Stability of Atmospheric Redox States of Early Mars Inferred from Time Response of the Regulation of H and O Losses

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Abstract:

Atmospheric losses including escapes to space and depositions to the surface play an essential role in the evolution of the Martian surface environment. Especially, a ratio of total losses of hydrogen and oxygen from the atmosphere is crucial to determine its atmospheric redox state. In the condition that H and O losses originate from H2O, an atmospheric redox state remains the same if the ratio is 2:1, otherwise it is driven into oxidizing or reducing. It was shown by McElroy. (1972) that Jeans escape flux of H and H2 and nonthermal escape flux of O were regulated to be in the ratio of 2:1 in a converged model of present-day Mars, which is called "self-regulation". Whether or not the self-regulation works in real atmospheres depends on its timescales, but time responses of the self-regulation are not well understood in different atmospheric conditions.

Here we study time responses of the self-regulation in different atmospheric conditions and discuss the stability of atmospheric redox states. We use a 1D time-dependent photochemical model for various atmospheric conditions and parameters, such as atmospheric CO2 pressure, surface temperature and O escape rate.

We find that the self-regulation timescale is essentially controlled by the net redox balance (pOx [mbar] = 2pO2 – pCO – pH2) in a converged state. The timescale gets longer as |pOx| increases, which suggests that redox-neutral atmospheres have the shortest timescale. We also find that the self-regulation can be classified into two regimes. First regime is the same as the one explained by Liu and Donahue. (1976), which tends to work in oxidizing atmospheres (pOx > 0) including present-day Mars in a way that H escape changes to reach the regulated state following a change in H2 transportation from the lower to upper atmosphere. Second one is likely to work in thicker and reducing atmospheres (pOx < 0) over a relatively long timescale. The regulation occurs dominantly by changes in CO abundance in the lower atmosphere. These results imply that thicker atmospheres in early Mars are less redox-stable than present-day Mars. Our model calculations also indicate that CO-dominated atmosphere of about 100 mbar might be possible at ~3 Ga. We finally discuss the redox stability of H2-rich CO2 atmosphere of early Mars.

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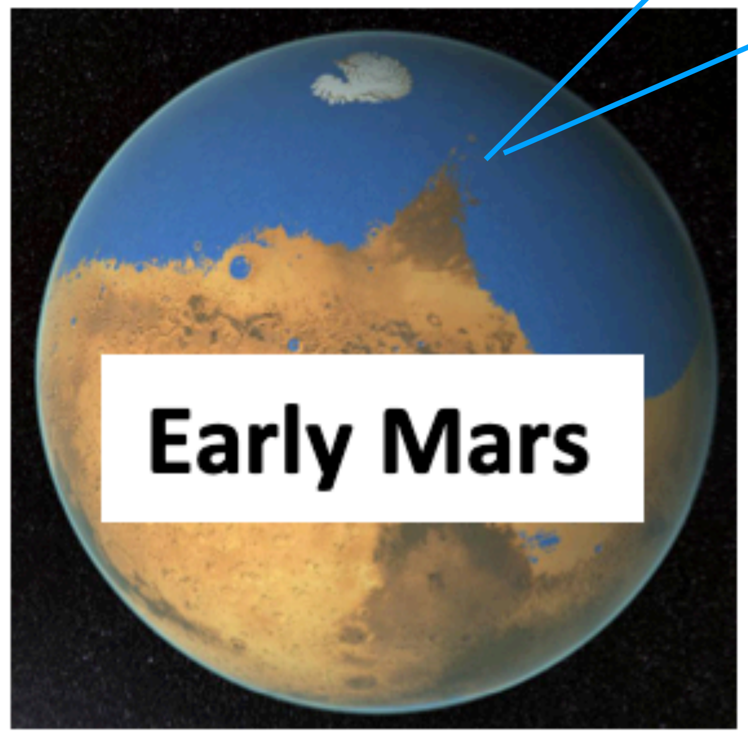
The effect of the ratio of H & O losses

- How did H_2O on early Mars go away?

H : O = 2 : 1 ?



Credits: NASA/GSFC

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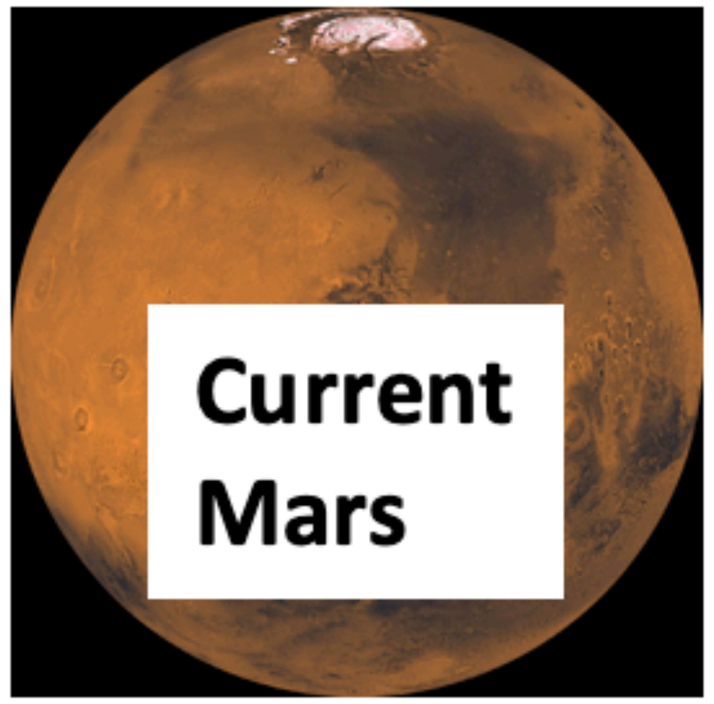


