Atmospheric Chemistry and Radiation in the Solar System as Guides to Exoplanet Atmospheres

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My homework assignment

From: david.crisp@jpl.nasa.gov
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“...overview talk on “Composition/chemistry/aerosols/radiation”... to identify critical processes that are common to the Earth, other planets in our solar system, and exoplanets, and to discuss their interactions...”
Outline

1) Atmospheric composition:
   - Why atmospheres exist (zero-order question of escape and retention)
   - The taxonomy of atmospheric composition
   - Earth as bio-atmospheric chemistry

2) Radiation and structure:
   Chemistry-radiation connection
   1st order commonalities in stratospheres, tropospheres

3) Conclusions
Part 1: Atmospheric composition
The existence of atmospheres

Nature *(volatile-rich origin)* vs. nurture *(evolution)*?

**Nurture** must ultimately rule because atmospheres must be stable against obliteration by:

1) Impact erosion – loss from large body impacts

2) Irradiation-driven hydrodynamic escape (thermal escape end-member)
Good versus bad neighborhoods


The diagram illustrates the relationship between escape velocity (km/s) and V_impact/V_escape for various celestial bodies. Bodies with higher escape velocity and lower V_impact/V_escape are considered to be in good neighborhoods, while those with lower escape velocity and higher V_impact/V_escape are in bad neighborhoods. The presence of an atmosphere is also indicated, with bodies that do not have an atmosphere marked as "no atmosphere."
Transiting exoplanets


prediction: no atmosphere

Some Super-Earths

Kepler 70b
Kepler 70c

Corot-7b
Kepler 10b
55 Cnc e
Kepler 9d

Kepler 42c
Kepler 42d
Kepler 11f
Kepler 11e
Kepler 30d

Estimated $v_{impact}/v_{escape}$ vs Escape velocity (km/s)
Thermal (hydrodynamic escape) stability

So, atmospheres will not exist if:

1) **Bad impact regime** (has received little attention)

- rocky planets in **M-star habitable zone** are vulnerable

- e.g. Earth @ 1/9AU from 1/3M⊙  
  Mars in same HZ,  
  \[ \frac{v_{\text{impact}}}{v_{\text{esc}}} \sim 3 \] => problem for complex life?  
  \[ \frac{v_{\text{impact}}}{v_{\text{esc}}} \sim 6 \] => I predict airless

- M-star planets form \(10^5-10^6\) yrs => migration is an *unlikely* savior; disk dissipation takes \(\sim 10^{6-7}\) yr from observations, so planet will be in its final orbit while impact regime is bad (Lissauer, 2007, *Ap. J.*).

- Lucky ones? Frozen volatiles on night-side; late slow, volatile-rich impactors

2) **Bad thermal regime** (prone to hydrodynamic escape)

- Pre-main sequence luminosity is under-appreciated

- e.g., a 1/3M⊙ M-star is \(\sim 10\times\) more luminous during first \(\sim 4\) Myr than on the main sequence, when planets have formed
Taxonomy of atmospheric compositions

( a Solar System perspective )

Fundamentally, two types:

1. Reducing
   - Titan
   - Pre-2.4 Ga Earth
   - Pre-4.3 Ga? Mars

2. Oxidizing
   - Post-2.4 Ga Earth
   - Venus (at altitude)
   - Mars

I’m ignoring
-very tenuous N₂ (CH₄) ice-vapor equilibria air of KBOs
(e.g., Triton, Pluto)
Fate of hydrogen in reducing atmospheres
a key difference in small vs. large bodies

Note: S forms polysulfur

From: Catling & Kasting (2014)
Atmospheric Evolution on Inhabited and Lifeless Worlds, Cambridge Univ. Press.
Snapshot of taxa: GJ1214b-type atmospheres

From R. Hu (2013), 44th LPSC, 1428

Elemental abundance, H

Elemental C/O ratio

Specified:
0.014 AU, M star
470 K top
800 K @1 bar
Fixed C-H-O

hydrocarbon if O-poor
C-oxide if O-poor

Solar
Sulfur in oxidizing atmospheres
differences in dry vs. wet worlds, cold vs. hot

Earth
oxidized S in oceanic SO$_4$(aq)
H$_2$SO$_4$ haze (Junge layer @20-25 km)
volcanoes:~1% of ~30% albedo

Venus (>30 km)
Sulfur in air given hot surface
SO$_2$, 3$^{rd}$ after CO$_2$, N$_2$ abundances
H$_2$SO$_4$ thick haze, important in IR,
dominates 76% visible albedo

Mars
oxidized S in soil, sedimentary SO$_4$(s)
H$_2$SO$_4$ haze early Mars, adds $\geq$10% albedo (Tian et al., 2010)
Earth: uniquely wet and O$_2$-rich...

