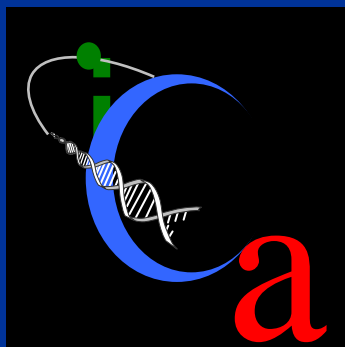
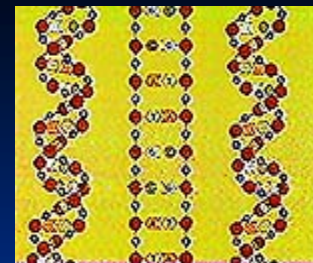
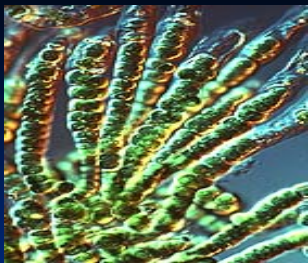


Astrochemistry

The Cradle of Life



Professor Nigel Mason
The Open University



Introduction

Perhaps the great unanswered questions of modern science is

- Where and how did life begin on Earth ?

And

- Is there life elsewhere in the universe ?

Introduction

Lets take a vote !

Who believes there is life elsewhere in
the universe ?

Introduction

Lets ask a slightly different question

Who believes there is intelligent life elsewhere in the universe which is able to establish a science programme to look for life ?

Introduction

To answer the questions

Where and how did life begin on Earth ?

And

Is there life elsewhere in the universe ?

We need to answer scientific questions

- Are the conditions for sustaining life common throughout the universe ?

Introduction

To answer the questions

Where and how did life begin on Earth ?

And

Is there life elsewhere in the universe ?

We need to answer scientific questions

- Are the conditions for sustaining life common throughout the universe ?
- How is the material needed for life (pre-biotic material) formed ?

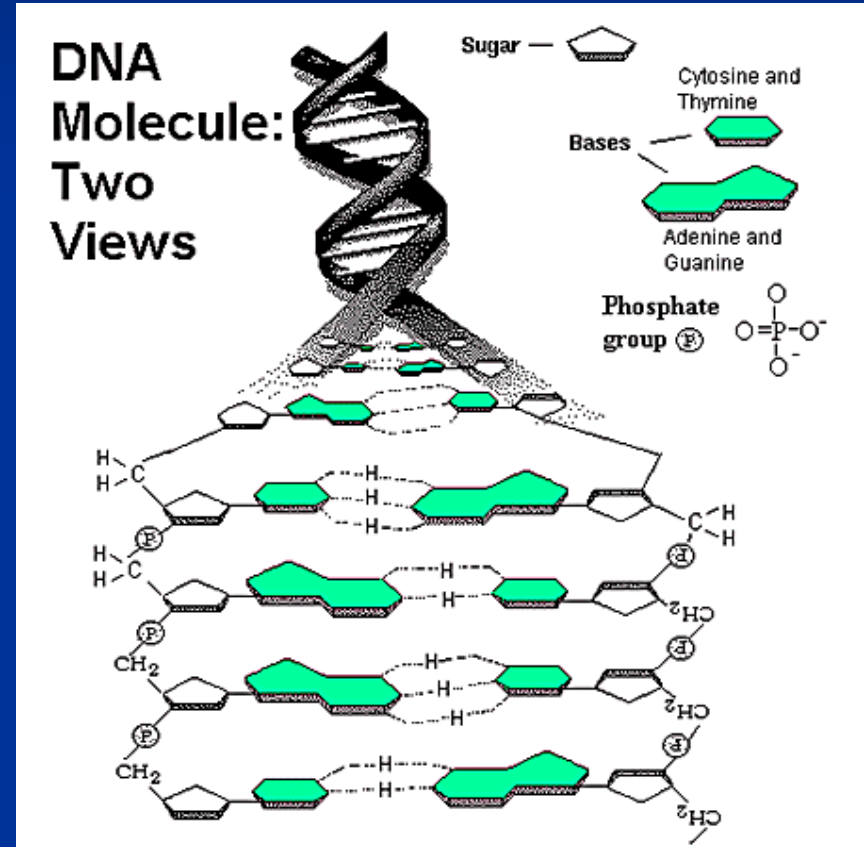
Chemical origins of life

- To understand how life was formed we need to know how and where chemical elements of life were made
- What are major chemical elements of life ?

Chemical origins of life

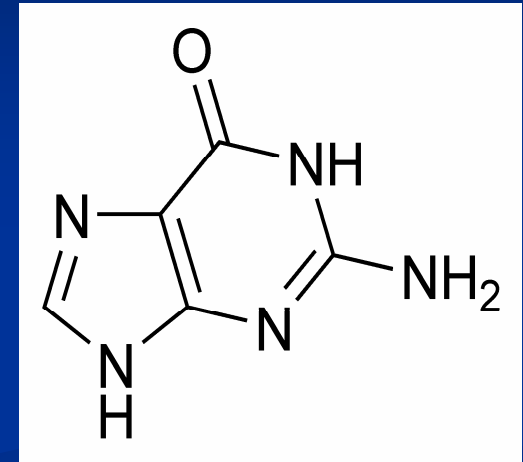
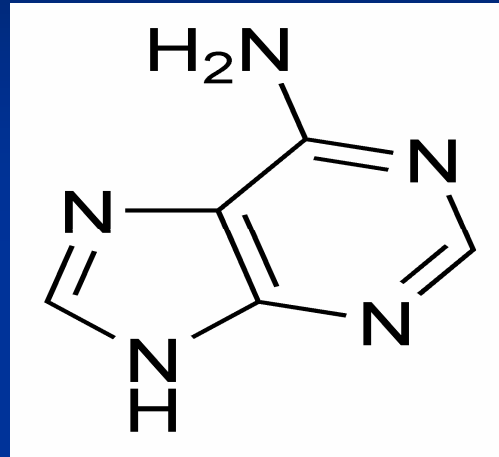
- The major molecule of life (as we know it) is **DNA**
Deoxyribonucleic acid

- Major elements are Carbon, hydrogen, oxygen, nitrogen and phosphorous.

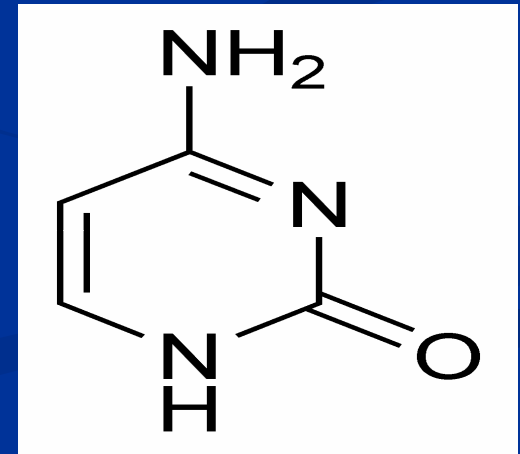
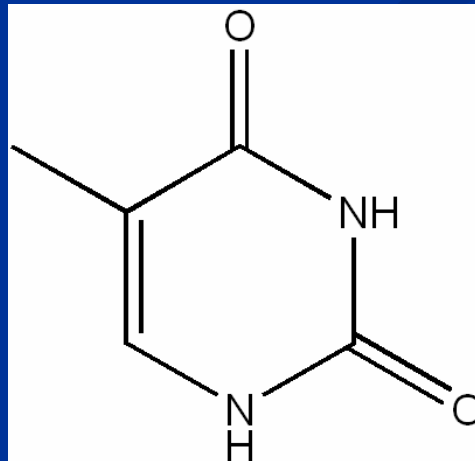


Nucleobases

- Adenine
- Guanine
- Thymine
- Cytosine



- Paired in DNA
- AT
- CG



Building DNA

DNA is made up of smaller molecules which must have assembled first from smaller molecules such as *Amino acids*

So if we want to know how DNA was formed we start by looking for how these smaller (prebiotic) molecules are formed

History of Origins of Life Research

Scientific investigation of origins of life are *recent*

Aleksandr Oparin 1894 -1980



Oparin considered how basic organic chemicals might form into larger chemical systems which were the possible precursors of cells - from which primitive living things could develop.

He suggested **life may have begun in early oceans** Since the surface was too exposed to UV light, volcanic eruptions acid rain and meteor impacts for life to survive,

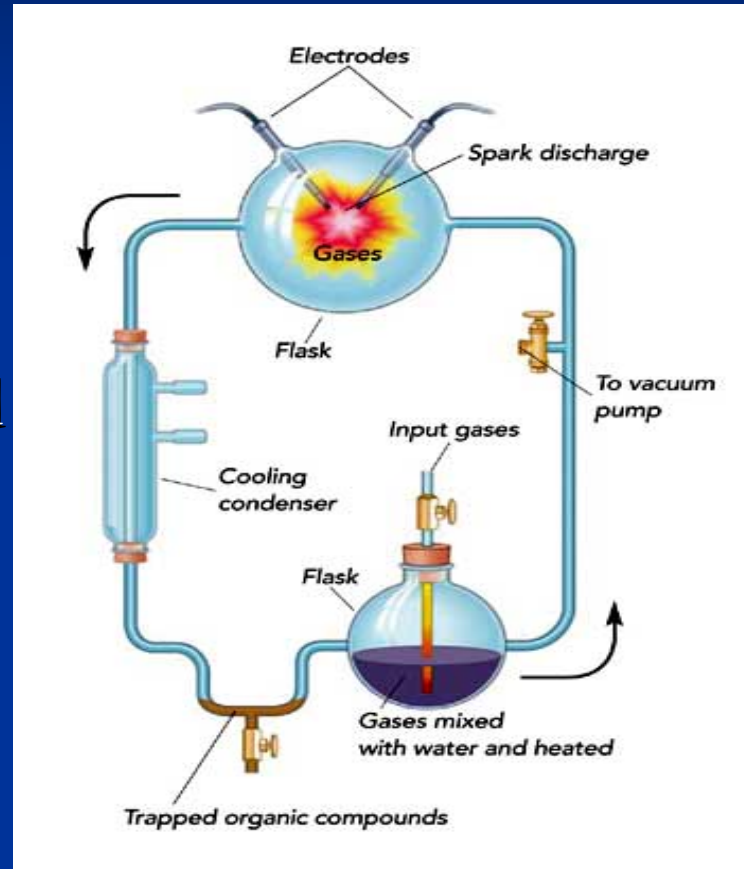
Exploring origins of life

Oparin's hypotheses were not tested for some 40 years until **Harold Urey and Stanley Miller** March 7, 1930 - May 20, 2007 performed a famous experiment to see if the **chemical ingredients of life can be made in the atmosphere of a planet** .

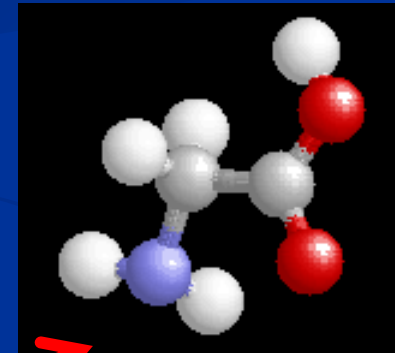
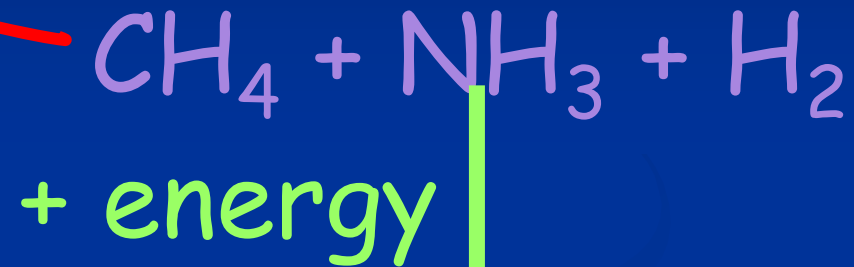
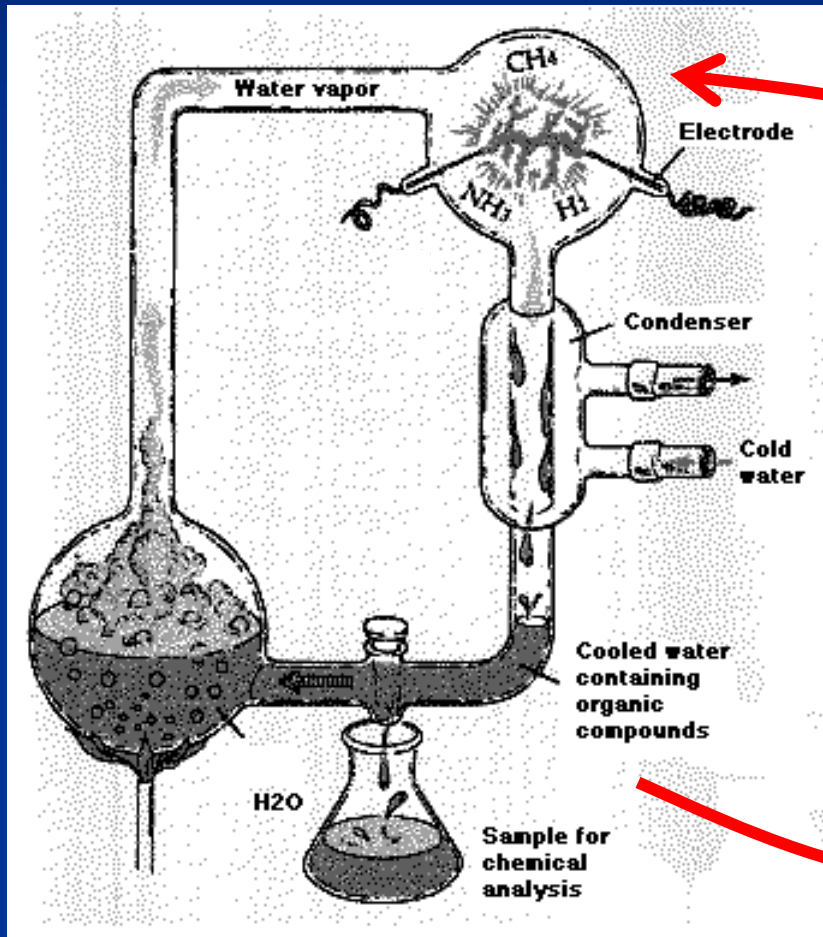


The UREY MILLER Experiment.

- The Urey Miller Experiment
- Mixture of Water, Hydrogen, Methane and Ammonia
- Generate a discharge as in lightening
- See what you make !



Molecules formed in planetary atmospheres - Urey Miller expts



Glycine
Amino acid

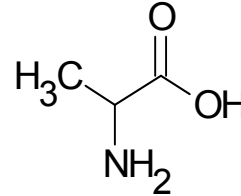
The OU Urey Miller experiment

- Similar in design to the original.
- 2 L glass bulb for the “atmosphere”
- 200 ml water bulb
- Heating provided by heating tapes

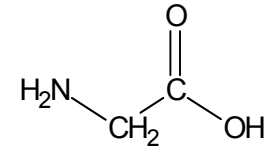


Urey Miller Results

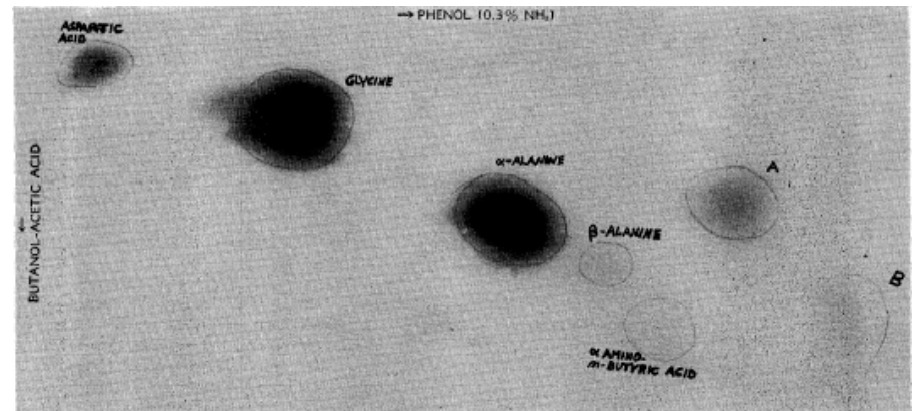
- Urey-Miller was run for a week, liquid was extracted from the flask
- Analysed with paper chromatogram
- 3 Amino acids identified, Glycine, α -alanine and β -alanine
- Hence it is possible to form prebiotic molecules from basic chemistry



Alanine (Ala)



Glycine (Gly)



But we now know ...

- These were not the gases in early earth atmosphere (more CO_2 and SO_2)
- It takes too long to build these molecules –
- Indeed according to our models we are not here yet !!!

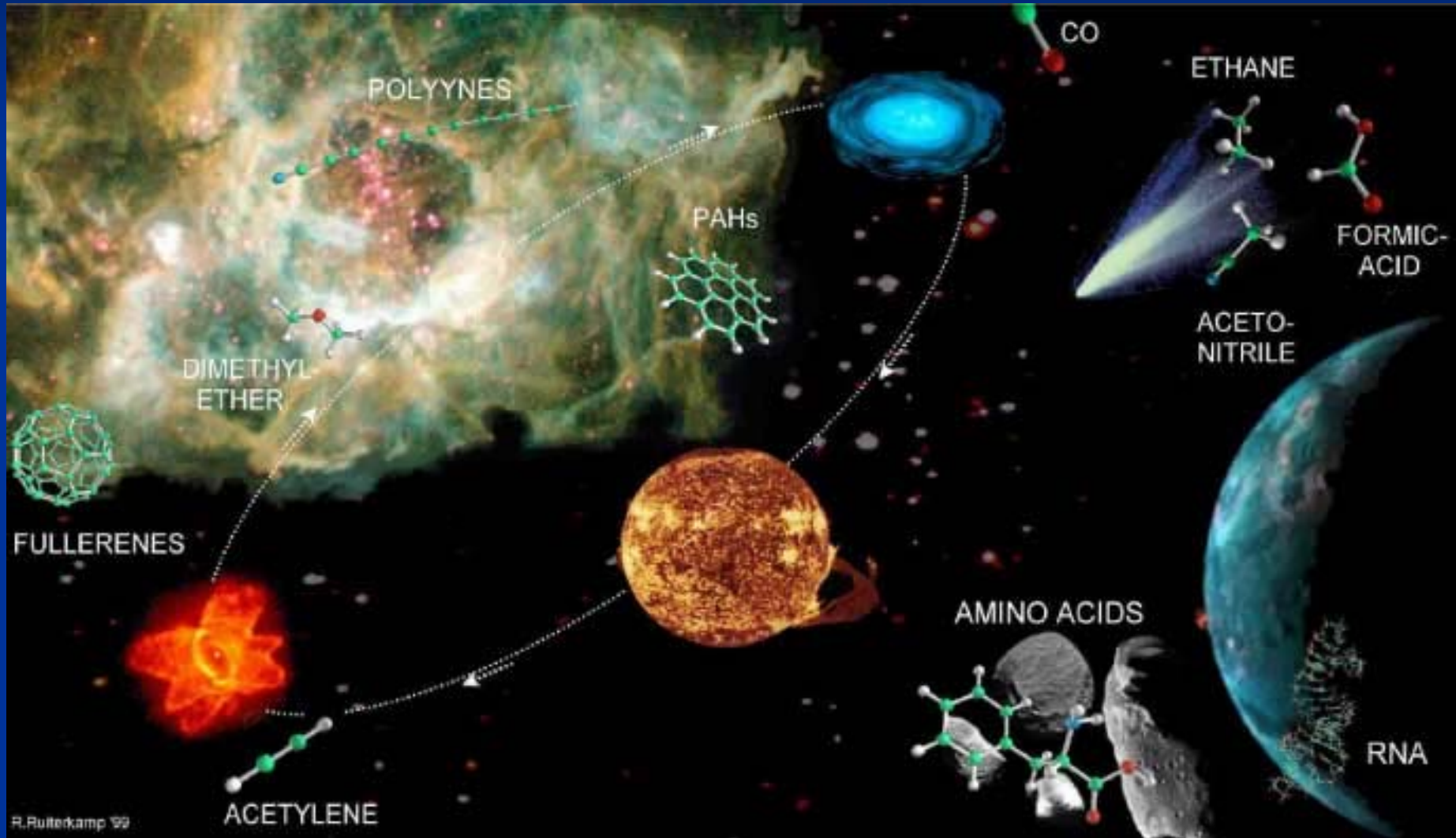
**But what if the 'building blocks' are
formed in space itself?**



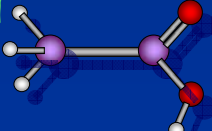

Are biomolecules transported to Earth on comets, meteorites ?

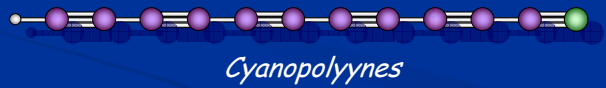
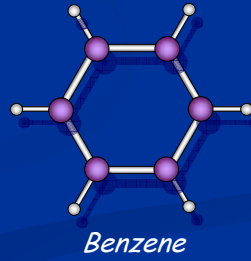
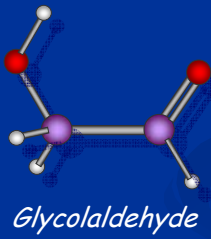
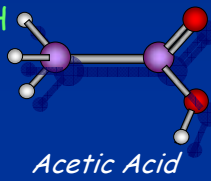
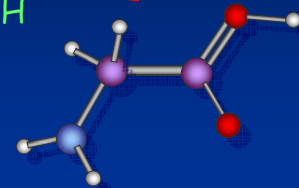
- Are biomolecules made in transit through Earth's atmosphere on comets etc ?
- Meteorites give evidence that **amino acids** are **present in large numbers** – some of which are not found naturally in terrestrial life
- **So are prebiotic molecules of life made in space ?**

The Interstellar Medium is **rich in molecules...**
from the simplest molecule (H_2)
to those necessary for the formation of life



>140 Interstellar and Circumstellar Molecules

2	3	4	5	6	7	8	9	10	11
H ₂	C ₃	c-C ₃ H	C ₅	C ₅ H	C ₆ H	CH ₃ C ₃ N	CH ₃ C ₄ H	CH ₃ C ₅ N?	HC ₉ N
AlF	C ₂ H	l-C ₃ H	C ₄ H	l-H ₂ C ₄	CH ₂ CHCN	HCOOCH ₃	CH ₃ CH ₂ CN	(CH ₃) ₂ CO	
AlCl	C ₂ O	C ₃ N	C ₄ Si	C ₂ H ₄	CH ₃ C ₂ H	CH ₃ COOH	(CH ₃) ₂ O	NH ₂ CH ₂ COOH?	12
C ₂	C ₂ S	C ₃ O	l-C ₃ H ₂	CH ₃ CN	HC ₅ N	C ₇ H	CH ₃ CH ₂ OH		C ₆ H ₆
CH	CH ₂	C ₃ S	c-C ₃ H ₂	CH ₃ NC	NH ₂ CH ₃	H ₂ C ₆	HC ₇ N		
CH ⁺	HCN	C ₂ H ₂	CH ₂ CN	CH ₃ OH	HCOCH ₃	CH ₂ OHCHO	C ₈ H		13+
CN	HCO	CH ₂ D ⁺ ?	CH ₄	CH ₃ SH	c-C ₂ H ₄ O				HC ₁₁ N
CO	HCO ⁺	HCCN	HC ₃ N	HC ₃ NH ⁺	CH ₂ CHOH				PAHs
CO ⁺	HCS ⁺	HCNH ⁺	HC ₂ NC	HC ₂ CHO					C60 ⁺
CP	HOC ⁺	HNCO	HCOOH	NH ₂ CHO					
CSi	H ₂ O	HNCS	H ₂ CHN	C ₅ N					
HCl	H ₂ S	HOCO ⁺	H ₂ C ₂ O						
KCl	HNC	H ₂ CO	H ₂ NCN						
NH	HNO	H ₂ CN	HNC ₃						
NO	MgCN	H ₂ CS	SiH ₄						
NS	MgNC	H ₃ O ⁺	H ₂ COH ⁺						
NaCl	N ₂ H ⁺	NH ₃							
OH	N ₂ O	SiC ₃							
PN	NaCN								
SO	OCS								
SO ⁺	SO ₂								
SiN	c-SiC ₂								
SiO	CO ₂								
SiS	NH ₂								
CS	H ₃ ⁺								
HF	SiCN								
SH									
FeO	AlNC								



What chemistry can occur in such environments ?



- Temperatures are low ... (As low as 10K)
- In the ISM the density is extremely low ... so probability of collisions is low
- Hence it appears impossible to support chemistry !

But evidence of molecular species shows there must be complex chemistry !

What chemistry can occur in such environments ?



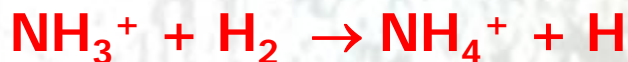
- At low temperatures there is little or no thermal/kinetic energy
- So chemistry must occur through reactions that need no energy.
- Or
- Reactions that are assisted e.g. by light

What chemistry can occur in such environments ?



Ion-Molecule reactions are a typical example of a reaction that do not require energy input

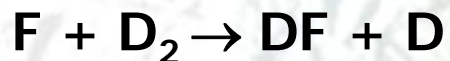
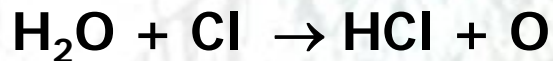
e.g.



What chemistry can occur in such environments ?



However neutral – neutral reactions can also occur at low temperatures.



Indeed the reaction rate may INCREASE as the temperature falls

What chemistry can occur in such environments ?

Supersonic crossed beam machine for radical-radical studies.

CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) to study neutral-neutral reactions and energy transfer processes in the gas phase down to temperatures as low as ~10 K. (Rennes)



What chemistry can occur in such environments ?



But such gas phase experiments can not explain all the chemistry in the ISM

E.g. the formation of H_2 the most common molecule in the ISM can not be formed in the gas phase

Instead it is formed by reactions on the surface of little dust grains made when stars die !

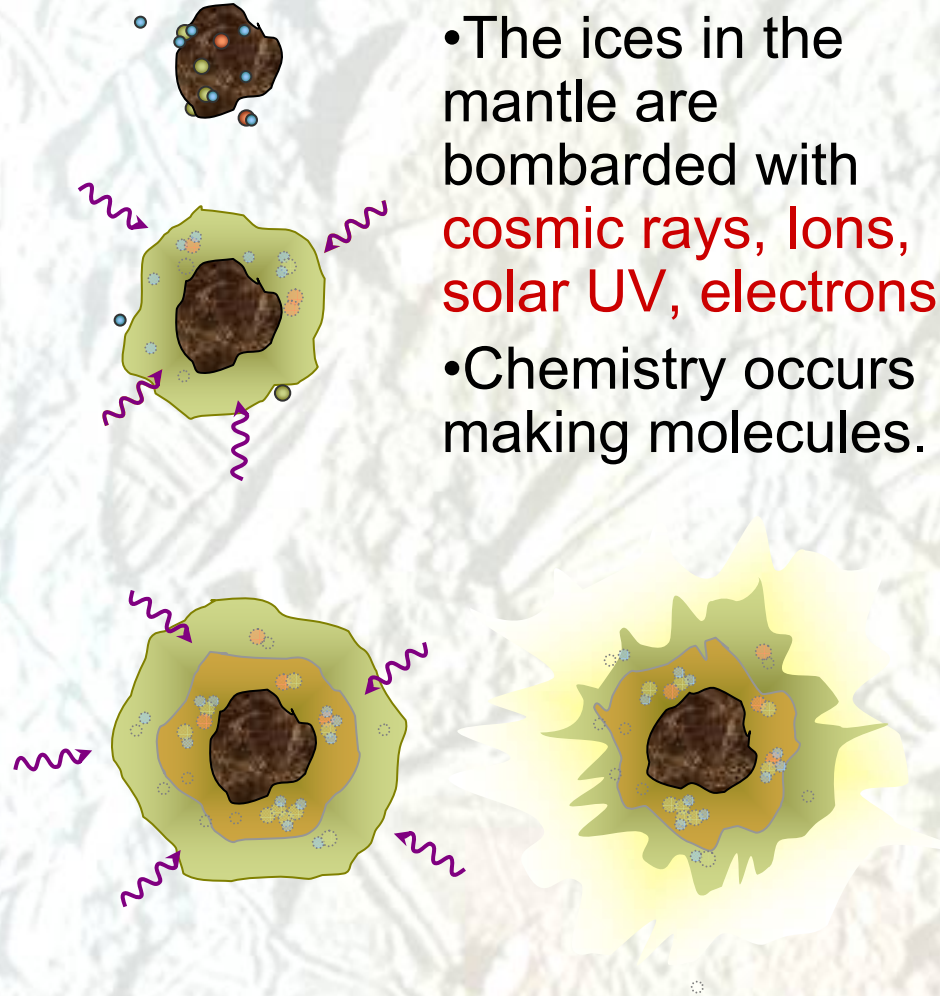
Little pieces of Carbon – like the soot on your Macdonalds 'flame grilled' burger

Or silicon (sand !!)

Chemistry on Dust grains

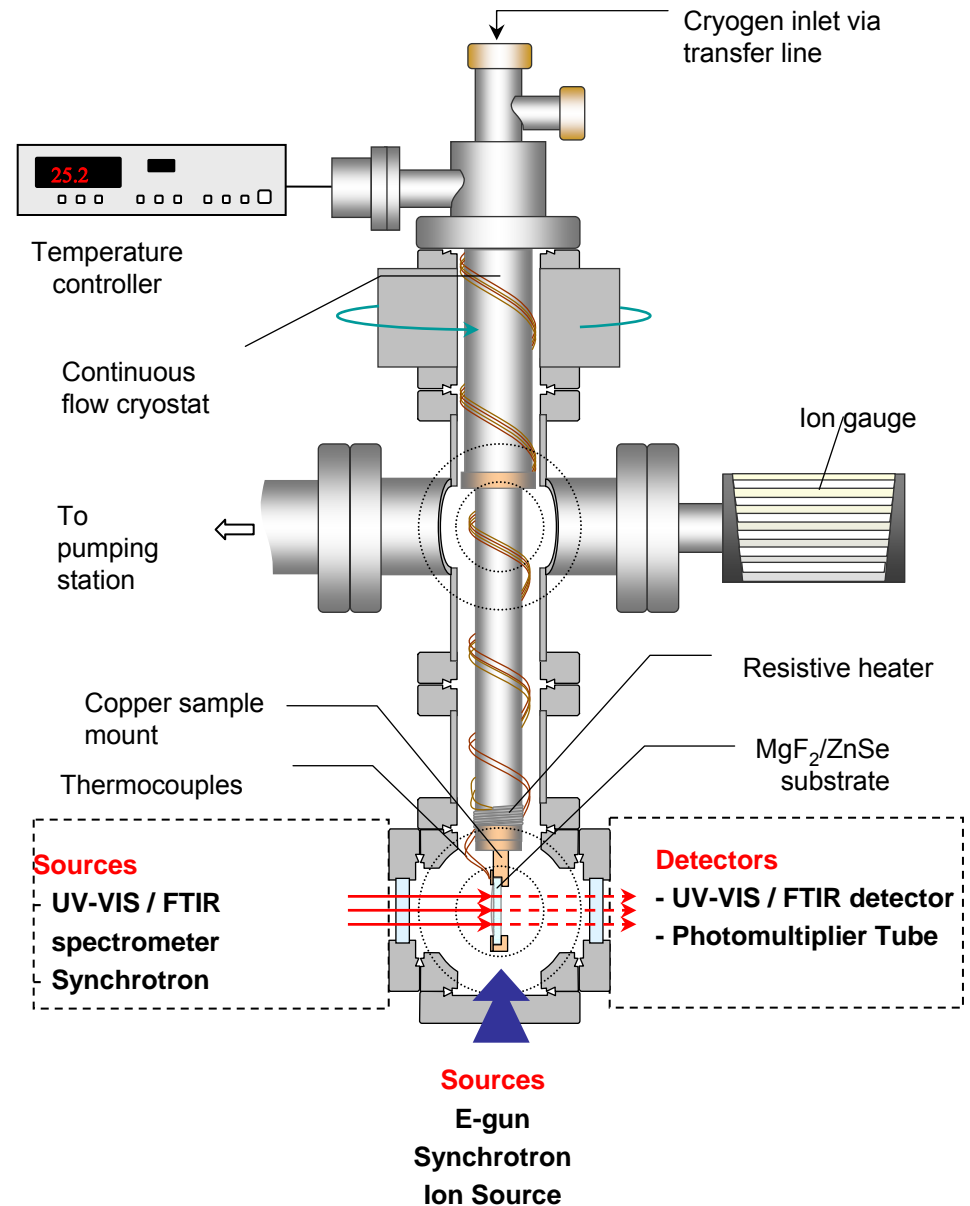


- Some of these grains are covered with an icy mantle formed by freezing out of atoms/molecules from the gas phase
- Hence we need to explore ice chemistry !



- The ices in the mantle are bombarded with **cosmic rays, ions, solar UV, electrons.**
- Chemistry occurs making molecules.

- **Vacuum chamber to mimic empty space:**
 - $P \sim 10^{-8} - 10^{-10}$ mbar
 - **Still > a million times higher than ISM!**
- **Temperature very cold in space**
 - Continuous flow LHe/LN2 cryostat
 - $12 \text{ K} < T < 450 \text{ K}$
- **Material to mimic grains**
- **Make ice Samples**
- **Use spectroscopy to see what you make**

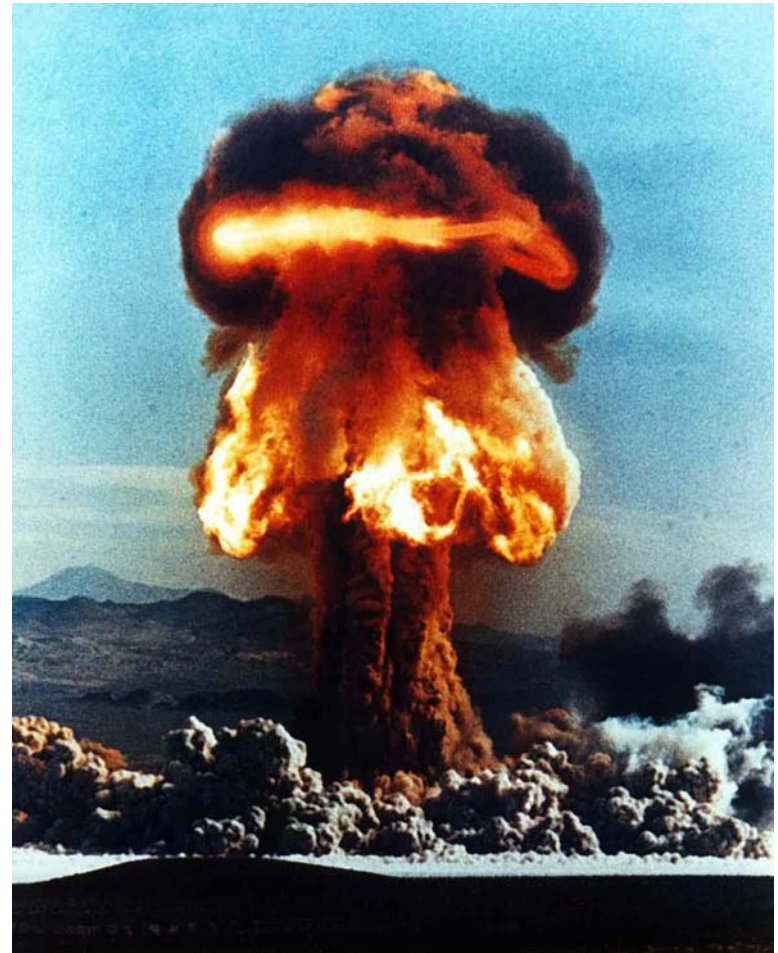


Experimental studies of chemical processing of astrochemical ices

First we need to find a
mimic of star light !

Stars are fuelled by
nuclear reactions

We can't use these in a
laboratory



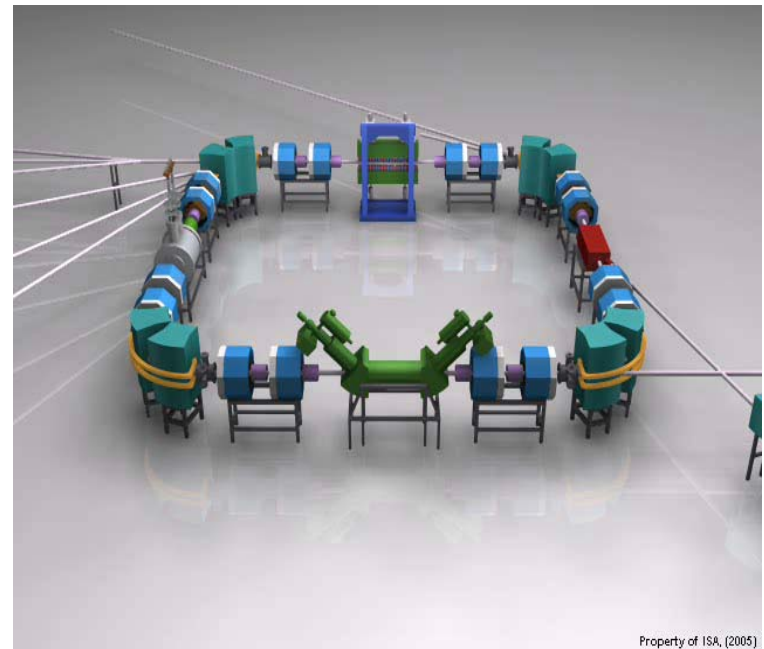
Experiments at Synchrotron Facilities

Mimicing star light

UK Daresbury

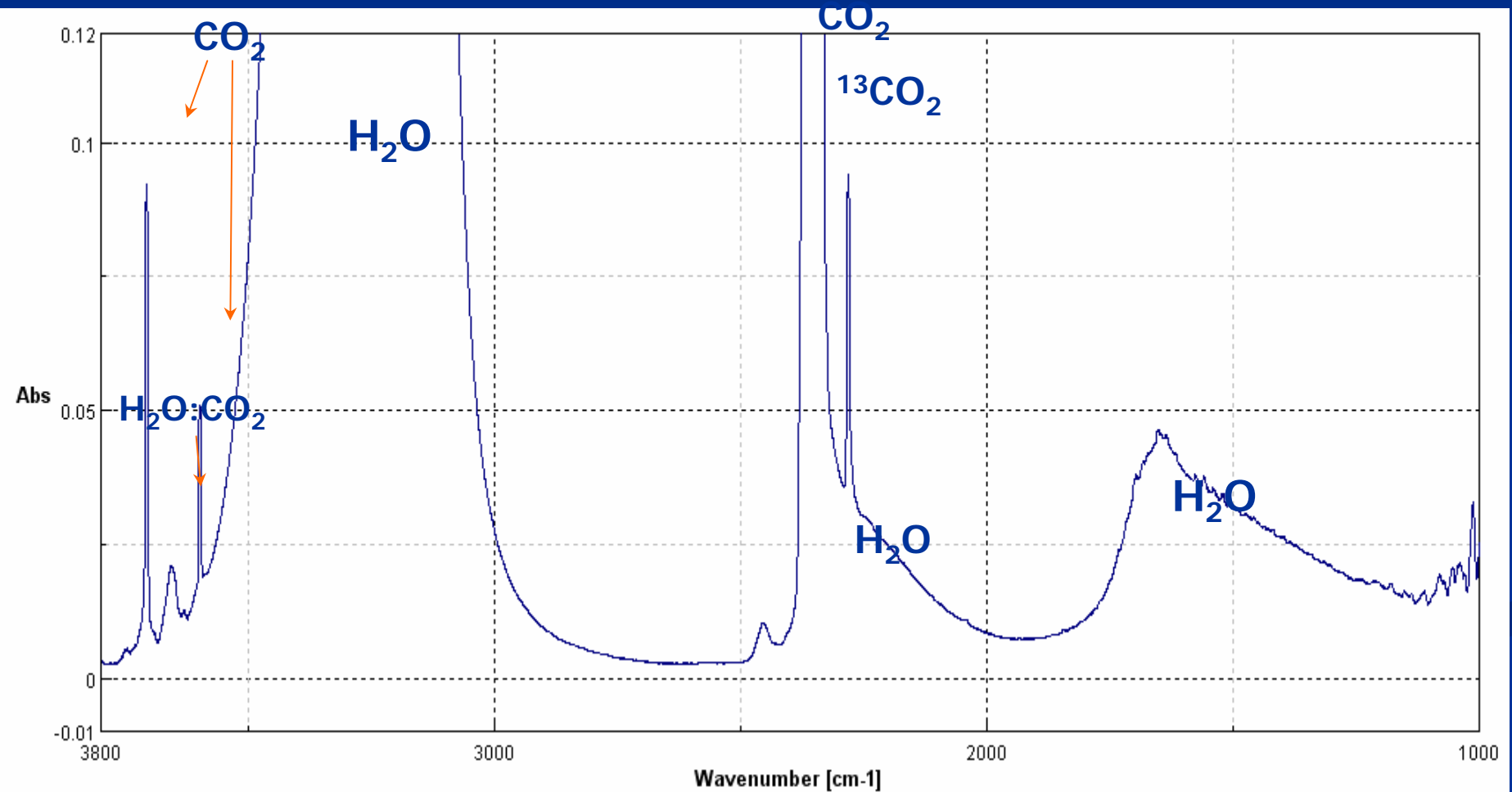


Aarhus Denmark



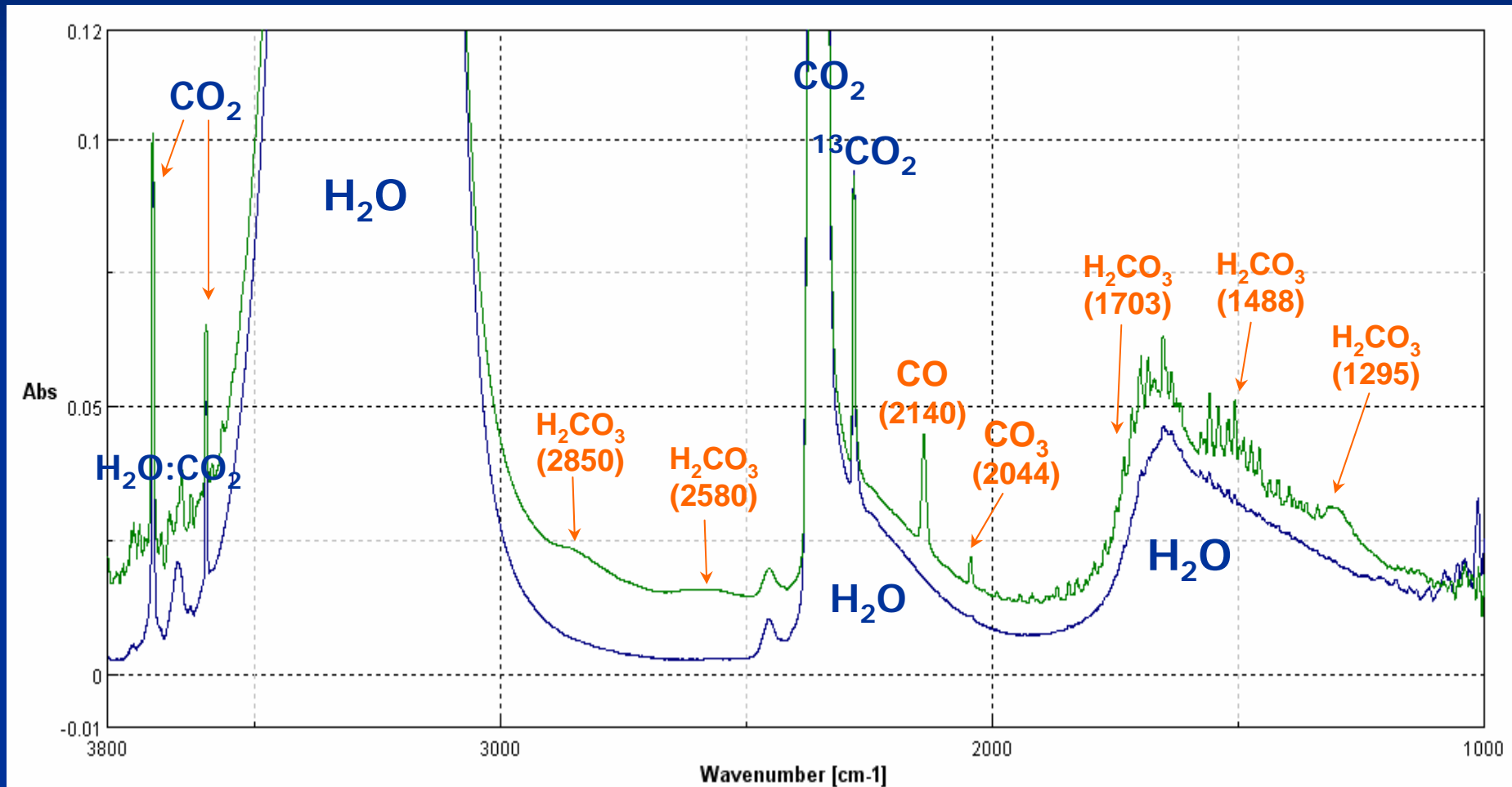
Irradiation of $\text{H}_2\text{O}:\text{CO}_2$ ice

Before irradiation



Irradiation of $\text{H}_2\text{O}:\text{CO}_2$ ice

After irradiation for 1 hour



T(K)

250

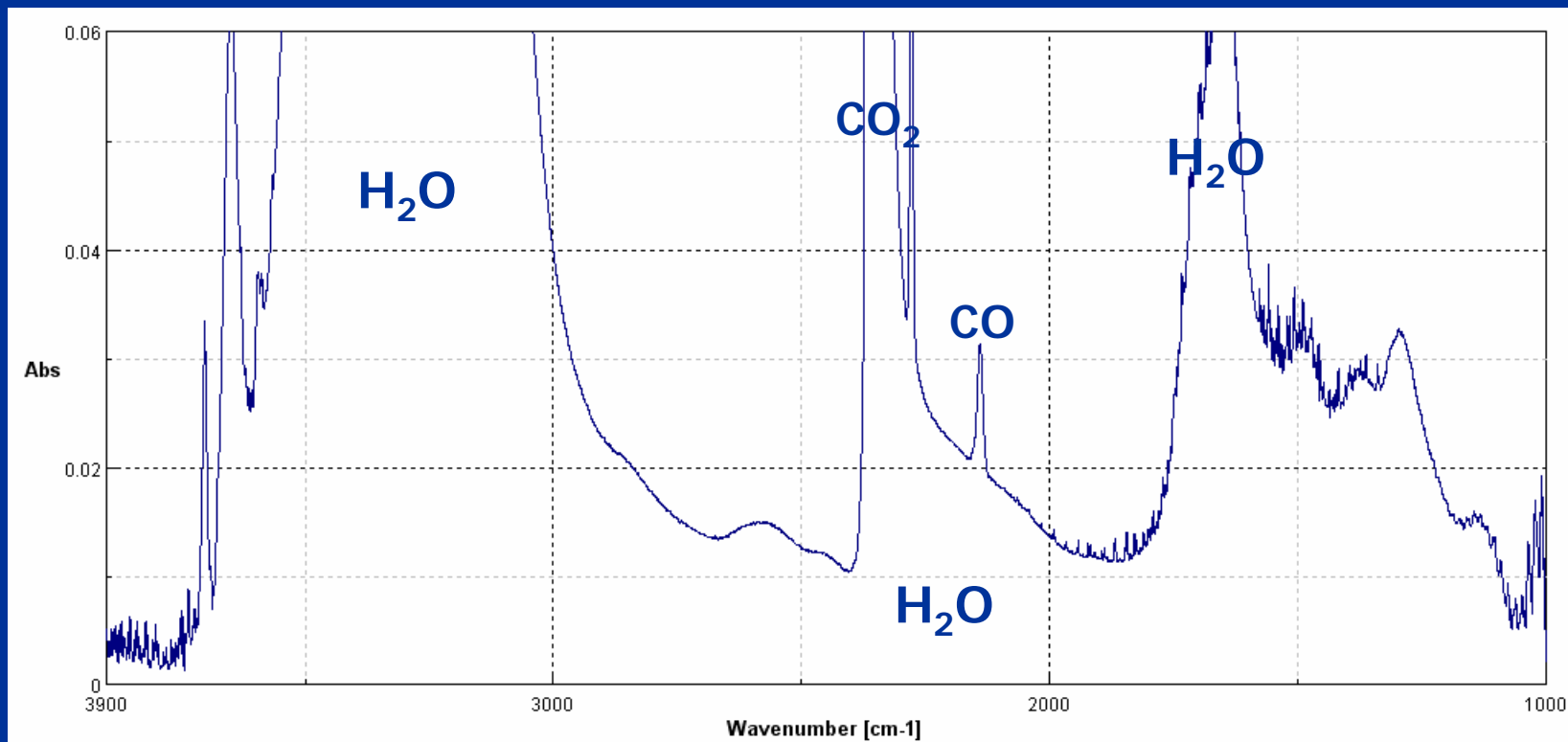
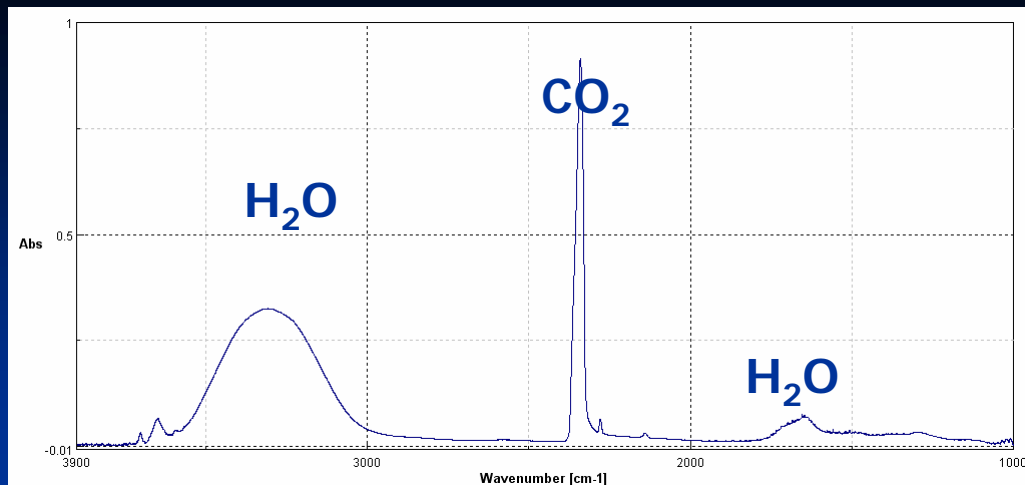
200

150

100

50

Warm-up
+Irradiation of
H₂O:CO₂ ice



T(K)

250

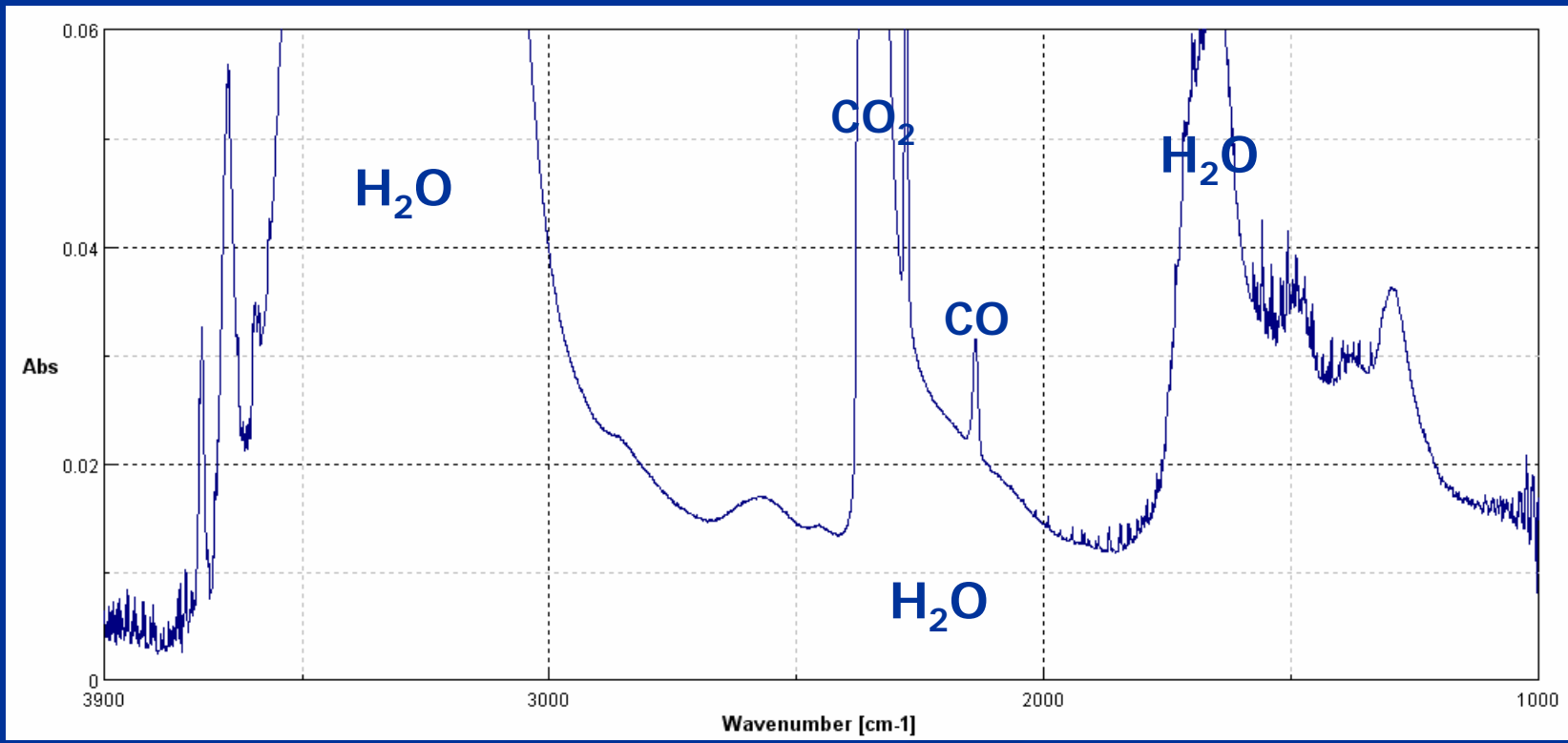
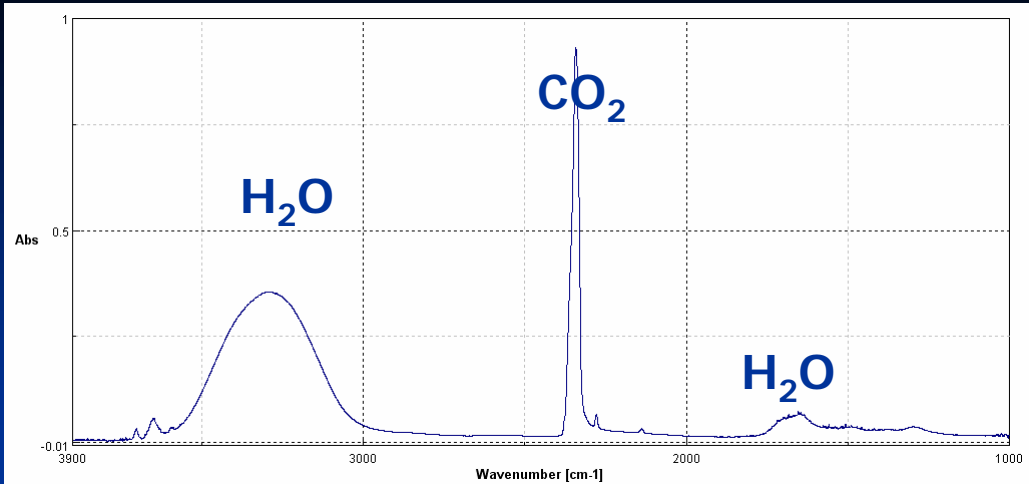
200

150

100

50

Warm-up after H⁺
Irradiation of
H₂O:CO₂ ice



T(K)

250

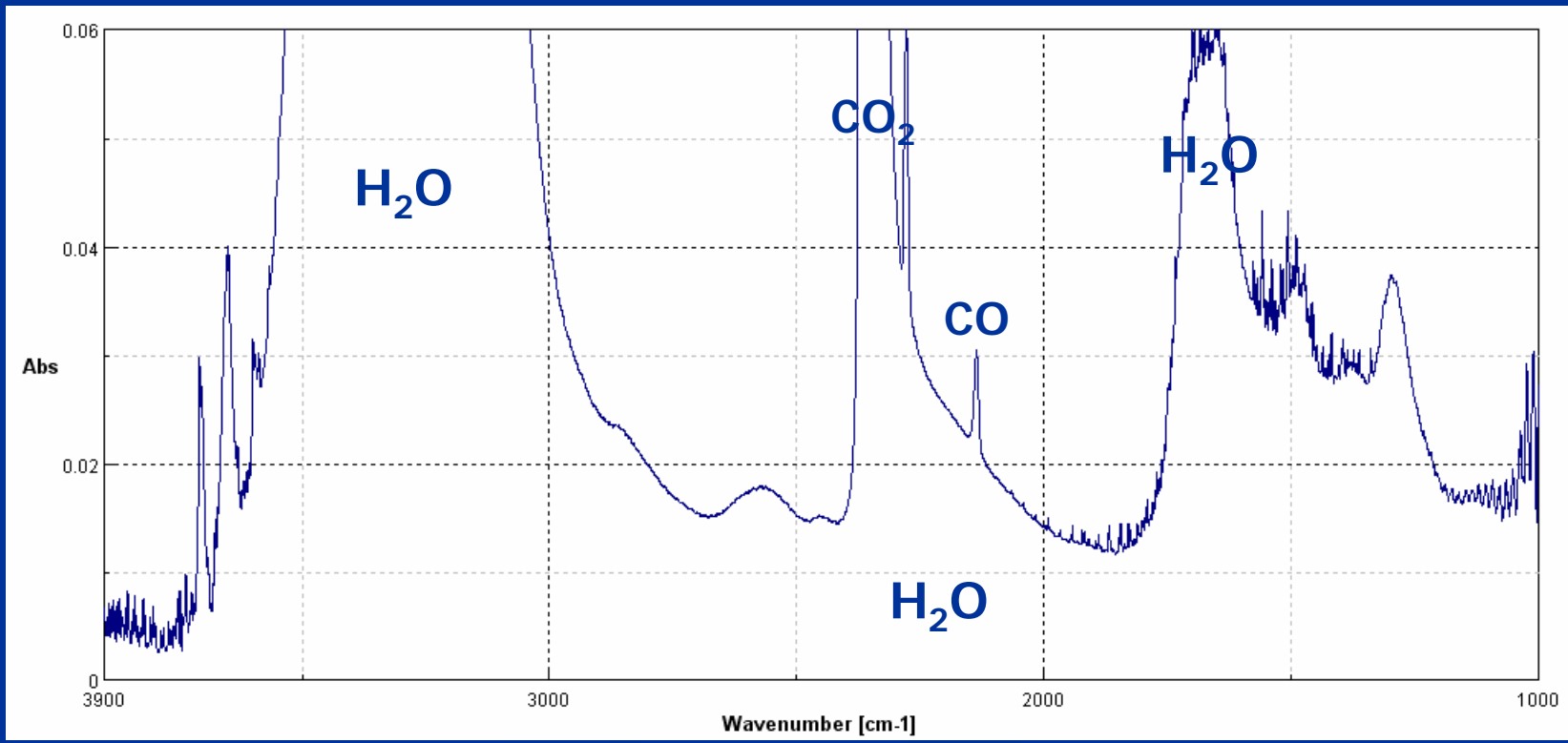
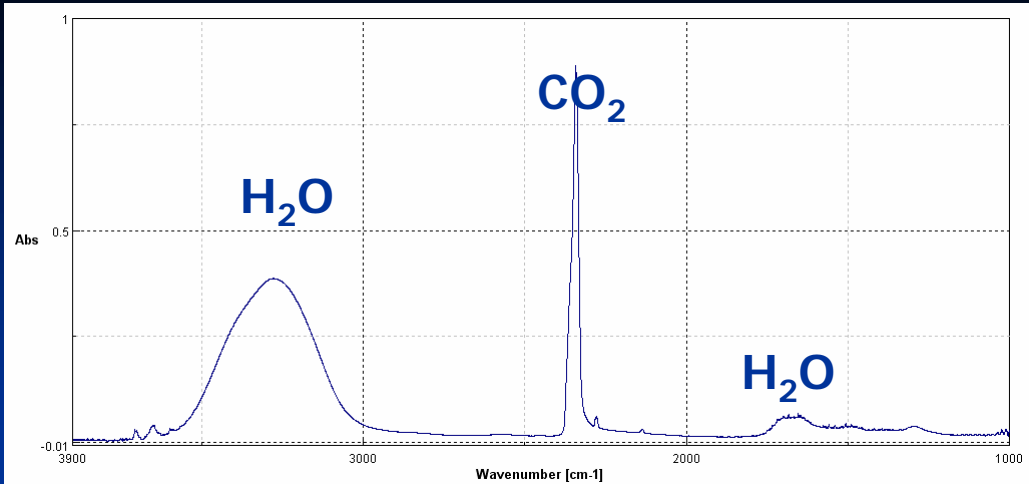
200

150

100

50

Warm-up after H⁺ Irradiation of H₂O:CO₂ ice



T(K)

250

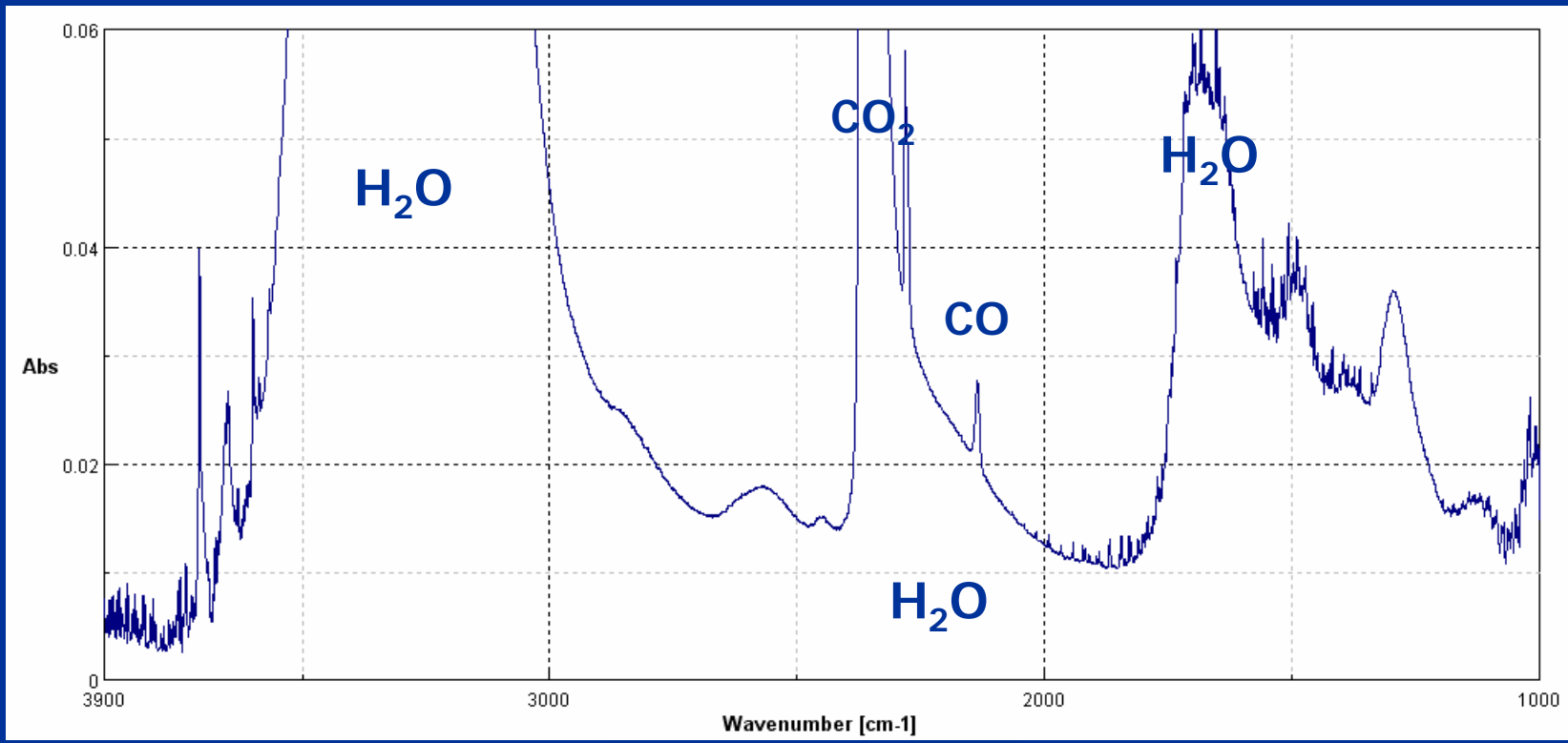
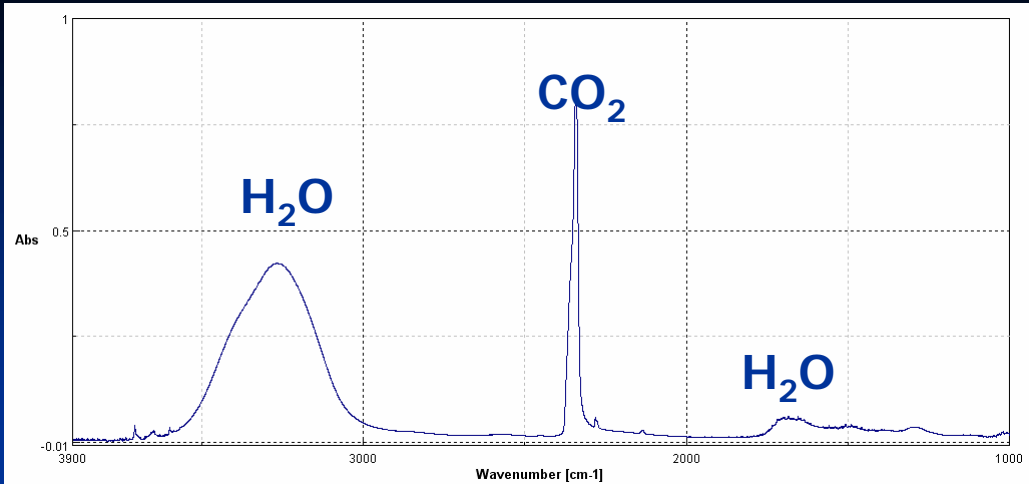
200

150

100

50

Warm-up after H⁺
Irradiation of
H₂O:CO₂ ice



T(K)

250

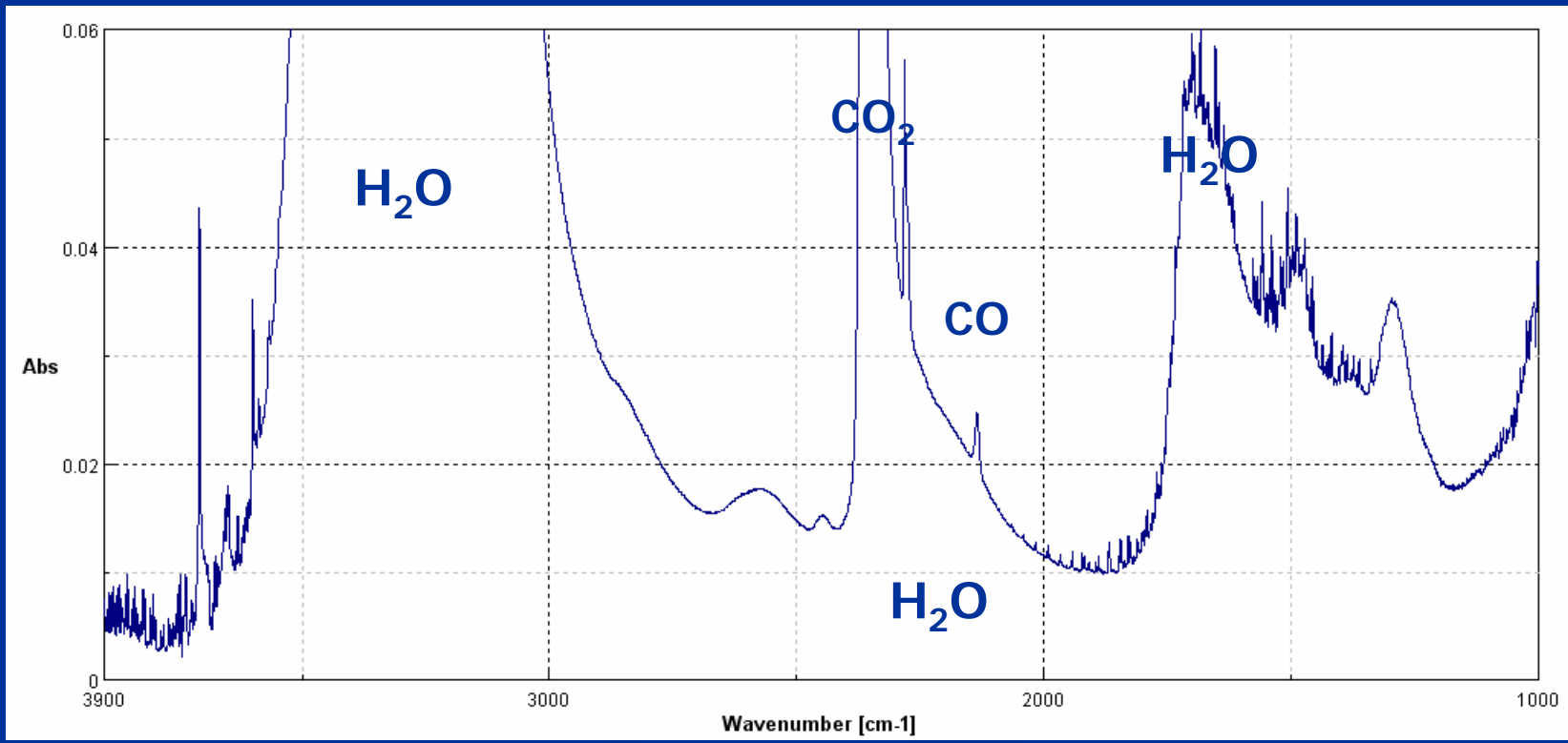
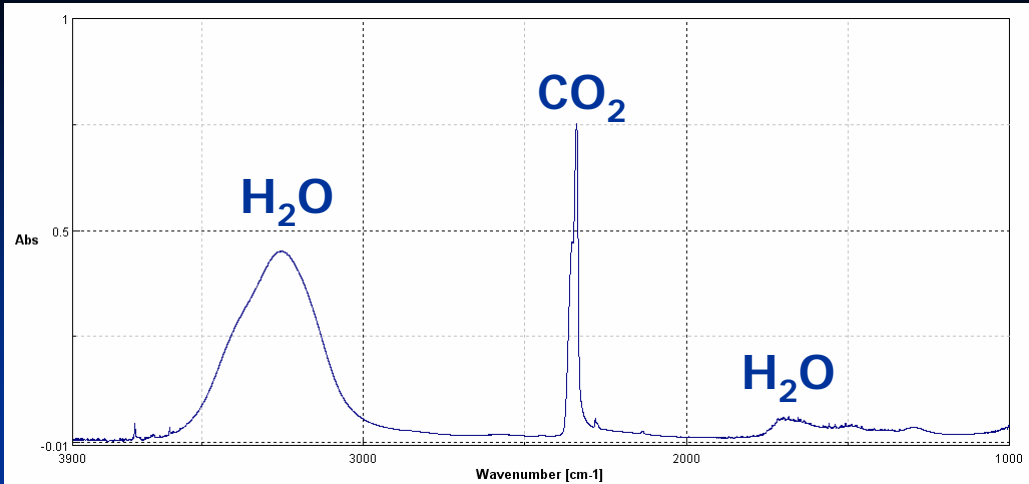
200

150

100

50

Warm-up after H⁺
Irradiation of
H₂O:CO₂ ice



T(K)

250

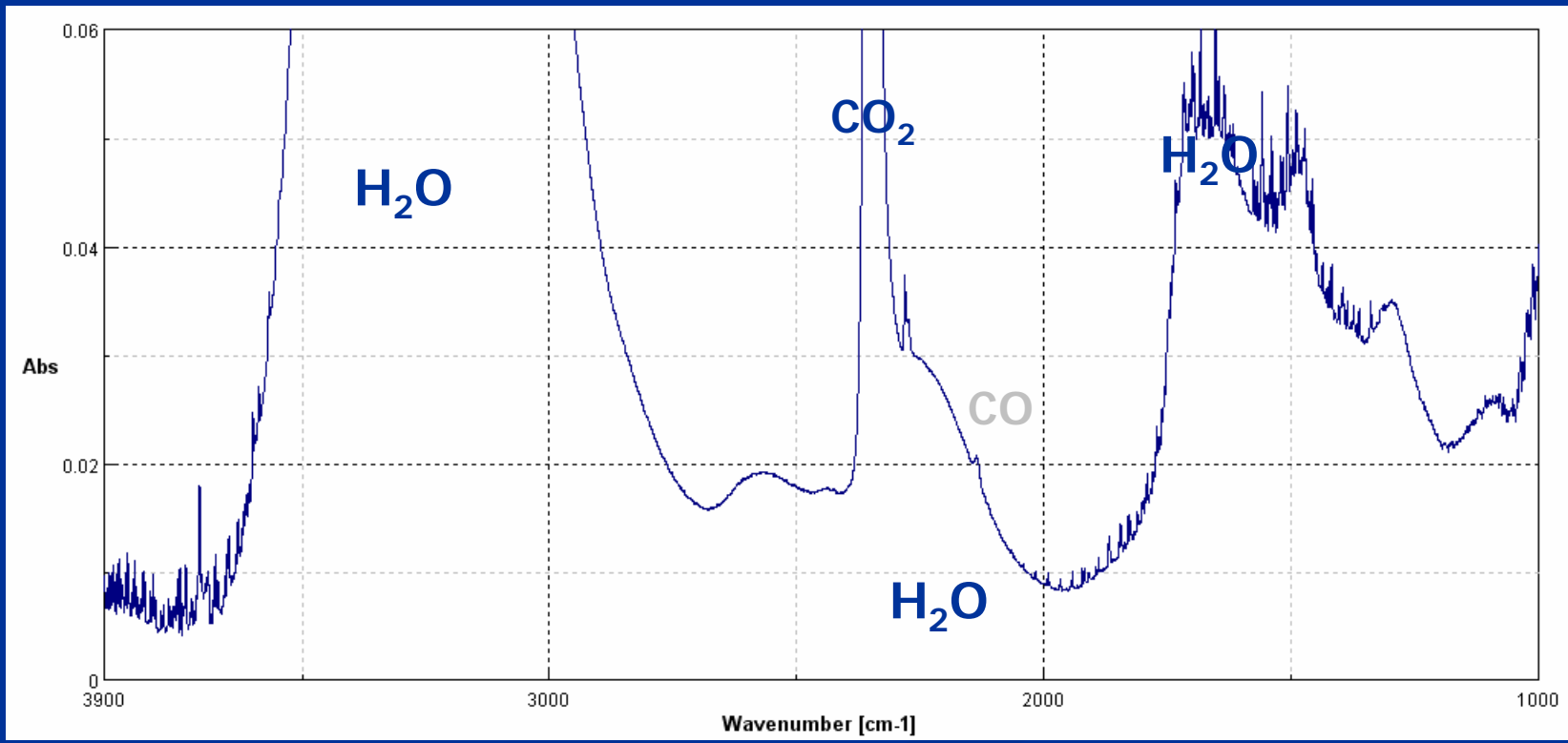
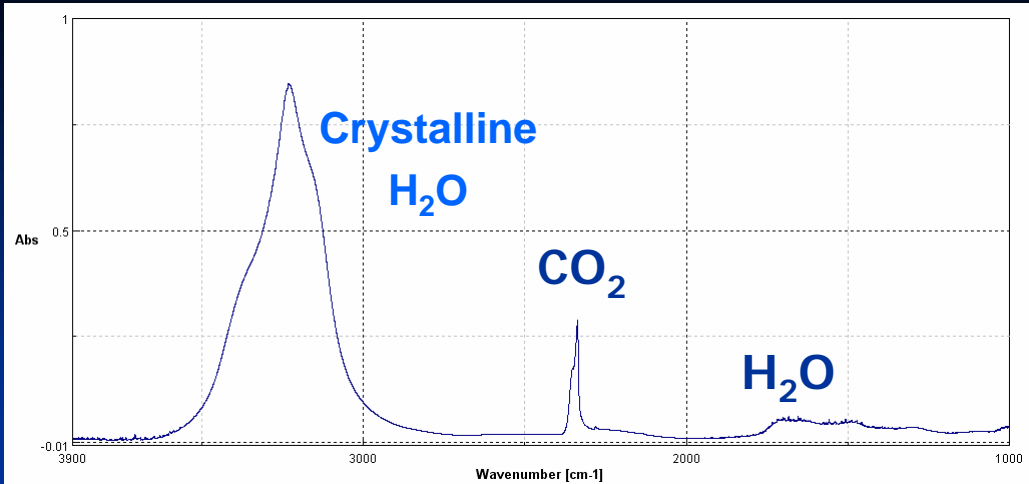
200

150

100

50

Warm-up after H⁺ Irradiation of H₂O:CO₂ ice



T(K)

250

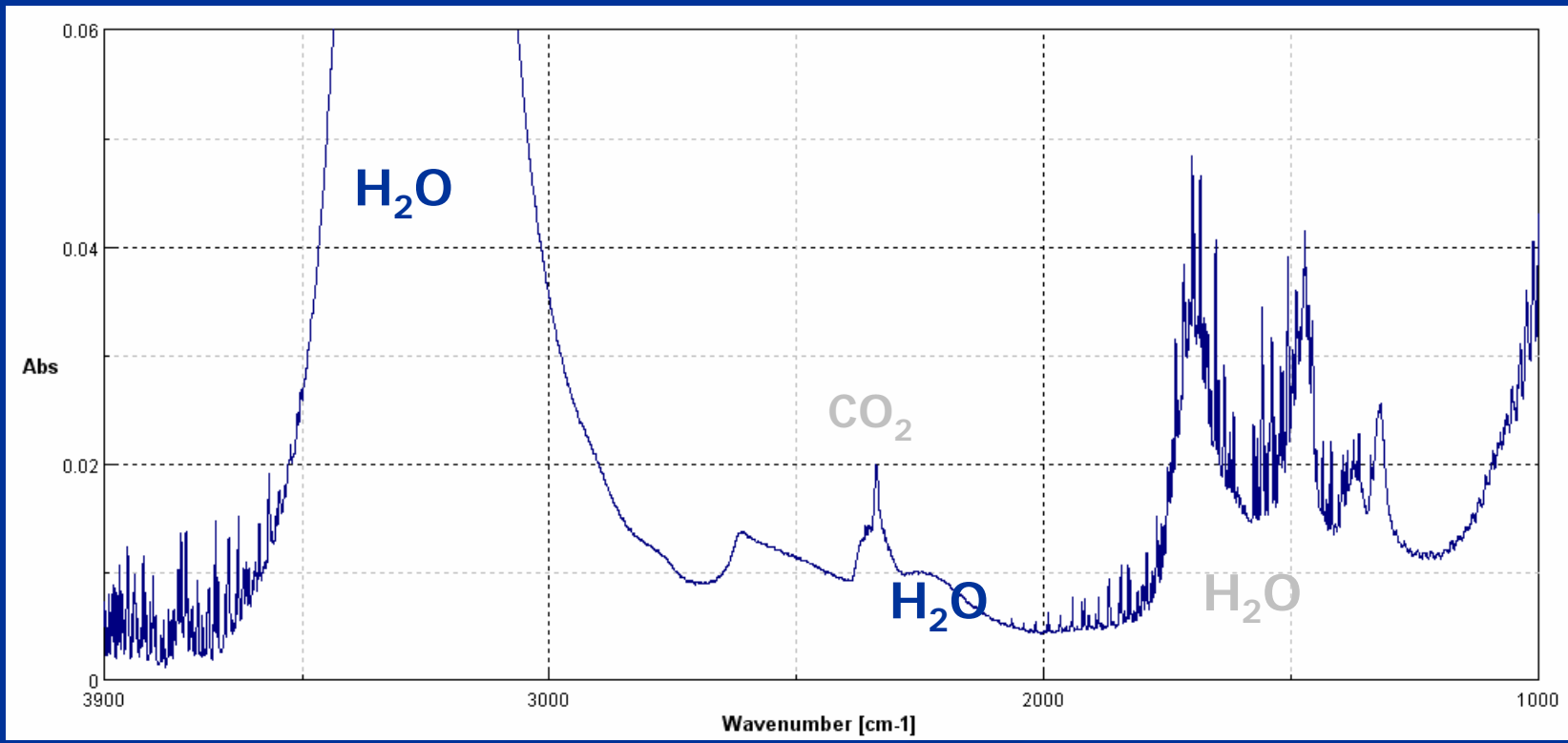
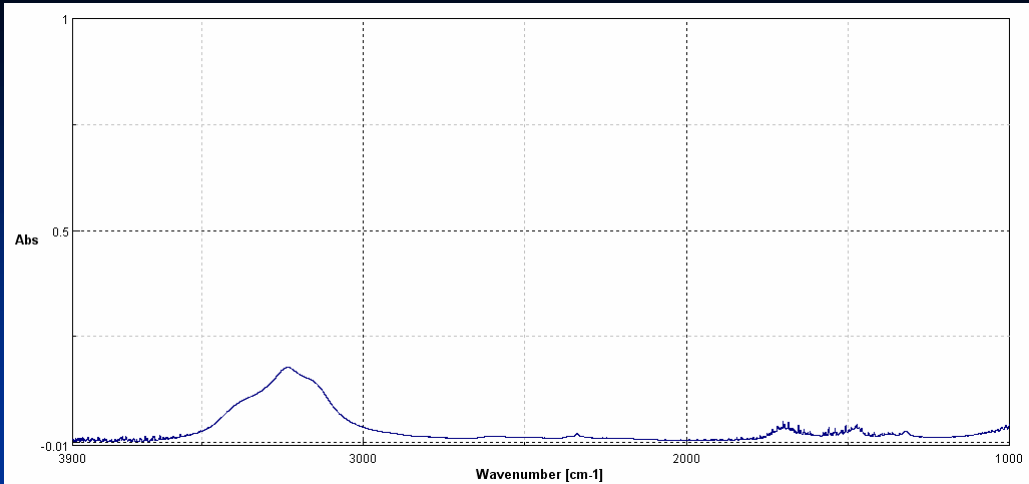
200

150

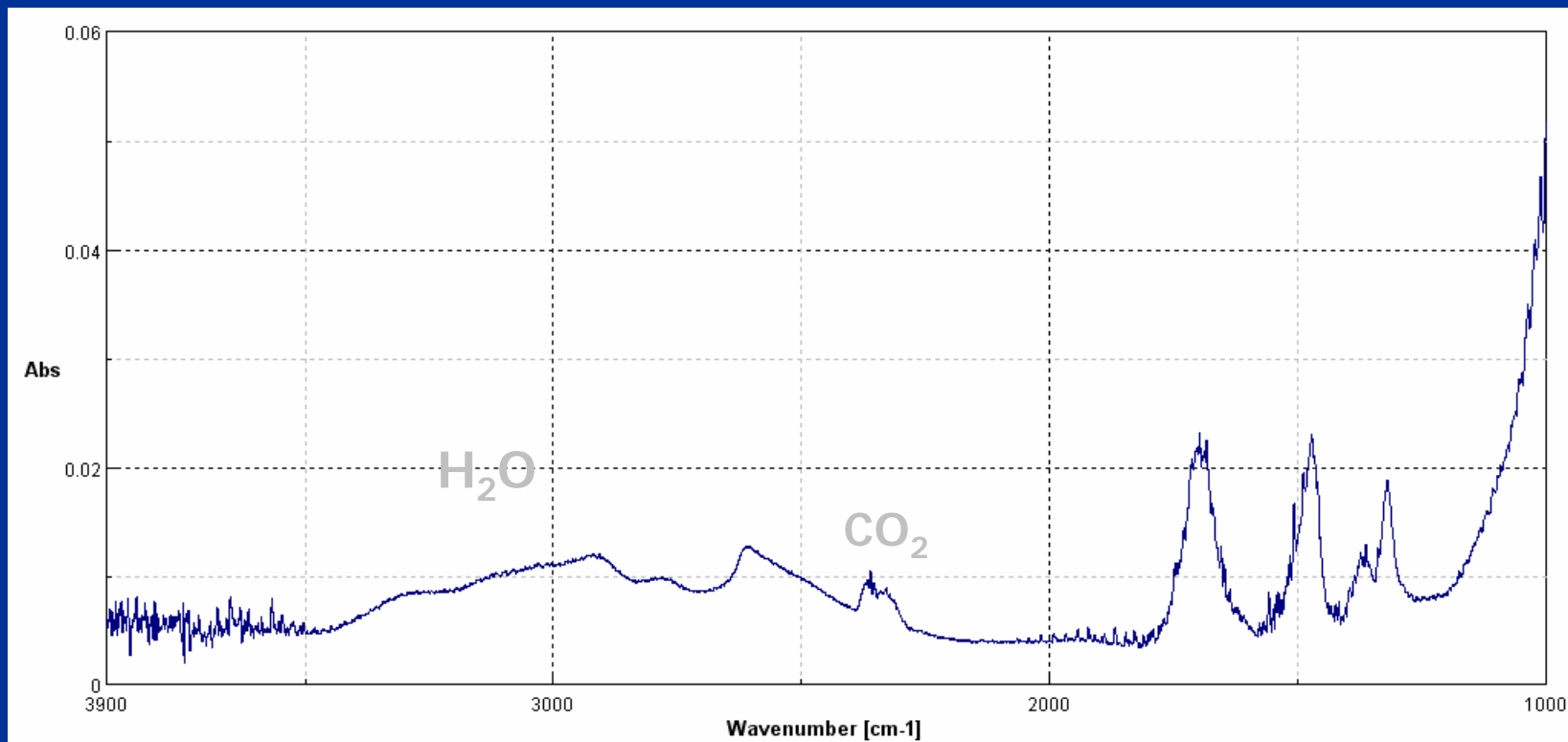
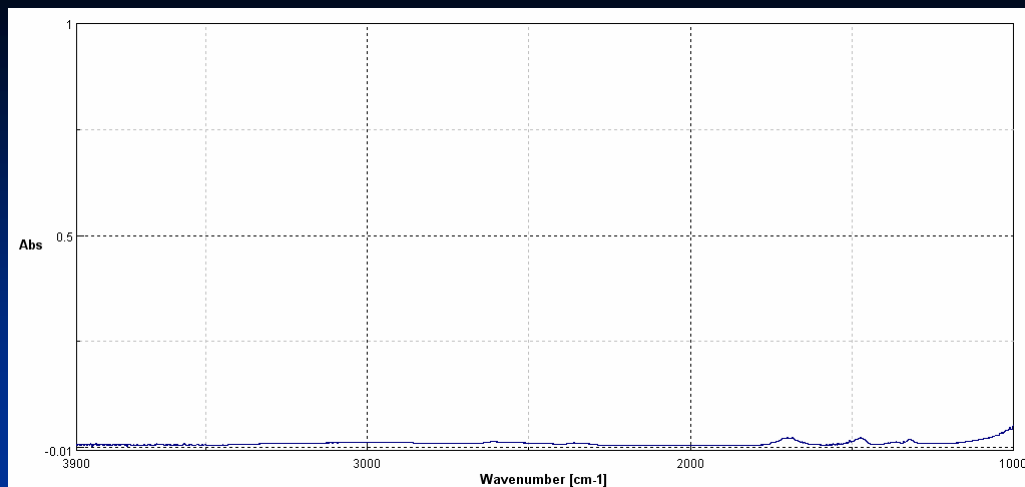
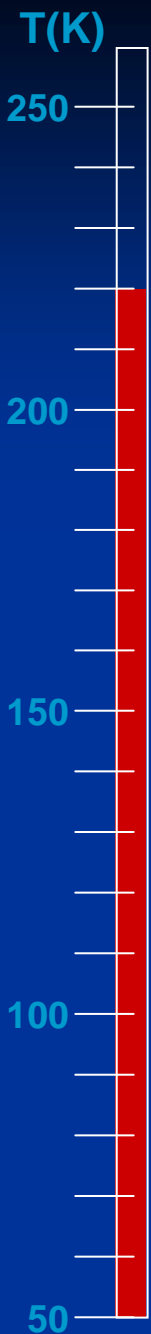
100

50

Warm-up after H⁺ Irradiation of H₂O:CO₂ ice



Warm-up after H⁺ Irradiation of H₂O:CO₂ ice



T(K)

250

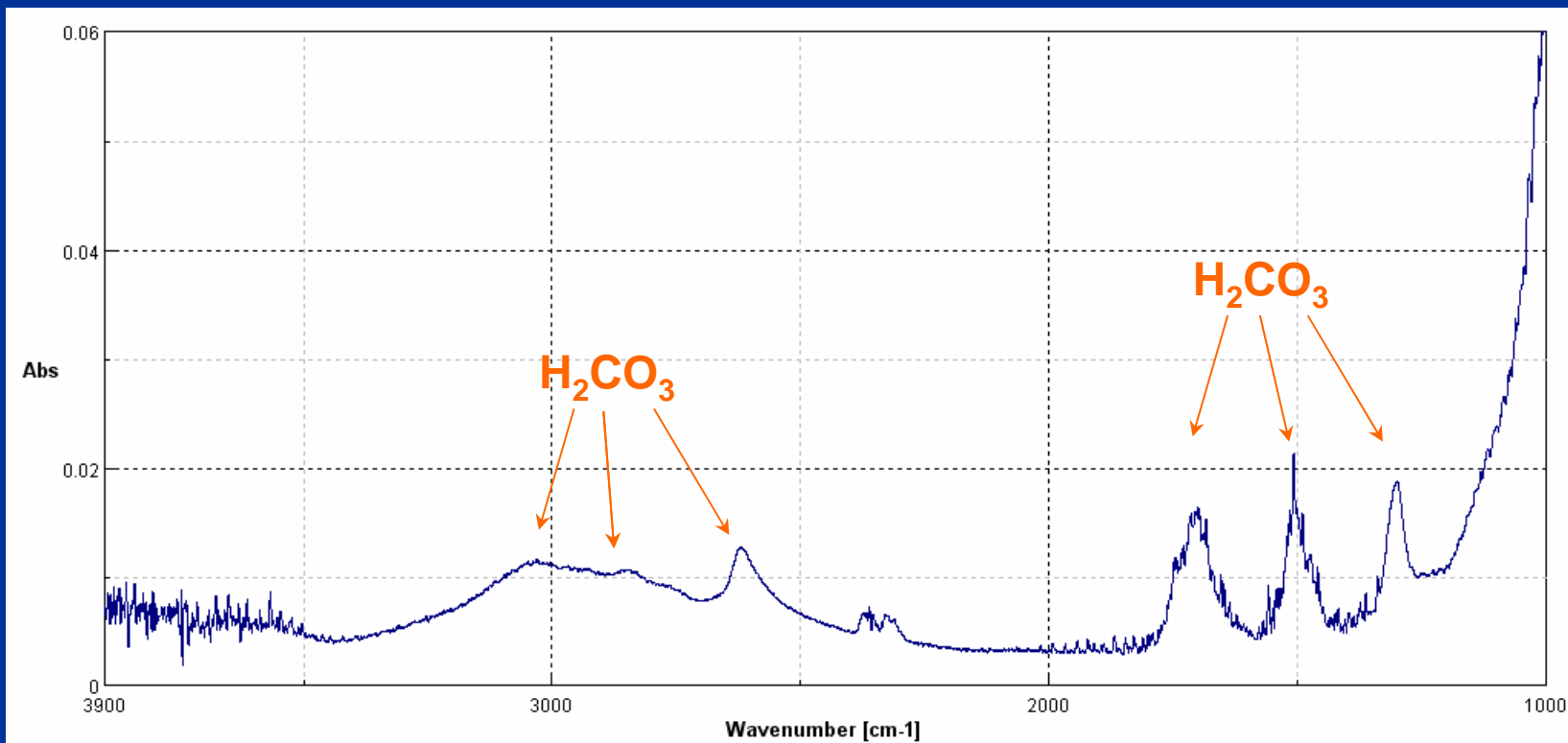
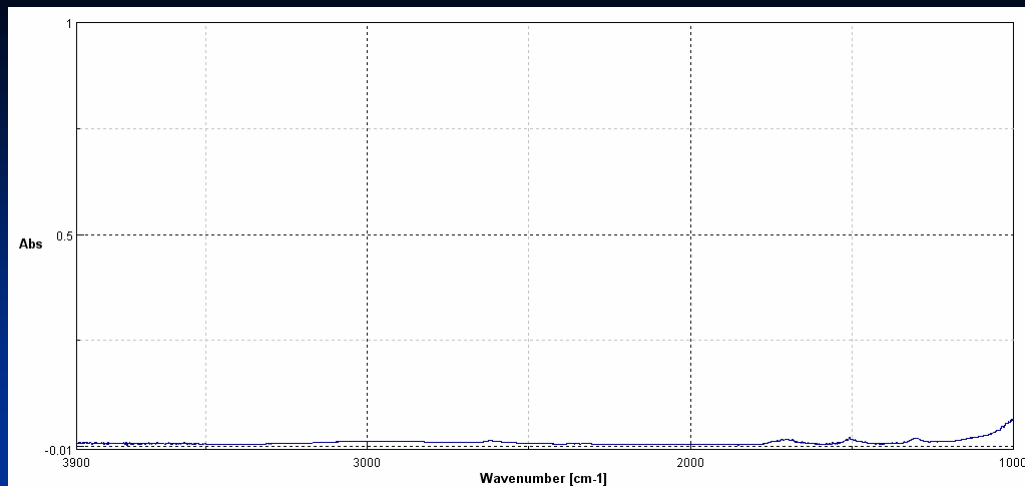
200

150

100

50

Warm-up after H⁺
Irradiation of
H₂O:CO₂ ice



Conclusions ?

- Experiments show possible to form molecules under conditions prevailing in the ISM
- But these are **small molecules**
- But can make larger (biological molecules) ?

So can we go on to make building blocks of life ?

- How to create an amino acid ?
- How to create a sugar in space ?
- Synthesis in the ice mantles ?

Electron Induced Chemistry



- Some examples of laboratory study of electron induced synthesis of molecules under astrochemical conditions.
- Chemical synthesis in **1:1 Mixture of NH₃:CO₂ Ice with 1 keV electrons at 30 K**

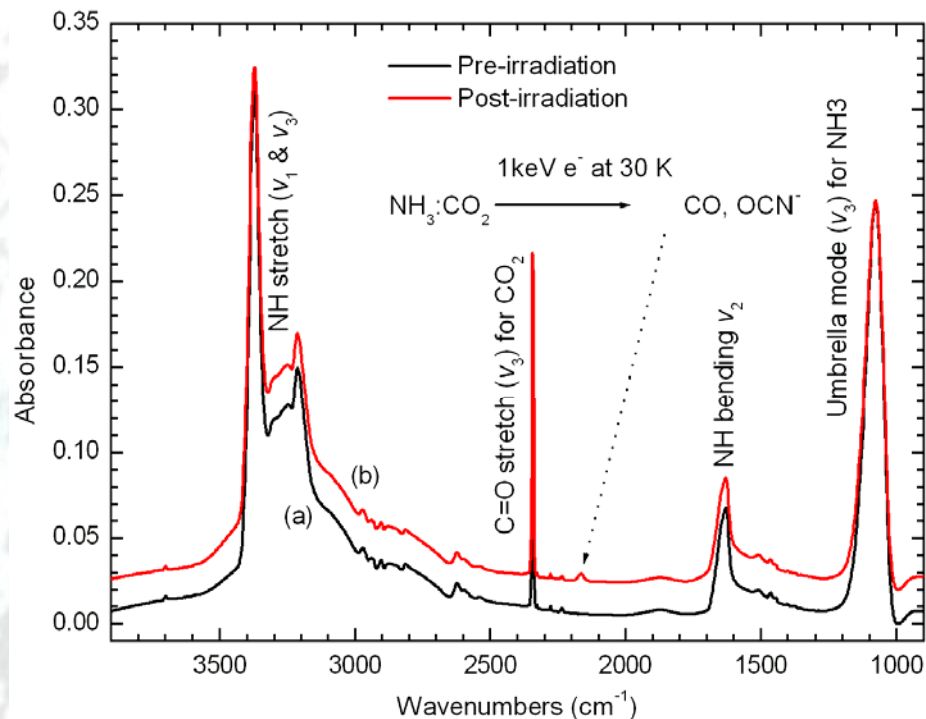


Fig 5-1: IR spectra of NH₃:CO₂ (1:1), (a) pre-irradiation (b) post irradiation (58 min). Both spectra at 30 K

OCN, CO production

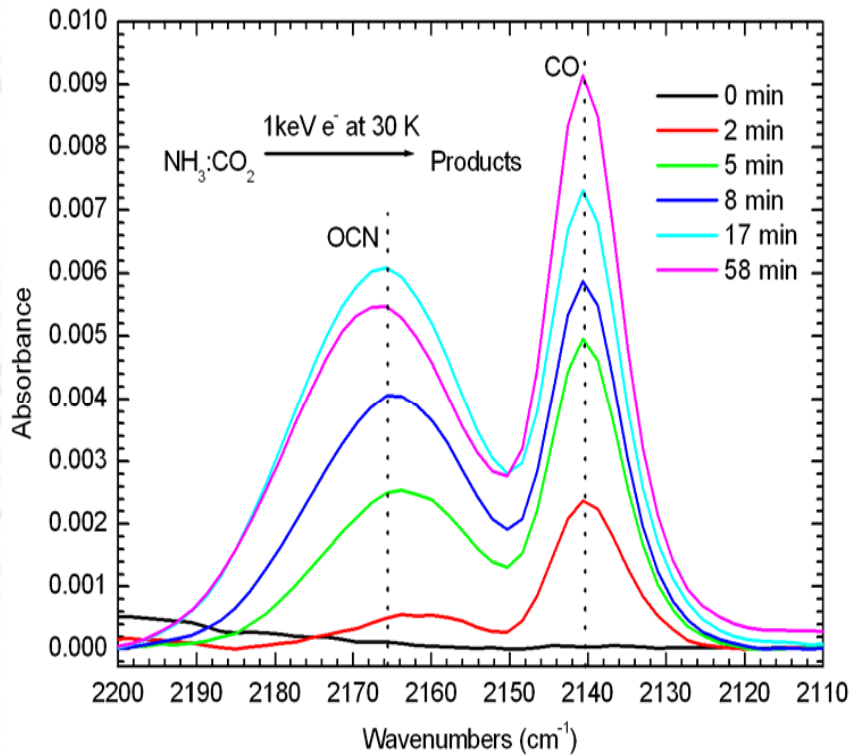


Fig. 5-2: IR bands observed for OCN (2165 cm^{-1}) and CO (2140 cm^{-1})

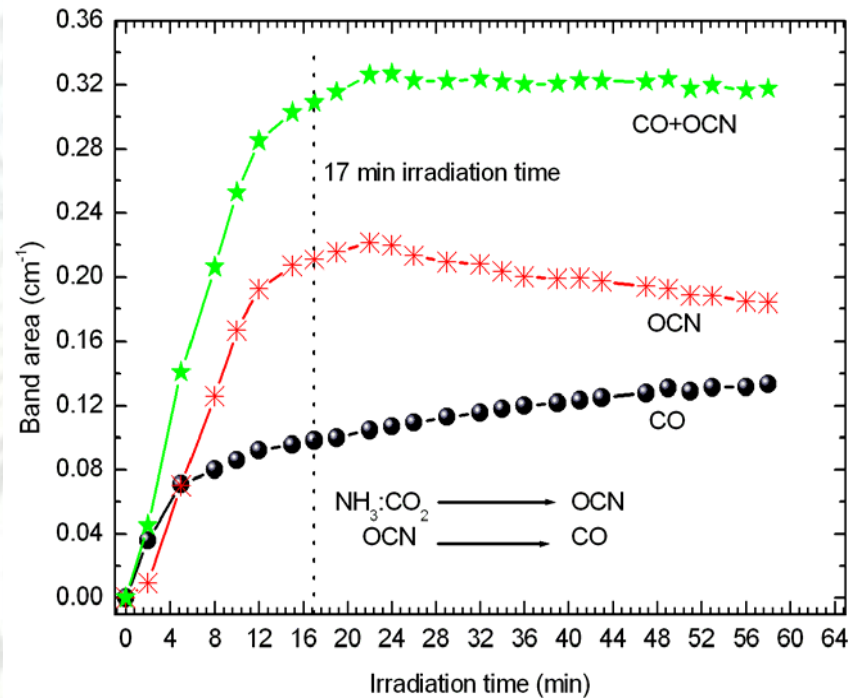


Fig. 5-9: Destruction of OCN during the irradiation of $\text{NH}_3:\text{CO}_2$ (1:1 ratio)

Formation of ammonium carbamate

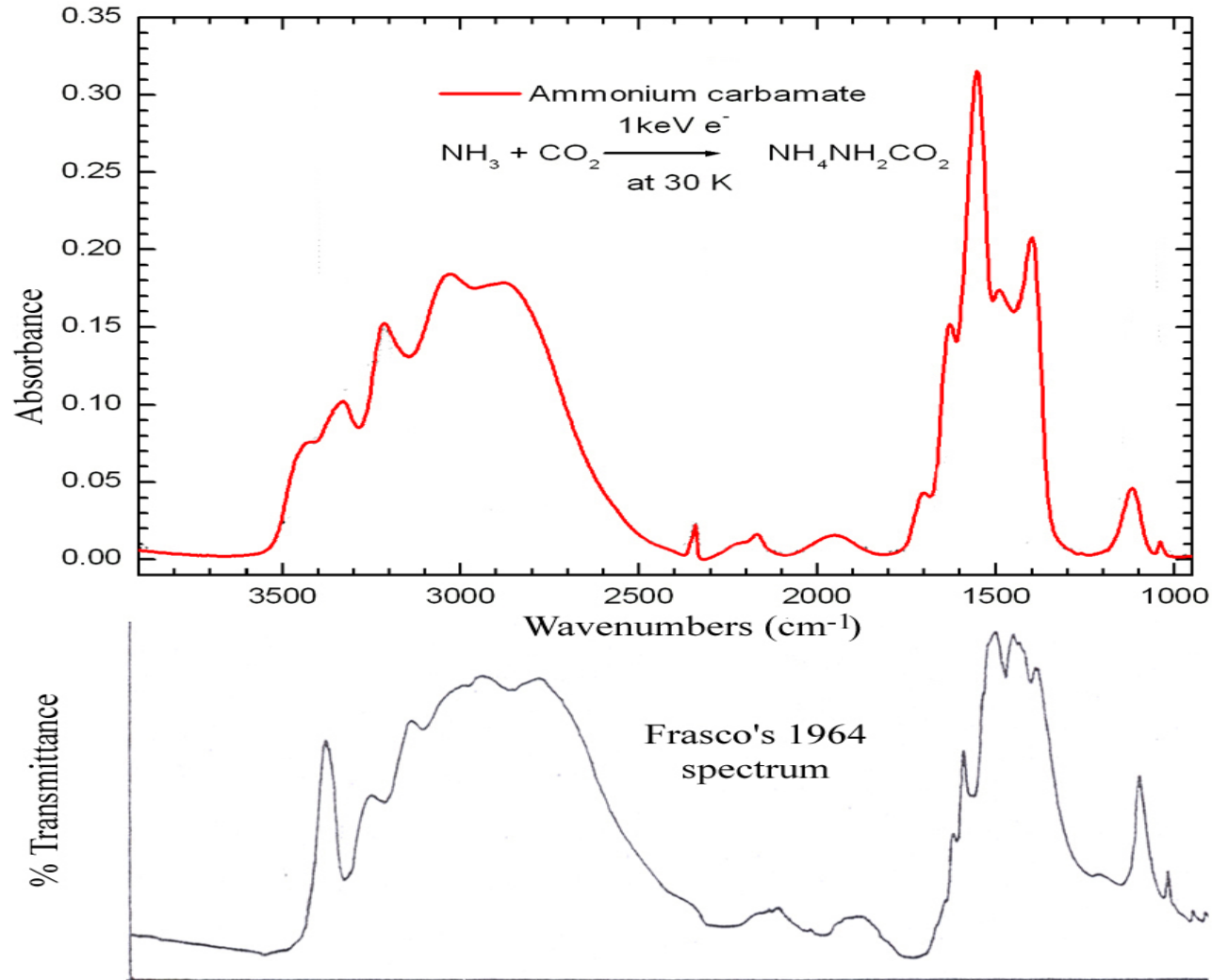


Fig. 5-5: IR spectra of $\text{NH}_3:\text{CO}_2$ (1:1), (a) post-irradiation (58 min) and after warm-up (220 - 270 K); and (b) comparing Frasco's actual 1964 experimental spectrum at 248 K

Electron Induced Chemistry



- Some examples of laboratory study of electron induced synthesis of molecules under astrochemical conditions.
- Chemical synthesis in **the Irradiation of 1:1 Mixture of NH₃:CH₃OH ice with 1 keV electrons at 20 K**

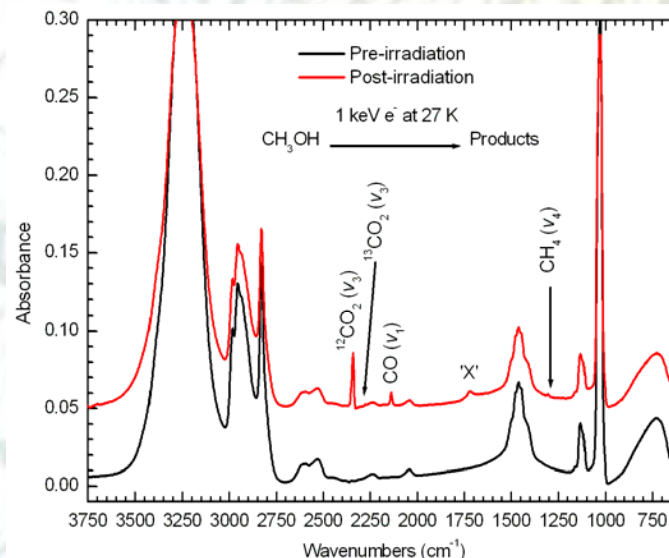


Fig. 6-2: Formation of new species during the irradiation of CH₃OH with 1 keV e⁻ at 27 K

Formation of ethylene glycol in pure methanol ice

HOH₂C-CH₂OH

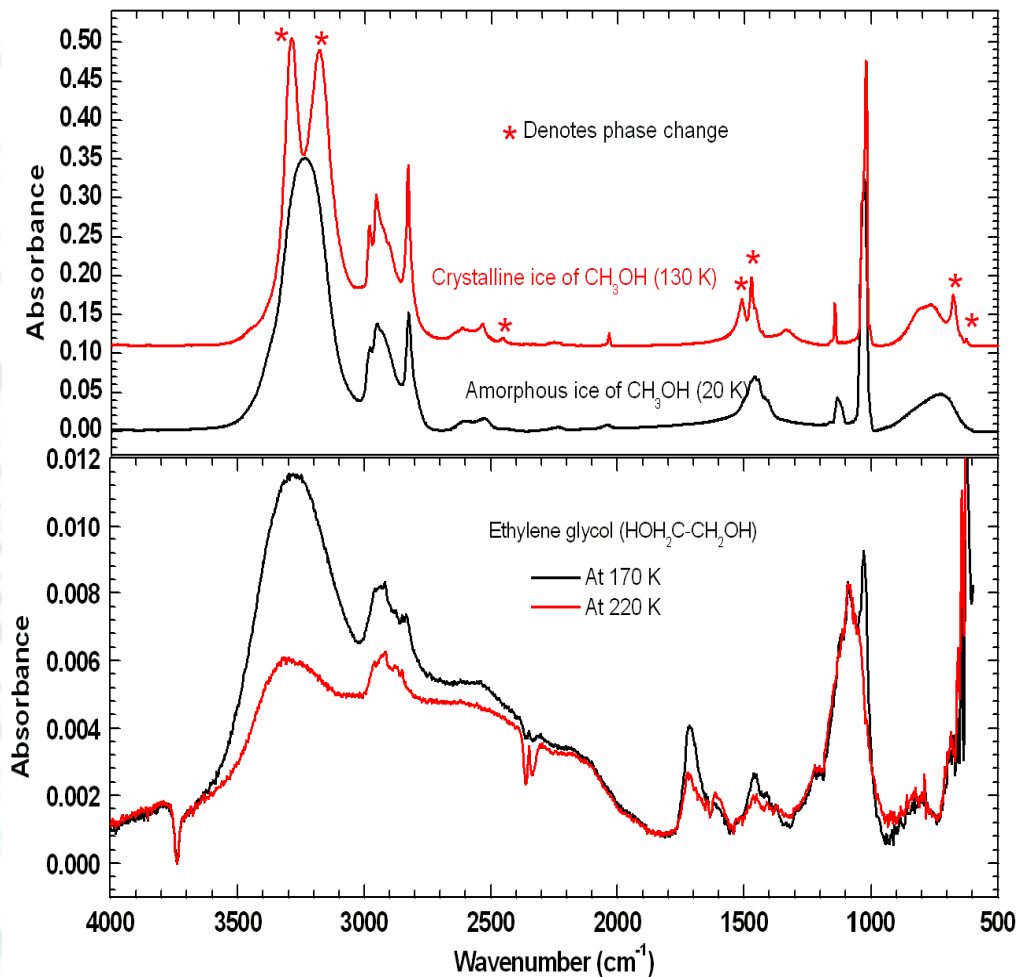


Fig. 6-3: Ethylene glycol was observed after irradiation of pure CH₃OH with 1 keV e⁻ at 30 K and then annealing process

Formation of methyl formate CH_3OHCO

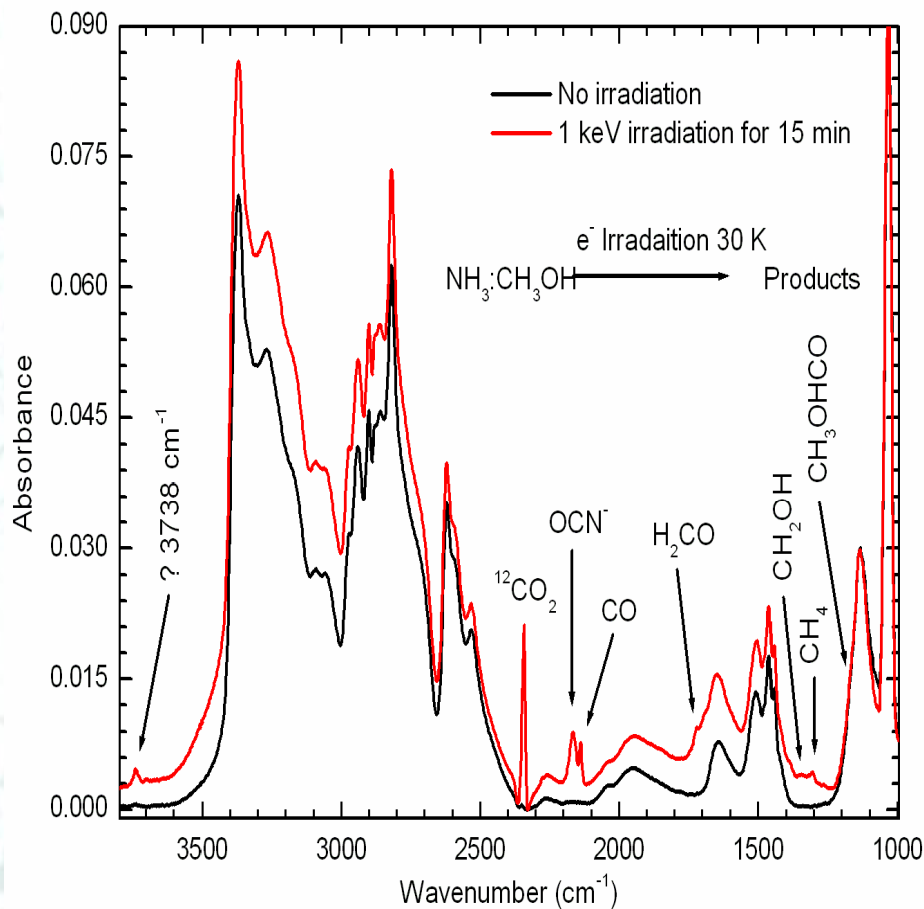


Fig. 6-9: Irradiation of 1:1 binary mixture of $\text{NH}_3:\text{CH}_3\text{OH}$ with $1 \text{ keV } e^-$ at 30 K

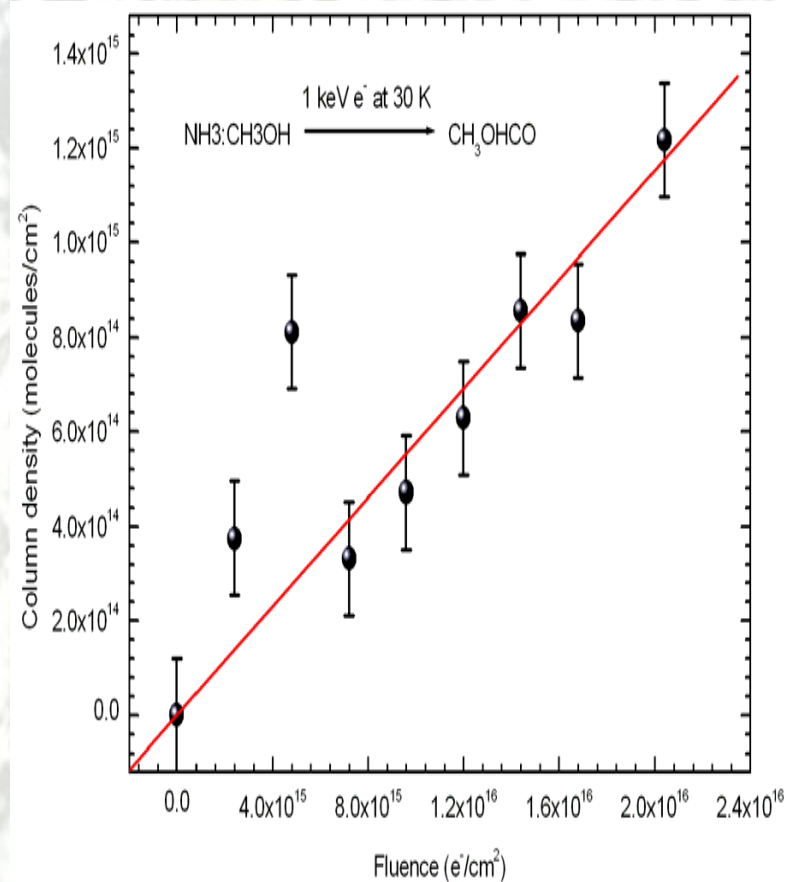


Fig 6-14: Formation of CH_3OHCO during the irradiation of binary mixture $\text{NH}_3:\text{CH}_3\text{OH}$ with $1 \text{ keV } e^-$ at 30 K



Formation of formamide HCONH_2

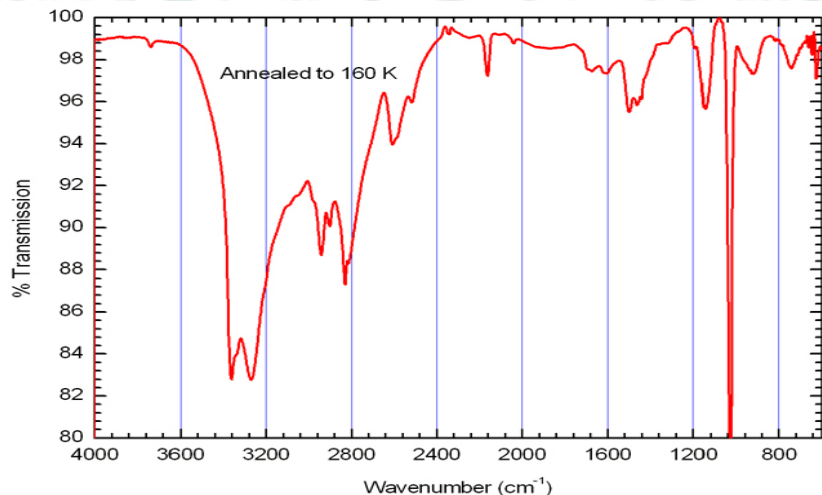


Fig. F6-16a: Spectrum of formamide formed during annealing to 160 K of irradiated ice of 1:1 binary mixture of $\text{NH}_3:\text{CH}_3\text{OH}$ with 1 keV e^- at 30 K

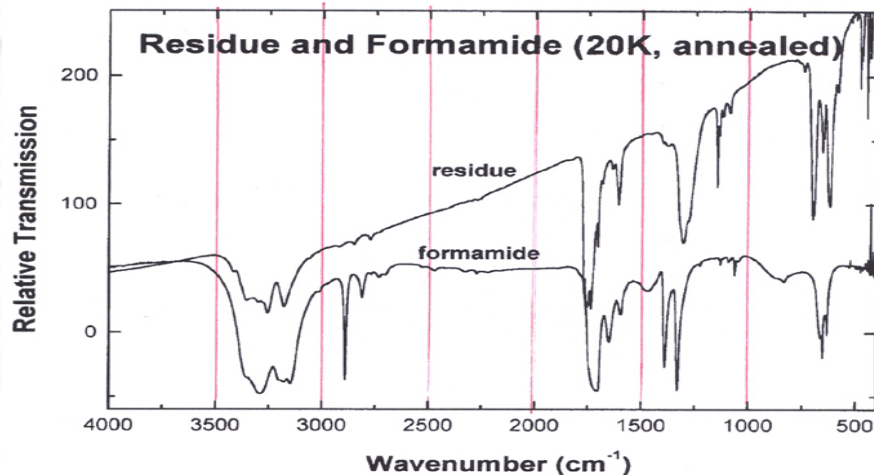


Fig. 6-16b: Comparison of infrared spectra of residue with formamide. Both deposits have been annealed (to 165 K) and recooled to 20 K to produce crystalline structure

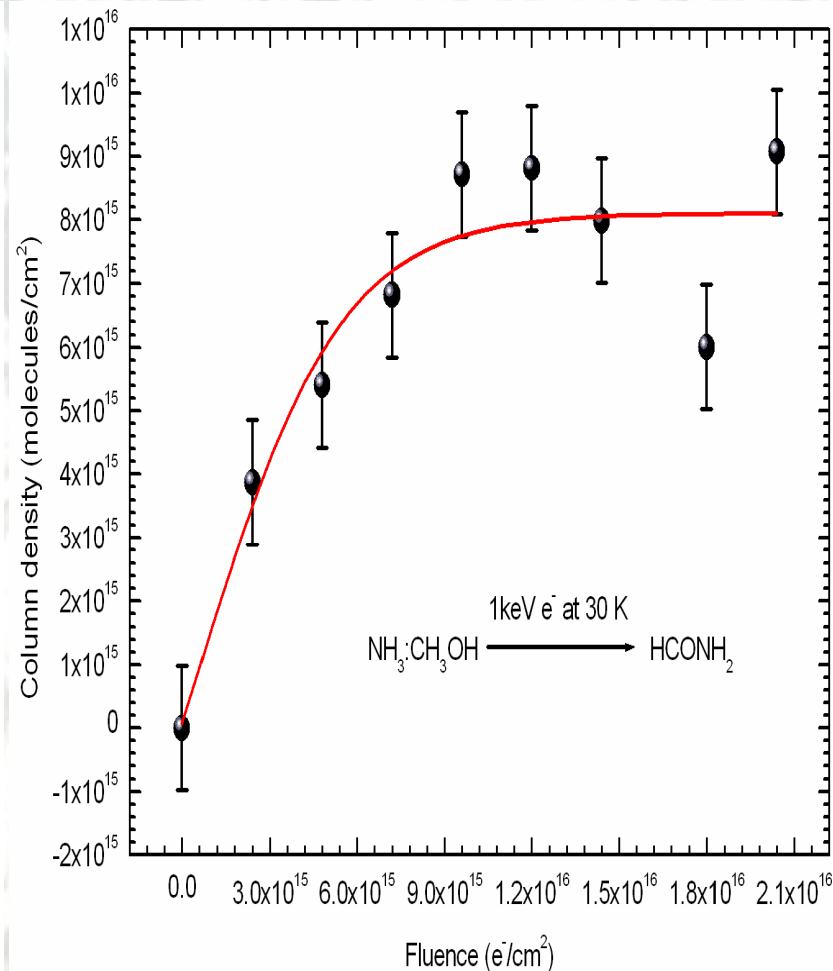


Fig. 6-15: Formation of HCONH_2 during the irradiation of 1:1 binary mixture of $\text{NH}_3:\text{CH}_3\text{OH}$ with 1 keV at 30 K

(Khanna, Lowenthal et al. 2002)

Irradiation of methylamine and carbon dioxide ice makes glycine simple amino acid

Effects of Irradiation

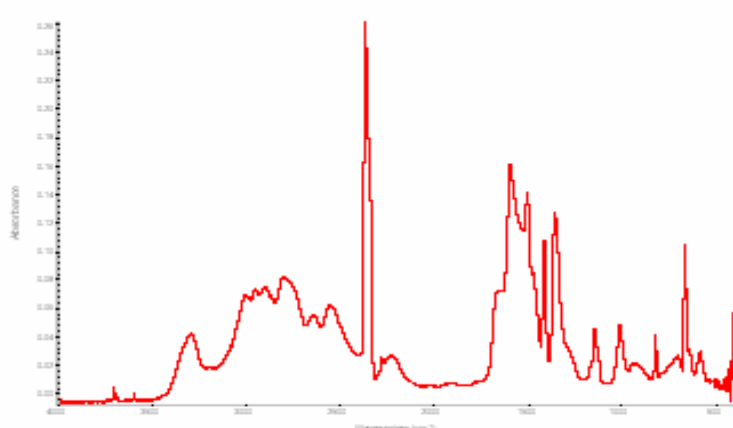


Figure 3 – Pristine CH_3NH_2 & CO_2
mixture

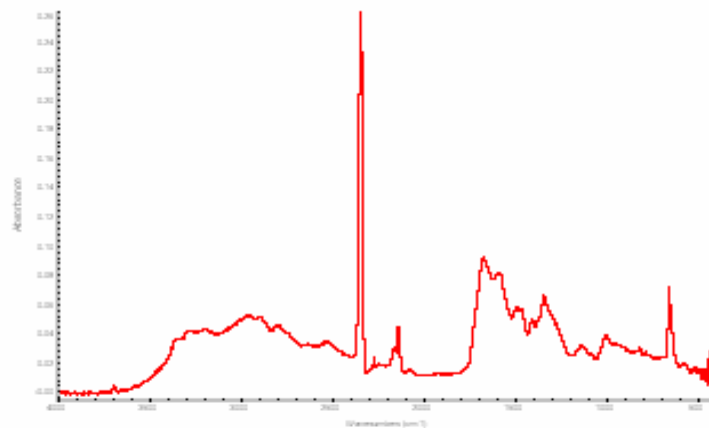


Figure 4 – 100 minute after
irradiation of the mixture

And So ?

- In the lab we can now simulate what happens in space
- We can show that the basic molecules of life can be made 'easily' throughout the universe by uniform process.
- So the chemistry for life exists 'everywhere'
- *But what does this tell us about the origins of life on earth/elsewhere ??*

We have the 'building blocks' but how do they assemble ?

- How do/did simple molecules assemble to make DNA ?

We have the 'building blocks' but how do they assemble ?

- How do/did simple molecules assemble to make DNA ?

WE DONT KNOW !!!!!!!

Science does not have all the answers !

There is still much to do



- There are known knowns

- Known unknowns

and

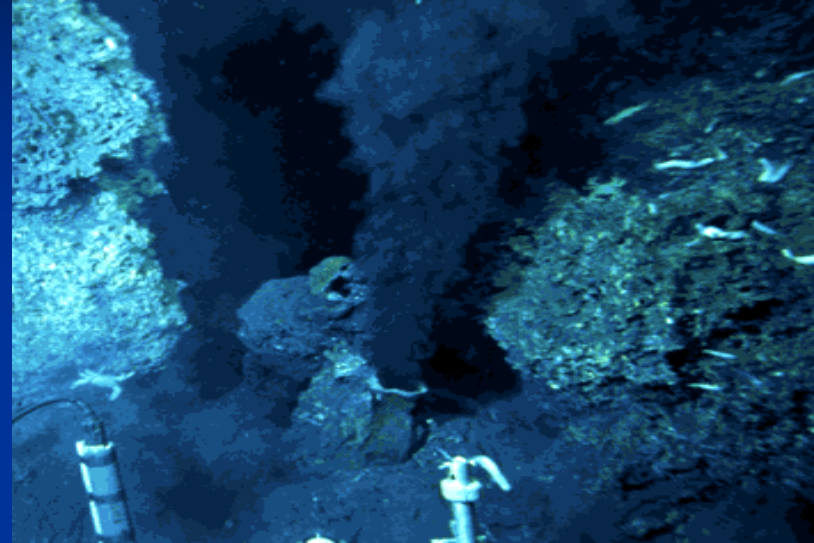
- Unknown unknowns

Known unknowns !

- The spontaneous formation of complex polymers from simple monomers is not simple and
- The physical/chemical conditions that allow the simple molecules to form (eg glycine) are the same that destroy larger molecules (DNA)
- So where do/did large molecules assemble ?

In a prebiotic soup

- Like the early oceans
**REMEMBER
OPARIN**
- Where they were
shielded from harsh
surface conditions
- **Smokers on seafloor**



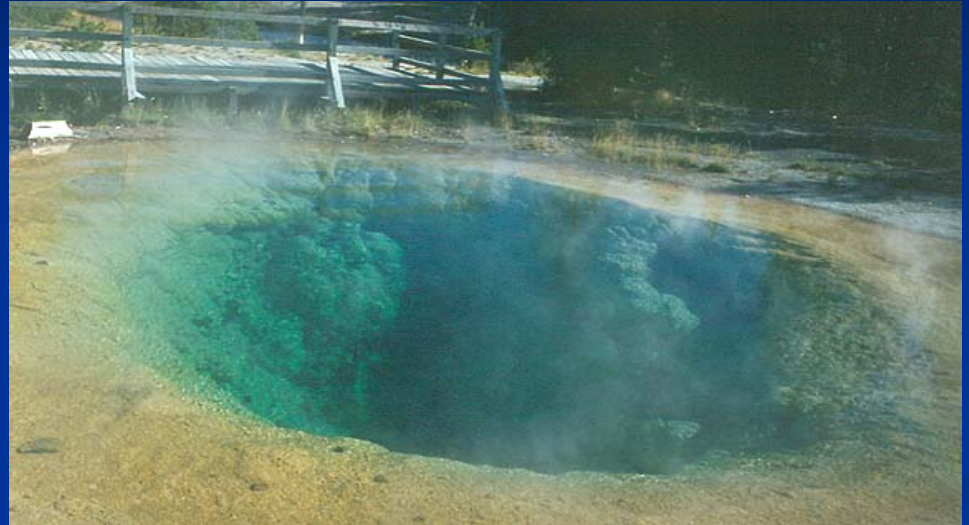
Other places where such assembly could begin

- **Clay world:** Chemical reactions taking place within clay substrates or on the surface of rocks which act as a 'template' for molecular assembly.



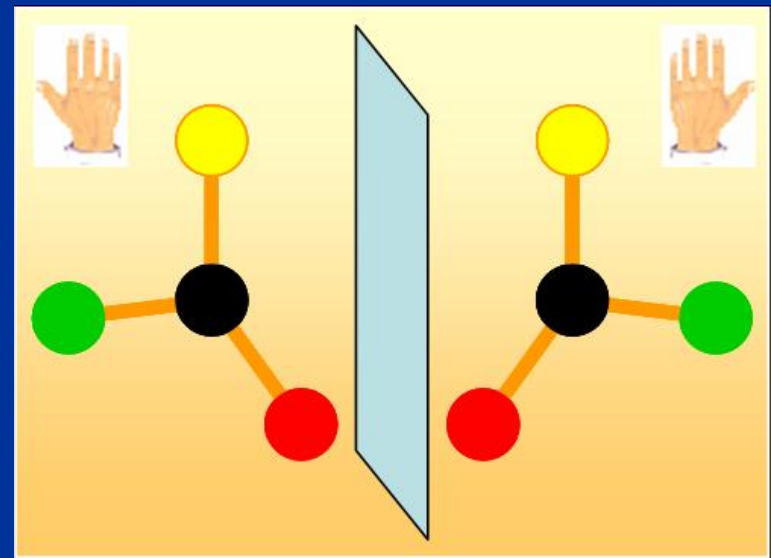
Other places where such assembly could begin

- In 'ponds': Chemical reactions taking place within pools around volcanic vents and geysers



One possible clue

Homochirality
Life is chiral !!



One possible clue

- Amino acids are left handed
- Nucleic acid sugars right handed.
- Homochirality is essential for the formation of functional proteins.
- How does/did homochirality arise ???
- We don't know but it might give us a clue as to way molecules are assembled

So back to opening question

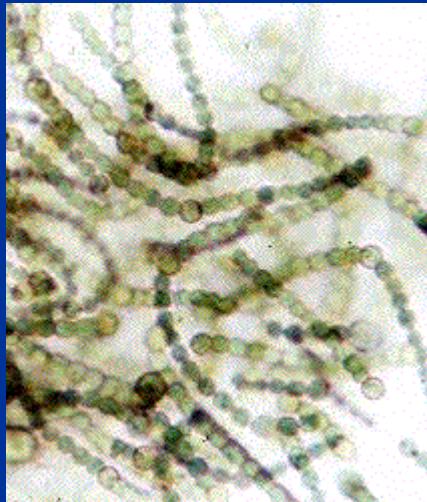
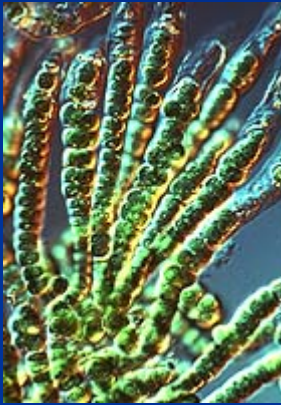
Is there life on another planet ??

The scientific search for Life

- Not aliens !
- More likely bacterial, photosynthetic

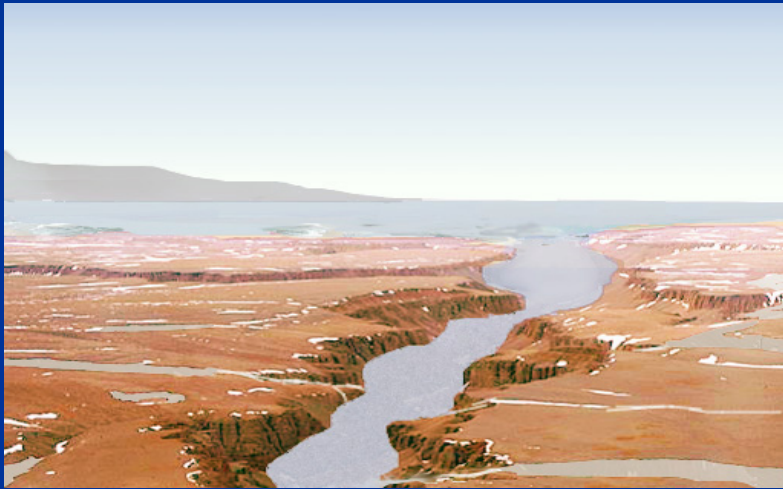
Cyanobacteria

Architects of earth's atmosphere



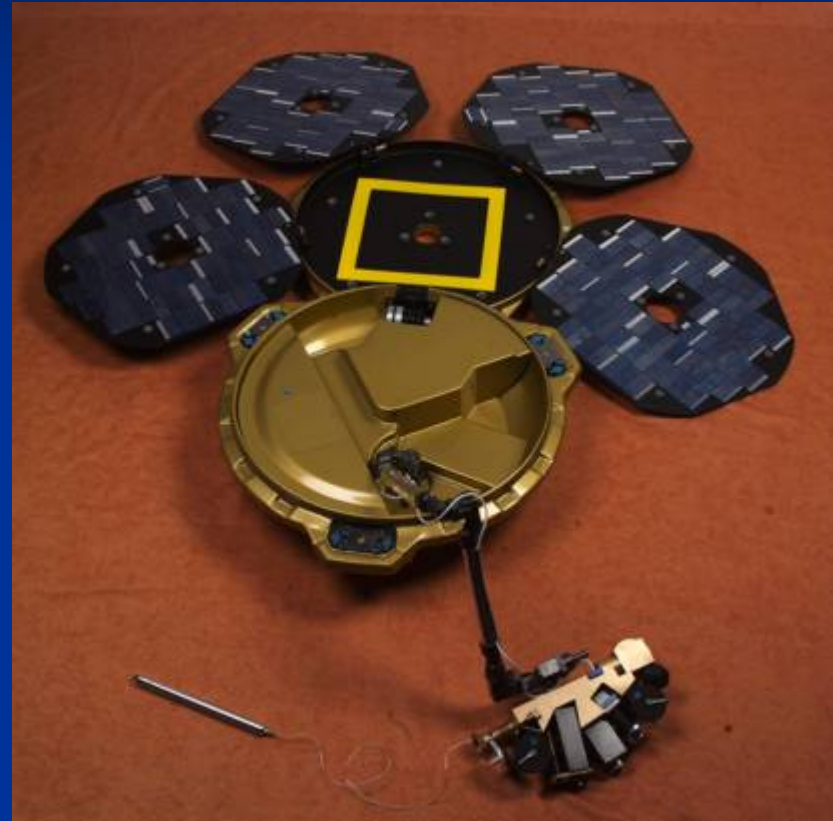
Life on Mars ?

More and more evidence suggests the
Martian Surface was once capable
of sustaining *flowing water*



ExoMars!

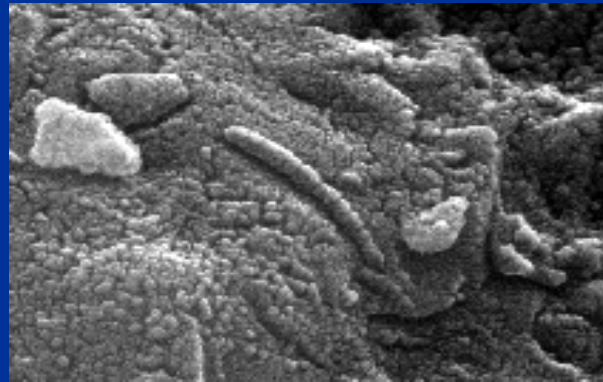
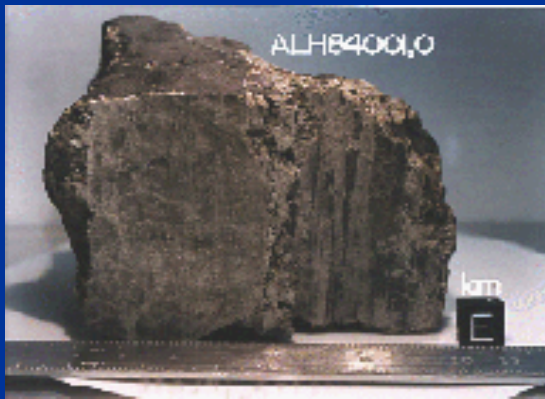
- Life on Mars ?
- Methane emissions
- Fossil evidence



Martian Meteorites



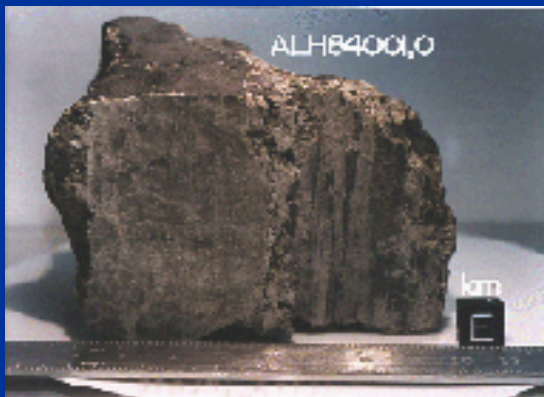
- Only 34 have been identified most since 2000
- Meteorite ALH 84001 in 1996 announce possible signs of fossil life



Martian Meteorites



Now not believed to be fossils of bacteria

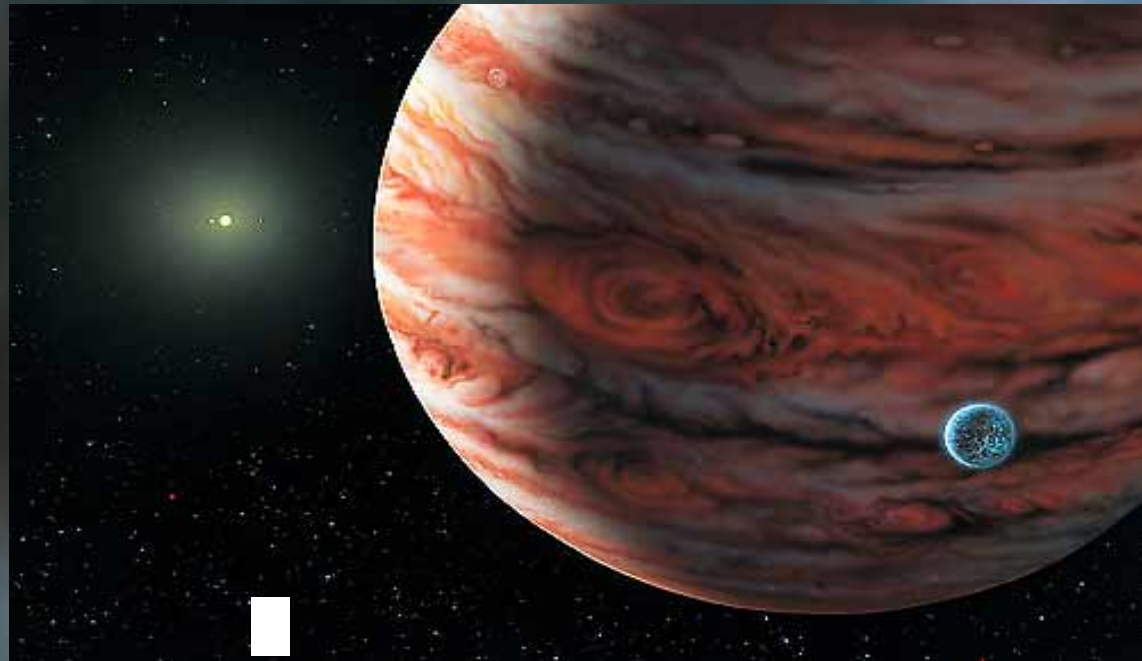


Search for Exoplanets

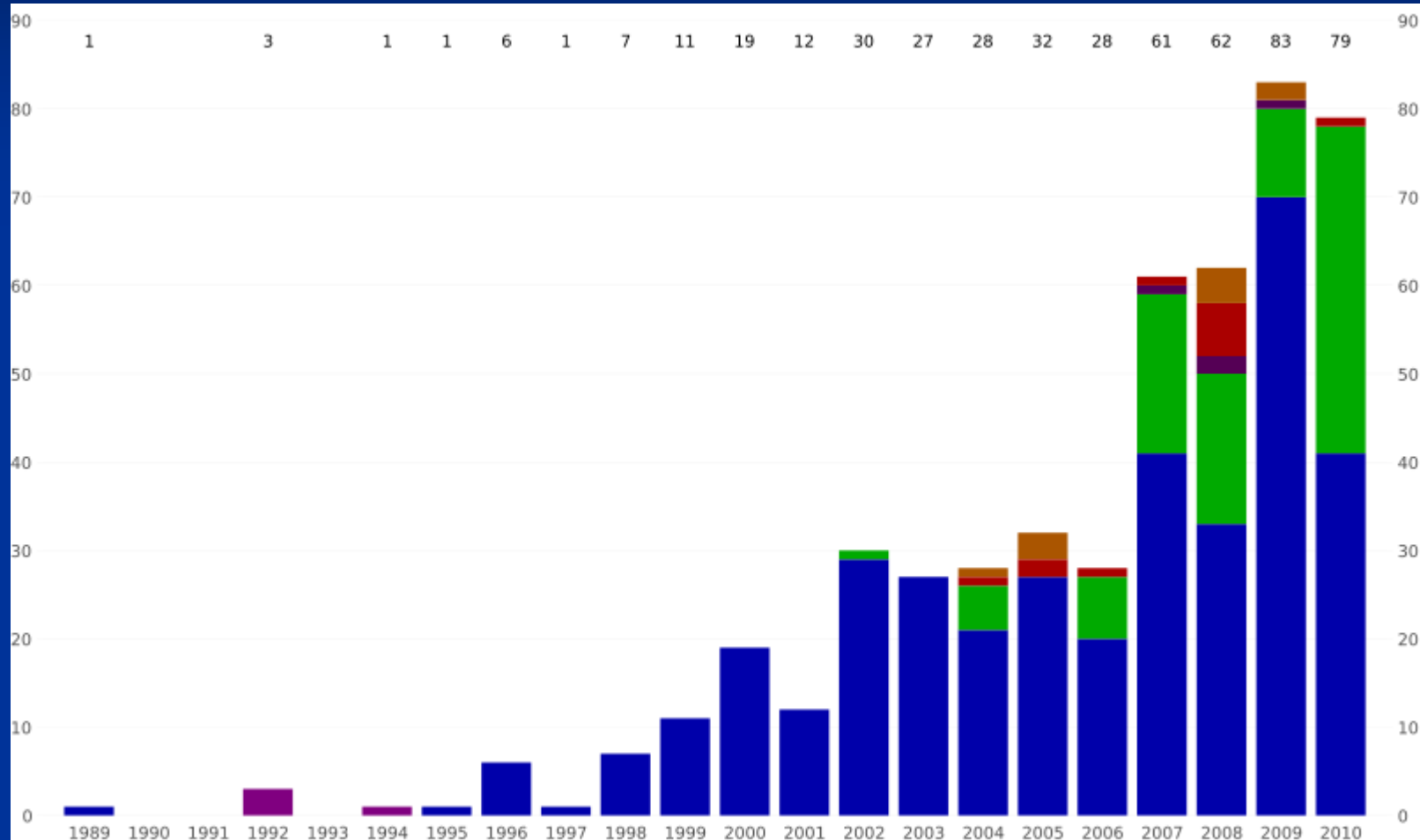
http://en.wikipedia.org/wiki/List_of_extrasolar_planets

http://en.wikipedia.org/wiki/Extrasolar_planet

We have already found **>500 extra-solar Planets**

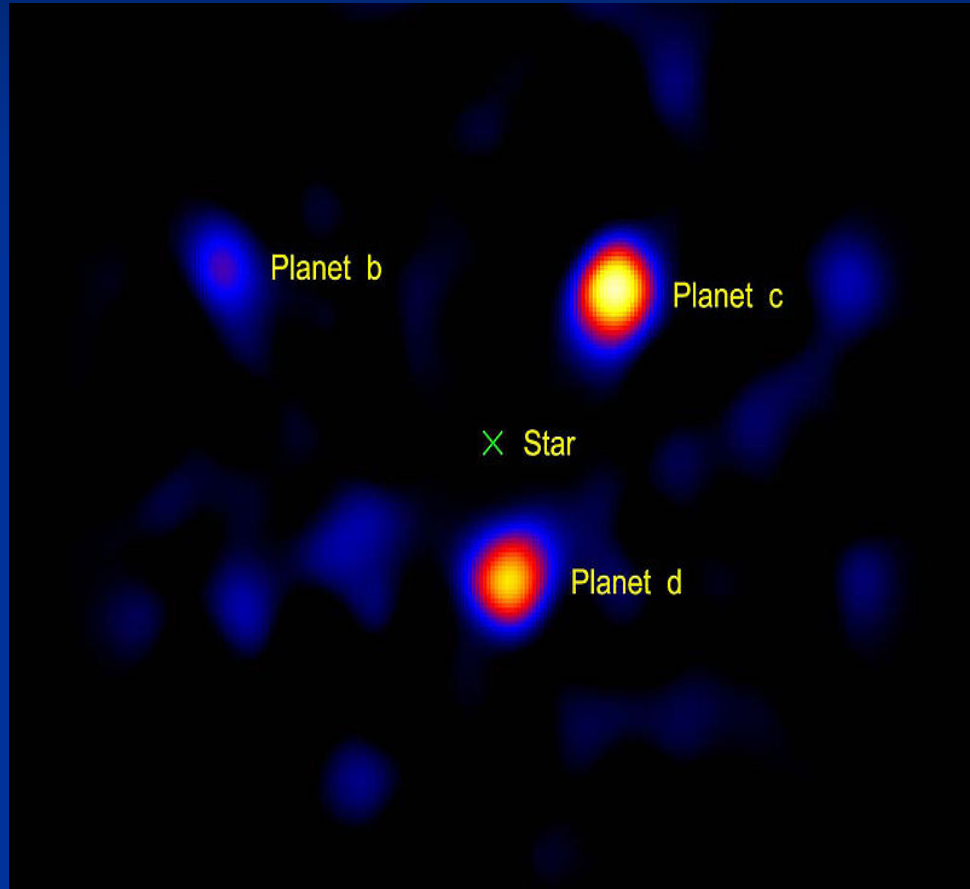


Number of extrasolar planet discoveries per year as of 3 October 2010, with colours indicating method of detection



Looking for planets

- Methods
- Radial velocity
/Doppler method
- Transit method
- Microlensing
- Astrometry

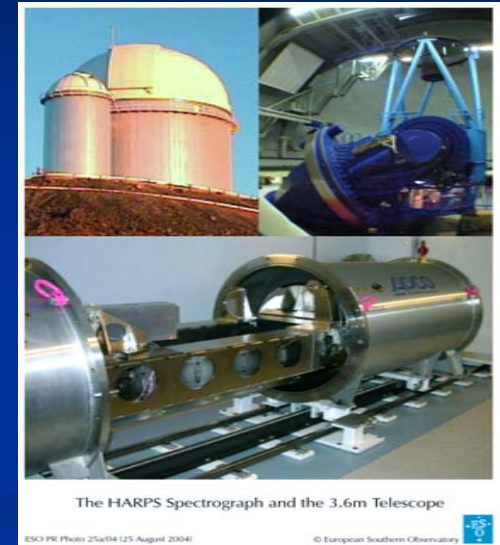


Direct image of exoplanets around the star HR8799 using Hale telescope

Looking for planets

Radial velocity/Doppler method

- This has been by far the most productive technique used by planet hunters. It is also known as Doppler spectroscopy. The method is distance independent, but requires high signal-to-noise ratios to achieve high precision, and so is generally only used for relatively nearby stars out to about 160 light-years from Earth.
- It easily finds massive planets that are close to stars, but detection of those orbiting at great distances requires many years of observation. Planets with orbits highly inclined to the line of sight from Earth produce smaller wobbles, and are thus more difficult to detect.
- One of the main disadvantages of the radial-velocity method is that it can only estimate a planet's minimum mass.



The **High Accuracy Radial velocity Planet Searcher (HARPS)** is a high-precision echelle spectrograph installed in 2002 on ESO's 3.6m telescope at La Silla

Observatory in Chile

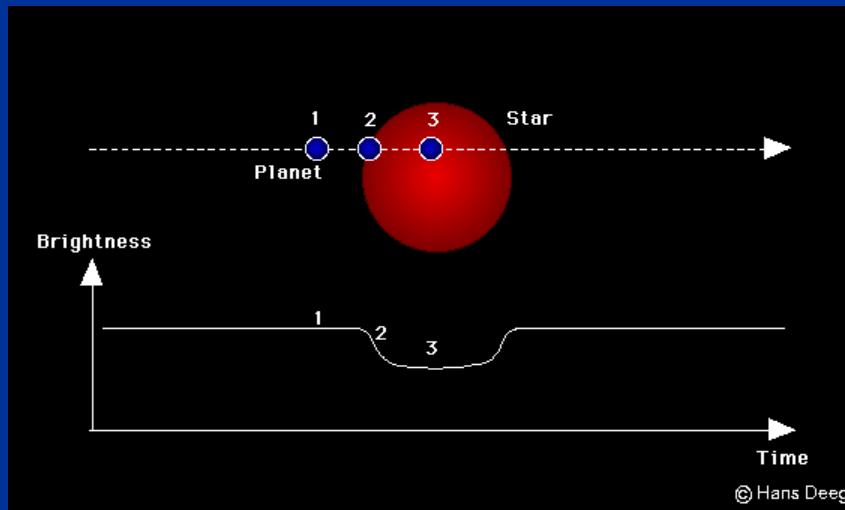
**16 exoplanets
found**

Looking for planets



UK University programme to look for planets using standard cameras

The Transit method



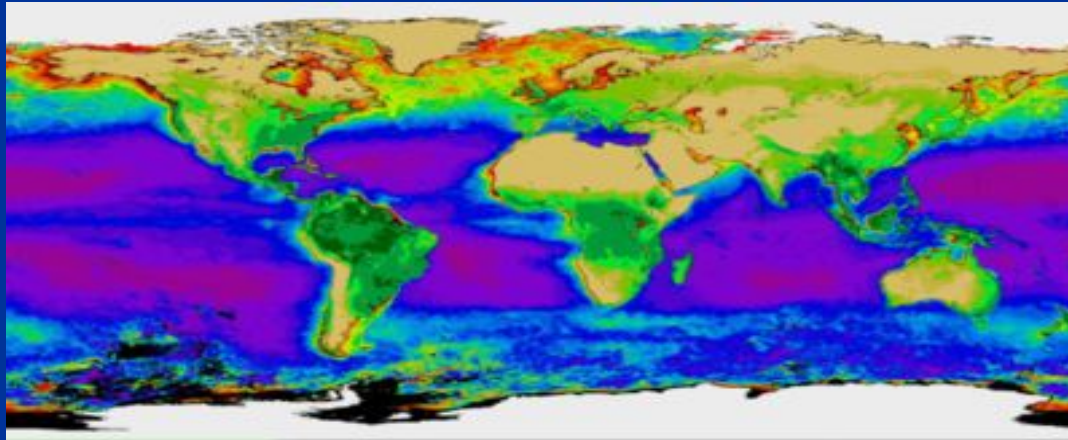
The future imaging the planet



A possible design for Darwin, a proposed ESA telescope to explore extrasolar planets

But what are biomarkers of life ?

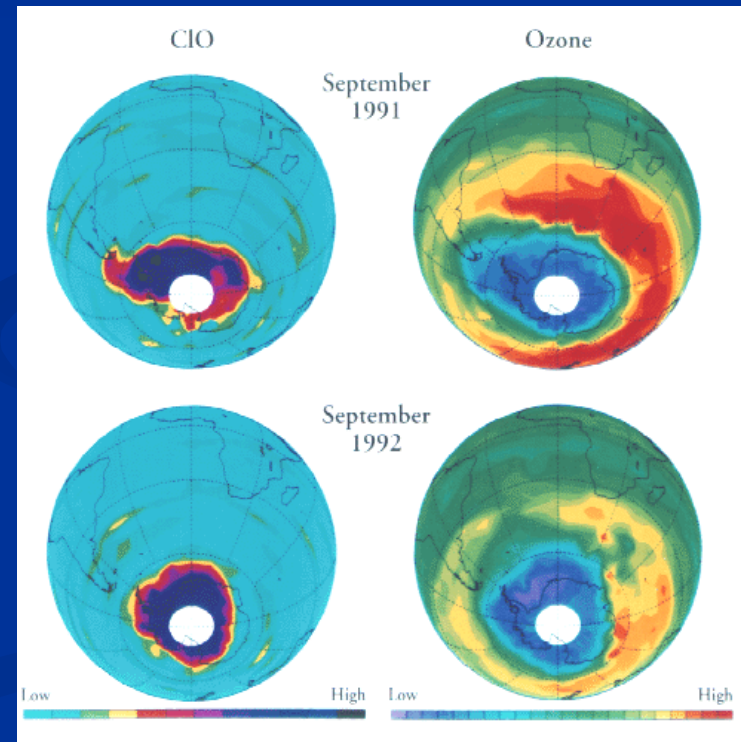
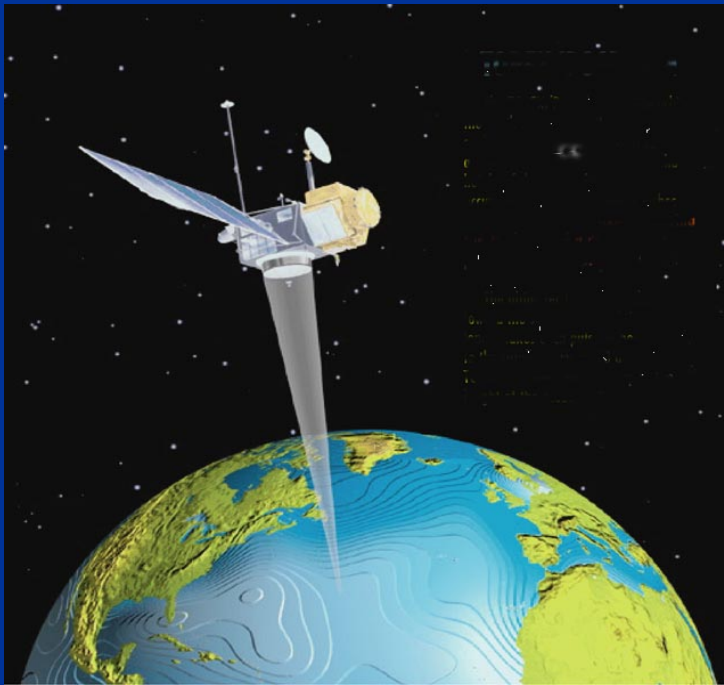
- CO₂/methane/water needed for life ?
- But have both biotic and abiotic sources



- but ozone was believed to be the BEST ***BIOMARKER***

Ozone is signature on Earth of molecular oxygen rich atmosphere

Prominence since 1980 due to problems of Ozone Depletion



Ozone formation

- Ozone is formed in a three body reaction since without a third body to stabilise the product ozone it would rapidly redissociate



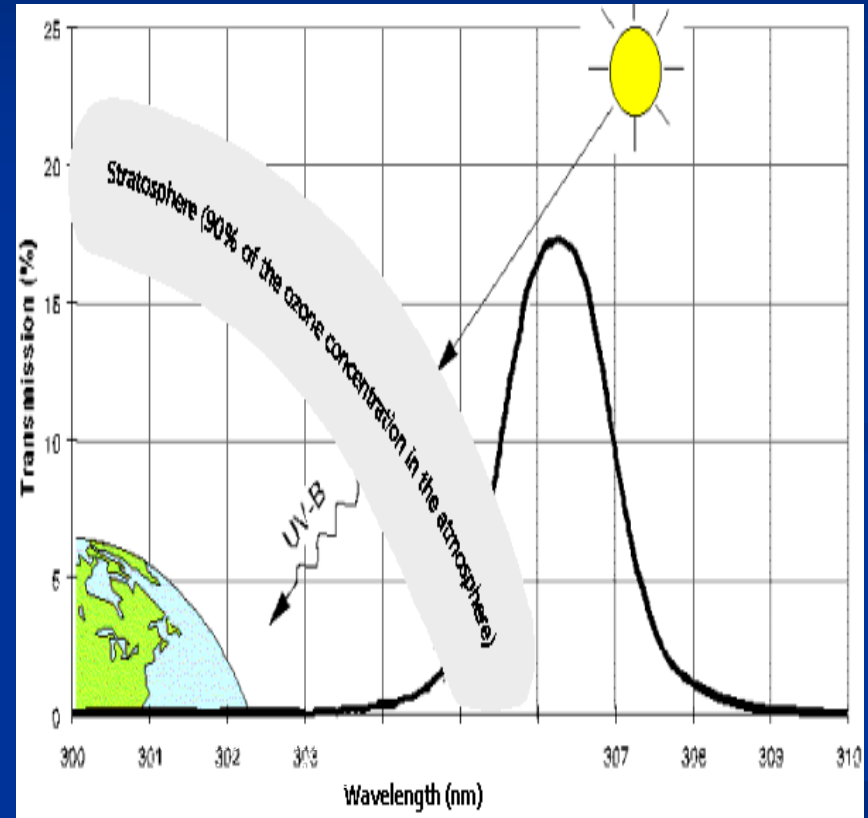
Ozone Destruction

OH radicals destroy ozone in a catalytic cycle;



Ozone Depletion Studies in the Ultra-Violet

- Ozone in the terrestrial atmosphere absorbs the solar UV preventing it from reaching the Earth's surface.
- Destruction of the ozone in the Earth's atmosphere leads to increased UV flux at the surface.



Ozone Depletion Studies in the Ultra-Violet

- UV leads to genetic (DNA) damage (erythema/sunburn)



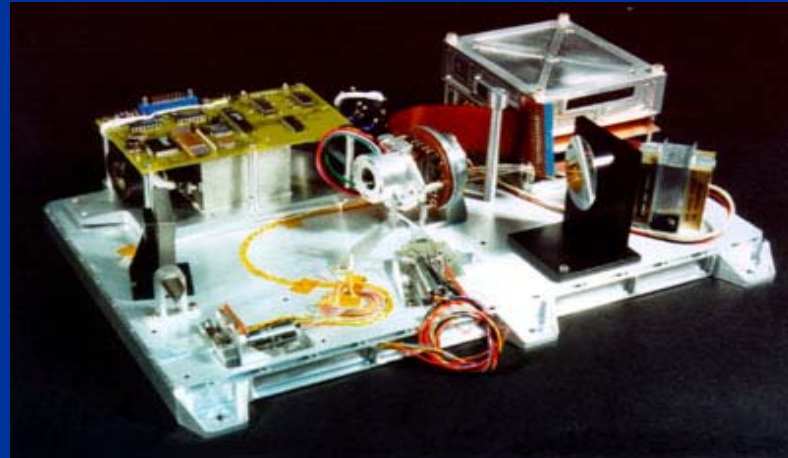
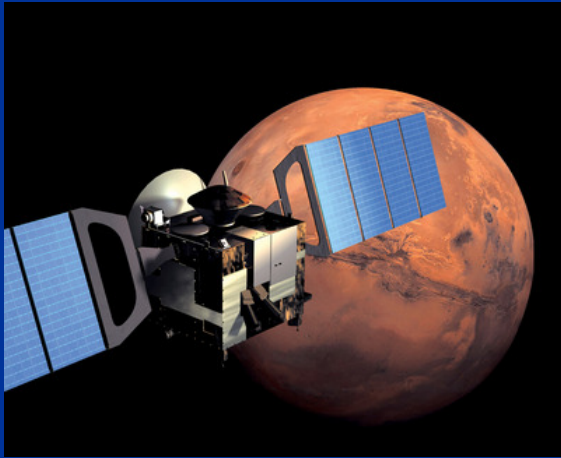
bse.unl.edu/.../images_undergrad/sunburn.JPG

So can ozone be formed on other planets ?

- Yes is found on Mars

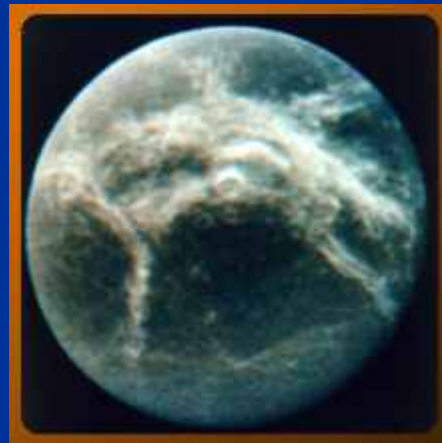
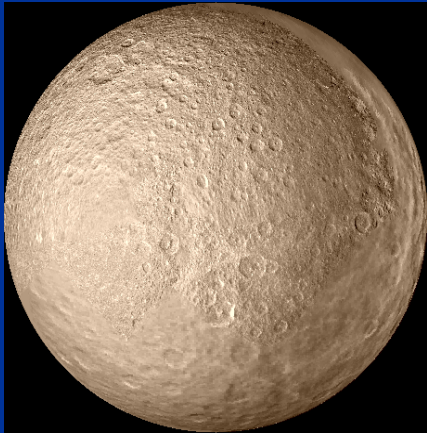
So could there ever have been a *significant*
ozone layer on Mars ?

- There are small quantities of ozone in Martian atmosphere
- SPICAM data from Mars Express



So can ozone be formed on other planets ?