Credits: NASA

- The ratio of total H and O outfluxes

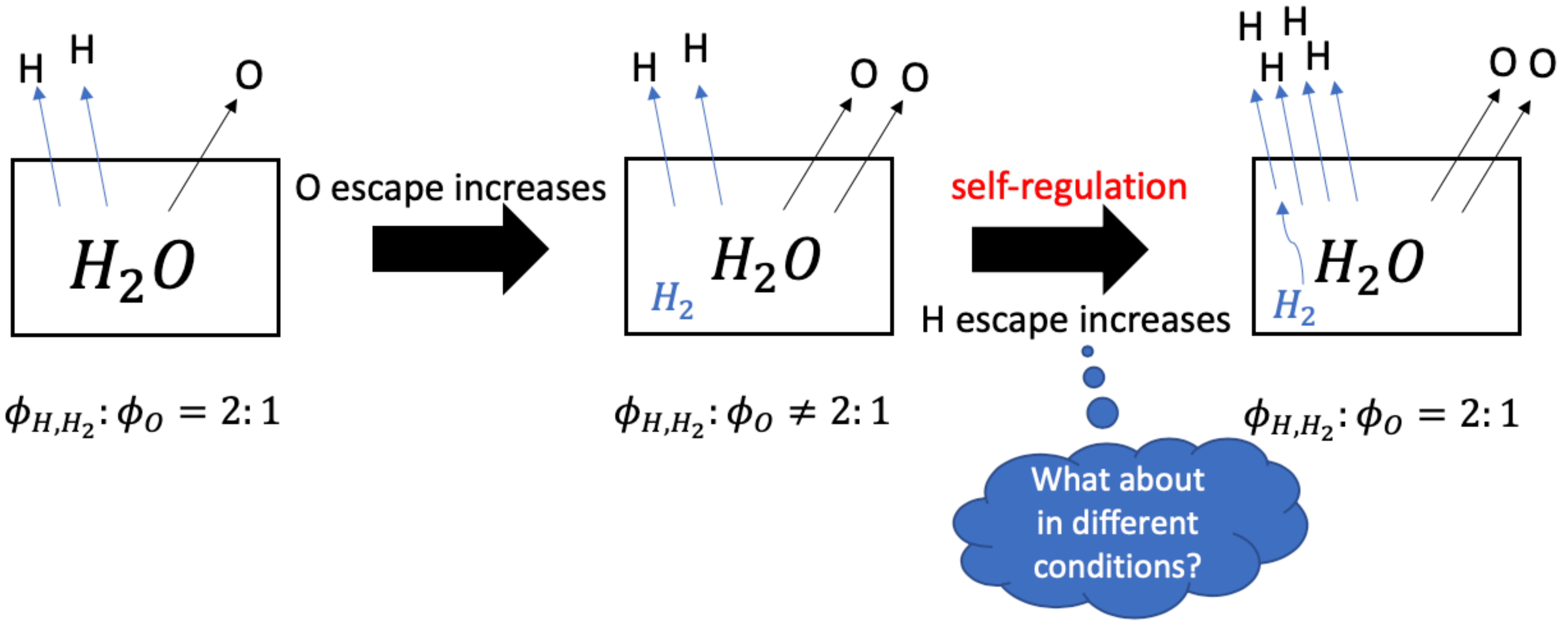
$\Phi_{total\ H} > 2\Phi_{total\ O}$ → Oxidizing atmosphere

$\Phi_{total\ H} < 2\Phi_{total\ O}$ → Reducing atmosphere

- Remain the same?
- More reducing?
- More oxidizing?

What is Self-regulation of H & O losses?

- Jeans escape flux of H and H_2 and nonthermal escape flux of O are regulated to be in the ratio of 2:1 in a converged model of present-day Mars.
  [McElroy, 1972; Liu & Donahue, 1976]



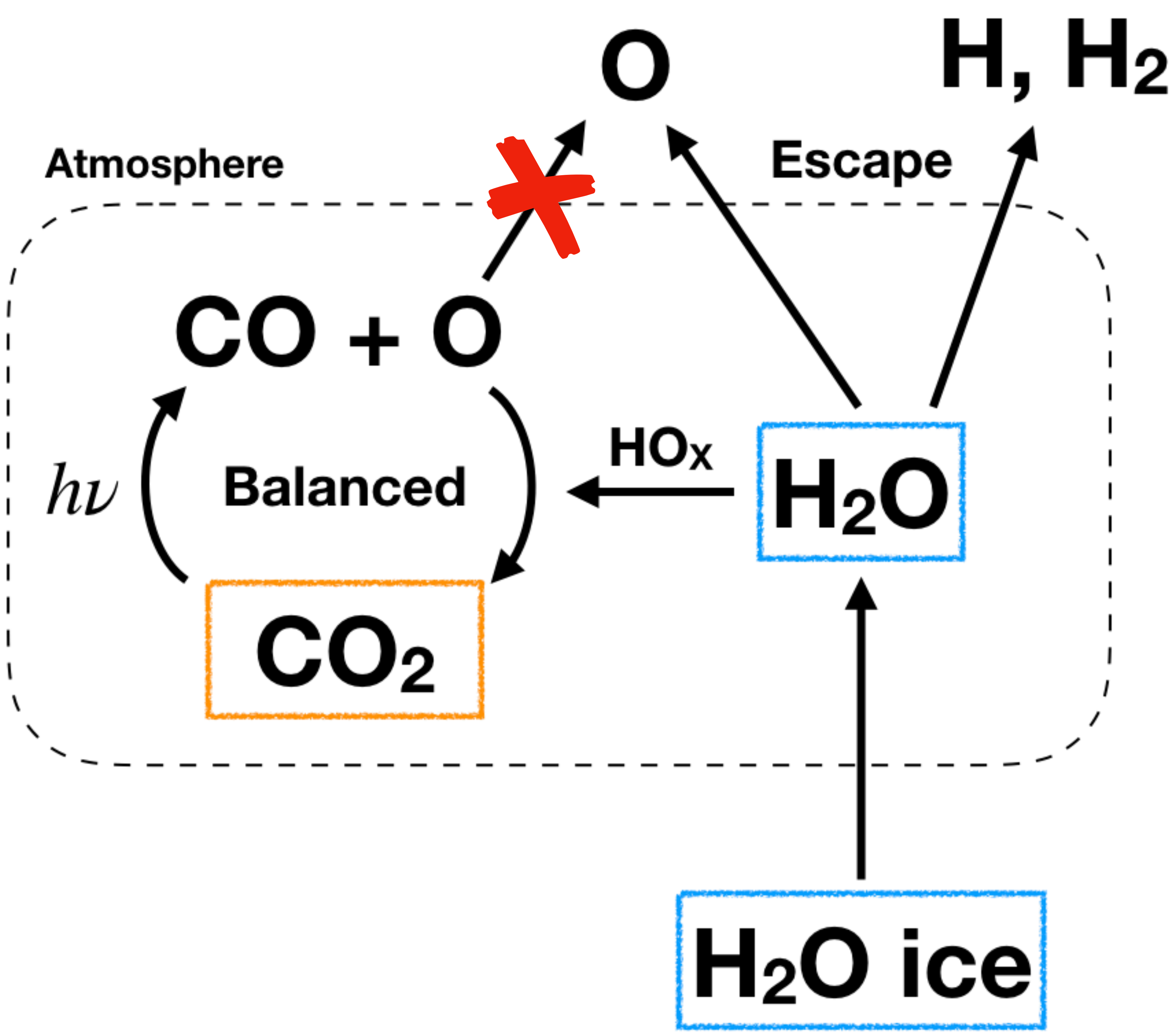
Self-regulation is not well understood in different conditions.

