Sputtering analysis of astrophysical solids by Plasma Desorption Mass Spectrometry - PDMS

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(Master Dissertation- 2015)

Solar das Andorinhas - 2016

Sputtering analysis of astrophysical solids by Plasma Desorption Mass Spectrometry - PDMS

1- Optical Spectroscopies – the main source of information

2- How Mass Spectrometry can be used in Astrophysics?

3- MS of cosmic rays

4- Mass spectrometers in space

5- MS of cosmic samples (our data)

6- MS of analogues (our data)

7- Final Comments

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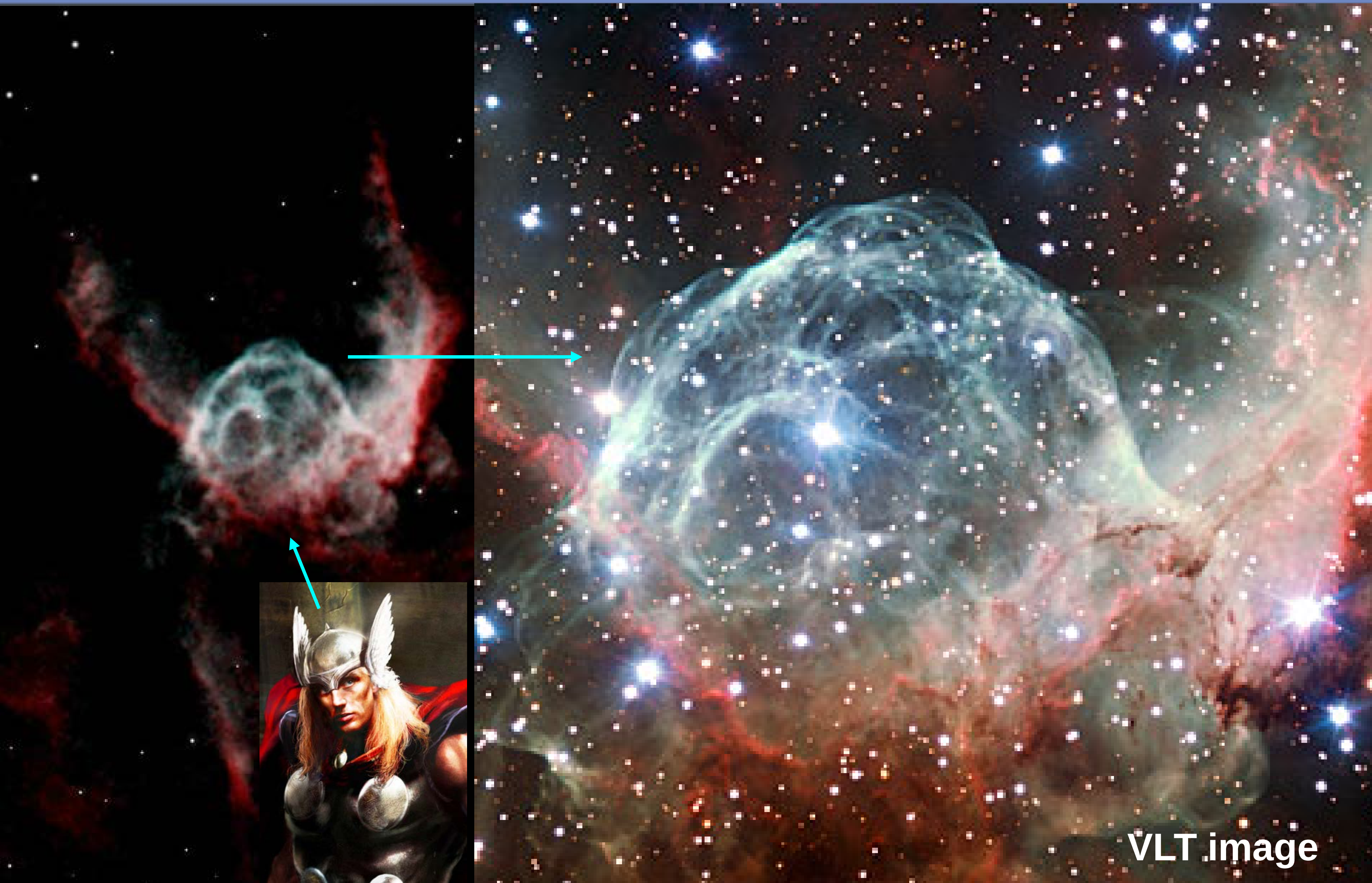
Because sources are too distant ,

