Modeling chemical uncertainties in a pale orange dot

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EARTH THROUGH TIME

From an atmospheric evolution...

origins of Life?  
traces of Life  
accumulation of $O_2$

4,5 4,0 3,5 3,0 2,5 2,0 0 Ga (present)

Impact rate  
X/EUV irradiation flux  
Reducing gas emissions  
Photochemistry

... to observable features evolution
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EARTH THROUGH TIME

Temperature (°C) vs. Time (Ga)

- Hren et al., *Nature* 2009
- Blake et al., *Nature* 2010

Present-day ocean temperatures range

pCO₂ (bar) vs. Time (Ga)

- Ohmoto et al., *Nature* 2004
- Rye et al., *Nature* 1995
- Hessler et al., *Nature* 2004
- Driese et al., *Precambrian Res.* 2011
- Sansjofre et al., *Nature* 2011
- Sheldon, *Precambrian Res.* 2006
- Rosing et al., *Nature* 2010
- Kah and Riding, *Geology* 2007

Solar luminosity vs. Time (Ga)

- 75%
- 80%
- 85%
- 90%
- 95%

15°C
EARTH THROUGH TIME

- Oxygen begins to appear in the atmosphere
- Oxygen-producing bacteria get their start
- Major CH₄ contributions to the atmosphere from methanogens
- First microscopic life begins consuming CO₂
- High CO₂ compensates for the faint young Sun

Kasting et al., 2004 - Sci. Am.
2.5
3.0
3.5

Time (Ga)

Relative concentration

CO₂

3000 ppmv

1000 ppmv

CH₄

Kasting et al., 2004 - Sci. Am.

Global ice ages

O₂

EARTH THROUGH TIME

Pavlov et al., 2001a
Trainer et al., 2006
Zerkle et al., 2012

Pavlov et al., 2001b
Haqq-Misra et al., 2008
Kurzweil et al., 2013

Trainer et al., 2004
Domagal-Goldman et al., 2008

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ARCHEAN EARTH
Impact on atmospheric chemistry?

Impact on planetary climate?

Impact on planetary spectrum?

Effective optical depth

0.01 0.1 1 10

Wavelength (μm)

0.0 0.5 1.0 1.5 2.0

Wolf and Toon, 2010 - Science

Less extinction at visible wavelengths

More extinction at UV wavelengths
Geochemical constraints

PHOTO - 1D photochemistry

CLIMA - 1D climate

Temperature
Pressure
Gases abundances
Haze abundance

SMART - Spectral Mapping and Atmospheric Transfer Code

Spectrum
P_{surf} = 1 \text{ bar, } P_{CO_2} = 0.018 \text{ bar}

- **Initiation of haze formation**
- **Cooling from haze**
- **Haze self-shielding**

Haze thickness
$P_{\text{surf}} = 1 \text{ bar}, P_{\text{CO}_2} = 0.018 \text{ bar}$

Wolf and Toon, 2014 - 62% ice free

Charley et al., 2013 - belt of equatorial open water
Mean surface temperature (K) at $P_{surf} = 1 \text{ bar}, P_{CO_2} = 0.018 \text{ bar}$

- **No haze**
- **Thin haze**
- **Thick haze**

Arney et al., submitted
Reflectance

Wavelength (μm)

No haze
Thin haze
Thick haze

Arney et al., submitted
PHOTO - 1D photochemistry

CLIMA - 1D climate

Geochemical constraints

SMART - Spectral Mapping and Atmospheric Transfer Code

Temperature
Pressure
Gases abundances
Haze abundance

Spectrum
Chemical models of planetary atmospheres are complex ([0-3]D chemical-dynamical codes with thousands of highly coupled nonlinear equations)

The chemical equations are based on empirical parameters:

- Photodissociations:
  \[ AB \xrightarrow{h\nu} A + B \]
  \[ \sigma_i(\lambda, T) \ q_{i,j}(\lambda, T) \]
  - Neutral-neutral thermal reactions:
  \[ A + B \xrightarrow{(+M)} C + D \]
  \[ k_i(T) = \alpha_i\left(\frac{T}{300}\right)^{\beta_i} \exp\left(-\frac{\gamma_i}{T}\right) \]

These empirical parameters are obtained from experiments, calculations and/or [ more or less [ but most often less ]] educated-guessed estimations:

- They are always evaluated with [ [very] large ] uncertainty
- Most of the cases, extrapolations of these parameters are mandatory
Photodissociations

\[ AB \xrightarrow{h\nu} A + B \]
\[ \sigma_i(\lambda, T) \quad q_{i,j}(\lambda, T') \]

Neutral-neutral thermal reactions

\[ A + B \xrightarrow{(+M)} C + D \]
\[ k_i(T) = \alpha_i \left( \frac{T}{300} \right)^{\beta_i} \exp\left( -\frac{\gamma_i}{T} \right) \]

PHOTOCHEMICAL MODELING

C\textsubscript{2}H\textsubscript{2}

Altitude (km)

Molar fraction

Observations

Modeling

Experiments and theoretical calculations

Measurements of the reaction parameters

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Photodissociations

$$AB \xrightarrow{h\nu} A + B$$

$$\sigma_i(\lambda, T) q_{i,j}(\lambda, T')$$

$$F_{\sigma_i}(\lambda,T) F_{q_{i,j}}(\lambda,T)$$

Neutral-neutral thermal reactions

$$A + B \xrightarrow{(+M)} C + D$$

$$k_i(T) = \alpha_i \left( \frac{T}{300} \right)^{\beta_i} \exp\left(-\frac{\gamma_i}{T}\right)$$

$$F_{k_i}(T)$$

Uncertainties of the reaction parameters

Experiments and theoretical calculations

Observations

Modeling chemical uncertainties

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« NEXT-GENERATION » PHOTOCHEMICAL MODELING
Photodissociations

\[
\begin{align*}
\text{AB} & \xrightarrow{h\nu} \text{A} + \text{B} \\
\sigma_i(\lambda, T) & q_{i,j}(\lambda, T) \\
F_{\sigma_i}(\lambda, T) & F_{q_{i,j}}(\lambda, T)
\end{align*}
\]