Two essential factors in other atmospheric conditions

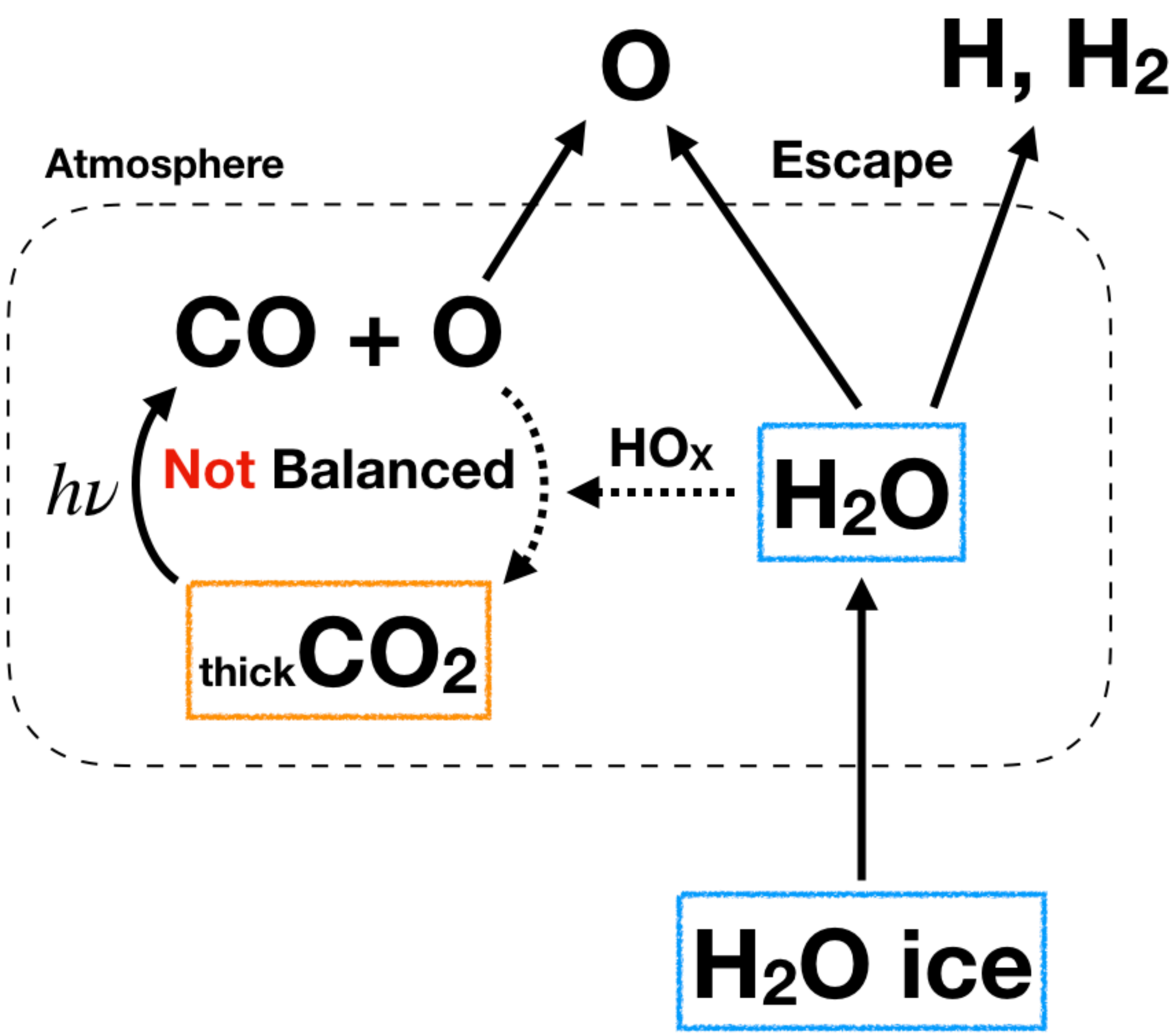
① **CO_2 stable or CO-runaway ?**

② Self-regulation timescale

CO_2 stable



CO-runaway

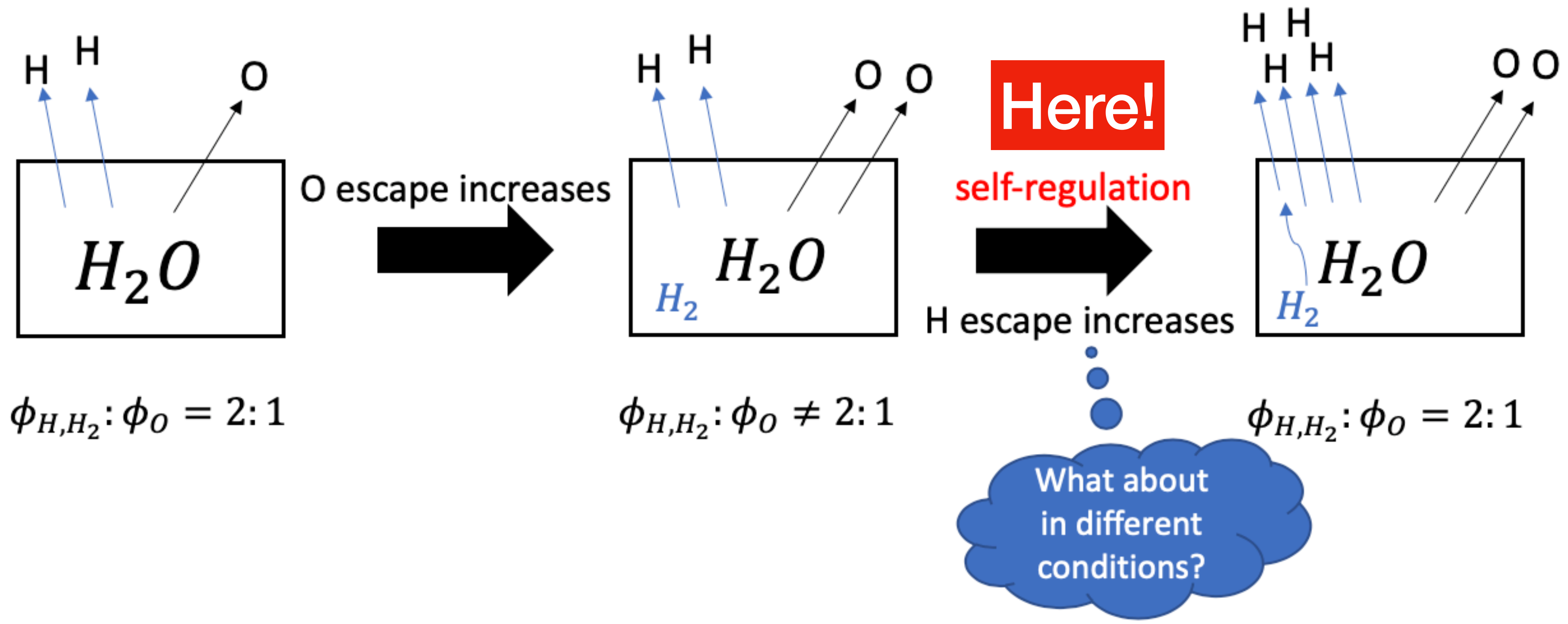


Two essential factors in other atmospheric conditions

① CO_2 stable or CO-runaway ?

② Self-regulation timescale

Shorter timescale → Redox state: more stable



Purpose

To investigate time responses of the self-regulation in different atmospheric conditions from present-day Mars

↓ **Timescales of the self-regulation**

Stability of atmospheric redox states in early Mars

1D-Photochemical model

modified after Chaffin et al. (2017)

❖ Basic model information

- Initial pCO_2 = 6.3mbar~3bar
- 13 species(C,H,O-bearing species)
- 52 reactions

❖ Boundary condition

Upper	O	$\Phi_{O_{esc}} = 1.2\times10^{8}\ cm^{-2}s^{-1}$
	H, H_2	Jeans' Escape
Lower	reactive species	deposition velocity $v_{dep} = 0.02cm\ s^{-1}$ [Zahnle et al., 2008]
	CO_2	Not fixed

Reactive species: O_3, H_2O_2, O,H,OH,HO_2,O1D

❖ Temperature profile

T_{surf} = 200-280K

Ex) CO_2:10mbar

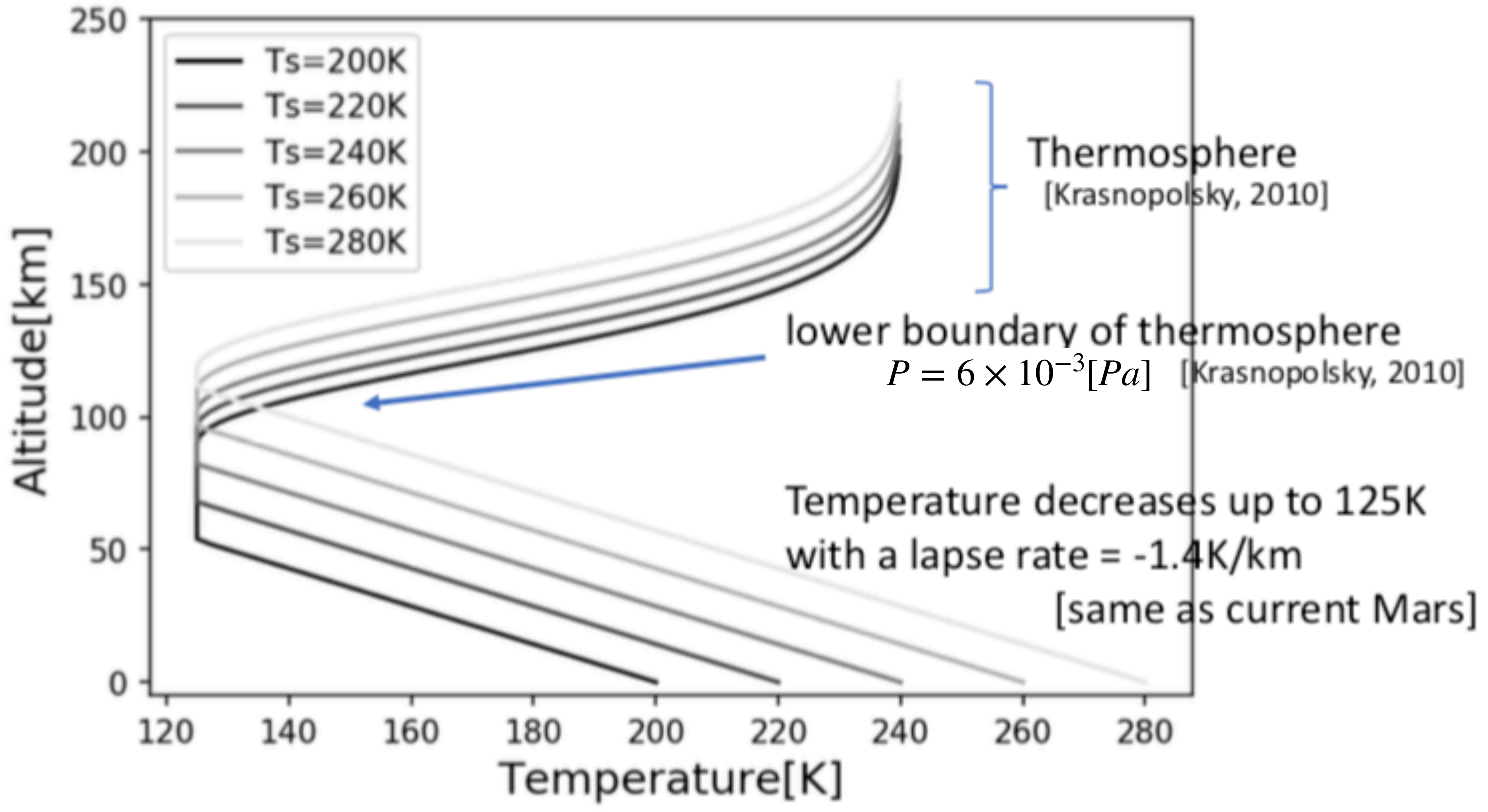


Fig. Vertical temperature profile.

❖ Water vapor profile

- Relative humidity is fixed at 0.22 near the surface
- Following the saturation water vapor curve above

Definition of Self-regulation timescale

At time zero, oxygen escape increases by a factor of two from a steady state, we define "timescale" of self-regulation as how long it takes to reach $\varepsilon < 0.01$.

