BORESKOV INSTITUTE OF CATALYSIS

Chemical base of hypothetical life on Venus

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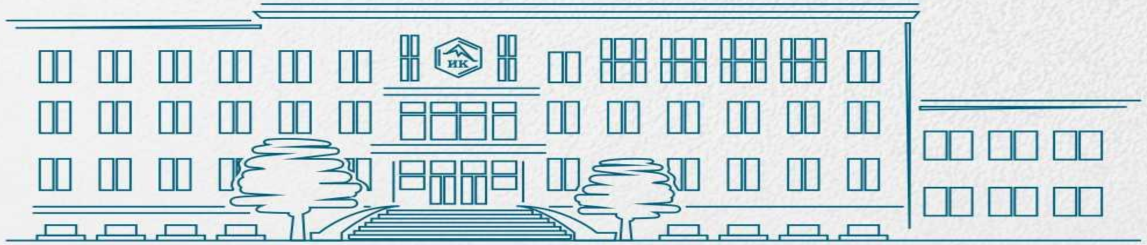


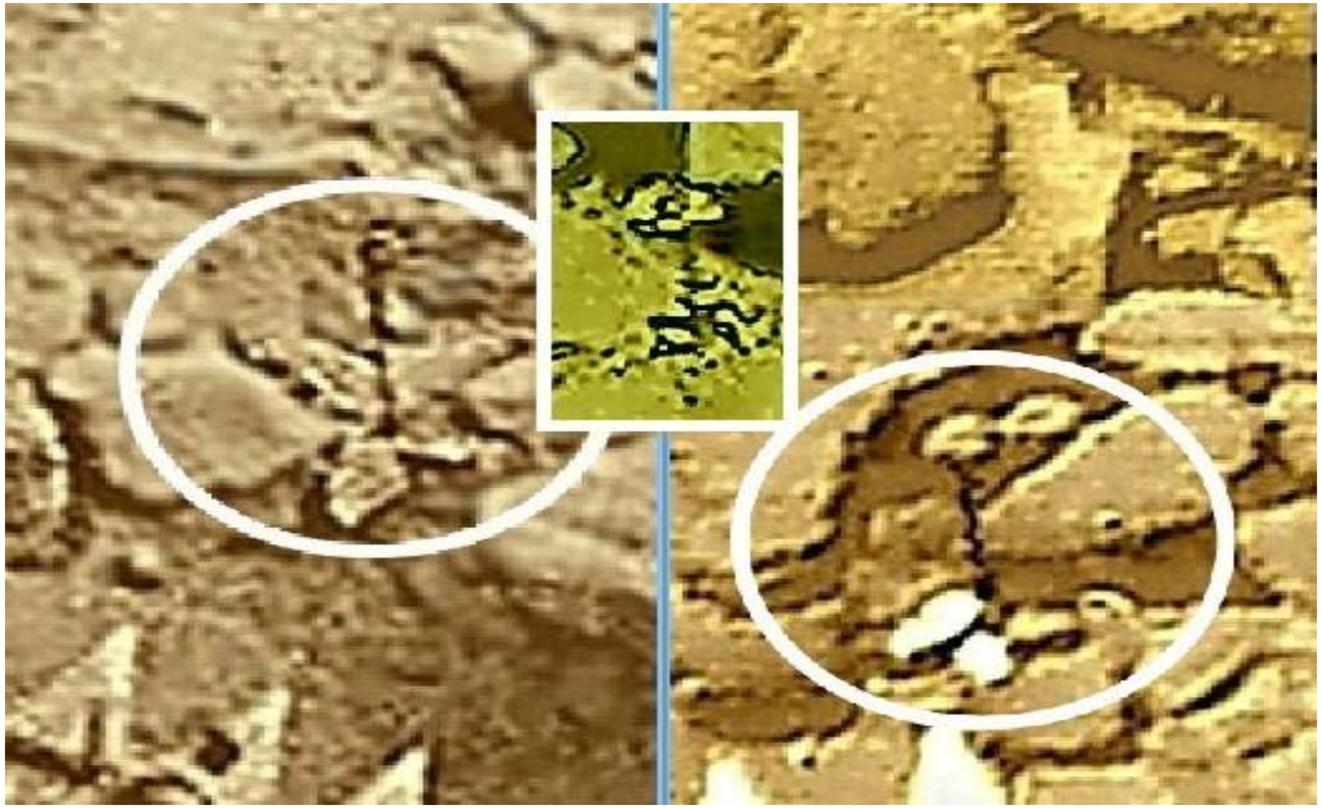
VENERA-D LANDING SITES SELECTION AND CLOUD LAYER HABITABILITY WORKSHOP 2019

In memory of the my co-author L.V. Ksanfomality 7.09.2019

Ksanfomality L.V., Zelenyi L.M., Parmon V.N., Snytnikov V.N. Hypothetical Signs of Life on Venus: Revising Results of 1975—1982 TV Experiments.
Physics-Uspekhi. 2019. V.62. N4. P.378-404.

“Flowers” on the surface of Venus

VENERA-14



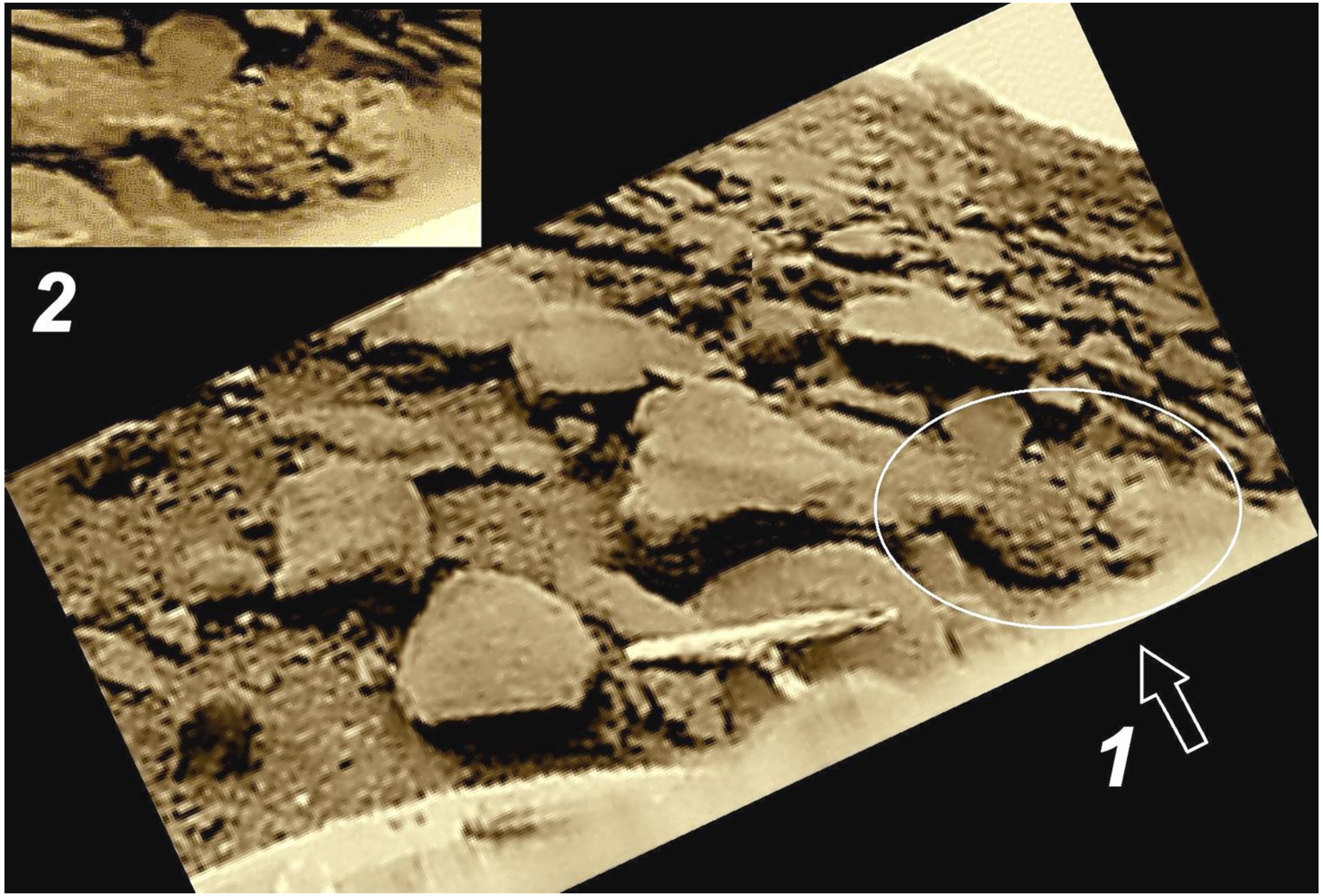
VENERA-13

Surface: temperature - 462ºC,
pressure 87 - 93 atmospheres.
Gas shell: density 65 кг/м^3,
CO_2- 96,5%, N_2 - 3,5% at the surface.

Surface:

462ºC,
87 - 93 bar.

CO_2- 96,5%,
N_2 - 3,5%



Question to me
L.V. Ksanfomality in 2011:

Where is the temperature boundary for the existence of organic life?

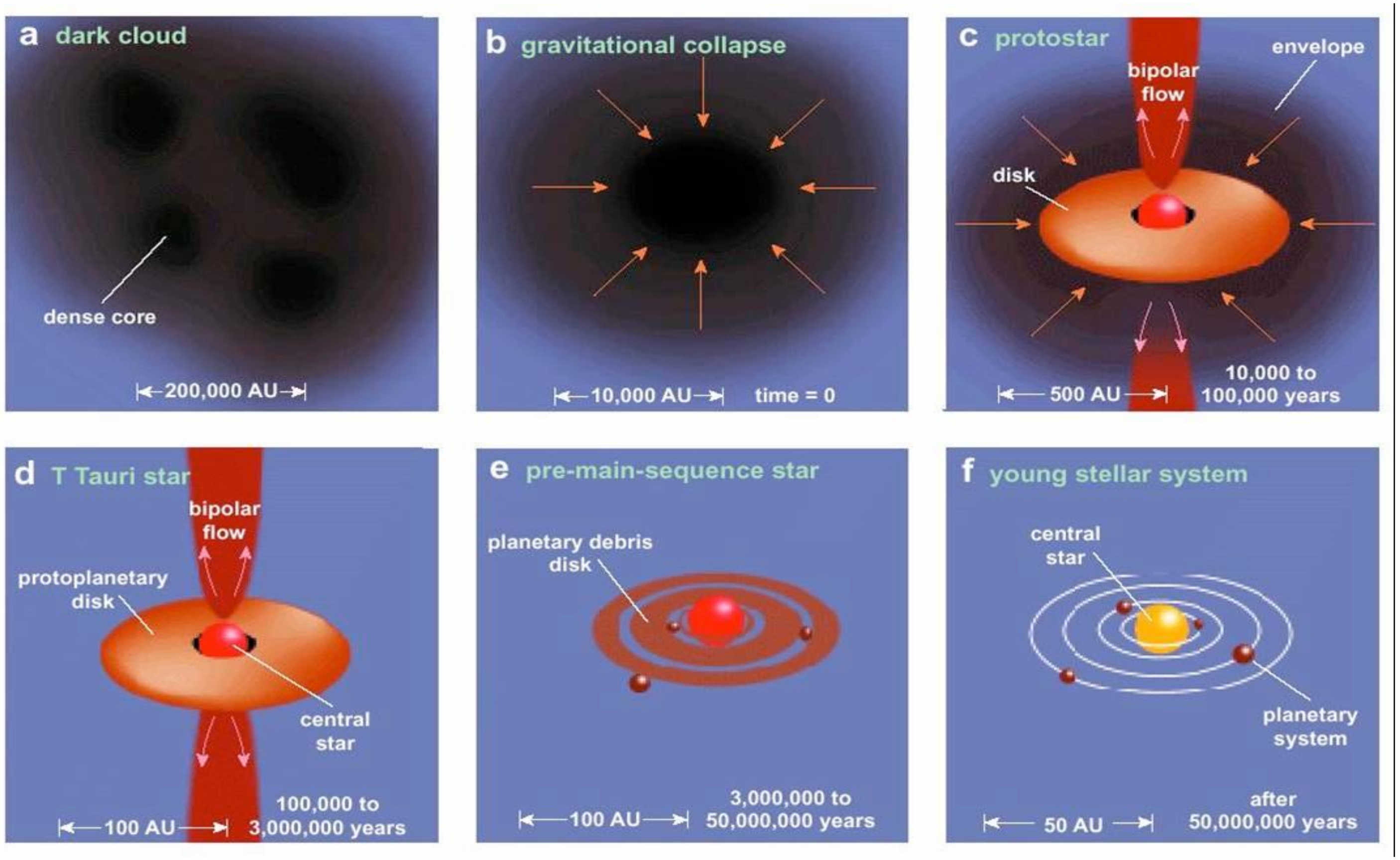
My answer was 550 – 600 ºC. There aren't stable organic polymers beyond this boundary.

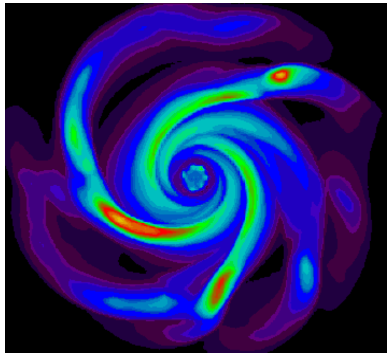
Life is evolution. What can be said about the formation of Venus?

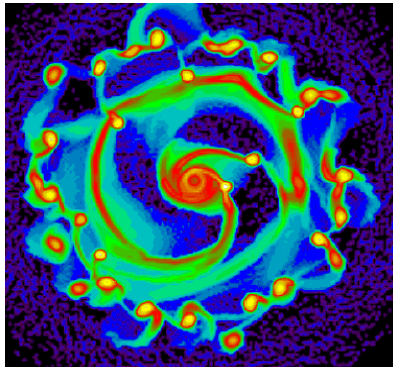
In a 1983 work by the geological group of K.P. Florensky, the authors wrote: "It is difficult to determine the shape of the" strange "stone ... The general roundness is combined with the spotted ... finely tuberous surface ... To the left of the described stone there is a light elongated formation that is decrypted as sticking out a stone rod-shaped protrusion of light material with a length of about 15 and a thickness of about 5 cm ... ".

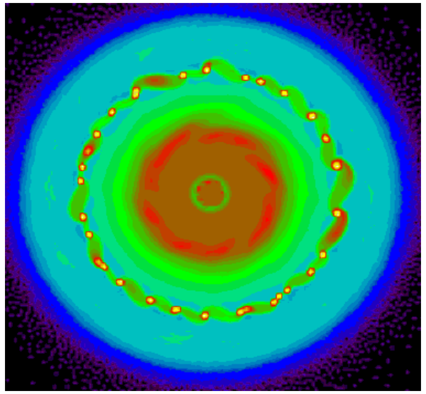
Planet formation

Rapid clump formation. Gravitational instability in massive circumstellar disc









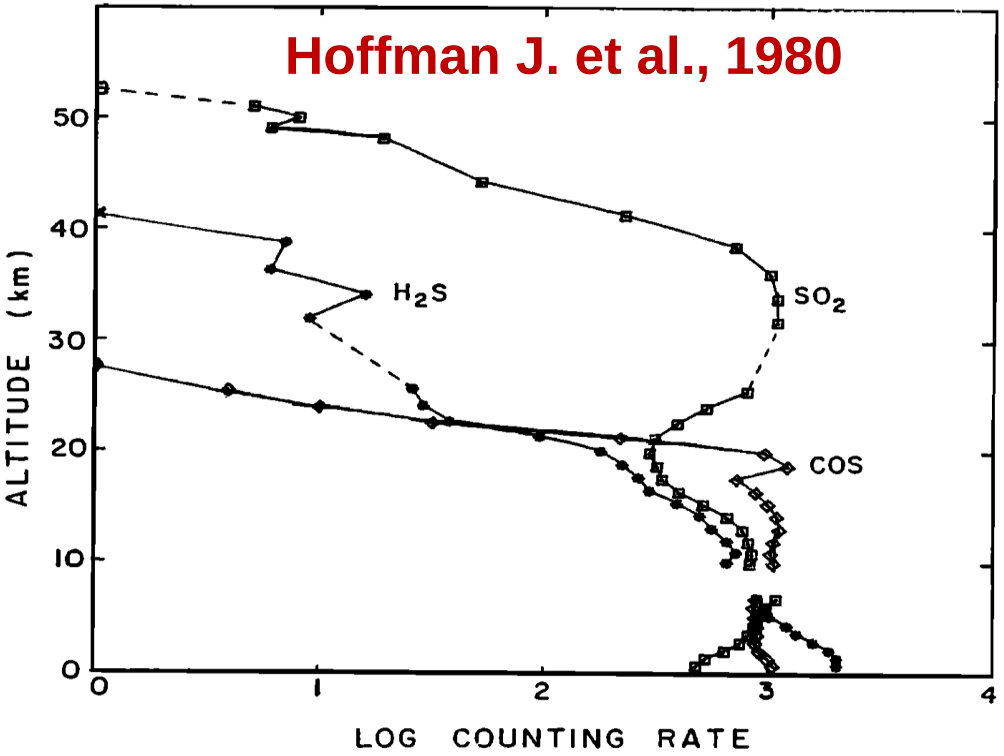
Computer simulation of quazi-3D dynamics of gas and solids in self-consistent gravitational field
Snytnikov V.N. …2006, 2014, 2016

High pressure more than 100 bar and moderate temperature in clumps.
The formation of the planets from the clamps. Loss of $\mathbf{H_2}$ **, He,** $\mathbf{H_2O}$ by Venus.

Atmosphere and Soil of Venus

Atmosphere

~96,5 % CO_2
~3,5 % N_2
~0,015 % SO_2
~0,007 % Ar
~0,002 % H_2O
~0,0017 % CO
~0,0012 % He
~0.0007 % Ne

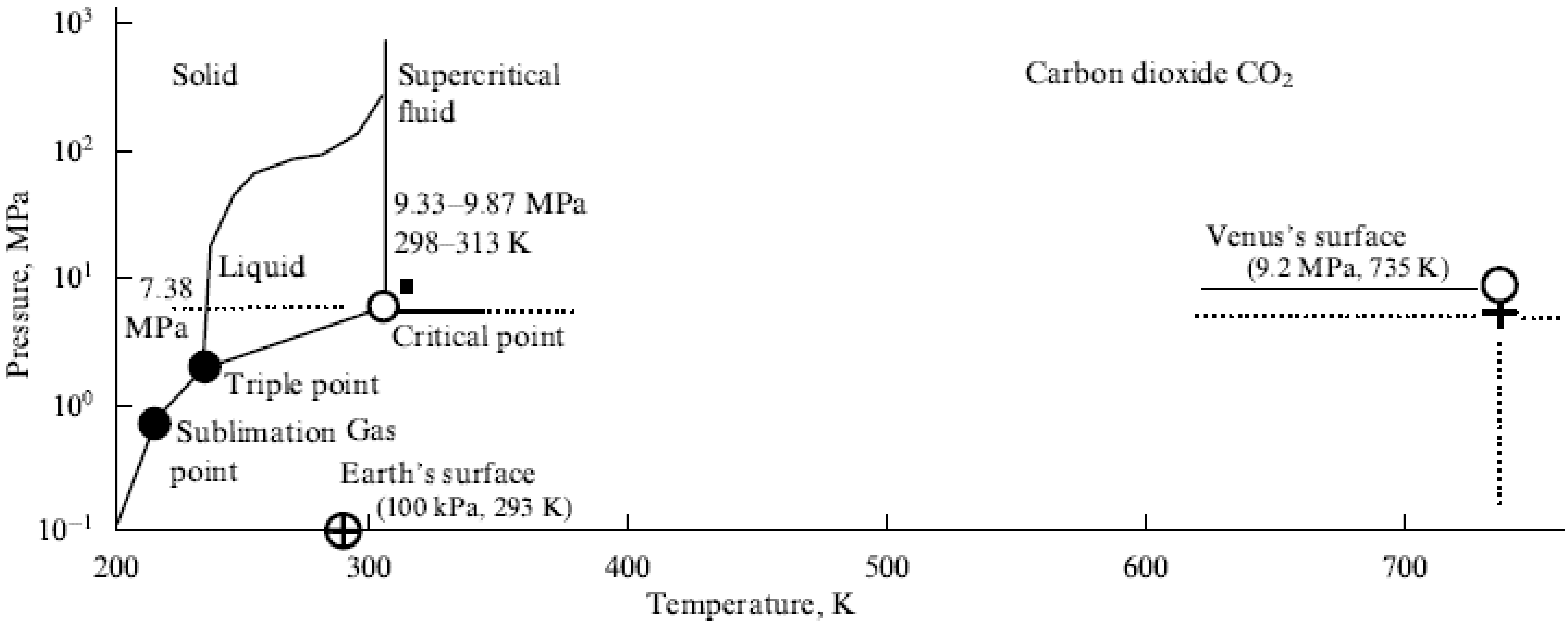


Soil, wt.%

Oxides	VENERA -13	VENERA -14	VEGA
SiO_2	45,1	48,7	46,5
Al_2O_3	15,8	17,9	16
MgO	11,4	8,1	11,5
CaO	7,1	10,3	7,5
FeO	9,3	8,8	8,6
K_2O	4,0	0,2	0,1
TiO_2	—	—	0,2
SO_3	—	—	4,7
MnO	0,2	0,16	0,14

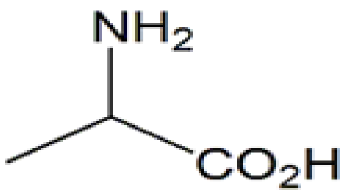
Temperature- 462ºC, Pressure 9,3 MPa

Near-surface atmosphere - supercritical fluid CO_2

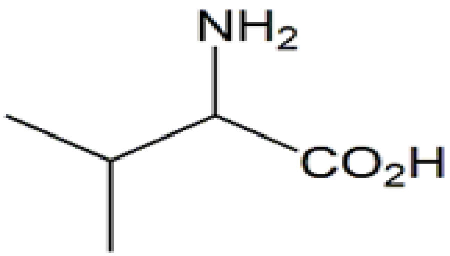


What are the data on physical and chemical processes in these conditions?

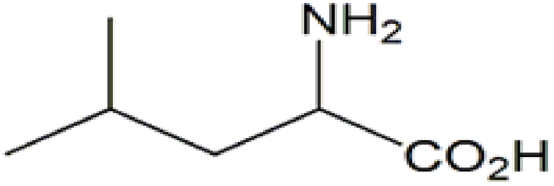
Amino Acids and Polymers
for Venusian Temperature



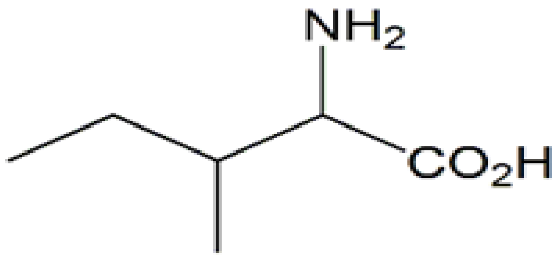
аланин



валин

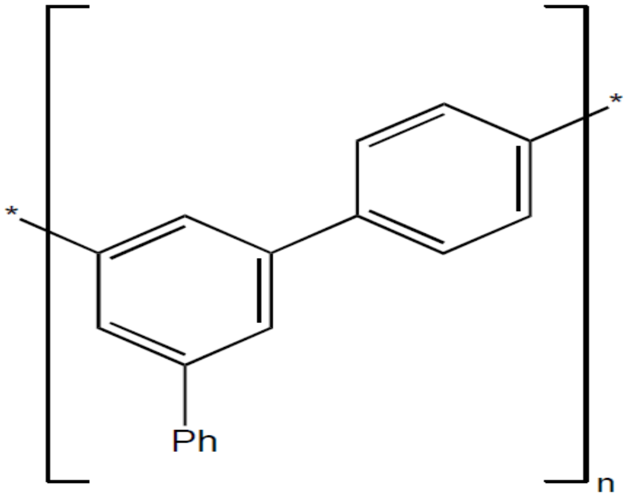


лейцин

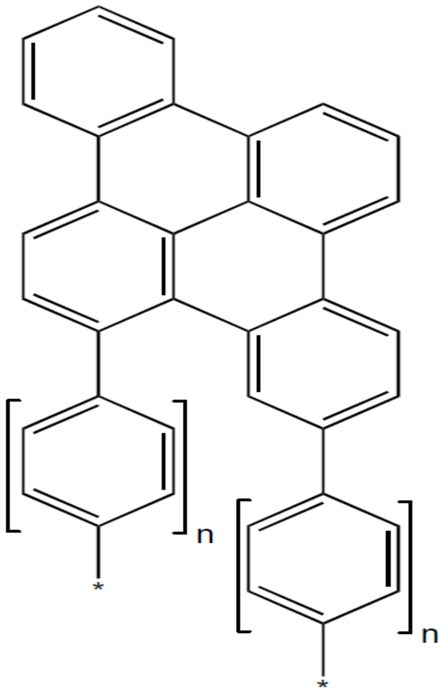


изо-лейцин

The study of the sublimation of protein amino acids at **T ~ 500-540 ° C, 1 bar**
Tarasevych A.V. et al. *ChemComm* **2015**



Diethinylbenzene or
Diethinylnaphthalene
>550° C



Poly-p-phenyl
>750° C

Nitrogen Activation ("Nitrogen Life"?)

Soil of composition $Fe – SiO_2 – Al_2O_3 – MgO – CaO – K_2O$

This is a typical catalyst for $N_2 + H_2 \rightarrow NH_3$

Yields of the order of 10-16%, 10 - 30 MPa , 300 - 550 ° C.

Shapatina E.N., Kuchayev V.L., Temkin M.I., 1988.

Iron nitrides FexN and intermediate complexes FexNH and FexNH2 are formed on the catalyst. The presence of sulfur in excess of 0.1% in the catalyst dramatically reduces its activity in the yield of ammonia. On Venus, we should expect the activation of nitrogen on reduced Fe and the formation of the complex FexNH. It further participates in the further synthesis of organic compounds and polymers.

A reactions may be carried out $N_2 + H_2S + Fe \rightarrow 2\ [NH] + FeS$

$$CO_2 + 4\ H_2S + 3\ FeS \rightarrow [CH_3SH] + 3\ FeS_2 + 2\ H_2O.$$

Synthesis of methyl sulfide [CH3SH] with the participation of iron is particularly effective in environments with low water content.

Chemical processes for Venusian Life

Photosynthesis on the Earth's surface - formaldehyde group [CH_2O]

$$H_2O + CO_2 \longleftrightarrow [CH_2O] + O_2.$$

Venus carbonyl sulfide [COS] :

$$H_2S + CO_2 \longleftrightarrow [COS] + H_2O$$

$\lg K_p = -2.02$ at 740 K

Krasnopolsky V.A. 1982.

Catalytic cycle $FeS \rightarrow FeS_2 \rightarrow FeS$:

$$H_2S + FeS \rightarrow FeS_2 + 2\,[H],$$
$$FeS_2 + CO_2 \rightarrow FeS + [COS] + [O],$$
$$2\,[H] + [O] \rightarrow H_2O$$
$$[S] + 2[O] \rightarrow SO_2.$$

The formation of FeS_2 on the surface of catalysts Fe_2O_3 / SiO_2 and Fe_2O_3 / Al_2O_3 in the presence of water vapor.

Bukhtiyarova G.A., et al. , 2000.

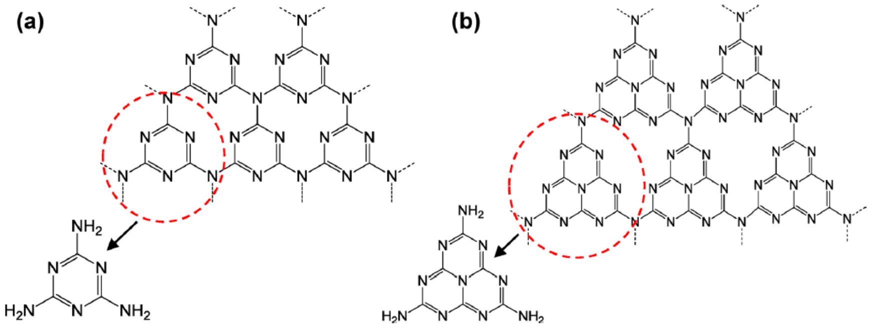
Chemical processes on Venus surface

$Fe + CO_2 \longrightarrow Fe_2(CO)_9$ or $Fe_3(CO)_{12}$???

The use of Fe - catalysts in the synthesis (low pressures and moderate temperatures):

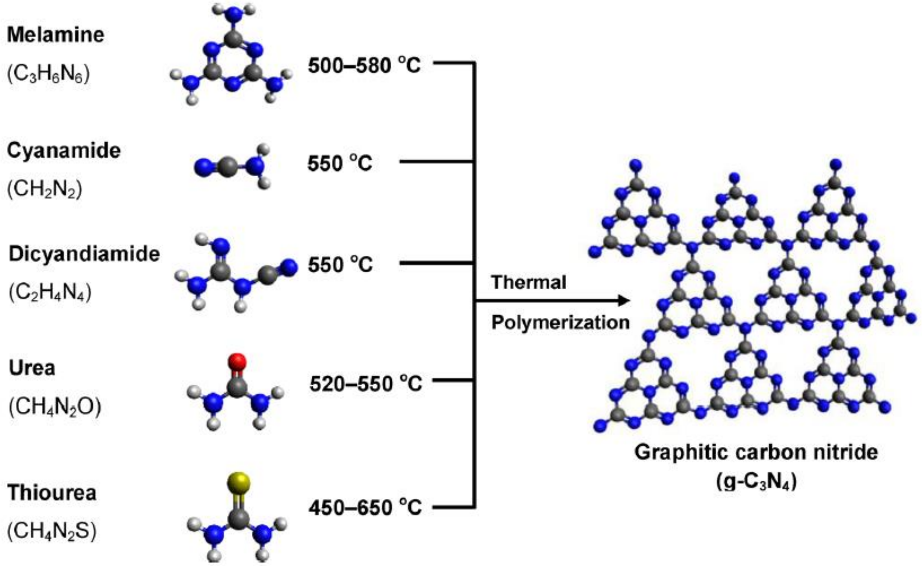
Bauer I. , Knolker H.J. Chem. Rev. , 2015. **Cheng-Jian Zhang et al. NATURE COMMUNICATIONS, 2018.**

g-C_3N_4 - photocatalysts



(a) Triazine and (b) tri-s-triazine (heptazine) structures of g-C_3N_4.

Wee-Jun Ong et all. Chem. Rev. 2016, 116, 7159-7329



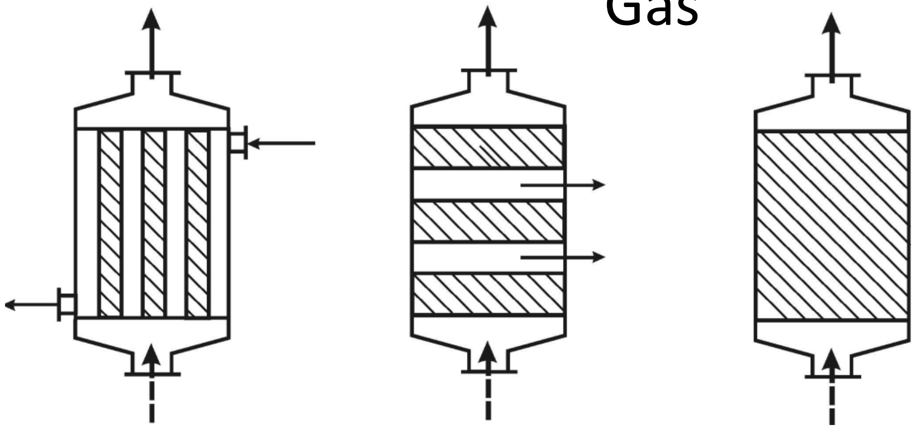
All these compounds, organic [COS] , [CH_2O], thiol [CH_3SH], nitrogen [NH] initiate chains of all further syntheses of substances on the catalyst surface. These substances may include other elements, such as Si, Fe, Mg, Ni, Zn and others that make up the Venusian soil. Among the total possible mass of compounds in the presence of a high-temperature fluid CO_2 and nitrogen remain stable substances, including some synthesized polymers.

Thus, the available data allow us to offer a venus - chemical “iron sulfur world” as a hypothesis about the basics of Venusian life.

Fixed bed catalytic reactors and fluidized bed reactor

Experience in the study of chemical processes on the surface of solids and gases for chemical technologies and industries.

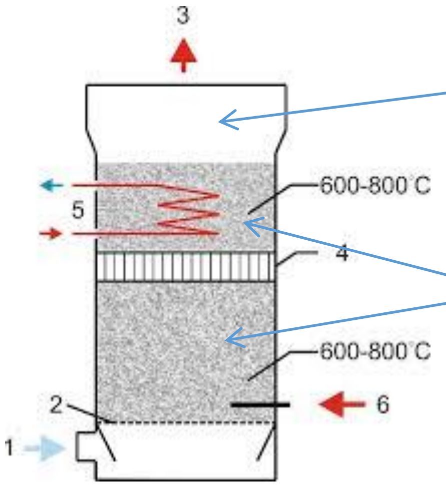
Gas



Gas, Liquids

Tubular Multilayer (Shelf) Adiabatic Reactors

Dust and gas



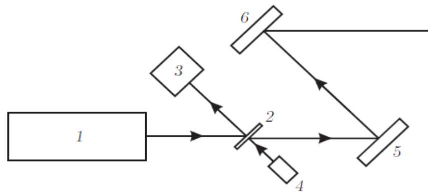
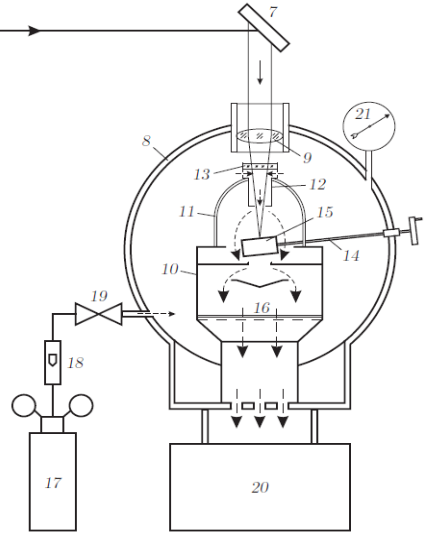
Catalysts

Gas

Fluidized bed reactor

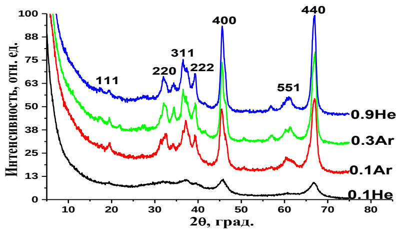
Temperature < 1000 ºC, pressure < 1000 atmospheres.

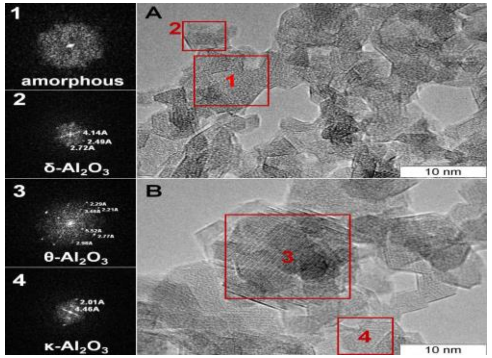
Device
for producing oxide nanoparticles

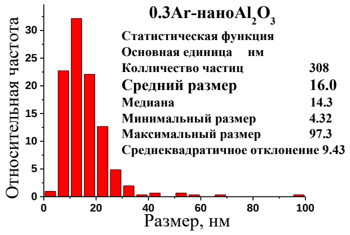



1 – непрерывный CO_2-лазер;
2 – делительная пластина
3 – калориметр;
4 – трассирующий полупроводниковый лазер;
5-7 – зеркала оптической трассы;
8 – вакуумная камера;
9 – объектив;
10 – испарительная камера;
11 – кварцевый колпак;
12 – сопловая насадка;
13 – защитная пластинка (KCl);
14 – шток для крепления и сканирования мишени;
15 – мишень;
16 – фильтр для сбора наночастиц;
17 – баллон с газом;
18 – ротаметр;
19 – вентиль;
20 – система прокачки газа;
21 – вакуумметр.
Сплошные стрелки – направление распространения излучения лазера, штриховые – направление движения потока газа

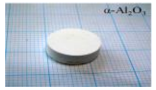
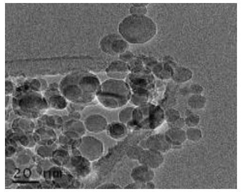
Условия испарения, газ и давление	$d_{сред.}$, нм
He, P= 0,034 атм.	3-4
He, P= 0,1 атм.	6
Ar, P= 0,1 атм.	15
Ar, P= 0,3 атм.	16
He, P= 0,9 атм.	21



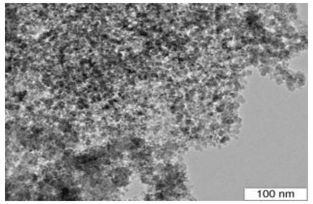
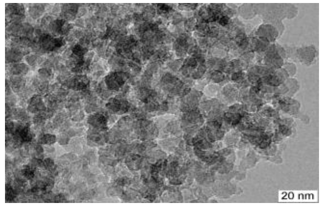




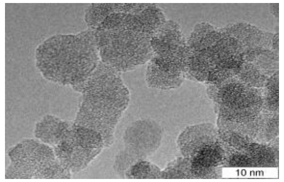
Al_2O_3 0,1 He

SiO_2

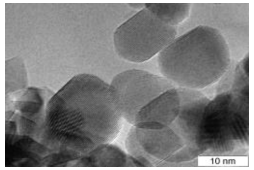
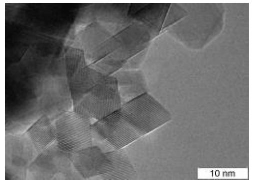
$Mg_xFe_y(SiO_4)$



Элемент	В нанопорошке, масс.%			
	Исходный состав	Содержание	Содержание	Содержание
Na	0,76	1,97	2,83	2,09
Mg	21,93	9,99	6,45	6,71
Al	0,05	0,04	0,07	0,14
Si	14,58	18,45	19,21	19,57
Cl	1,22	1,92	3,09	1,63
K	0,06	0,17	0,27	0,15
Mn	0,09	0,11	0,11	0,12
Fe	20,98	27,00	28,15	29,01

Изменение состава образца после лазерного синтеза нанопорошка
Аморфное фазовое состояние у наночастиц

CeO_2

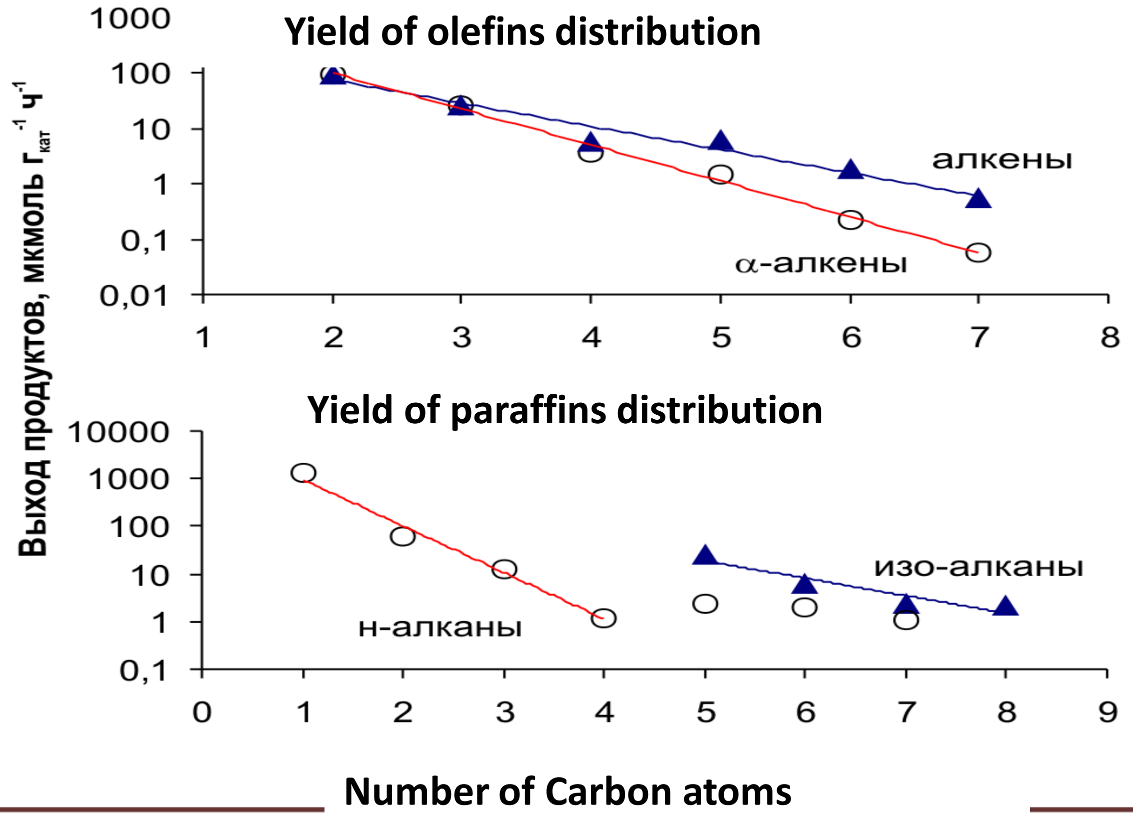
Kostyukov A., Baronskiy M., Rastorguev A., Snytnikov V., Snytnikov V., Zhuzhgov A., Ishchenko A. Photoluminescence of Cr3+ in Nanostructured Al_2O_3 Synthesized by Evaporation Using a Continuous Wave CO_2 Laser // RSC Advances. 2016. V.6. N3. P.2072-2078

"FT" Synthesis

$$CO + H_2 \longrightarrow C_xH_y + H_2O$$

Catalytic active nanomaterials

Products distribution of FT-Synthesis over Meteorite Tsarev, T=642 K



	Meteorite Tsarev	Dolerit
SiO_2	40,6	41,6
TiO_2	0,12	1,04
Al_2O_3	2,5	12,2
Cr_2O_3	0,5	0,02
FeO_x	**14,0**	**25,3**
MnO	0,34	0,18
MgO	25,2	9,0
CaO	2,0	6,3
Na_2O	0,7	1,0
K_2O	0,10	0,47
P_2O_5	0,3	0,09
S	1,92	0,98
Fe (сулф.)	3,36	0
Fe^0	**6,51**	**0**
Ni	**1,08**	**0,17**
Co	**0,048**	**0**
Cu	0,013	0,13

Conclusion

1. A complex of chemical reactions of organic synthesis of complex organic compounds catalyzed by iron-containing compounds can take place on the surface of Venus . Photocatalytic processes may also occur.

2. From the Venus-D mission, we are waiting for
- data on the altitude content of gases **H_2, He, H_2O, C_xH_y , Ne , OCS, H_2S , HCN, Ar , SO_2 …** near the surface of Venus;
- data on carbon and nitrogen compounds on the surface of Venus;
- data on inorganic surface material;
- data on compounds adsorbed on inorganic surface material;
- data on the composition of dust on the surface.

3. Venus is an ancient cooling Earth before condensation of water.
The study of Venus opens the way to the knowledge of the pre-epochal era of the hot Earth in the first 600 million years from the origin of the Earth to the appearance of the oldest rocks 3.95 billion years.

4. Studies of chemical catalytic processes on the surface of Venus for supercritical fluid CO_2 will find their application in the creation of new chemical technologies and the synthesis of new materials for high-temperature applications.

Thank you for attention!

Acknowledgment
Presidium Program (coordinator L.M. Zelenyi).

Chemical reactions

Syntheses of active molecules (C_2H_4, NH_3, HCN, H_2O…)

$CO + H_2 \rightarrow H_2CO$ (gas discharge of low pressure)

$CO : H_2 = 1 : 8$, $H_2CO : CO = 7:100$ (plasma-chemical reactions) *Rusanov V.D., Fridman A.A., 1984*

$CO + H_2 \rightarrow H_2CO$ MgO, T< 500-600K *Hattory H., Wang G.W., 1984*

$N_2 + 3H_2 \rightarrow 2NH_3$ Fe, Ni

$CO + NH_3 \rightarrow HCN + H_2O$

Reactions of polymerization with mass increasing

H_2O with organic matter, T< 200°C

$n(C_2H_4) \rightarrow (C_2H_4)_n$, Fe, UV

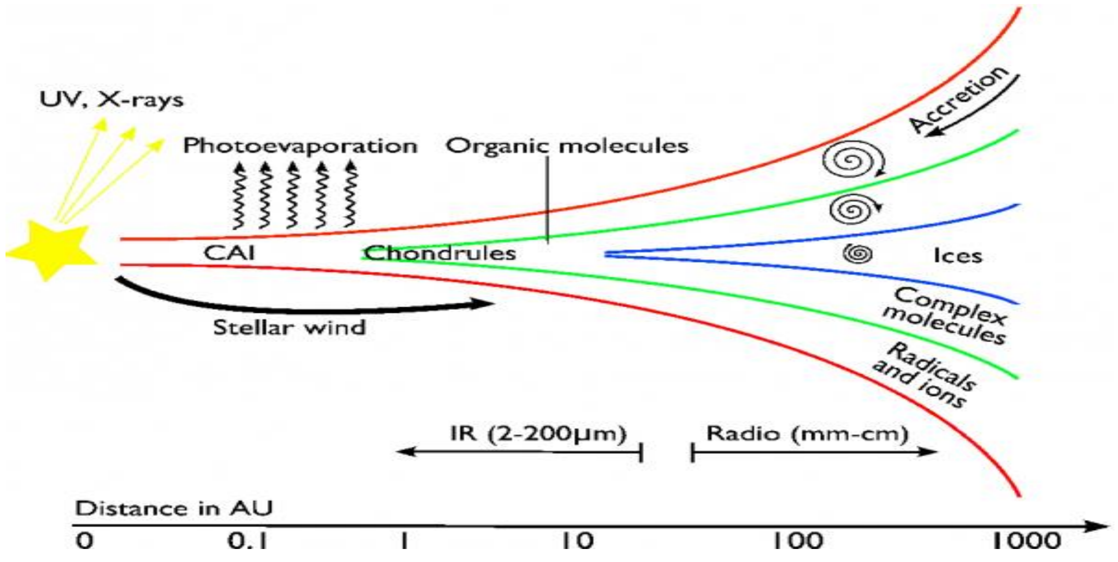
$n(HCN) \rightarrow (HCN)_n$

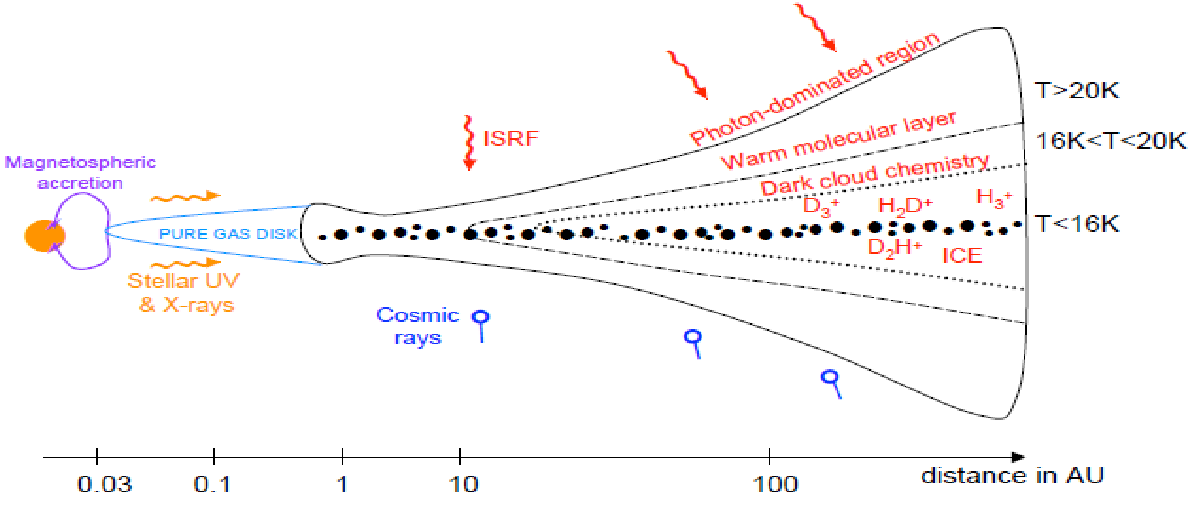
$n(H_2CO) \rightarrow (H_2CO)_n$, OH^-, Me^{2+} (Mg^{2+}, …)

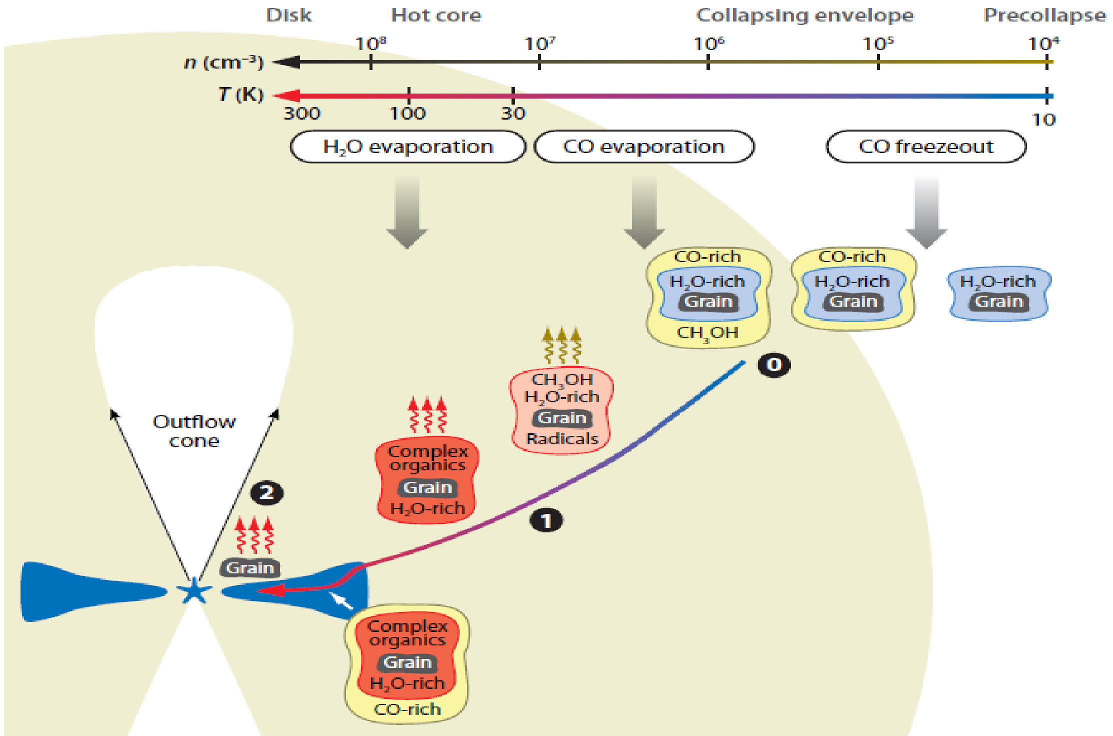
……………………………………………………………….

CO/H_2 for molecular clouds not equal to CO/H_2 in discs!!!

Структура диска







Трехфазная среда

плазма – газ – твердая фаза

Газ: концентрация от 10^3 cm-3 до 10^{21} cm-3

Температура от 20 K до 100 000 K

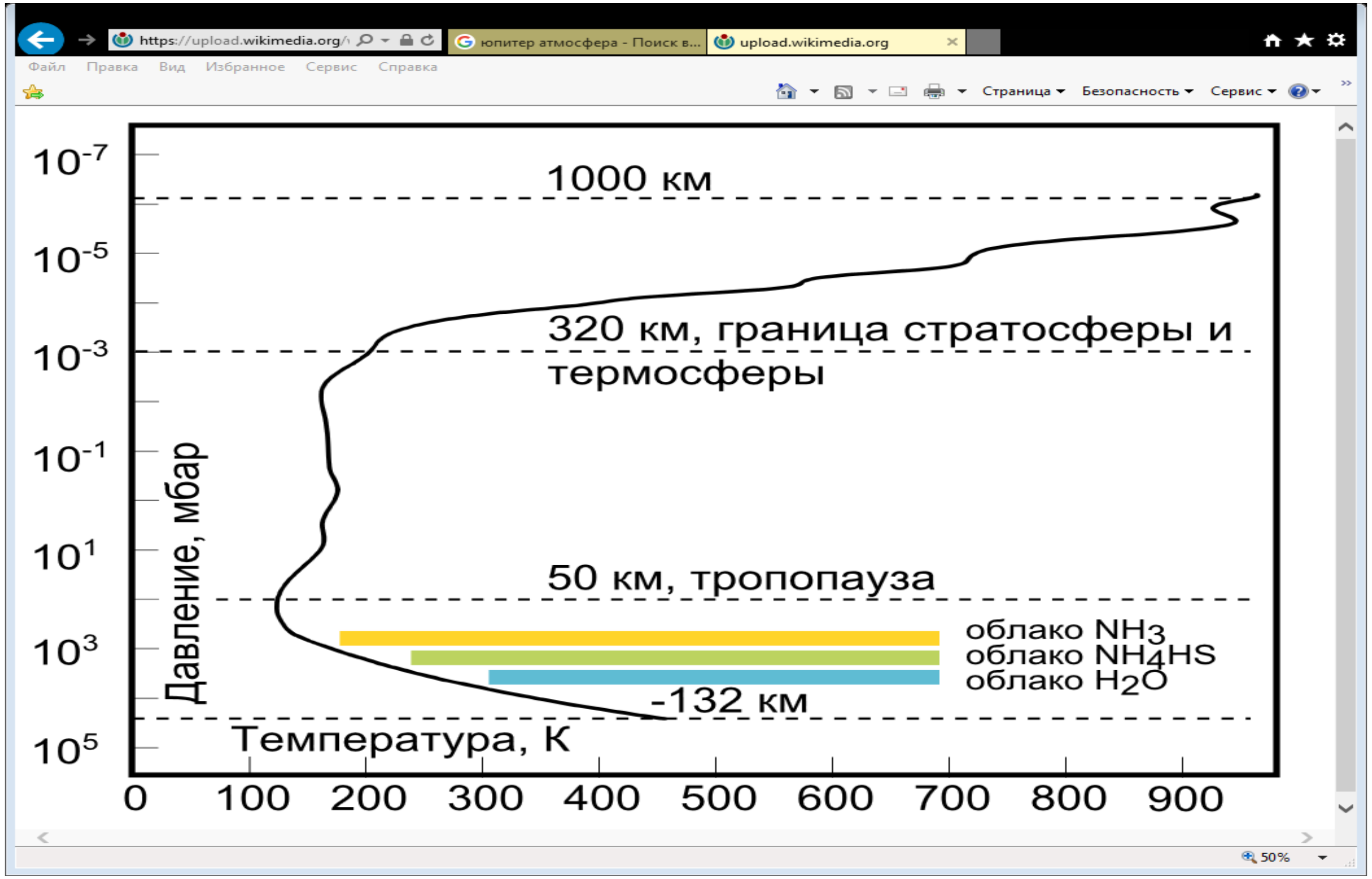
Давление до 10^{-3} атм и выше (?)

Внеземная жизнь в Солнечной системе

Объекты для исследований
Результат изменений за 4,56 млрд лет

Метеориты
Кометы
Космическая пыль
Луна
Марс
Венера
Юпитер + Европа
Сатурн + Титан

Внеземная жизнь в Солнечной системе. Юпитер и Сатурн



Идея Саган К. искать жизнь в переходном слое атмосферы Юпитера.

Снытников В. Протожизнь околозвездного диска

Вода, метан (CH_4), сероводород (H_2S), аммиак (NH_3) и фосфин (PH_3).
Их относительное количество в глубокой (ниже 10 бар) тропосфере подразумевает, что атмосфера Юпитера в 3-4 раза богаче углеродом, азотом, серой и, возможно, кислородом , чем Солнце.

Астрокатализ.
Эволюция биоценозов в Солнечной системе

Юпитер и Сатурн

Первичные восстановительные атмосферы околозвездного диска

Ю: Температура −107 °C (1атм) и +153 °C (22 атм)

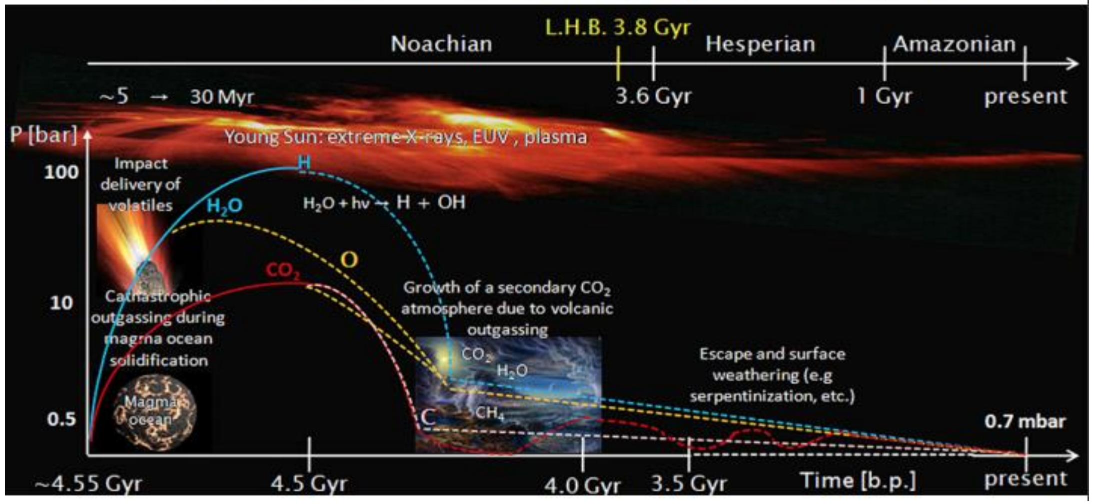
С: Температура −130 °C при давлении 1атм

Состав атмосферы H_2, He (CH_4, H_2S, NH_3 , PH_3 …)

Гипотеза о сохранении протожизни околозвездного диска (???)

$H_2S + CO_2$ <--> [COS] + H_2O и $H_2O + CO_2$ <--> [CH_2O] + O_2

Эволюция атмосферы Марса



Температура от -150 °C до +20 °C, средняя – 50 °C и давление 6 мбар

Состав атмосферы 95,3% CO_2, 2,7% N_2

Гипотеза о жизни в подповерхностных слоях. Как обеспечить в них энергетику ???)

Астрокатализ.
Эволюция биоценозов в Солнечной системе

Земля: потеря первичных H_2, He и H_2O

4,56 – 3,95 млрд лет назад:

Падение температуры к, условно, 100 °С, давление выше 30 бар

Состав атмосферы H_2, He, H_2O + к*(96% CO_2 + 4% N_2)

Геобиохимический синтез, «железо-серный мир»

$H_2S + CO_2 <--> [COS] + H_2O$ и $H_2O + CO_2 <--> [CH_2O] + O_2$

3,95 млрд лет назад:

Температура ниже 100 °С, жидкая вода на поверхности !!!

«Конденсация» CO_2 с образованием осадочных пород,

$$\mathbf{CO_2 + H_2O\ (liquid) + CaSiO_3 \longrightarrow SiO_2 + CaCO_3 + H_2O\ (liquid)}$$

Переход от венерианского фотосинтеза к земному

3,5 млрд лет назад, «геологические времена» :

Температура ниже 100 °С, давление около 1 бар

Формирование состава атмосферы, 80% N_2 , 20% O_2

Геобиохимический фотосинтез, формирование биосферы

$H_2O + CO_2 <--> [CH_2O] + O_2$

Астрокатализ.
Эволюция биоценозов в Солнечной системе

Венера:

Потеря первичных H_2, He и H_2O

Температура   475 °C, давление   92 бар

Состав атмосферы 96% CO2, 4% N2

Геобиохимический синтез

$$H_2S + CO_2 \;\text{<-->}\; [COS] + H_2O$$

Впервые обнаружены внеземные организмы !!!