- **2 key consequences for chemistry**: (1) a strong control on trace gases via the hydroxyl radical OH (2) rainfall

1) **CLEAR OUT THE MUCK BY OXIDATION; PLUS RAIN OUT**

O$_3$ absorption <340 nm generates O($^1D$)

$$H_2O + O(^1D) \rightarrow OH + OH$$

**Oxidizes** H$_2$S, COS, DMS to sulfate (NH$_3$ to NH$_3$-sulfate in troposphere) which rains out.

**Oxidizes** CO, CH$_4$ and other hydrocarbons to CO$_2$ and H$_2$O

=> air transparent to visible

=> sunniest planet in Solar System with an atmosphere

2) **IF THERE WERE A LACK of ‘OH’ => HAZE WOULD BUILD UP**

e.g., Archean Earth: CH$_4$ and associated hydrocarbons + haze
Thick sulfate aerosol haze

Indicates a dry, volcanic planet
Sort of anti-biosignature.

Venus: nailing $H_2SO_4$ required polarized reflected light as a function of phase angle (Young, 1973; Hansen & Hovenis, 1974).

Exoplanets: ~45 micron sulfate feature, MIR OCS, SO$_2$ proxies.

(Conversely, S$_8$ absorption edge@300-400 nm)
Part 2: Radiation, structure

• Chemistry-radiation connection

• 1st order commonalities and differences in stratospheres, tropospheres, tropopauses
<table>
<thead>
<tr>
<th>World</th>
<th>Stratospheric Heating</th>
<th>Stratospheric Cooling</th>
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</thead>
<tbody>
<tr>
<td>Venus</td>
<td>( \text{CO}_2 )</td>
<td>( \text{CO}_2 )</td>
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<tr>
<td>Earth</td>
<td>ozone (UV)</td>
<td>( \text{CO}_2 )</td>
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<tr>
<td>Jupiter</td>
<td>aerosols (UV/vis); methane (NIR)</td>
<td>acetylene ((\text{C}_2\text{H}_2)) 13.7 (\mu\text{m}) ethane ((\text{C}_2\text{H}_6)) 12.2 (\mu\text{m})</td>
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<tr>
<td>Saturn</td>
<td>aerosols (UV/vis); methane (NIR)</td>
<td>acetylene ((\text{C}_2\text{H}_2)); ethane ((\text{C}_2\text{H}_6))</td>
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<tr>
<td>Titan</td>
<td>haze; methane (NIR)</td>
<td>acetylene ((\text{C}_2\text{H}_2)); ethane ((\text{C}_2\text{H}_6)); haze</td>
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<tr>
<td>Uranus</td>
<td>aerosols (UV/vis); methane (NIR)</td>
<td>acetylene ((\text{C}_2\text{H}_2)); ethane ((\text{C}_2\text{H}_6))</td>
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<tr>
<td>Neptune</td>
<td>aerosols (UV/vis); methane (NIR)</td>
<td>acetylene ((\text{C}_2\text{H}_2)); ethane ((\text{C}_2\text{H}_6))</td>
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<tr>
<td>World</td>
<td>Key greenhouse</td>
<td>Cooling factors</td>
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<td>------------------------------------------------------</td>
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<tr>
<td>Venus</td>
<td>CO$_2$ (15 μm)</td>
<td>huge SO$_4$ haze albedo</td>
</tr>
<tr>
<td>Earth</td>
<td>H$_2$O (continuum)-CO$_2$ (15 μm) (CH$_4$, O$_3$ N$_2$O)</td>
<td>H$_2$O cloud albedo, small SO$_4$ haze</td>
</tr>
<tr>
<td>Jupiter</td>
<td>H$_2$-H$_2$, H$_2$-He CIA; NH$_3$, CH$_4$</td>
<td>cloud, haze albedo</td>
</tr>
<tr>
<td>Saturn</td>
<td>H$_2$-H$_2$, H$_2$-He CIA; PH$_3$, CH$_4$</td>
<td>cloud, haze albedo</td>
</tr>
<tr>
<td>Titan</td>
<td>N$_2$-N$_2$, N$_2$-CH$_4$, N$_2$-H$_2$, CH$_4$-CH$_4$ CIA</td>
<td>haze ‘anti-greenhouse’ absorbs solar in IR optically thin region</td>
</tr>
<tr>
<td>Uranus</td>
<td>H$_2$-H$_2$, H$_2$-He CIA; CH$_4$</td>
<td>cloud, haze albedo</td>
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</table>
Oxidizing
Absorption, oxidized gas: $CO_2$ (+$H_2O$ +$O_3$ for Earth)
+band center emission (stratosphere)