At time=0

$$\Phi_{O_{esc}} \rightarrow 2\Phi_{O_{esc}}$$

② **Self-regulated state**

$$\varepsilon = \left| 2 - \frac{\Phi_{\mathrm{total\ H}}}{\Phi_{\mathrm{total\ O}}} \right| < 0.01$$

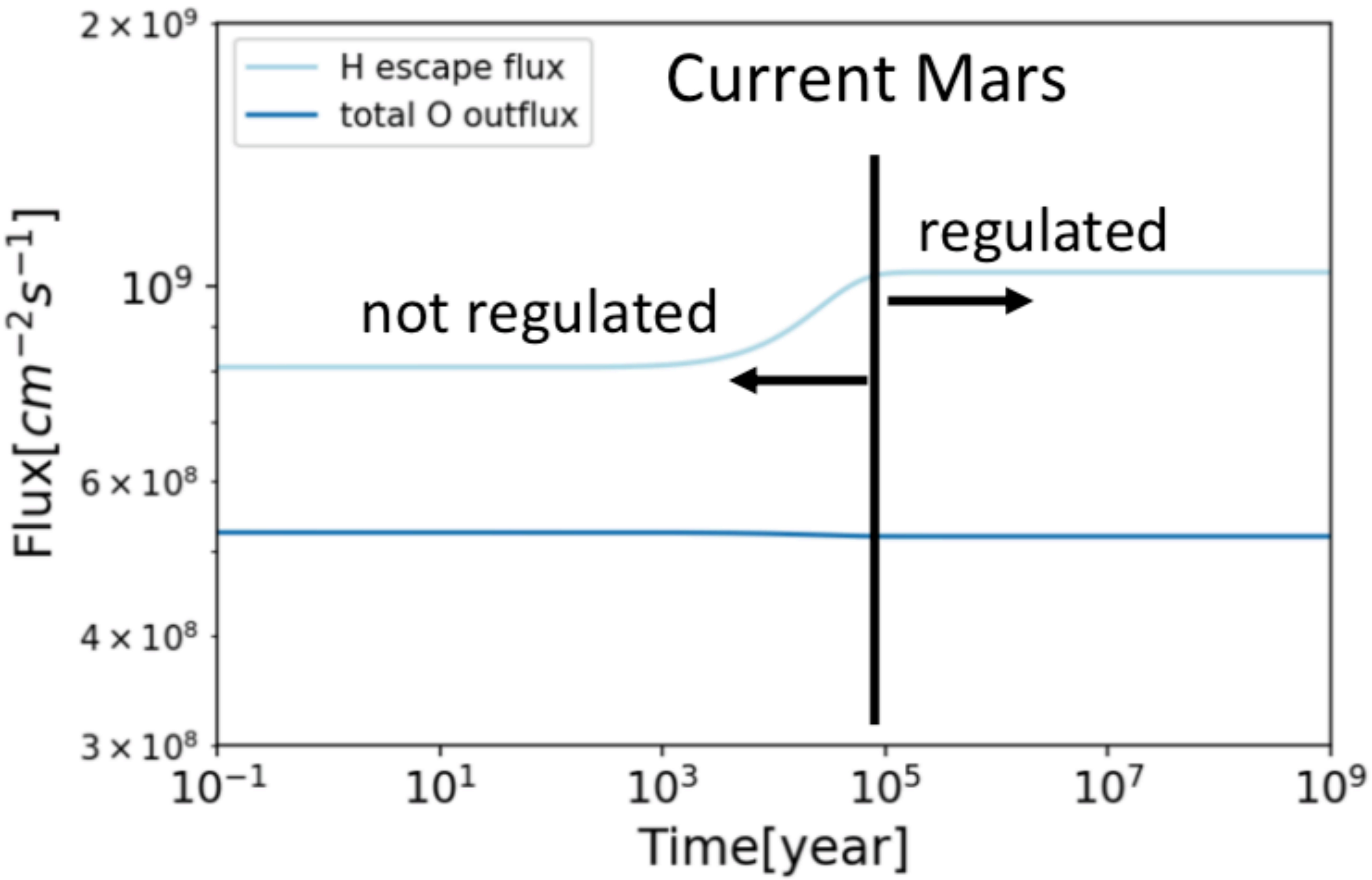
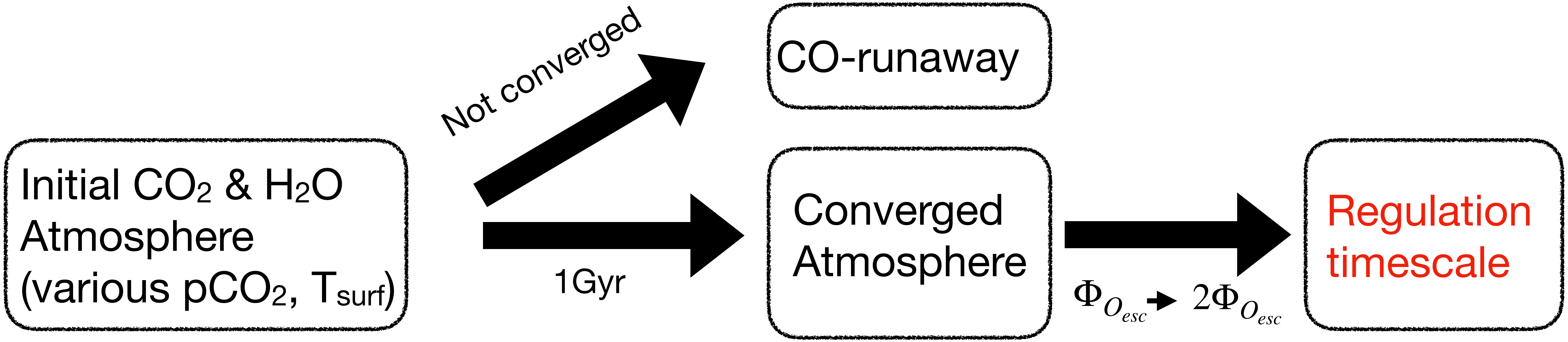


Fig. $\Phi_{O_{esc}} = 1.2\times10^8 \rightarrow 2.4\times10^8\ cm^{-2}s^{-1}$ at time zero under current Martian atmospheric condition

