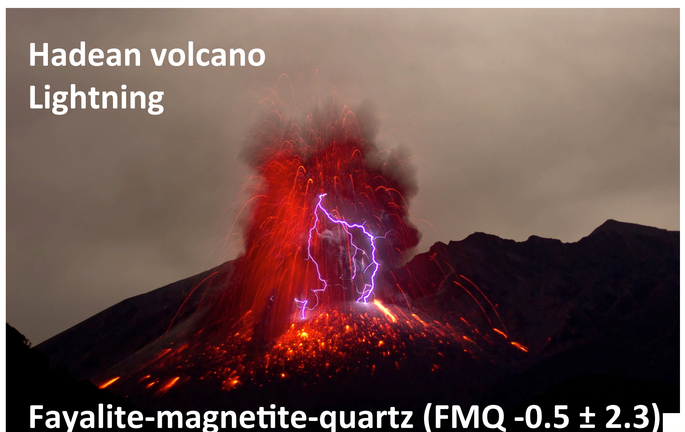
Origins: Chemistry that Could Not *Not* have happened

Steven Benner, Elisa Biondi, Hyo-Joong Kim

…in this geological context



Few reduced gasses gives little atmospheric production of RNA base precursors HCN, HCCCN, $NCNH_2$, NCCN …

NH_3 NH_3 H_2S CH_4 CO

H_2O N_2 SO_2 CO_2

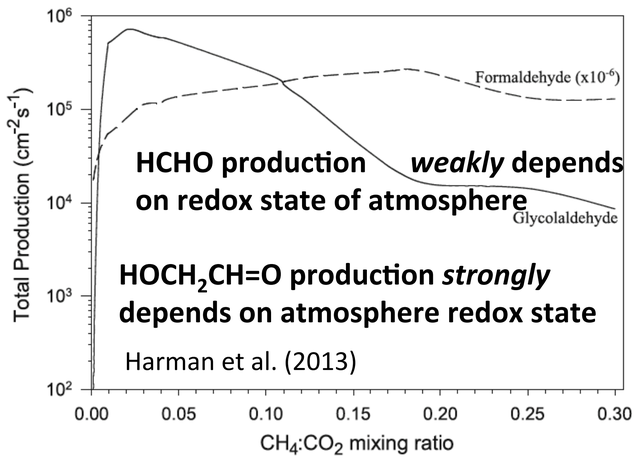
UV light
Electrical discharge

3 x 10^9 kg/yr (feedstock)

~ 10^3 kg/yr (catalytic)

$H_2C{=}O$ formaldehyde

$HOCH_2CH{=}O$ glycolaldehyde



Could not *not* have formed

Could not *not* have formed

With 5-carbon carbohydrates as an end point, the ratio of stabilized carbohydrates on Hadean surfaces is unknown. But they must have been there. *Chirality* remains unsolved.

Nature of phosphate on Hadean surfaces unknown. Here trimetaphosphate and/ or lüneburgite (see also Hud) giving inevitable chemistry.

Could not *not* have rained on to subaerial surfaces (unknown area). In basalt (pH 7-9), reverse of bisulfite addition leads unavoidably to higher carbohydrates captured by SO_2 and borate; these accumulate.

bleed C=O back

Bisulfite & borate mineral organic reservoirs.
~ 3 mg/m²/yr

ribose

Krishnamurthy et al. 2000
water, 25 °C

Ca^{2+} urea evap. H_2O
Kim & Kim 2019

glycosidic bond formation

A: ~ 17%
G: ~ 0.5%
C: ~ 7 %
U: ~ 0.5%

Kim & Benner 2017

Lüneburgite
Kim et al. 2016

Borate Ni^{2+}

silicates
Biondi et al. 2017

Oligomeric RNA

Cytosine Uracil Adenine Guanine

A. Partitioning of ions without **borate**

Ca^{2+} PO_4^{3-} ⇩ apatite

SO_4^{2-} Mg^{2+} ⇩ epsomite

B. Partitioning of ions with **borate**

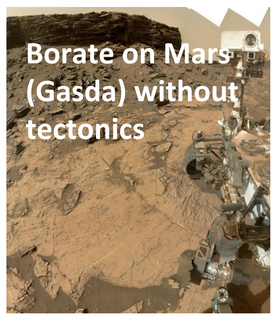
Ca^{2+} SO_4^{2-} ⟹ gypsum

PO_4^{3-} BO_3^{3-} Mg^{2+} ⟹ lüneburgite

phosphorylating agent for ribonucleosides

C. Lab separation of gypsum/lüneburgite

D. Natural lüneburgite from three locales



Where do nucleobases come from?