Reducing
Absorption, reducing gas:
• $H_2$ on giants
• $NH_3$, on all giants (1400-1800 cm$^{-1}$); $PH_3$ on Saturn
• $CH_4$, $H_2$ operating with $N_2$ on Titan
Emission: $C_2H_2$ (729 = 13.7 μm) $C_2H_6$ (820 = 12.2 μm), $CH_4$
Commonalities in atmospheric structure
A note on terminology I’m using

Radiative-convective boundary

tropopause

gray radiative profile

convective profile

Altitude

Temperature
Commonalities in structure: Terminology

1) temperature minimum ‘tropopause’

2) Shockingly: let’s call the radiative-convective boundary... the “radiative-convective boundary”
Global mean tropopause minima @ ~0.1 bar

Pressure [bar]

Temperature [K]

McClatchey+ (1972); Lindal+ (1983); Moroz & Zasova (1997); Moses+ (2005)
I know, I know…

Yes, dynamics modulates the tropopause pressure on Earth by $\pm x2$ and is important for latitudinal differences on Venus.

Here I’m concerned with a $1^{st}$ order global mean state set by radiative-convective equilibrium.
Why ~0.1 bar tropopauses?  
First, some wrong answers:

1) where the IR absorption by gas changes from pressure to Doppler broadening?

2) Where IR optical depth drops below ~1?  
(National Academy atmos. physicist)  
(but on the right track)
1. With $T$ and flux continuity, solve for IR optical depth $\tau_{IR}$ at (i) radiative-convective boundary (ii) 1 bar
2. Relate optical depth to pressure to get profile

How molecular absorption of IR comes in

\[ \tau = \tau_0 \left( \frac{p}{p_0} \right)^n \]

1 bar reference pressure

\( n = 2 \) in TROPOSPHERES & LOWER STRATOSPHERES:

- pressure broadening (molecules gain or lose energy during collisions so absorption over a wider range of photon energies)
- collision-induced broadening (collision-induced dipoles allow non-polar molecules to be greenhouse gases; also dimers or symmetry-breaking for forbidden transitions)

\( n = 1 \) in UPPER STRATOSPHERES (Doppler broadening)
Simple model is decent match to tropospheres and lower stratospheres of Titan, Venus, Earth + 4 giants


Unselfish cooperation in research: IDL source online
Ref: from Robinson & Catling (2013) Explanation of a common 0.1 bar tropopause in thick atmospheres of planets and large moons., Nature Geosci., in revision.
So, why the \(~0.1\) bar tropopause?

1. minima in $T$ occur at $\tau_{IR} \approx 0.05$ (enough IR transparency for shortwave heating to start dominance)

2. pressure broadening and/or collision-induced absorption relate optical depth to pressure

$$\tau \sim p^2 \Rightarrow p \sim \tau^{1/2}$$

3. atmospheres are IR-optically thick at 1 bar

$$\frac{p_{\text{tropo}}}{(p_0 = 1 \text{ bar})} \approx \left( \frac{\tau_{\text{tropo}} \sim 0.05}{\tau_0 \sim \text{a few to several}} \right)^{1/2}$$ is always $\sim 0.1$ bar

Ref: from Robinson & Catling (2013) Explanation of a common 0.1 bar tropopause in thick atmospheres of planets and large moons., *Nature Geosci.*, *in revision*. 
Gray optical depths at 1 bar are always \( \sim 2-10 \) for hypothetical Titan-like, Earth-like, and Jupiter-like worlds.