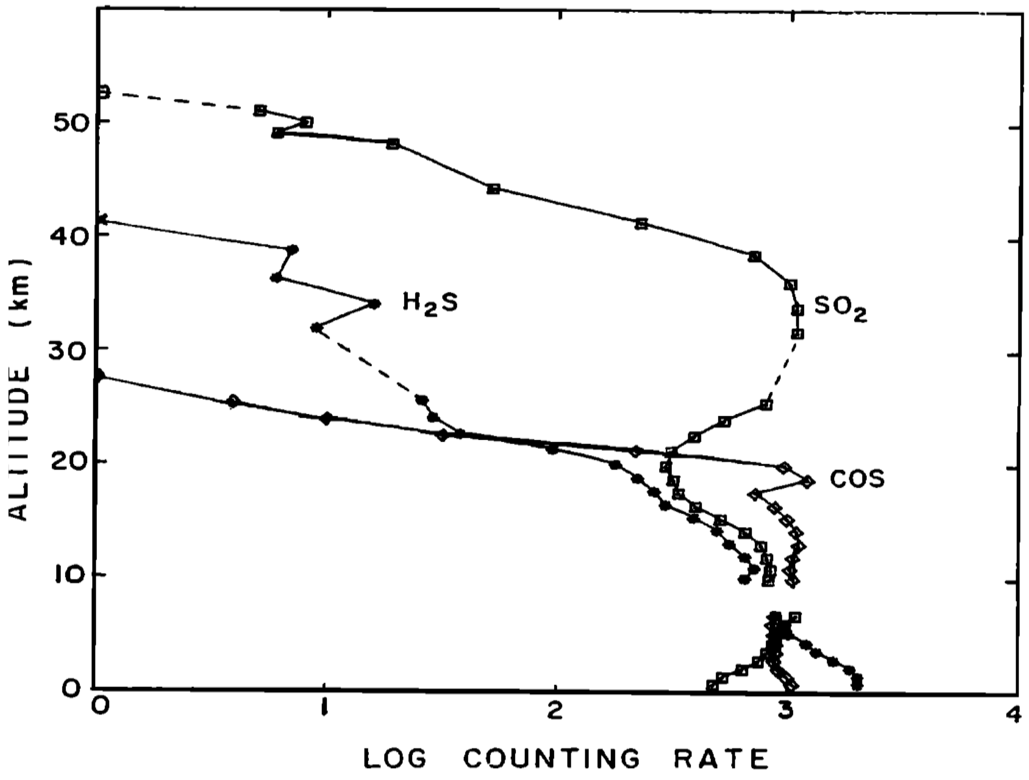
Ксанфомалити Л.В. , 2011 г.

TABLE 2. Volume Mixing Ratios of Gases Found in the Venus Atmosphere

Gas*	Venus Atmosphere Mixing Ratio, ppm	Earth Atmosphere Mixing Ratio, ppm
^{20}Ne	9†	16
^{22}Ne	1†	2
Total Ne	10†	18
^{36}Ar	30_{-10}^{+20}	31
^{38}Ar	6†	6
^{40}Ar	31†	0.93%
Total Ar	40–120†	0.93%
^{84}Kr	<0.2	0.5
N_2	4 ± 2%	78%
O_2	<30	21%
SO_2 55 km	<10	
Below 24 km	<300	
COS Above 24 km	<3	
Below 20 km	<500	
H_2S	3†	
C_2H_6	2†	
H_2O	<1000	
Cl	<10	
Hg	<5	

*In those rows where altitude is unspecified, result is average value from 24 km to surface.

†Deduced from ratio to ^{36}Ar.



ltitude profiles of COS, SO_2, and H_2S. Maximum in the SO_2 profile at 33 km is from evaporation from the
:t on the leak. The peak in COS at 20 km is an artifact. Dashed portions of curves indicate times when low
;y data were taken (not plotted).

Water in biocenoses

The absolute water content on Venus is 0.1 g/m3 (about 20 ppm H2O)

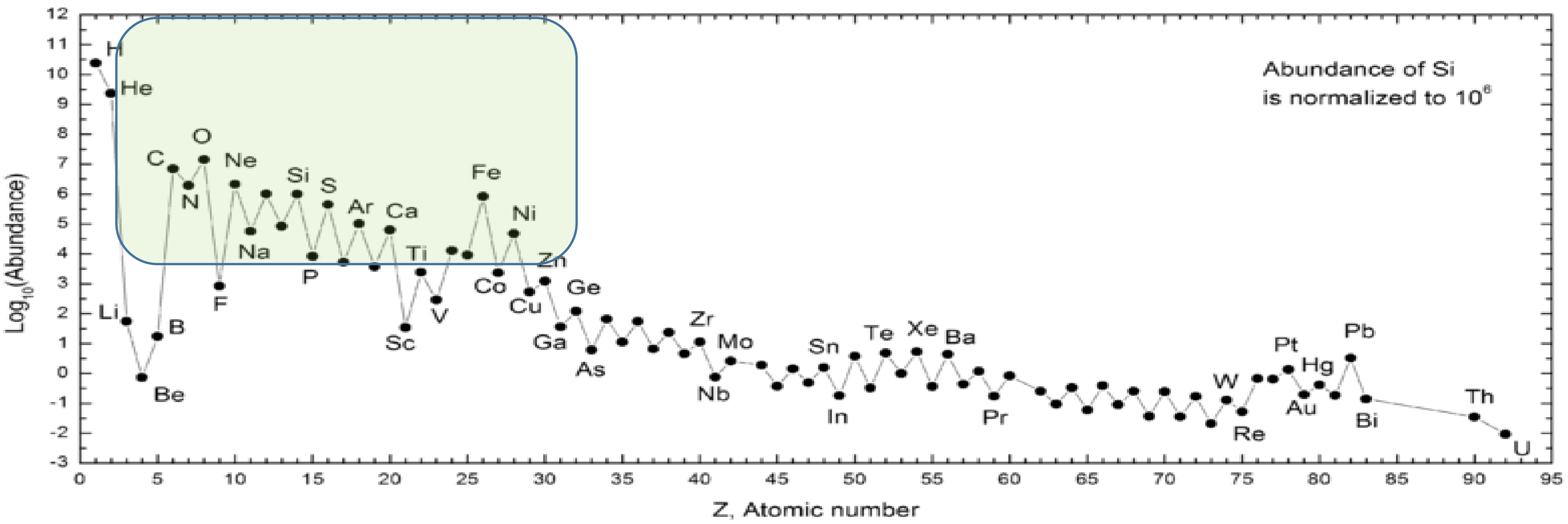
Water, functions in biocenoses		
	Earth	Venus
Structural component in cells	Yes	May be
Habitat and breeding of unicellular organisms	Yes	No, CO_2-N_2
Multicellular component	Yes	May be, CO_2-N_2
The basis of chemo- and photo synthesis	Yes	Yes, H_2S – CO_2

-31°C	0,301 g/m³
-32°C	0,271 g/m³
-33°C	0,244 g/m³
-34°C	0,220 g/m³
-35°C	0,198 g/m³
-36°C	0,178 g/m³
-37°C	0,160 g/m³
-38°C	0,144 g/m³
-39°C	0,130 g/m³
-40°C	**0,117 g/m³**
-41°C	0,104 g/m³
-42°C	0,093 g/m³
-43°C	0,083 g/m³
-44°C	0,075 g/m³
-45°C	0,067 g/m³
-46°C	0,060 g/m³
-47°C	0,054 g/m³
-48°C	0,048 g/m³
-49°C	0,043 g/m³
-50°C	0,038 g/m³
-51°C	0,034 g/m³
-52°C	0,030 g/m³
-53°C	0,027 g/m³
-54°C	0,024 g/m³
-55°C	0,021 g/m³
-56°C	0,019 g/m³
-57°C	0,017 g/m³
-58°C	0,015 g/m³
-59°C	0,013 g/m³
-60°C	0,011 g/m³

Maximum absolute humidity g/m³ of air depending on temperature, 0.1 MPa

https://www.dpva.ru/Guide/GuidePhysics/Humidity/MaximumMoistureContentAir/

Elements Abundance



I. ***H + He*** – **98%,**

Another elements – **1-2%,** *among them*

II. ***Organics*** (**H, O, C, N,**…) **> 90%**

III. Inorganics (**Mg, Si, Fe, O,** …) **< 10%**

H_2(2) , He (4), H_2O (18), CH_4(16) , Ne (20) , NH_3,(17) , N_2(28), H_2S (34), Ar (40), CO_2 (44), …

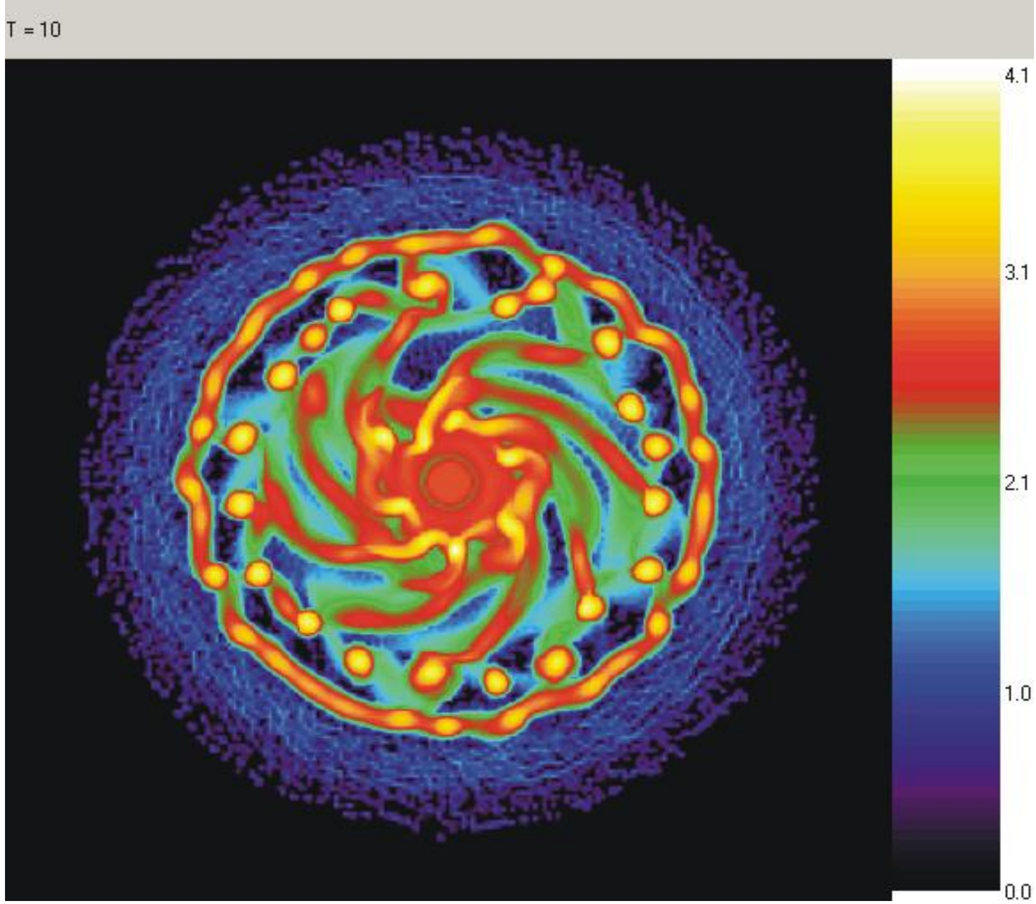
light gases **moderate mass gases** **heavy gases**

$MgH_2 + SiH_4 + FeH + H_2O$ --> $(Mg,Fe)_2SiO_4$ and $(Mg,Fe)_6Si_4O_{10}(OH)_8$

in the crust $(CH_2O)_{106}(NH_3)_{16}H_3PO_4$ and Organics <—> $CO_2 + H_2O + N_2 + CH_4 + [PO_3]^{3-}$

Astrocatalysis.
Chemical evolution in pre-planetary circumstellar disks.

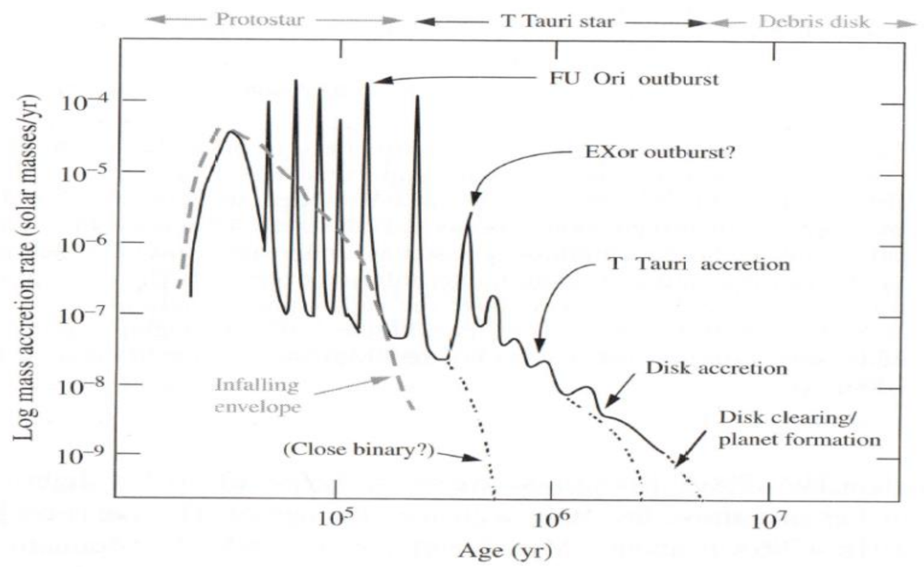
The logarithm of the gas density in the disk. Clumps.



Two-phase model of a disk of gas and solids.

Snytnikov V.N. Paleontological journal, 2010, etc.

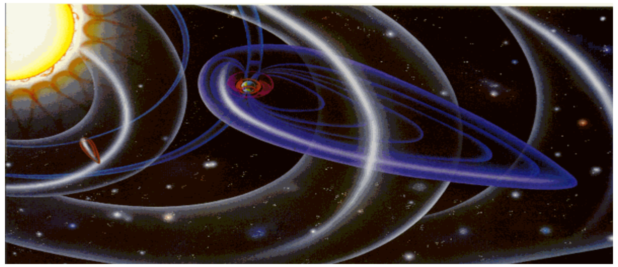
$$L_{acc} = f_{acc}\frac{GM_*\dot{M}_{acc}}{R_*}, + L_s$$



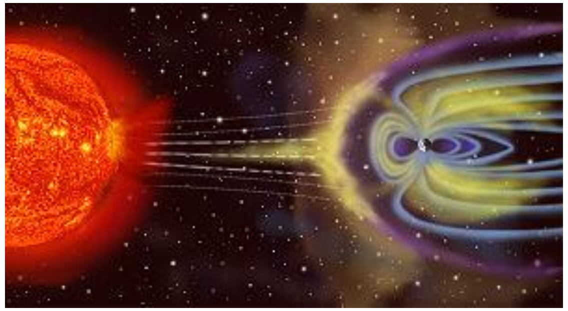
L. Hartmann, *Accretion ..., 2008*

Periodic increase in pressure over the body surface from **$(Mg,Fe)_2SiO_4$ и $(Mg,Fe)_6Si_4O_{10}(OH)_8$** as it moves from one bunch to another in the first million years. High-pressure wave reactors P> 100 atm in H_2 and He for the “RNA world”.

Gas collapse and body assembly in one bunch.



Formation of Planet atmospheres in the Solar system



Radiation Flux from the Sun,

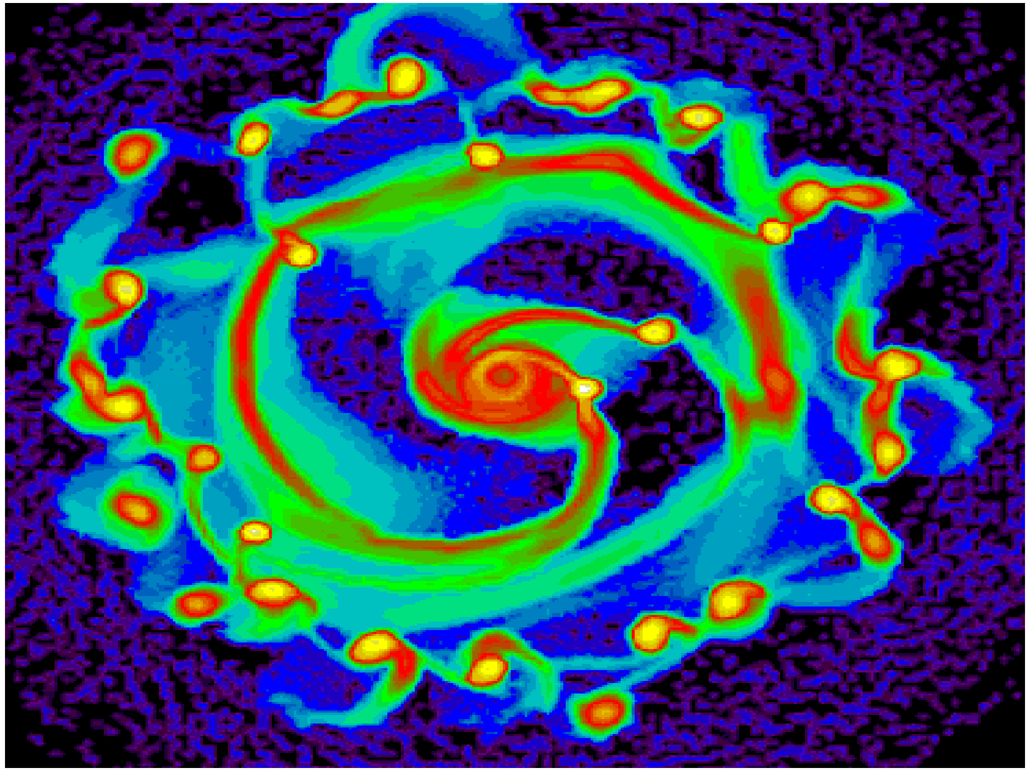
Mass of protoplanets and Solar wind

Computer simulation: $P_i / P0 \sim \exp(-mGM/TR)$; R ,M- body radius and mass, T - temperature

Initial composition **H_2 (2), He (4), CH_4 (16), NH_3 (17), H_2O (18), Ne (20), N_2 (28), O_2 (32), H_2S (34), Ar (40), CO_2 (44), …** **As a result:**

F, Flux from the Sun	M, Mass of protoplanet	Young planet, previously 100 million years	Modern planet, 4.56 billion years evolution
low, long distances	Large, Jupiter, Saturn	Jupiter, Saturn H_2, He, + (CH_4, NH_3, H_2S, PH_3 ….)	Jupiter, Saturn H_2, He, + (CH_4, NH_3, H_2S, PH_3 ….)
moderate	Low, Mars	Loss H_2, He, CH_4 Condensation **H_2O**	Mars : Loss of **H_2O** 95,3% CO_2, 2,7% N_2
moderate	Moderate, Earth	Loss H_2, He, CH_4 Condensation **H_2O**	Earth: **CO_2** - Chemical Condensation. **N_2 , + O_2 from H_2O** and **CO_2**
High	Moderate, Venus	Loss H_2, He, CH_4, **H_2O**	Venus 96,5% CO_2, 3,5% N_2

SUBDISK
RNA World



Gravitational instability
Time of the Clump was 1-10 years
RNA World was during 1 Million Years

Creation of primary bodies with size about 1 and more kilometers

Catalysts and organics compounds

Drastic change of physical and chemical conditions

RNA world

Ancient RNA world was a precursor of the Life on the Earth

Ribonucleic acids are capable to perform all basic functions characteristic of both DNA and proteins.