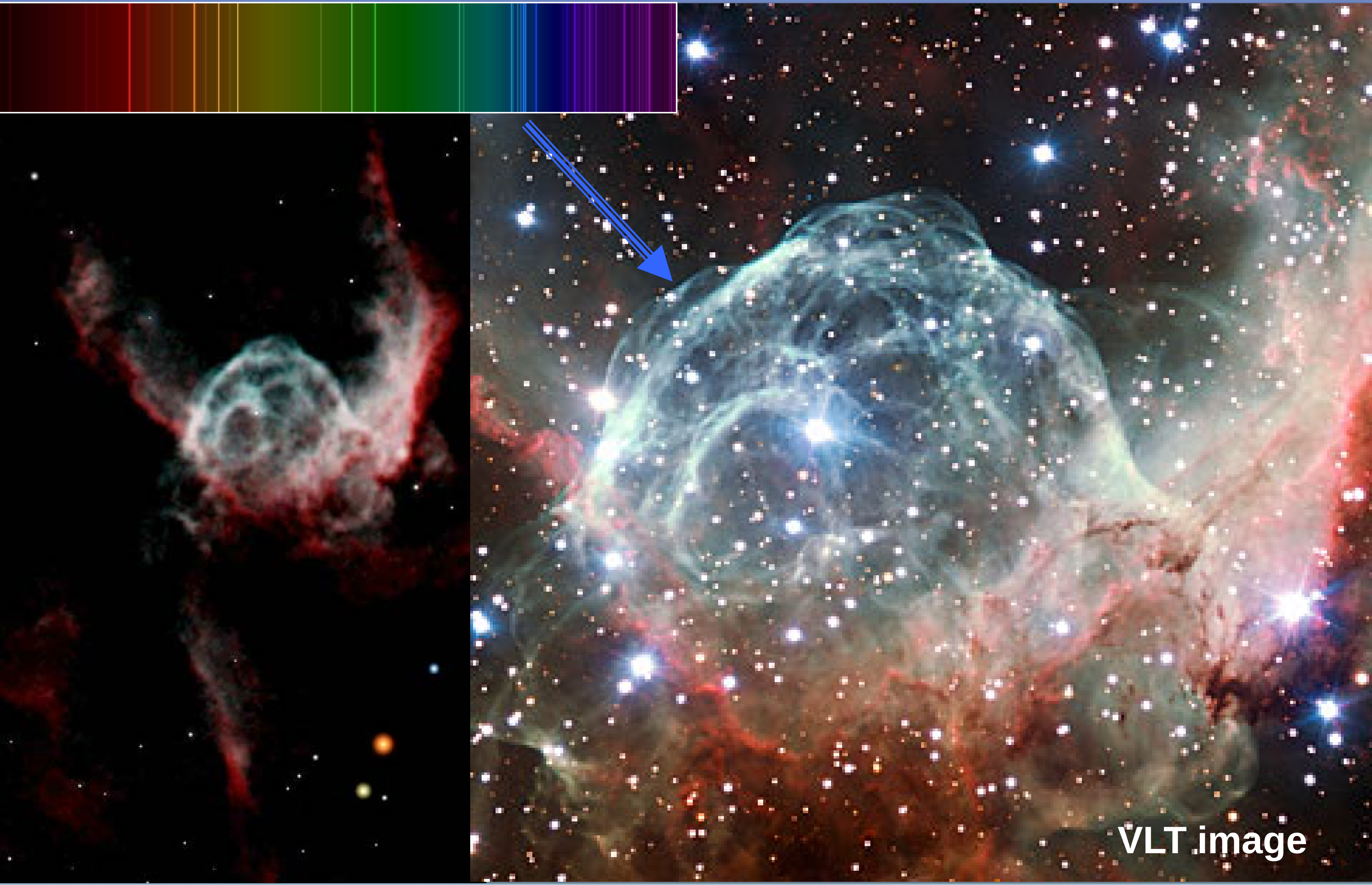
most of the information from the Universe comes by electromagnetic waves

Ex.: image acquired by the Very Large Telescope, Chile



Thor's Helmet Nebula (near Sirius – Canis Major)

The blue color reveals an oxygen cloud expanding



Thor's Helmet Nebula (near Sirius – Canis Major)

Optical Spectroscopies are very important but, nevertheless,

Relevant cosmic information also comes via:

- **gravitation (now: waves !)**
- **neutrinos**
- **electrons**
- **cosmic rays (ions)**
- **cosmogenic and cosmic materials**
- **space missions**

More analytical techniques are necessary, in particular

Mass Spectrometry (MS)

How MS can be used in Astrophysics?

Direct use:

a) **cosmic rays*** arriving on Earth and on artificial satellites

b) **secondary ions** produced by natural ionizing radiation impinging on planets, satellites, grains, asteroids and comets

c) **cosmogenic materials** (e.g. ^{14}C produced in atmosphere)

d) **cosmic samples** (measurements in situ) and meteorites or material brought to Earth by missions

Indirect use:

study of **cosmic analogue samples** ← laboratory data

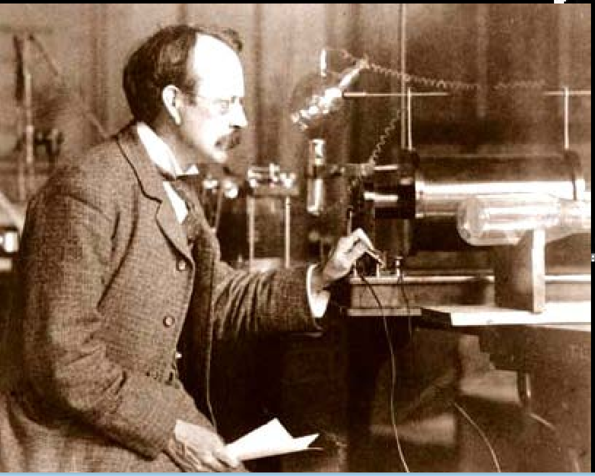
* Primary CR: e^-, H, He and heavy (C → Fe) ions; Secondary CR: Li, mesons, e^+

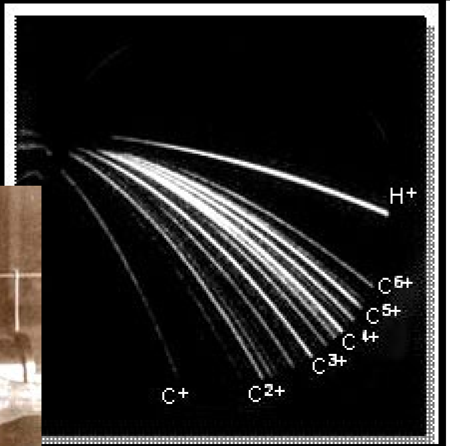
How MS can be used in Astrophysics?

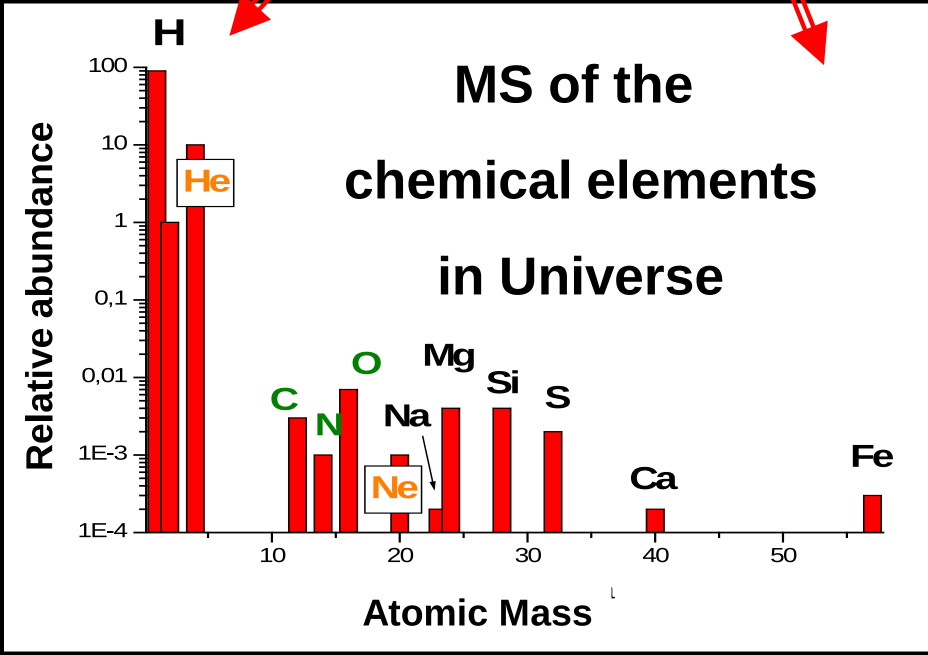
Mass Spectrometry →

- mass determination of:
- elementary particles, atoms and molecules
- measurement of their abundance