- Recently found on
- Ganymede- moon of Jupiter
- Dione and Rhea moons of Saturn



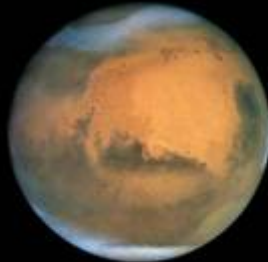
Ices in the Solar System



Mercury



Earth



Mars



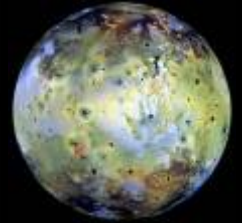
Europa



Ganymede



Callisto



Io



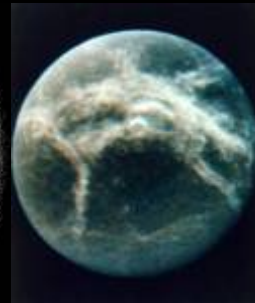
Saturn



Dione



Enceladus



Rhea



Tethys



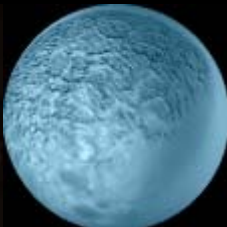
Mimas



Miranda



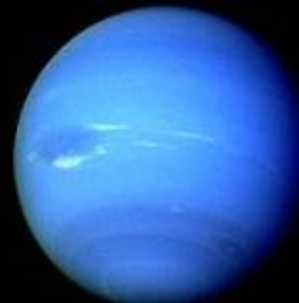
Ariel: CO₂



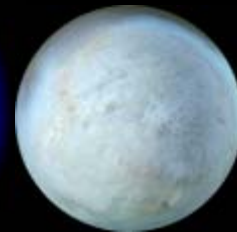
Umbriel



Oberon



Neptune



Triton



Pluto & Charon

Ices in the Outer Solar System



Ehrenfreund and Fraser (2003)

Planet	Satellite	Ices
Jupiter	Io	SO ₂ , SO ₃ , H ₂ S?, H ₂ O?
	Europa	H ₂ O, SO ₂ , SH, CO ₂ , CH, XCN, H ₂ O ₂ , H ₂ SO ₄
	Ganymede	H ₂ O, SO ₂ , SH, CO ₂ , CH, XCN, O ₂ , O ₃
	Callisto	H ₂ O, SO ₂ , SH, CO ₂ , CH, XCN
Saturn	Mimas	H ₂ O
	Enceladus	H ₂ O
	Tethys	H ₂ O
	Dione	H ₂ O, C, HC, O ₃
	Rhea	H ₂ O, HC?, O ₃
	Hyperion	H ₂ O
	Iapetus	H ₂ O, C, HC, H ₂ S?
	Phoebe	H ₂ O
	Rings	H ₂ O
Uranus	Miranda	H ₂ O, NH ₃
	Ariel	H ₂ O, OH?
	Umbriel	H ₂ O
	Titania	H ₂ O, C, HC, OH?
	Oberon	H ₂ O, C, HC, OH?
Neptune	Triton	N ₂ , CH ₄ , CO, CO ₂ , H ₂ O
Pluto	Charon	H ₂ O, NH ₃ , NH ₃ hydrate
		N ₂ , CH ₄ , CO
KBOs		H ₂ O, HC-ices (CH ₄ , CH ₃ OH), HC, silicates

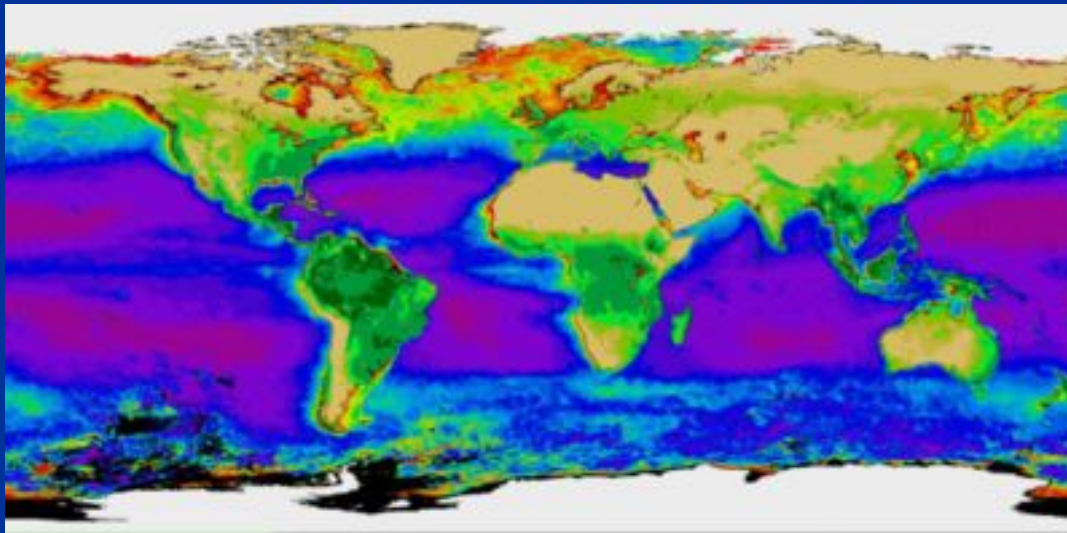


But ...

- Ozone on such moons is not formed in the 'lunar' atmosphere but rather by ion bombardment of the icy surfaces
- So ozone is **not a unique biosignature** and does not indicate oxygen atmosphere or photosynthesis

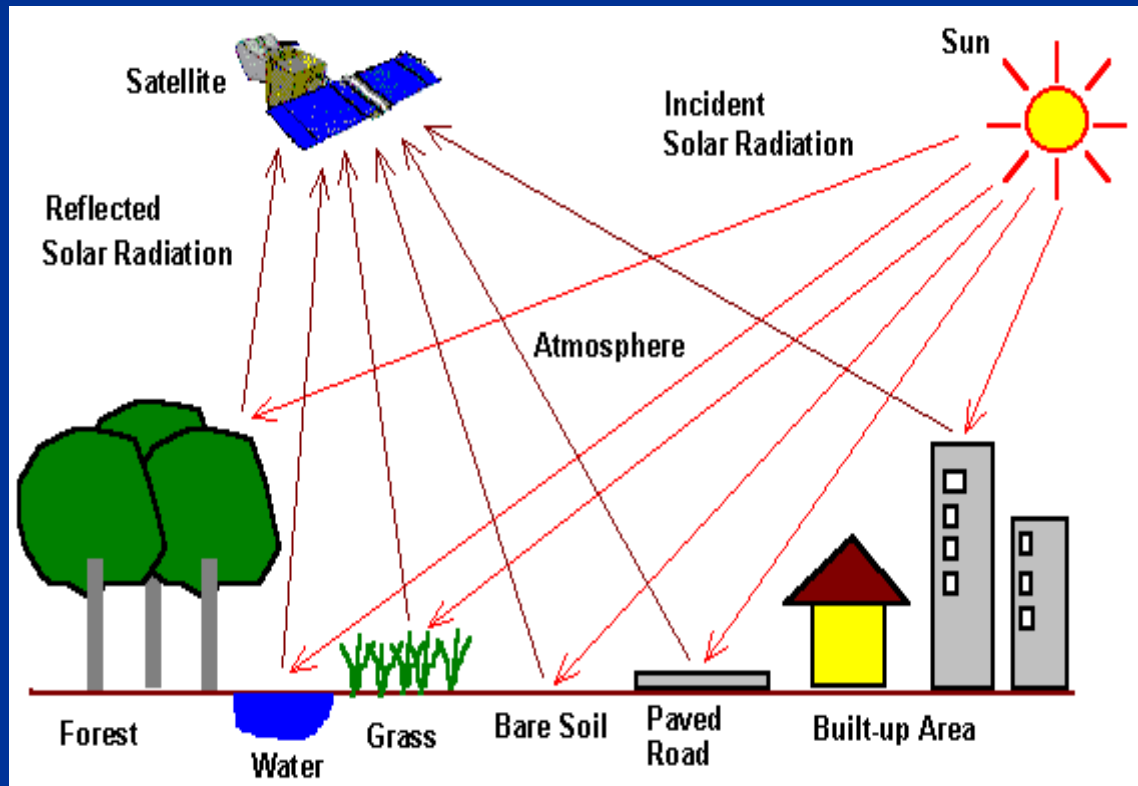
But what to look for ?

- So how about looking for a real biomarker
- Eg chlorophyll a pigment in plants ?

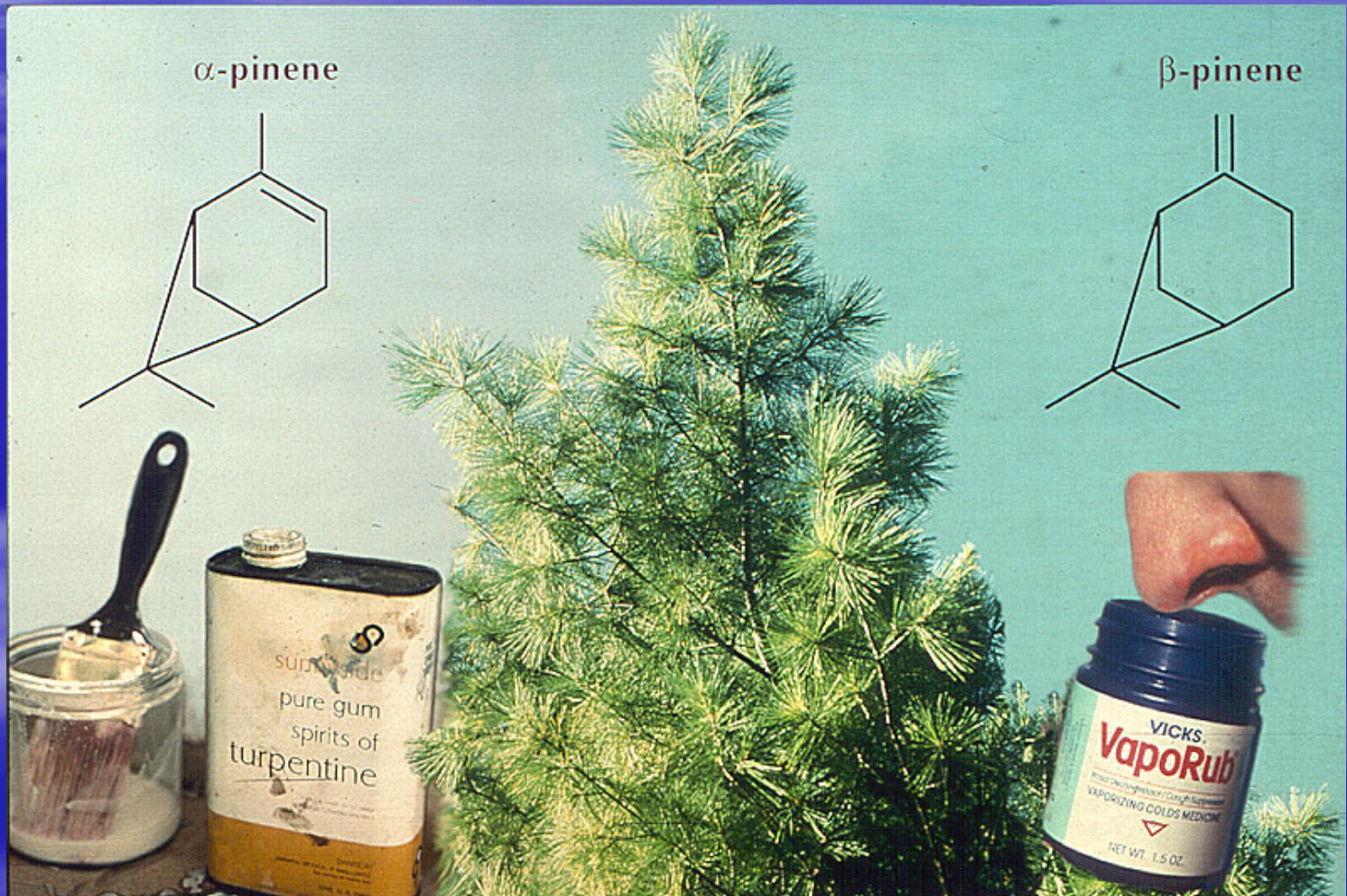


Remote Sensing

Identifying life on Earth from Space



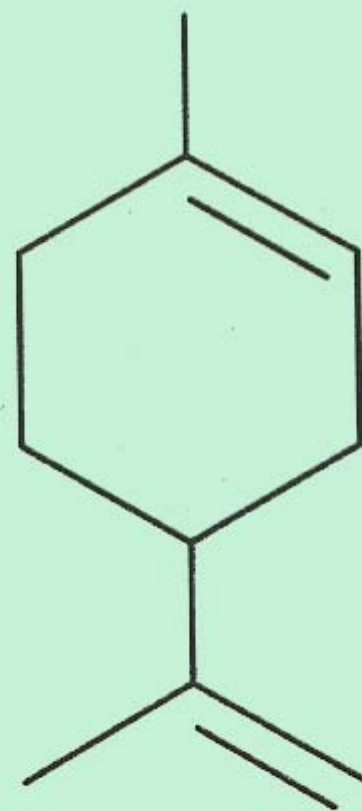
Monoterpenes



The citrus smell



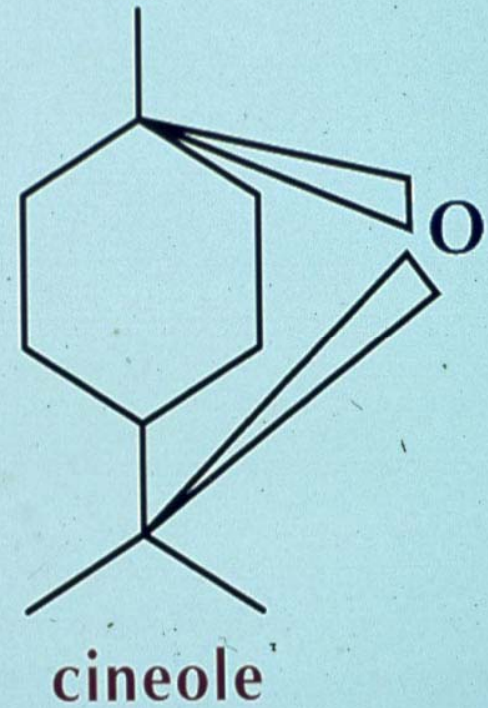
Limonene



Eucalyptus smell

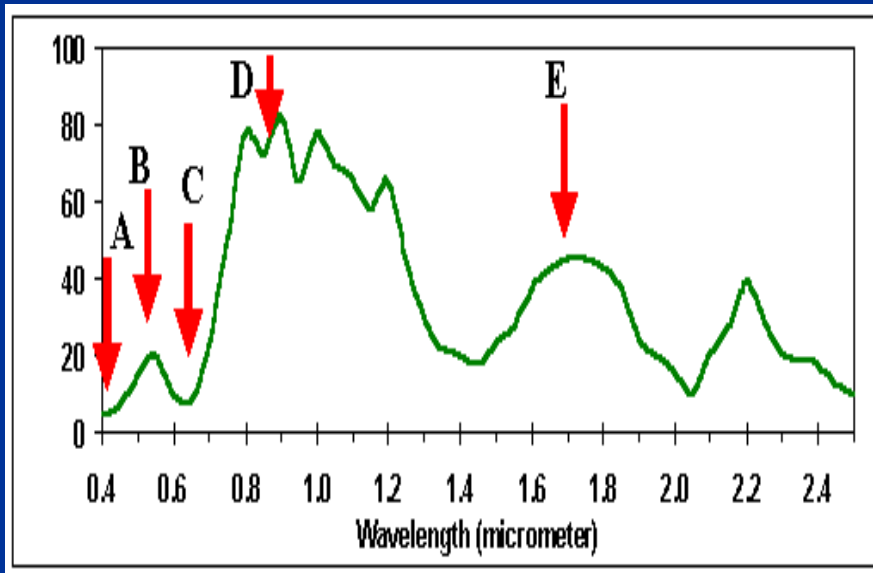


Eucalyptol



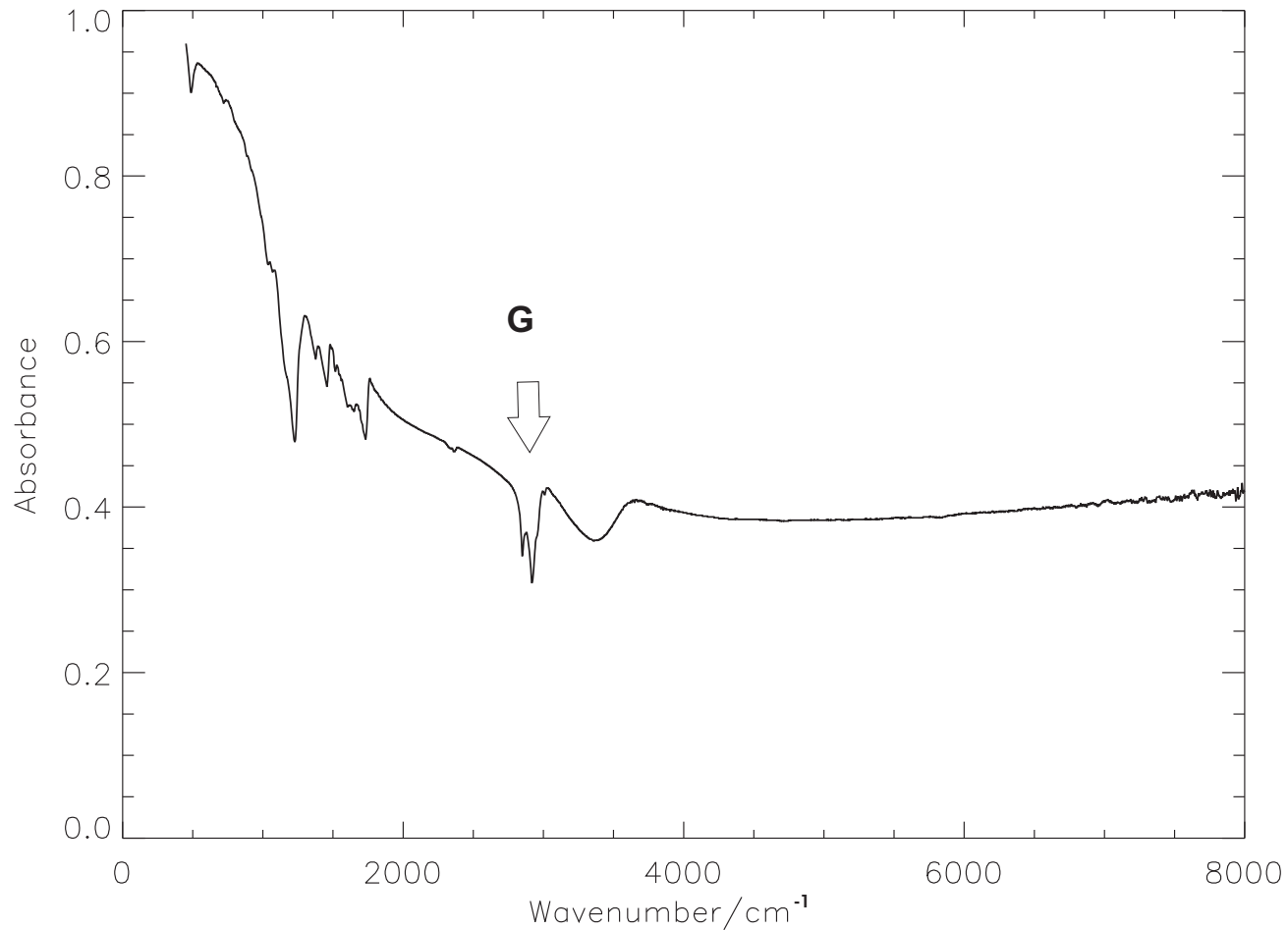
Can we adopt techniques from environmental research ?

- Measure the reflectance spectra



Typical Reflectance Spectrum of Vegetation.
Common wavelength bands used in optical remote sensing of vegetation:
A: blue band, B: green band;
C: red band;
D: near IR band; E: short-wave IR band

The absorbance spectrum of coarsely separated chlorophyll from common box leaves.



And how do we find out more of early life on earth ??

- Need more field studies to look for fossils
- And to develop more computer models of the developing early terrestrial atmosphere (using ideas of sophisticated climate programmes).

And how do we find out more of early life on earth ??

- Stromatolites -- are these what we look for ?



So there is much to be done

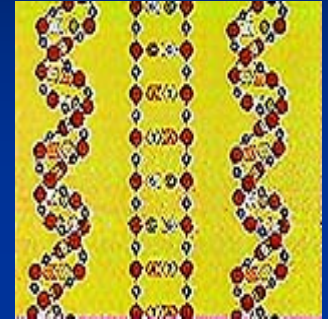
and there is a new name for this research field

ASTROBIOLOGY



Astrobiology has come of age

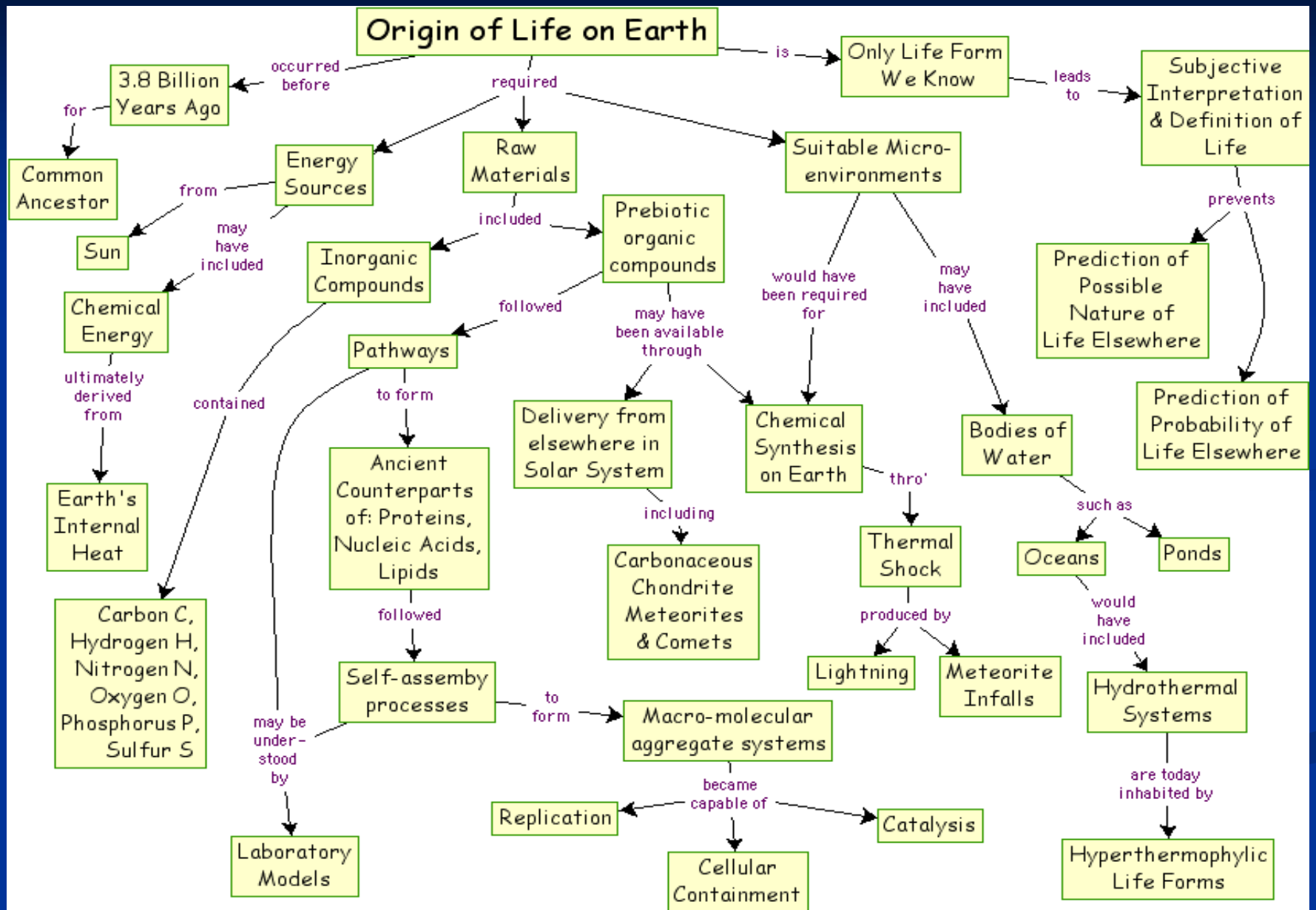
- And it is an exciting (the most exciting ?) area of scientific research....
- Bringing together researchers in a truly interdisciplinary programme **INTERNATIONALLY!**



The Open
University

CEPSAR

Centre for Earth, Planetary, Space & Astronomical Research



ASTROBIOLOGY

A field combining astronomy, biology, Chemistry and physics

This century we may answer the questions

Is there life on other planets in other solar systems

And

we may understand the chemistry of how life begins