present CH₄ release rate, the CH₄ released since the last obliquity transition (3 Myr ago) results in a superficial CO₂ ice layer on the south polar cap similar to the observed one (10 m thick).
- The preferred value of the molar fraction of CH₄ in the vented gas is ≈1 (not 0.1 like on Earth), with therefore no simultaneous H₂ release.

Chassefière and Leblanc, 2011
CO$_2$ ice layer of $\approx 10$ m thickness
No south polar cap at high obliquity.
Deposition of south polar cap 3 Myr ago/
Subsequent deposition of $\approx 10$ m thick layer of CO$_2$ ice due to CH$_4$ release (?).
Why no significant $\text{H}_2$ release?

(AT LEAST) THREE POSSIBLE REASONS:

- $\text{CH}_4$ stored in subsurface clathrates (unlike $\text{H}_2$ rapidly outgassed during hydrothermal events).
- $\text{CH}_4$ formed by direct thermodynamical equilibration of carbon dissolved in deep hot fluids, no $\text{H}_2$ released (Lyons et al., 2006).
- $\text{H}_2$ consumed by microbes before reaching the surface (C. Muller, personal communication, 2010).
A few suggestions

• \( \text{CH}_4 \) release at present rate since several thousand or million years.

• Subsurface \( \text{CH}_4 \) clathrate-rich cryosphere could serve as intermediate reservoir for \( \text{CH}_4 \).

• An active long-term carbon cycle, progressively decreasing with volcanic/hydrothermal activity, may occur through various reservoirs: carbonates, clathrates, atmosphere.

• The lack of present \( \text{H}_2 \) release could also sign a volcanic and/or biotic origin.
Seasonal cycle of CH$_4$ over the last 5 seasonal cycles: why?
Seasonal correlation of methane with water and ice optical depth

Geminale et al, 2008
Local time variations

Longitudinal variations

CH₄

H₂O

Geminale et al, 2008
Correlation coefficients

Data from Geminale et al, 2008

Chassefière, Icarus, 2009
Recent reanalysis of PFS data

Seasonal/latitudinal maps of CH$_4$ and H$_2$O observed by the same instrument (PFS/ Marx Express).

Geminale et al., 2011
Release of methane under the form of metastable clathrate particles

• Anomalous preservation of clathrates (Stern et al., 2001, and ref. therein). *Clathrates more difficult to dissociate than to build.*

• Ultra-stability of very pure clathrate crystals (Zhang et Rodgers, 2008): <1% dissociation at 1 bar & 268 K in 10 days.

• Atmospheric gaseous methane could be released from metastable clathrate particles suspended in the atmosphere.

→ The cause of particle decomposition could be water condensation, explaining the CH$_4$/H$_2$O global correlation (Chassefière, 2009).
« Anomalous preservation » of clathrates

- Anomalous preservation of clathrates (Stern et al. 2001 and ref. therein)

- Ultra-stability of very pure clathrate crystal aggregates (Zhang and Rodgers, 2008): <1% dissociation at 1 bar/268 K during 10 days.
Present methane cycle according to the hypothesis of clathrate particle release

Chassefière, 2009
Potential role of serpentinization in storing water in the crust

- Release of CH\(_4\) and H\(_2\) by serpentinization → thermal escape of H atoms → **increase of the D/H ratio**.

\[
\text{Mg}_{1.5}\text{Fe}_{0.5}\text{SiO}_4 + 1.17\text{H}_2\text{O} \rightarrow 0.5\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 0.17\text{Fe}_3\text{O}_4 + 0.17\text{H}_2
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\]

- A model calculating the D/H ratio due to serpentinization since the late Noachian has been implemented.

Chassefière and Leblanc, EPSL, in press, 2011
Possible scenario of water history

• A maximum serpentinization rate resulting in the present D/H value (≈5 SMOW) can be calculated.
• A H$_2$O global equivalent layer of ≈400 m depth could have been removed during the last 3.8 Gyr, most of it being stored in subsurface serpentine.

Chassefière and Leblanc, EPSL, in press, 2011