W. Wien	1898
A. Dempster	1918
F. Aston	1919



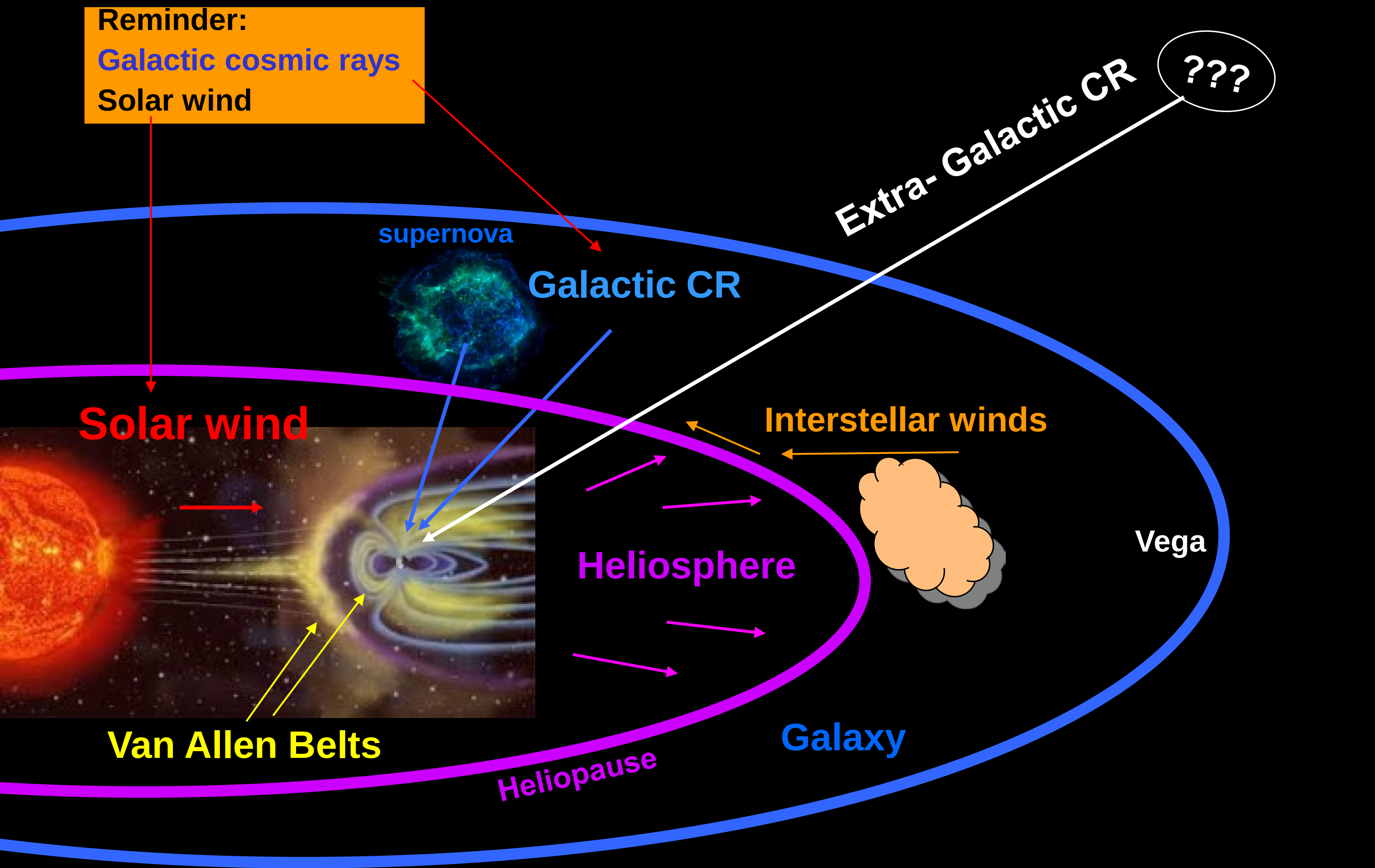




Thomson (1912) : first mass spectrum

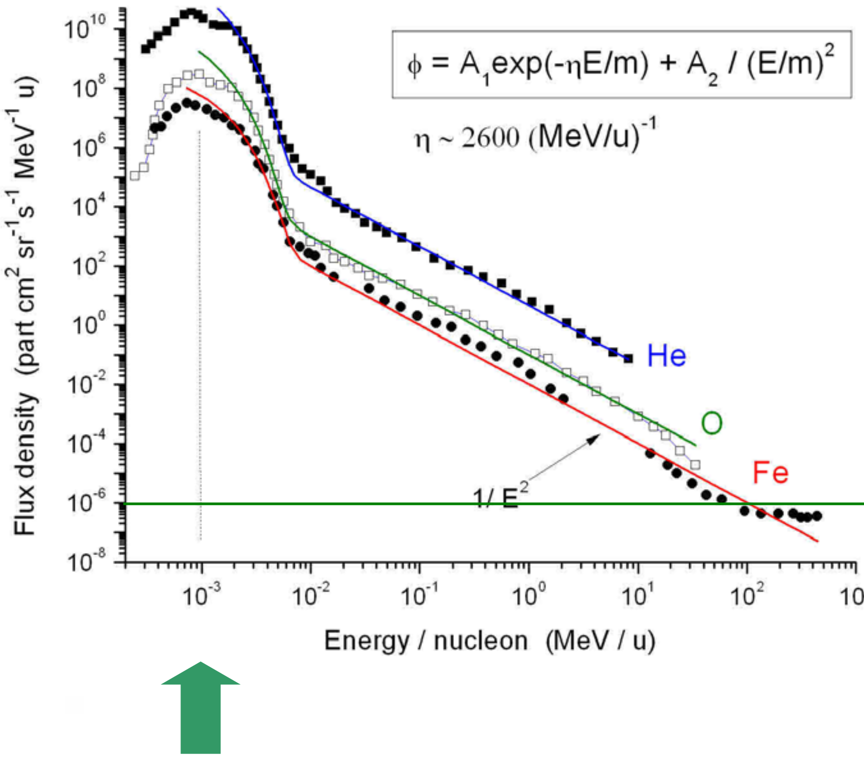
How to get his?

Primary Cosmic Ray (CR) Species



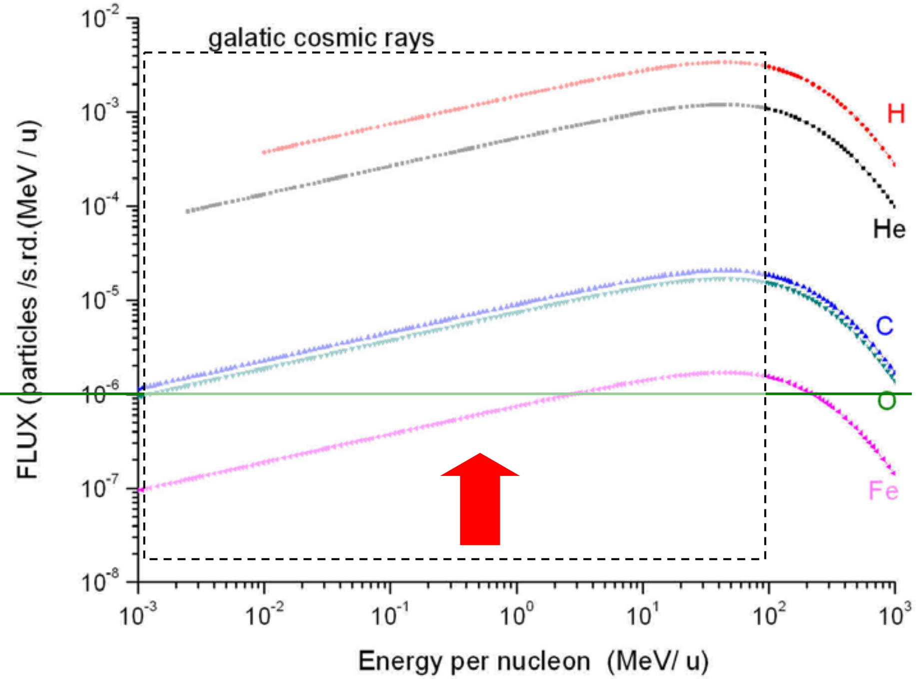
V_{SW} = 400c km/s V_s = 100 km/s V_{apex} = 16 km/s

Solar wind on Earth orbit



MS easy

Galactic cosmic rays



MS difficult

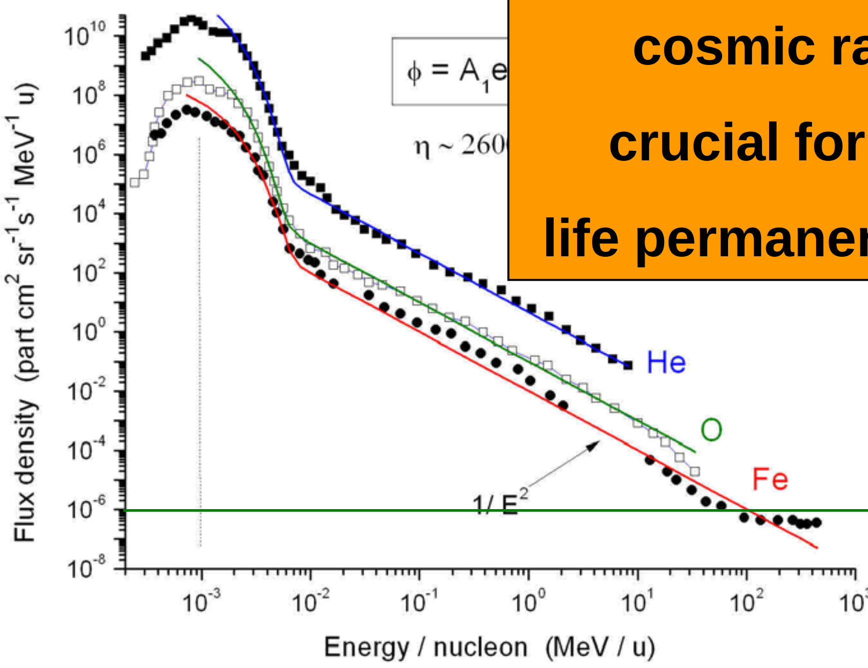
(very large spectrometers)

Solar Wind & Galactic CR

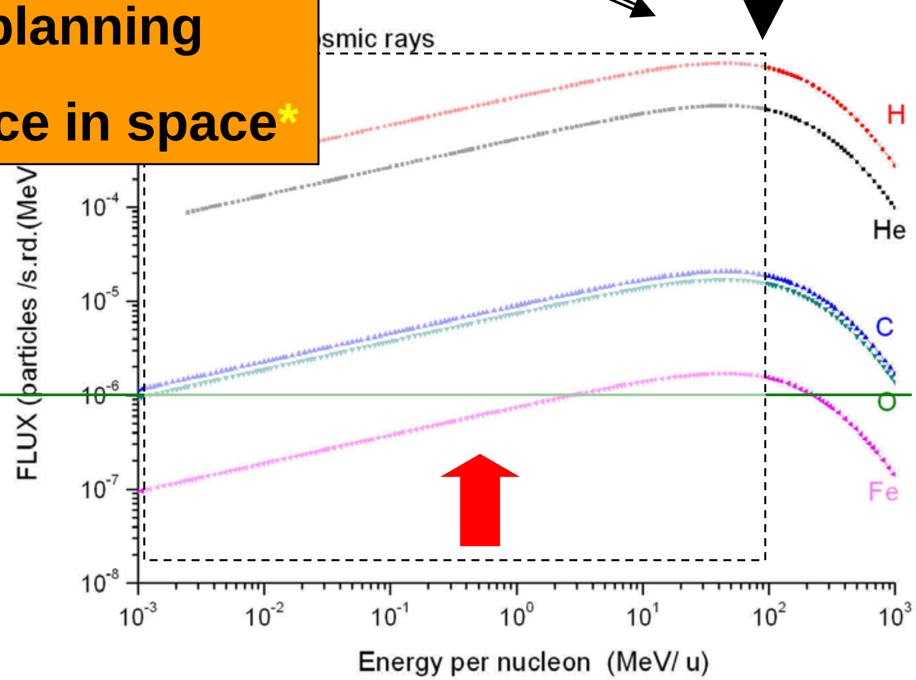
Solar wind on Earth orbit

Galactic cosmic rays

0.1 GeV protons



The knowledge of cosmic ray flux is crucial for planning life permanence in space*



MS easy

MS difficult
(very large spectrometers)

b) Mass Spectrometers in Space

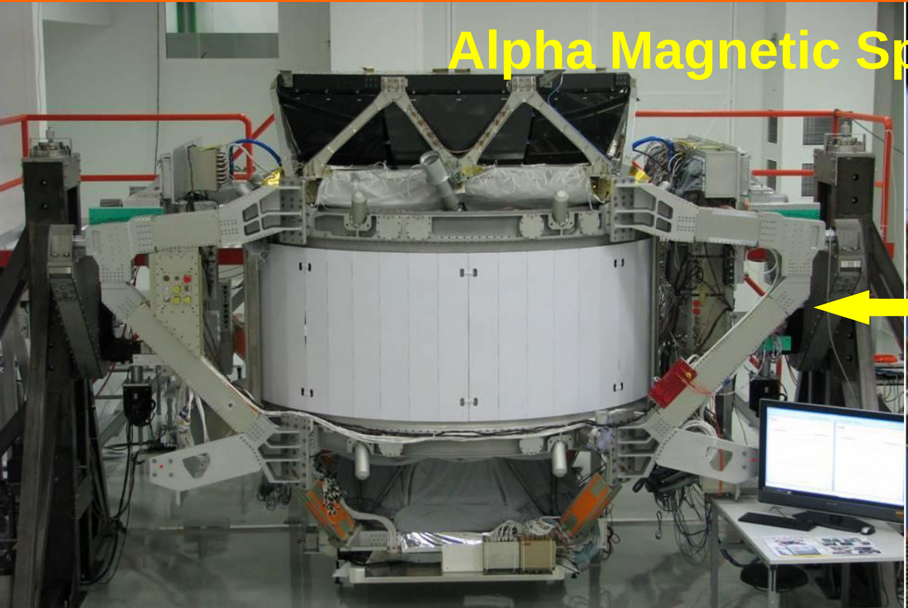
The Viking Gas Chromatograph Mass Spectrometer

(1971)

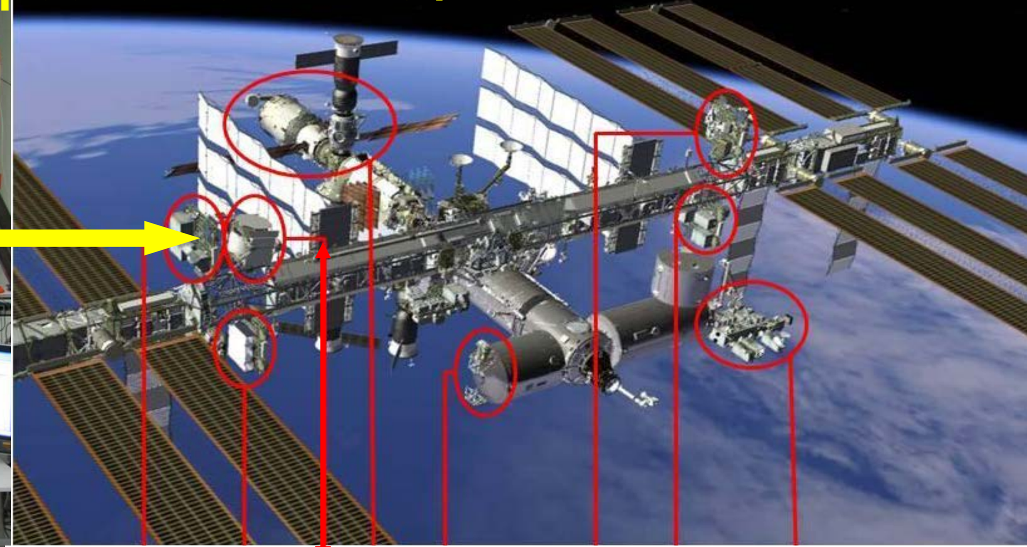
A gas chromatograph uses a thin capillary fiber known as a column to separate different types of molecules, based on their chemical properties.

→ **Searching for Life on Mars**

Alpha Magnetic Spectrometer: $\overline{He}$ / He **Launch: May 2011**



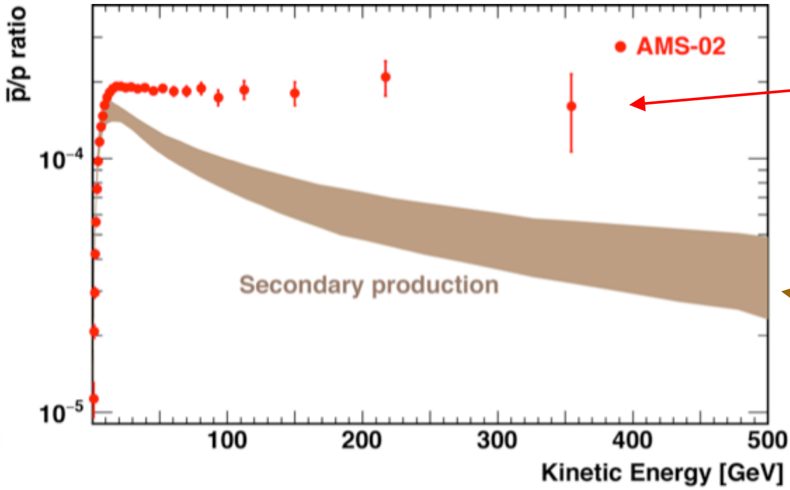
Mass: 8.5 ton



AMS @ Internl. Space Station (ISS)

AMS: Searching for antimatter, dark matter and measuring cosmic rays

b) Mass Spectrometers in Space



antiproton / proton ratio

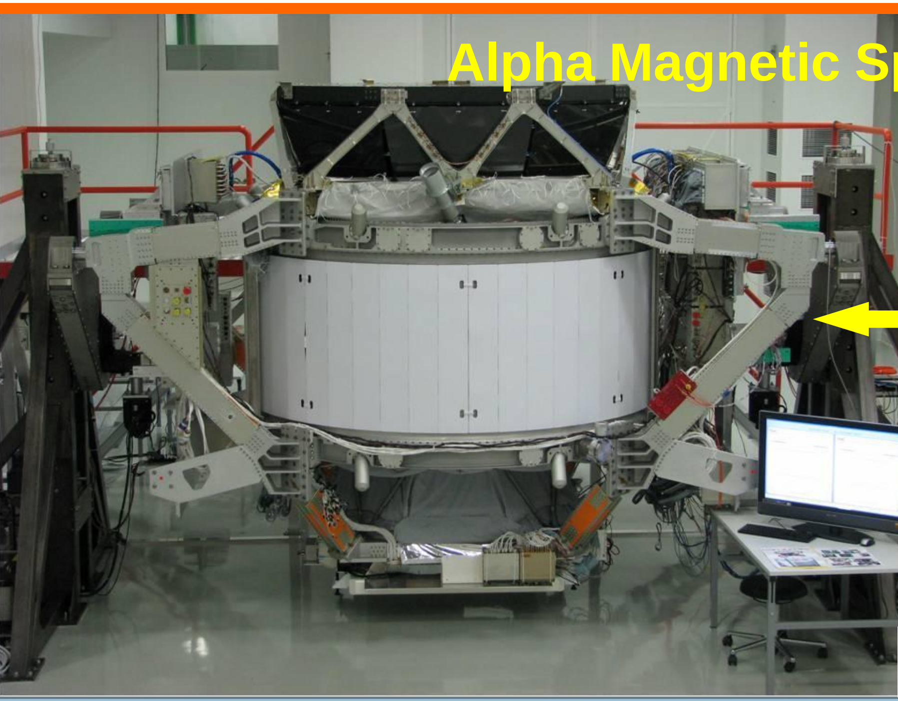
(2015 AMS-02 data)