Summary of what we did

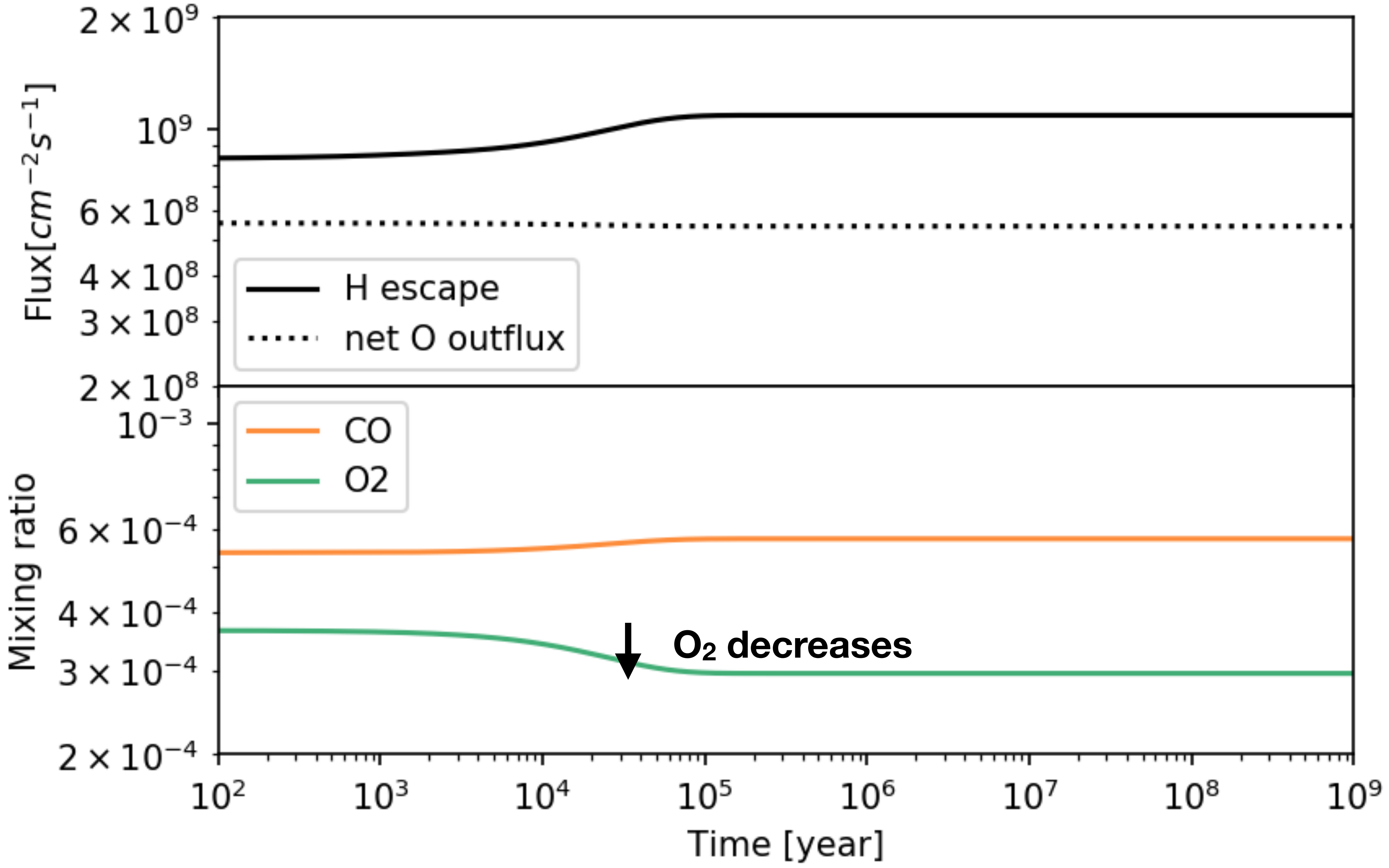


Result 1

Two Regulation regimes

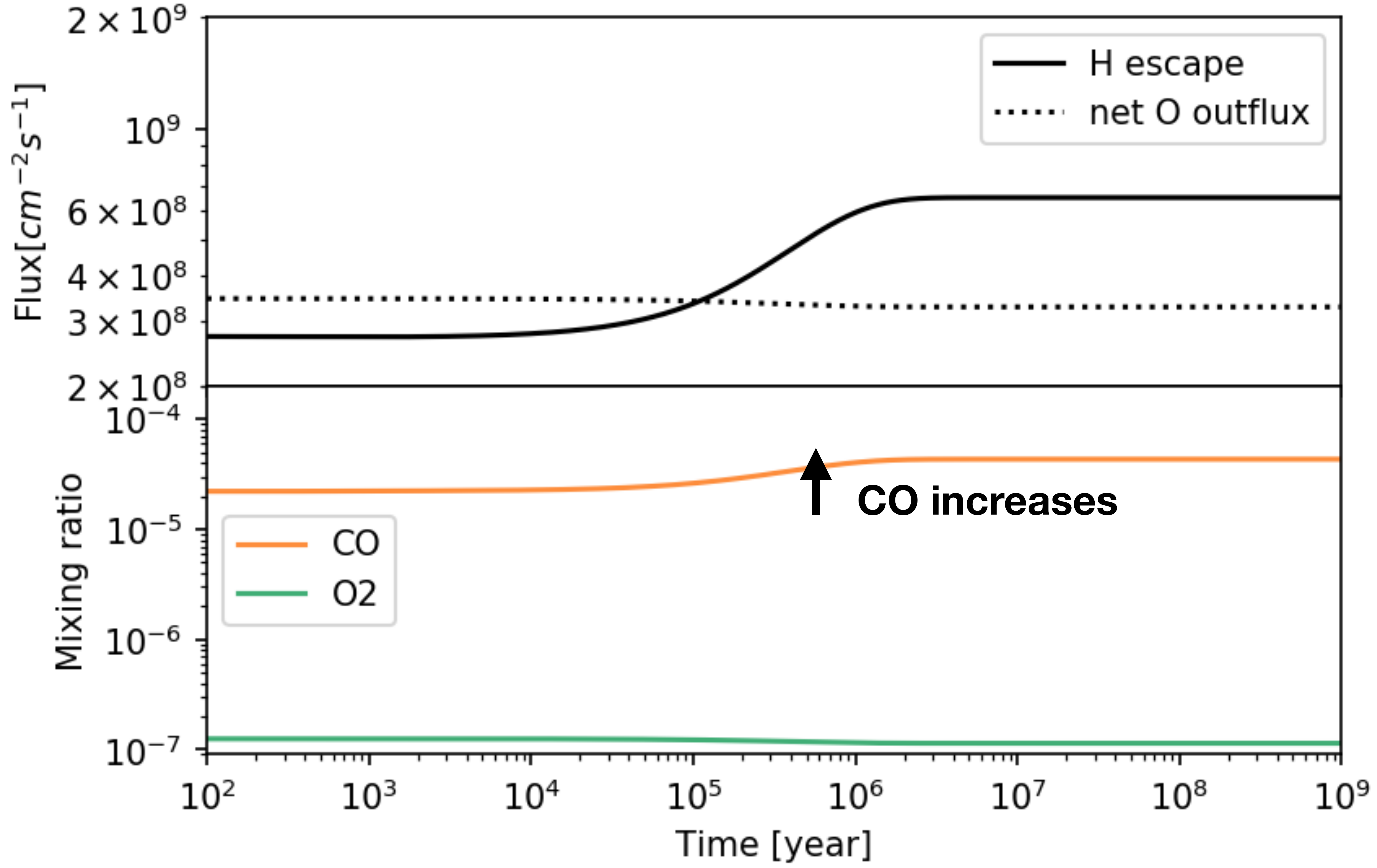
Regime 1

Ts: 210K
CO2: 10mbar



Regime 2

Ts: 260K
CO2: 1bar



H + O_3 -> OH + O_2 ↓
H ↑
H +HO_2 -> H_2 + O_2 ↑