From: Robinson & Catling (2013), *Nature Geosci.*, in revision
Aside: Hot Jupiters are far from the norm

0.5-1% of all planets (Howard, 2013, Science)

So, I choose to focus on the other ones.

OCCUPY THE SOLAR SYSTEM:
Favor the 99% not the 1%!
What’s the condition for a stratospheric inversion to exist? It’s analytic

A tropopause minimum: differentiate and set to 0, gives:

\[ \tau_{tp} \approx \frac{1}{k_{strato}} \ln \left( \frac{F^\odot_{strato}}{F^\odot_{tropo} + F_i} \left( \frac{k_{strato}^2}{D^2} - 1 \right) \right) \]

\[ \approx 0.05 \]

where \( k_{strato} \) = \frac{\text{shortwave optical depth}}{\text{infrared optical depth}} \) of stratosphere

Only has a physical solution if \( k_{strato} > D \approx 1.7 \), usu. \( \approx 10^2 \)

Hence no global mean stratospheric inversion on Venus
THE USER MANUAL:

this “0.1 bar” tropopause minimum rule does not apply when there’s no minimum,

i.e., when the condition for a stratospheric inversion fails
e.g., pump up CO$_2$ on Earth; make moist stratosphere

Stratospheric inversion and tropopause minimum vanish, consistent with theory: At 64xCO$_2$, ~10x H$_2$O in stratosphere

$$k_{strato} = \frac{\text{shortwave optical depth}}{\text{infrared optical depth}}$$

goes from ~90 to < 2, the value needed for a tropopause minimum.

Hence no 0.1 bar tropopause minimum at high CO$_2$ because THERE IS NO MINIMUM
Extend to exoplanets?

~0.1 bar tropopause minima of Earth, Titan, giants from
(1) a common IR transparency requirement and
(2) a common pressure dependence on the IR opacity

TESTABLE HYPOTHESIS:

A ~0.1 bar tropopause minimum is an emergent “rule” arising from common physics that will apply to many exoplanets and exomoons with thick atmospheres

From: Robinson & Catling (2013) Explanation of a common 0.1 bar tropopause in thick atmospheres of planets and large moons., Nature Geosci., in revision.
Conclusions

• Atmospheres may not exist in bad impact erosion or thermal escape regimes
  - e.g., double whammy for M-dwarf planets

• No Super-Earth examples in our Solar System (notably present as exoplanets), but the bodies/models at least provide points of reference for exoplanet atmospheres.

• Atmospheres we know are: (1) reducing with organic hazes +/- poly-S, poly-P, or (2) oxidizing with sulfate hazes of variable radiative significance that can be high vis. albedo
  - Reasonable to expect to such hazes on similar exoplanets – can we see sulfate or $S_8$?
  - Reasonable to expect corresponding absorption / emission features of common reducing or oxidizing gas suites

• Structure:
  ▪ Reducing atmospheres we know have stratospheric inversions from methane+hazes
  ▪ Oxidizing atmospheres we know do (Earth) or don’t (Venus) have strat. inversions

• Stratospheric inversions require IR-optically thin stratospheres and absorbers strong in SW relative to IR. Combined with pressure-broadening or CIA => common ~0.1 bar level for tropopause minima. Testable hypothesis: Plausibly true in many exoplanet atmospheres

• Didn’t talk about evolution. But observing runaway Venuses (future Earths) states on exoplanets would clearly be an extremely valuable confirmation of theories.
References

ON IMPACT EROSION AND HYDRODYNAMIC ESCAPE OF ATMOSPHERES:


OVERVIEW OF THE CHEMISTRY, RADIATION AND EVOLUTION OF ATMOSPHERES:

RADIATION, ATMOSPHERIC STRUCTURE, and COMMON TROPOPAUSE MINIMUM LEVEL: