

# High-Pressure and High-Temperature Behavior of Venus's Atmosphere Near the Surface: A Thermo-Gravitational Study

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## Abstract

Though Venus's atmospheric conditions and composition have been directly measured, the composition of the Venus lower atmosphere near the surface is generally still poorly known. It was extrapolated from observational data at other altitudes by assuming the constancy of elemental composition without condensation (Krasnopolsky 2007). Both in-situ measurement and remote-sensing observations reveals the most abundant components that exceed the mixing ratio of  $10^{-4}$  to be  $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{SO}_2$  (Bezard & de Bergh 2007, JGR 112, E04S07). Water and formation of photochemical  $\text{H}_2\text{SO}_4$  — and condensation of cloud-forming  $\text{H}_2\text{SO}_4$  — is only important at higher altitudes (Krasnopolsky 2012, Icarus 191, 25). In this work, the balancing of chemical-gravitational-thermal diffusive potentials for the ternary mixture of  $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{SO}_2$ , which represent the neutral Venusian lower atmosphere near the surface, is addressed to obtain the composition grading and to evaluate the tendency toward supercritical density-driven separation of  $\text{CO}_2$  and  $\text{N}_2$  (Lebonnois & Schubert 2017, Nat. Geosci. 10, 473). Even though dynamic atmospheric systems, including advective mixing, are more realistic, the static cases evaluated in this work provide stationary states where every dynamic process would eventually proceed to. Hence, our modeling is of a limiting case of the systems of interest, which could help explain some indications of compositional grading. The CRYOCHEM equation of state, which has been successfully applied in describing phase equilibria of Titan's atmosphere and the surface liquid (Tan & Kargel 2018, Fluid Phase Equilib. 458, 153), as well as that involving solid phases on Pluto's surface (Tan & Kargel 2018, MNRAS, 474, 4254), is used in this work on the supercritical Venus's lower atmosphere. In the absence of direct measurement of composition of the lower atmosphere, as well as no lab evidence of  $\text{CO}_2$  and  $\text{N}_2$  separation under Venusian surface conditions (Lebonnois et al. 2020, Icarus 338, 113550), the results from this study may at least introduce some new concepts that would entail some tendency for molecular fractionation.



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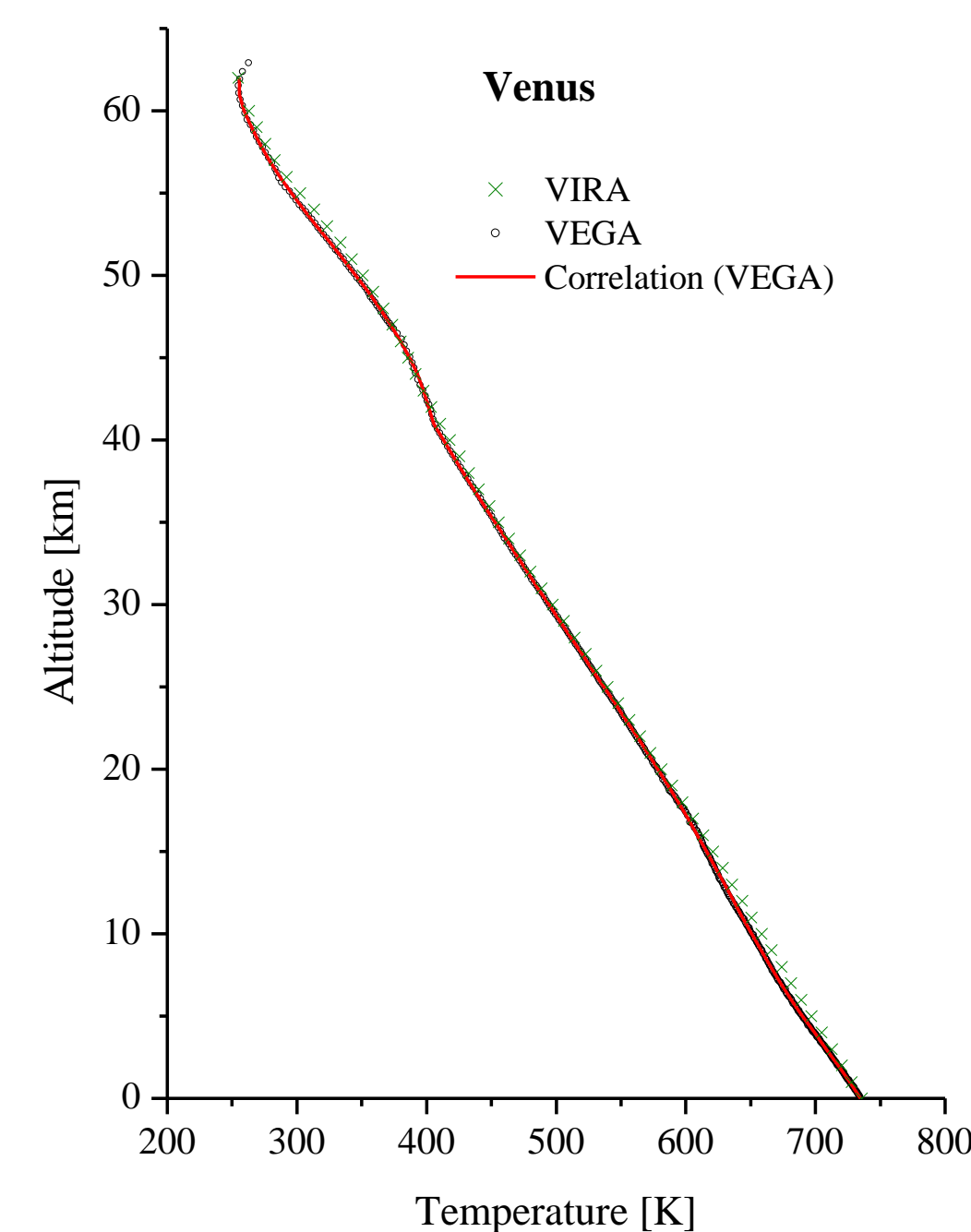
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## Venus's atmosphere: CO<sub>2</sub> / N<sub>2</sub> / SO<sub>2</sub>

- The temperature profile of the atmosphere at low latitudes was measured by VEGA (*Linkin et al., Kosmich. Issled. 1987, 25, 659*) and modeled by VIRA (*Seiff et al., Adv. Space. Res. 1985, 5, 3*).
- The temperature profile  $T(h)$  by VEGA is correlated using polynomials:

$$T(h) = \sum_{i=0}^8 c_i (h - h_0)^i \quad [\text{K}]$$

in two parts corresponding to the altitude ranges of  $h = 0$ -41 km ( $h_0 = 0$ ) and 41-62 km ( $h_0 = 41$ ) as seen in the figure. The correlation has an accuracy of 0.08%. The constants  $c_i$  is tabulated below the figure.



$i$	Altitudes	
	0 – 41 km	41 – 62 km
0	734.863249	406.773623
1	-7.642702	-6.755073
2	-0.71474	2.42324
3	0.12952	-0.931572
4	-0.009494	0.15933
5	3.553979E-4	-0.015415
6	-7.160138E-6	8.545841E-4
7	7.310104E-8	-2.511086E-5
8	-2.897589E-10	3.027652E-7

- Total composition of CO<sub>2</sub>/N<sub>2</sub>/SO<sub>2</sub> in the atmosphere: {96.45%, 3.54%, 0.014%} is assumed at the altitude of 41 km. The mole fraction of N<sub>2</sub> is from *Oyama et al. (JGR 1980, 85, 7891)*, and SO<sub>2</sub> is from *Arney et al. (JGR Planets 2014, 119, 1860)*.
- Calculations were started from the altitude of 41 km down to the surface as well as up to the altitude of 62 km (near tropopause).
- The gravity of Venus is from VIRA as a linear function of the altitude ( $h$  in km):  
 $g(h) = 8.8691 - 0.00289 h \quad [\text{m/s}^2]$

## Thermo-gravitational effects

- In a stable phase  $\alpha$  that is subject to gravity and thermo-diffusion:  
$$d\mu_i^\alpha = M_i g dh - \frac{Q_i}{T} dT \quad i = 1, \dots, N$$
where:  
 $\mu_i$  – chemical potential of component  $i$   
 $N$  – the number of components  
 $T$  – absolute temperature  
 $M_i$  – molar mass of component  $i$   
 $g$  – gravity  
 $h$  – altitude  
 $Q_i$  – heat due to diffusion of component  $i$  (*Firoozabadi et al. AIChE J. 2000, 46, 892*):  
$$\frac{Q_i}{RT} = -\frac{\bar{U}_i^R}{4RT} + \frac{1}{4RT} \sum_j \frac{\bar{v}_i}{z_j \bar{v}_j} \sum_j z_j \bar{U}_j^R$$
  
 $R$  – gas constant  
 $\mathbf{z} = \{z_i\}$  – composition ( $\sum z_i = 1$ )  
 $\bar{U}_i^R$  – partial molar residual internal energy of component  $i$   
 $\bar{v}_i$  – partial molar volume of comp  $i$
- For calculations on the vertical profiles of fluid properties, the applied algorithm is the same as that in the AGU Fall Meeting 2020 with the application for Titan's subsurface liquid (*Tan & Kargel, paper # P067-0002*).

## Without thermal diffusion

- To see whether the thermal diffusion is significant,  $Q_i$  is set to zero ( $Q_i = 0$ ). This is called the zeroth-order approximation or the passive thermal diffusion.

## Without SO<sub>2</sub>: binary CO<sub>2</sub>/N<sub>2</sub>

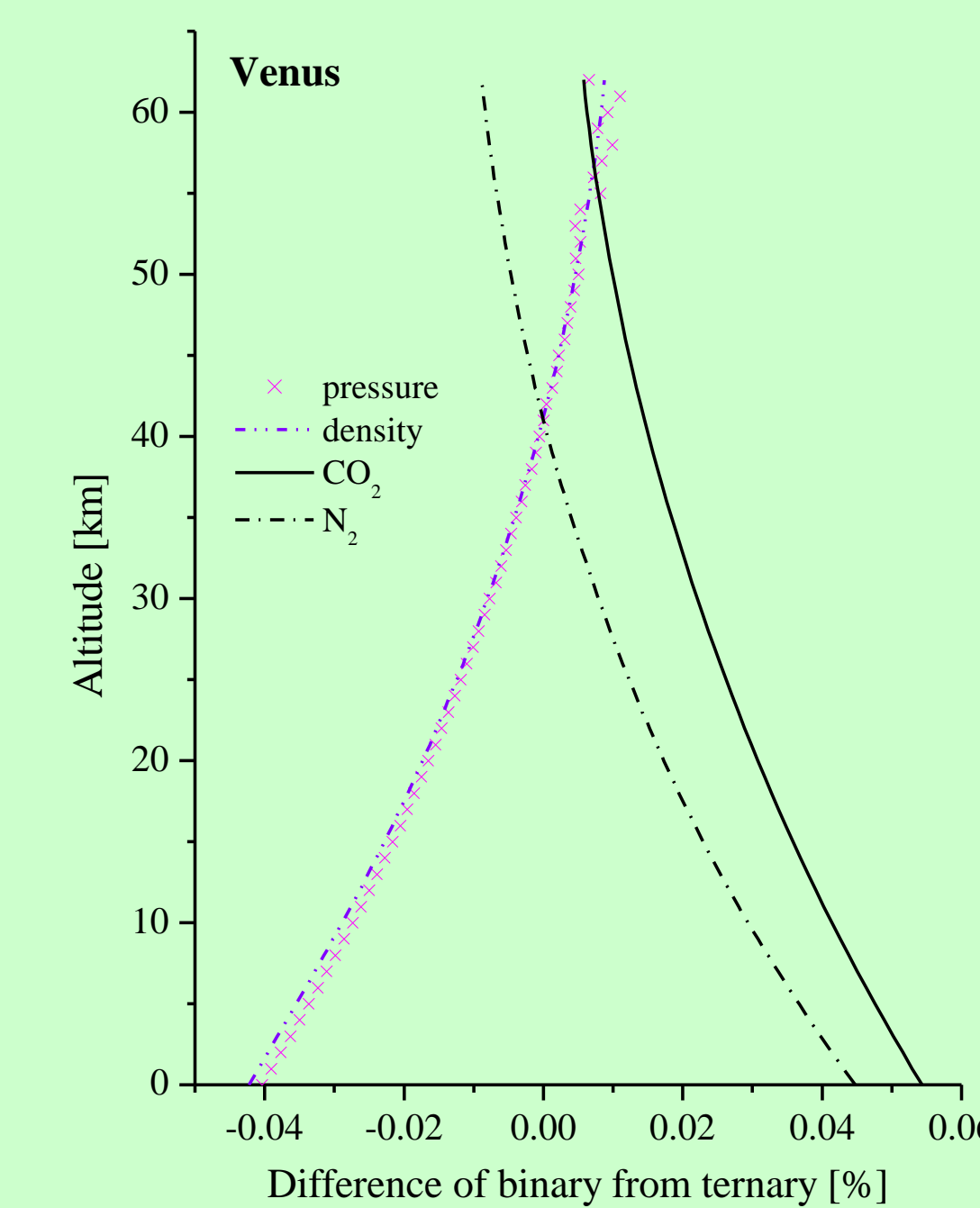
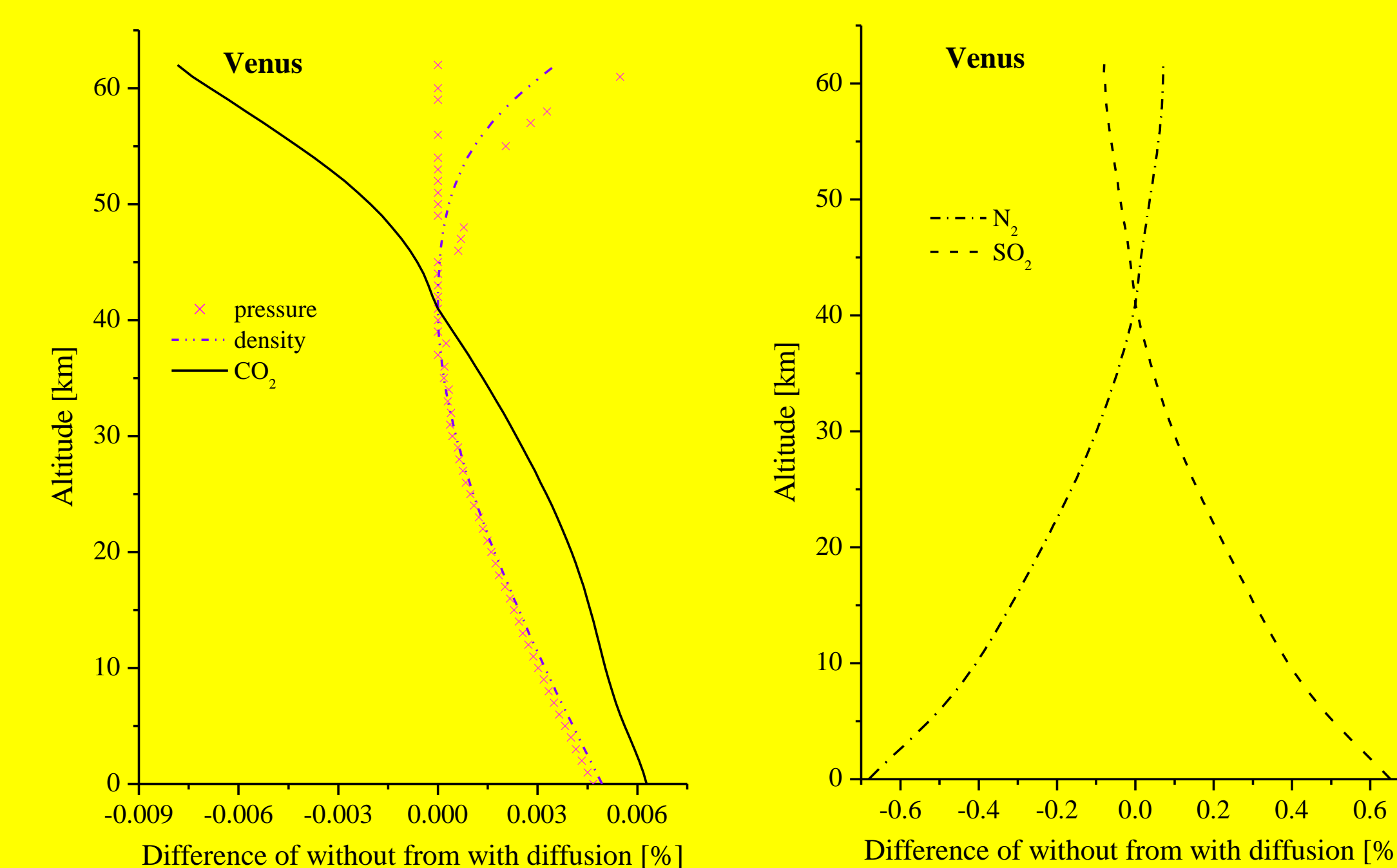
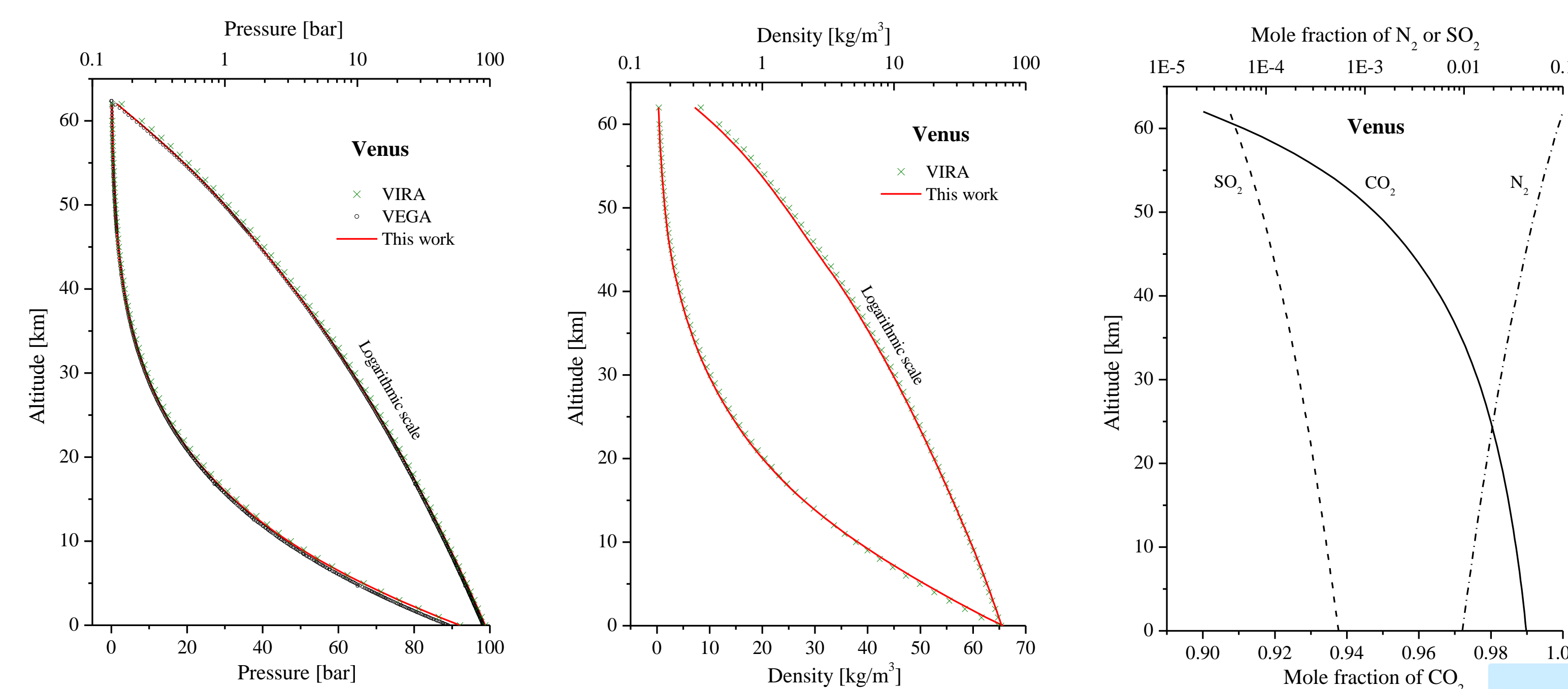
- Due to the tiny mole fraction of SO<sub>2</sub>, it is of modeling interest to see the effect of the inclusion of SO<sub>2</sub>.

## Equation of state

- The equation of state (EOS) used in the calculation is the PC-SAFT (*Gross & Sadowski, 2001, Ind. Eng. Chem. Res., 40, 1244*).

## Results and Discussion

- The resulting pressure profile agrees well with both VEGA and VIRA, particularly in the higher altitudes with VEGA and lower latitudes with VIRA.
- The resulting density profile agrees well with VIRA.
- The resulting compositional grading due to the thermo-gravitational effects reveals that CO<sub>2</sub> and SO<sub>2</sub> decrease while N<sub>2</sub> increases with altitudes, which implies the dominance of gravitational effects over the thermal diffusion counterpart as N<sub>2</sub> is the lightest component.

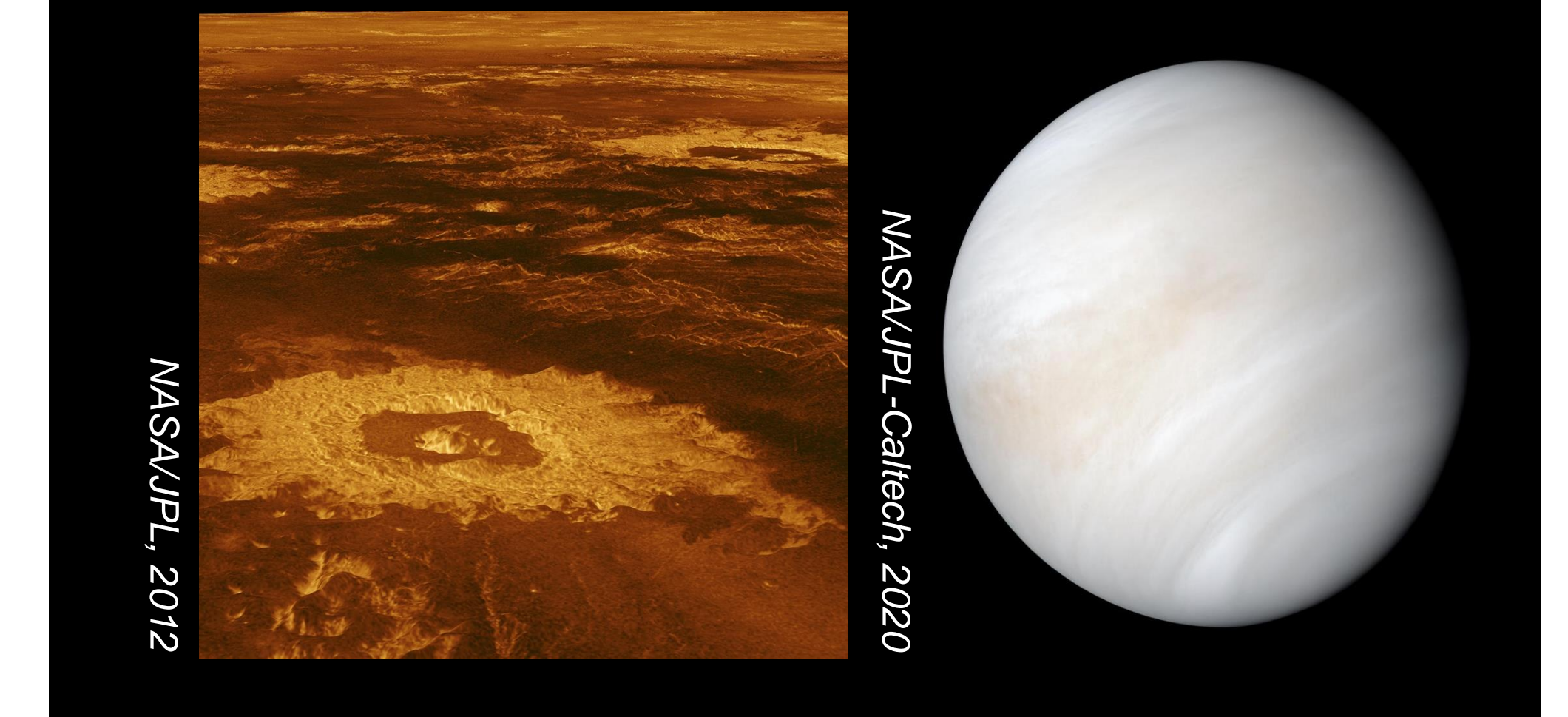


The omission of thermal diffusion makes:

- The pressure and density to overestimate by 0.005% on the surface.
- CO<sub>2</sub> to underestimate by 0.008% at the altitude of 62 km and overestimate by 0.006% on the surface.
- N<sub>2</sub> and SO<sub>2</sub> to underestimate and overestimate by about 0.65% on the surface, respectively.