H escape ↑

Timescale

$\propto total\ O_2\ /\ \Phi_{O_{esc}}$

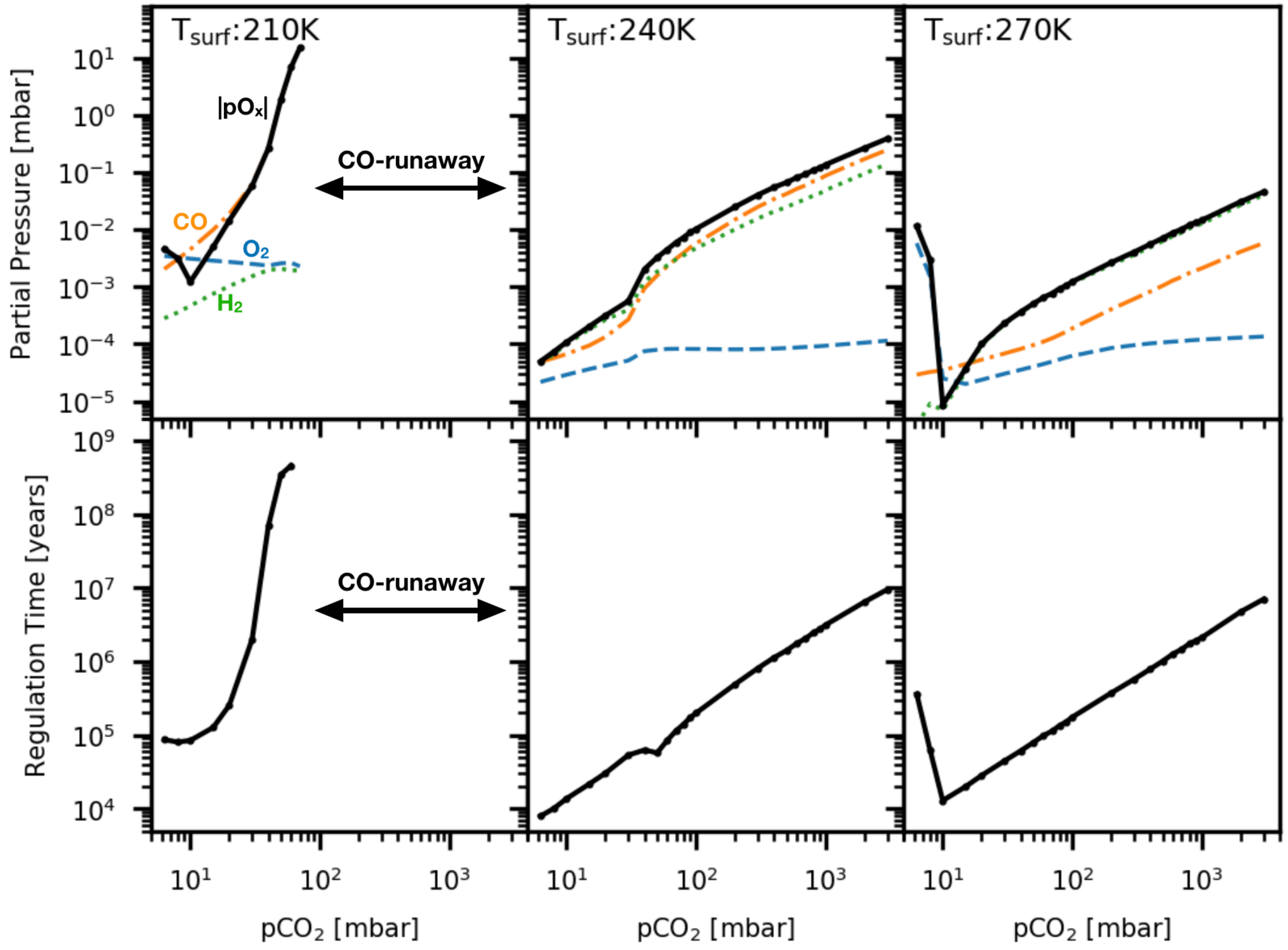
CO + OH -> CO_2 + H ↑
H +HO_2 -> H_2 + O2 ↑
H escape ↑

Timescale

$\propto total\ CO\ /\ \Phi_{O_{esc}}$

Result 2

Self-regulation timescales



Net oxidation:

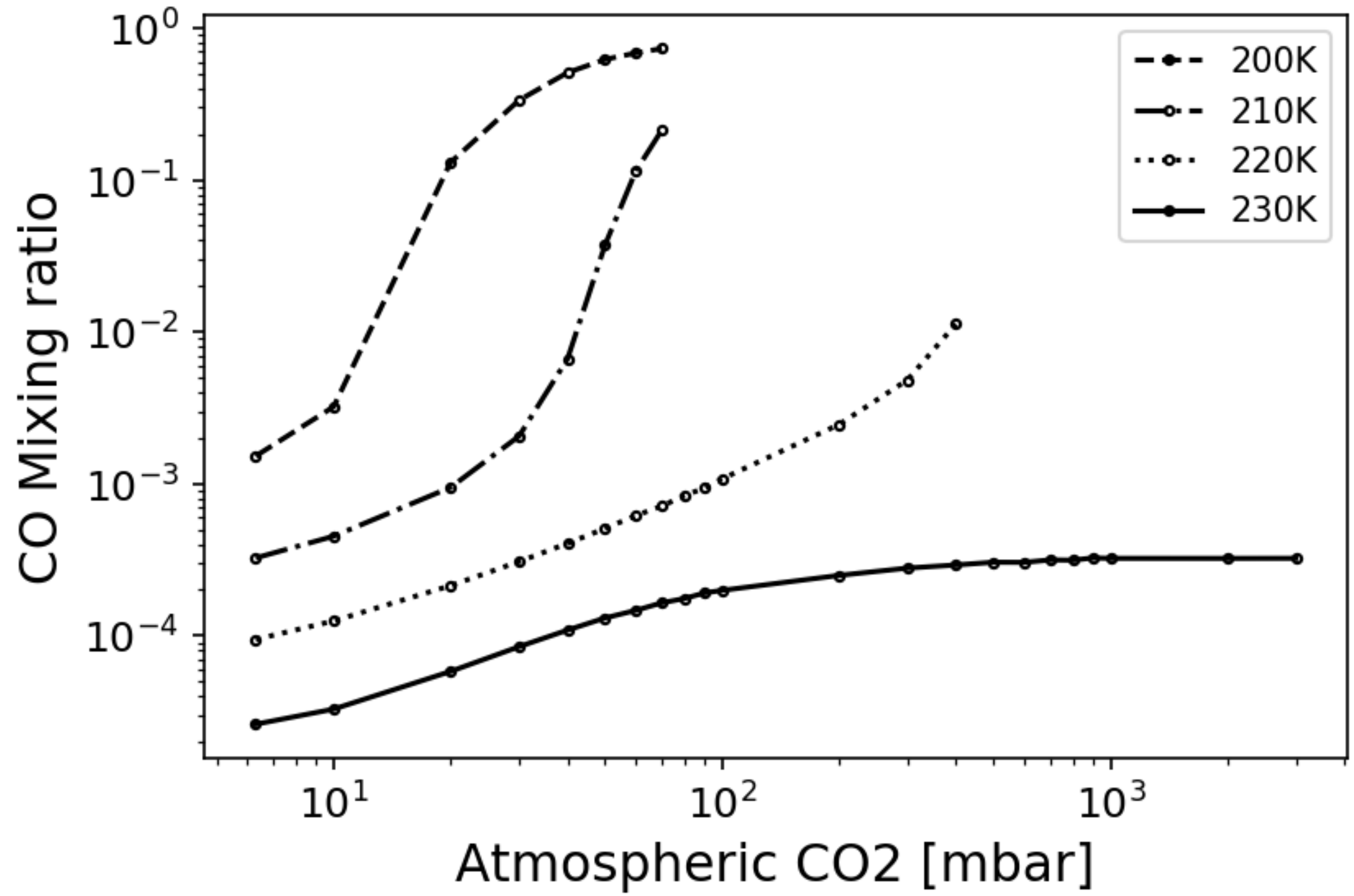
$$pOx = 2pO_2 - pCO - pH_2$$

[Zahnle et al., 2008]

- **Self-regulation timescale is likely to be controlled by |pOx|.**
- **The atmosphere with more CO_2 on early Mars has the longer timescale than the present.**

Discussion 1

CO possibility on early Mars

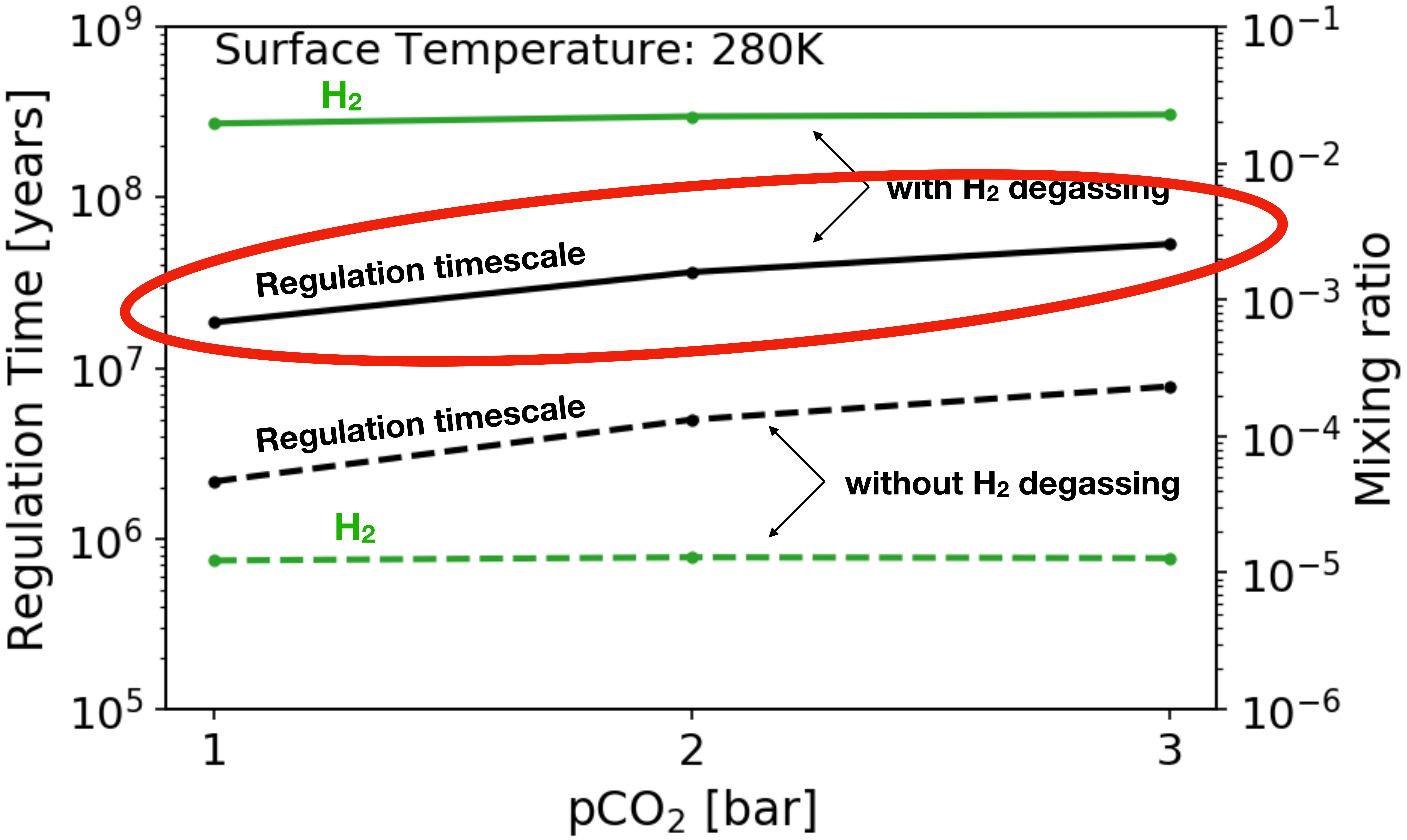


- **CO2 atmosphere of 100mbar is converted to CO-main atmosphere in several hundred million years with Tsurf=200K in our calculation.**
- **CO-main atmosphere of about 50-150mbar might be possible around 3 Ga**

[Kurokawa et al., 2017; Kasting, 1991; Feulner, 2011]

Discussion 2

Implication for H_2-rich CO_2 atmosphere scenario of early Mars



H_2 degassing rate:

$1 \times 10^{11} cm^{-2} s^{-1}$

[Batalha et al., 2015]

The redox state of H_2-CO_2 atmosphere is less stable than current Mars

-> The imbalance of H and O losses may have a large impact on its redox state.

Summary

- We calculated self-regulation timescales for various atmospheric conditions.
- The regulation timescale is likely to be controlled by net oxidation(|pOx|)
- Denser CO_2 atmospheres on early Mars are less redox-stable (longer timescale) than present-day Mars
- CO-main atmosphere might be possible around 3 Ga.
- The imbalance of H and O outfluxes ratio in H_2-CO_2 atmosphere might have a large effect on its H_2 abundance.