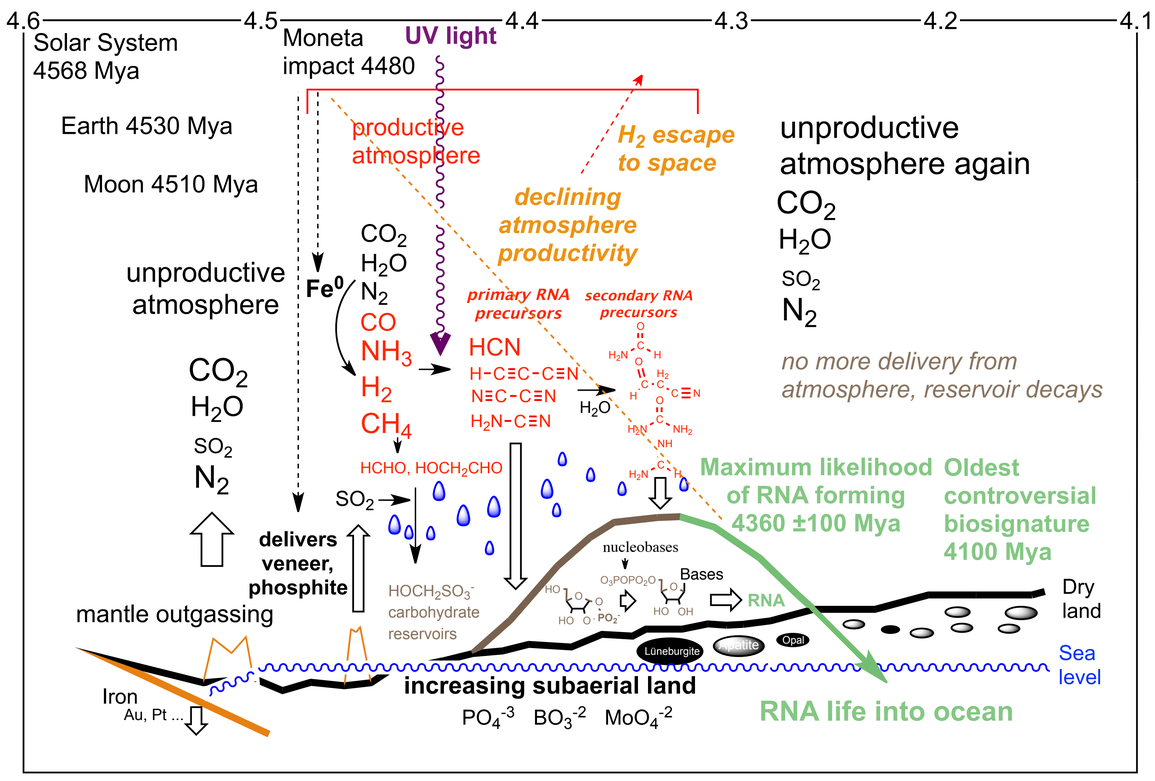
Easily made from RNA base precursors HCN, HCCCN, $NCNH_2$, NCCN …, but the absence of reduced gasses gives little atmosphere production of these precursors.

Earth **certainly** had mid-sized impacts that delivered molten iron to the Earth's atmosphere that could **not not** have transiently generated a productively reducing atmosphere. We have some choices starting at ~ 4.7 Ga and ending ~ 4.2 Ga.

- **Moneta** (~10^{23} kg, Moon-sized) delivering veneer siderophiles. Too small to re-open the core, created lava oceans, sterilizing. Resets clock and makes productive atmosphere that decays with $t_{1/2}$ ~ 40 million years.
- **Ceres**-sized (10^{21} kg) sterilizing/non-sterilizing boundary; reducing atmosphere without resetting clocks. A still smaller 10^{20} kg
- **Vesta**-sized (10^{20} kg) impactor, not sterilizing, productive atmosphere decays with $t_{1/2}$ ~ 40 thousand years.

Productive atmosphere supported RNA formation, also needed to feed first RNA-based Darwinism.

Thus, the most probably relevant impactor is the last sterilizing impactor.



Conclusion. Relatively direct way for RNA-based Darwinism to emerge 4.35 ± 0.10 Ga.

Amount of subaerial land for its chemistry is unknown.

Benner, S. A., Bell, E. A., Biondi, E., Brasser, R., Carell, T., Kim, H.-J., Mojzsis, S. J., Omran, A., Pasek, M. A., Trail, D. (2019) When did Life Likely Emerge on Earth in an RNA-First Process? ChemSystChem doi:10.1002/syst.201900035
Benner, S.A., Kim, H.J. (2019) Prebiotic chemistry that could not not have happened. *Life* **in press**