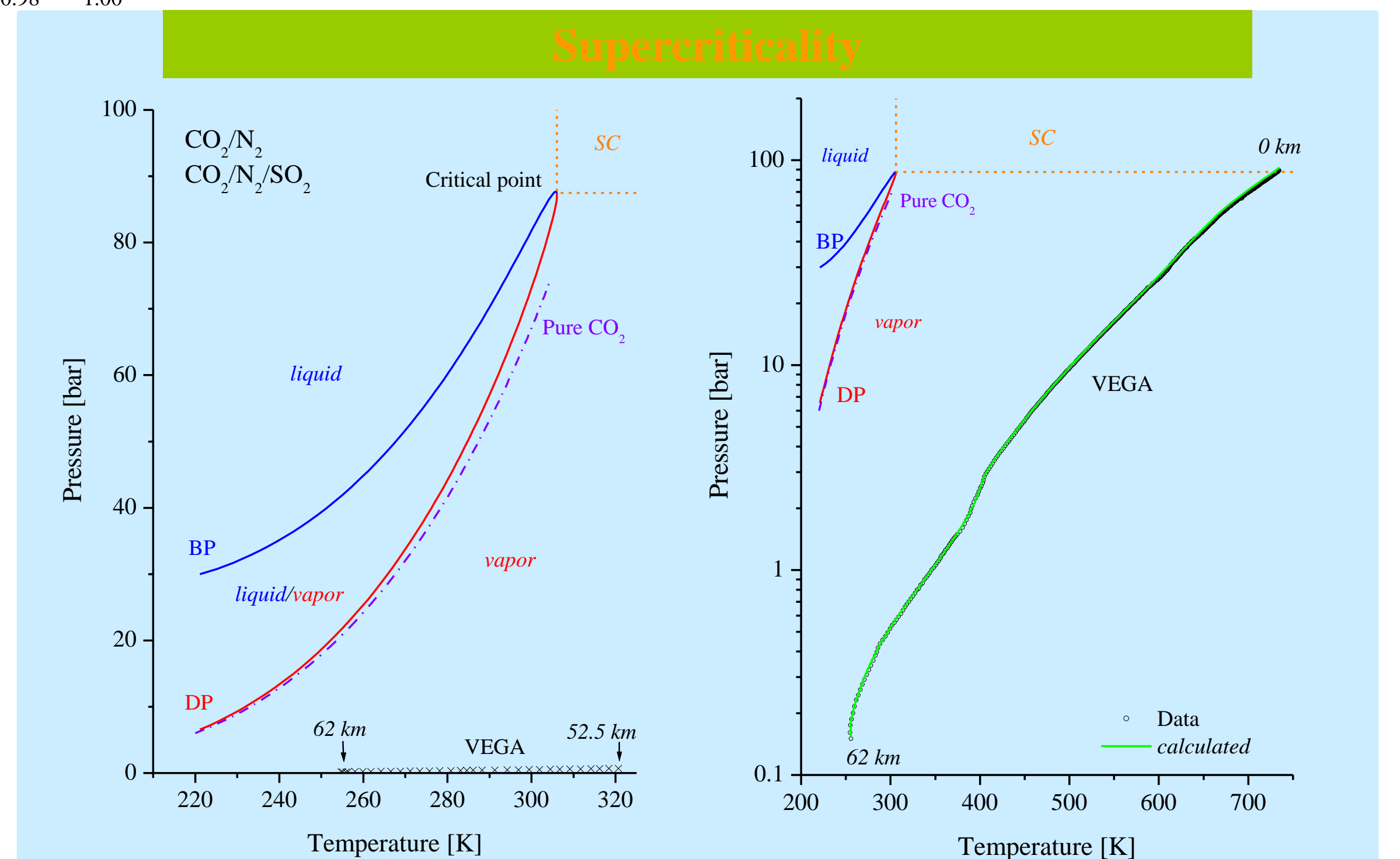
The use of binary CO<sub>2</sub>/N<sub>2</sub> instead of ternary CO<sub>2</sub>/N<sub>2</sub>/SO<sub>2</sub> makes:

- The pressure and density to underestimate by 0.04% on the surface.
- CO<sub>2</sub> and N<sub>2</sub> to overestimate by 0.054% and 0.045% on the surface, respectively.



- The atmospheric properties at the surface and the altitudes of 41 km and 62 km are tabulated below.

	Altitudes		
	0 km	41 km	62 km
Temperature [K]	734.86	405.60	255.44
Pressure [bar]	92.12	2.94	0.1534
CO <sub>2</sub> [mole fraction]	0.9898	0.9645	0.9001
N <sub>2</sub> [mole fraction]	0.0096	0.0354	0.0999
SO <sub>2</sub> [mole fraction]	5.42E-4	1.40E-4	0.43E-4
Density [kg/m³]	65.75	3.81	0.31



- Vapor (low density) and liquid (high density) phases can only coexist between the dew-point curve (DP) and bubble-point curve (BP) on the  $P$ - $T$  phase diagram forming the so-called phase envelope.
- The phase envelop of ternary CO<sub>2</sub>/N<sub>2</sub>/SO<sub>2</sub> with the total composition of {96.45%, 3.54%, 0.014%} is indistinguishable from that of binary CO<sub>2</sub>/N<sub>2</sub> with a total composition of {96.46%, 3.54%} on the diagram.
- The supercritical region of the atmosphere (SC) is located above the critical point (where DP meets BP) on the phase diagram.
- The  $P$ - $T$  relationship of the atmosphere (green curve) is mostly in the vapor phase, except for that in the lowest of 6-7 km, where the atmosphere becomes supercritical.
- There is no indication of "gas-gas" equilibrium along the  $P$ - $T$  function of the atmosphere as it must be above the phase envelope.