Neutral-neutral thermal reactions

\[
\begin{align*}
\text{A} + \text{B} & \xrightarrow{(+M)} \text{C} + \text{D} \\
k_i(T) & = \alpha_i \left( \frac{T}{300} \right)^{\beta_i} \exp\left( -\frac{\gamma_i}{T} \right) \\
F_{k_i}(T)
\end{align*}
\]

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« NEXT-GENERATION » PHOTOCHEMICAL MODELING
Photodissociations

\[ AB \xrightarrow{h\nu} A + B \]

\[ \sigma_i(\lambda, T) \quad q_{i,j}(\lambda, T) \]

Neutral-neutral thermal reactions

\[ A + B \xrightarrow{(+M)} C + D \]

\[ k_i(T) = \alpha_i \left( \frac{T}{300} \right)^{\beta_i} \exp\left( -\frac{\gamma_i}{T} \right) \]

\[ F_{\sigma_i}(\lambda, T) \quad F_{q_{i,j}}(\lambda, T) \]

\[ F_{k_i}(T) \]

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« NEXT-GENERATION » PHOTOCHEMICAL MODELING

Observations

Experiments and theoretical calculations
Uncertainties of the reaction parameters

RANDOM SAMPLING BASED UNCERTAINTY PROPAGATION
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« NEXT-GENERATION » PHOTOCHEMICAL MODELING

\[ \text{AB} \xrightarrow{h\nu} \text{A} + \text{B} \]

\[ \sigma_i(\lambda, T) \quad q_{i,j}(\lambda, T) \]

\[ F_{\sigma_i}(\lambda, T) \quad F_{q_{i,j}}(\lambda, T) \]

Photodissociations

\[ \text{A} + \text{B} \xrightarrow{(+M)} \text{C} + \text{D} \]

\[ k_i(T) = \alpha_i \left( \frac{T}{300} \right)^{\beta_i} \exp\left( -\frac{\gamma_i}{T} \right) \]

\[ F_{k_i}(T) \]

Neutral-neutral thermal reactions

HCAER

Observations

Modeling

Experiments and theoretical calculations

Random sampling-based uncertainty propagation

Molar fraction

Altitude (km)

68% (1\(\sigma\))

95% (2\(\sigma\))

99% (3\(\sigma\))

\(10^{-12}\) \(10^{-10}\) \(10^{-8}\) \(10^{-6}\) \(10^{-4}\) \(10^{-2}\) \(10^0\)
Photodissociations

\[ \text{AB} \xrightarrow{h\nu} \text{A} + \text{B} \]
\[ \sigma_i(\lambda, T), q_{i,j}(\lambda, T') \]
\[ F_{\sigma_i}(\lambda, T), F_{q_{i,j}}(\lambda, T') \]

Neutral-neutral thermal reactions

\[ \text{A} + \text{B} \xrightarrow{(+\text{M})} \text{C} + \text{D} \]
\[ k_i(T) = \alpha_i \left( \frac{T}{300} \right)^{\beta_i} \exp\left( -\frac{\gamma_i}{T} \right) \]
\[ F_{k_i}(T) \]

« NEXT-GENERATION » PHOTOCHEMICAL MODELING

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« NEXT-GENERATION » CLIMATE MODELING

$P_{surf} = 1 \text{ bar, } P_{CO_2} = 0.018 \text{ bar, } CH_4/CO_2 = 0.2$
« NEXT-GENERATION » CLIMATE MODELING

Wavelength (μm)

Wavelength (μm)
Flux (W m$^{-2}$ μm)

P$_{\text{surf}}$ = 1 bar, P$_{\text{CO}_2}$ = 0.018 bar, CH$_4$/CO$_2$ = 0.2

Kahre et al. [1984]
Mahjoub et al. [2012] - 1% CH$_4$
Mahjoub et al. [2012] - 2% CH$_4$
Mahjoub et al. [2012] - 5% CH$_4$
Mahjoub et al. [2012] - 10% CH$_4$
NOA ROSES-EXO

CHEMICAL FORMATION PATHWAYS AND OPTICAL PROPERTIES FOR EARLY EARTH’S ORGANIC HAZE:
A COMBINED THEORETICAL AND EXPERIMENTAL APPROACH

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Science PI: Eric Hébrard (NASA-GSFC)
Co-Is: Shawn D. Domagal-Goldman, Thomas Gautier and Jennifer C. Stern (NASA-GSFC)
Collaborator: Giada Arney (University of Washington, Seattle, WA)

+ vplanet

PHOTO - 1D photochemistry
CLIMA - 1D climate
SMART - Spectral Mapping and Atmospheric Transfer Code
HYDROCARBONS HAZES DO NOT PRECLUDE HABITABLE SURFACE TEMPERATURES

HYDROCARBONS HAZES HAVE STRONG, DETECTABLE SPECTRAL FEATURES AT SHORT WAVELENGTHS

A BETTER KNOWLEDGE OF THEIR CHEMICAL FORMATION PATHWAYS AND OPTICAL PROPERTIES ARE NEEDED