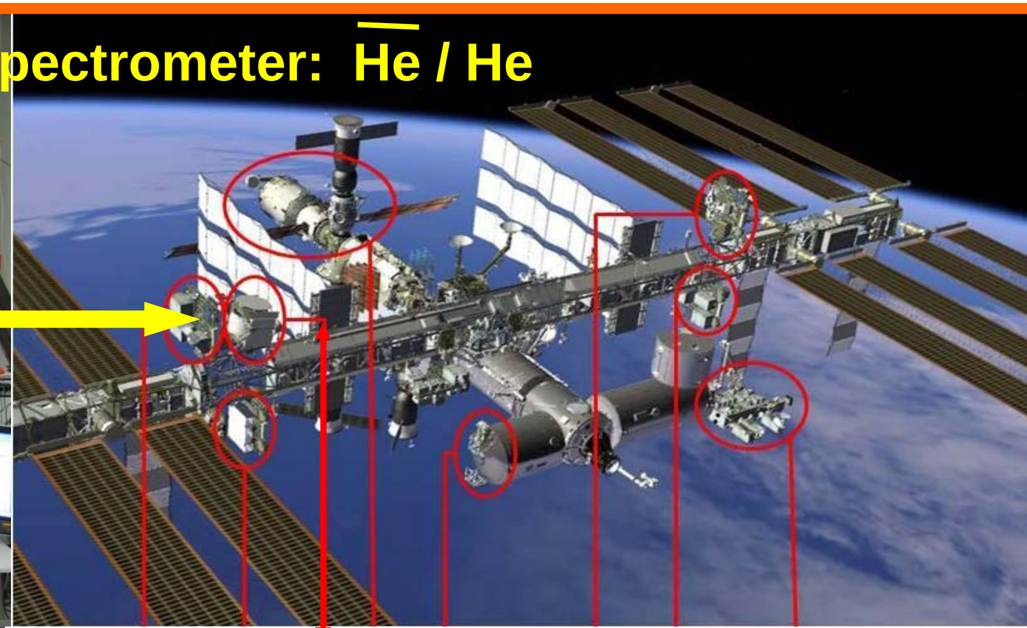
antiproton secondary production

from ordinary cosmic ray collisions

(expected)

Alpha Magnetic Spectrometer: $\overline{He}$ / He

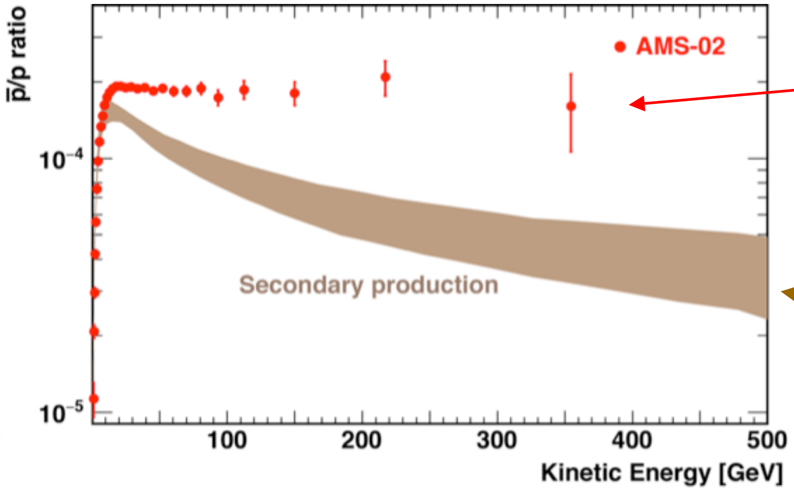




AMS @ Internl. Space Station (ISS)

AMS: preparing for Mars mission. Measuring GeV cosmic rays

b) Mass Spectrometers in Space



antiproton / proton ratio

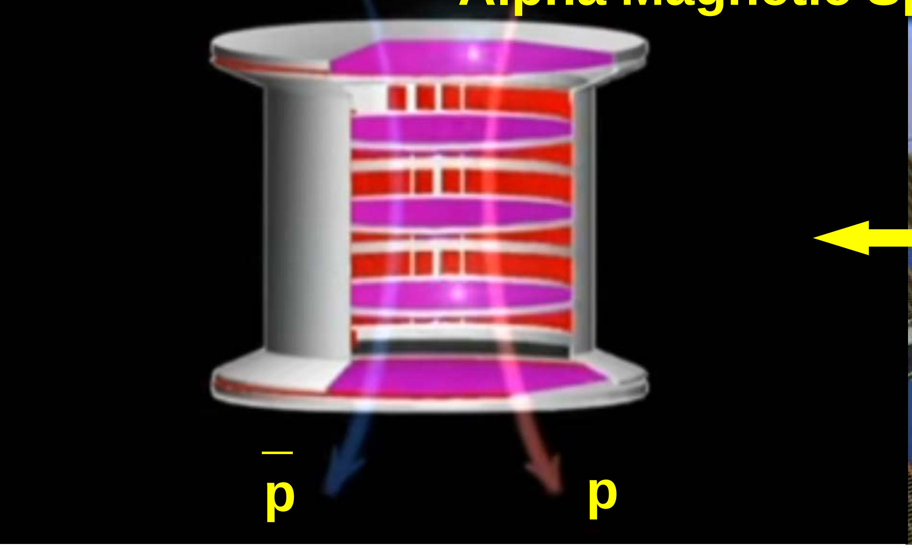
(2015 AMS-02 data)

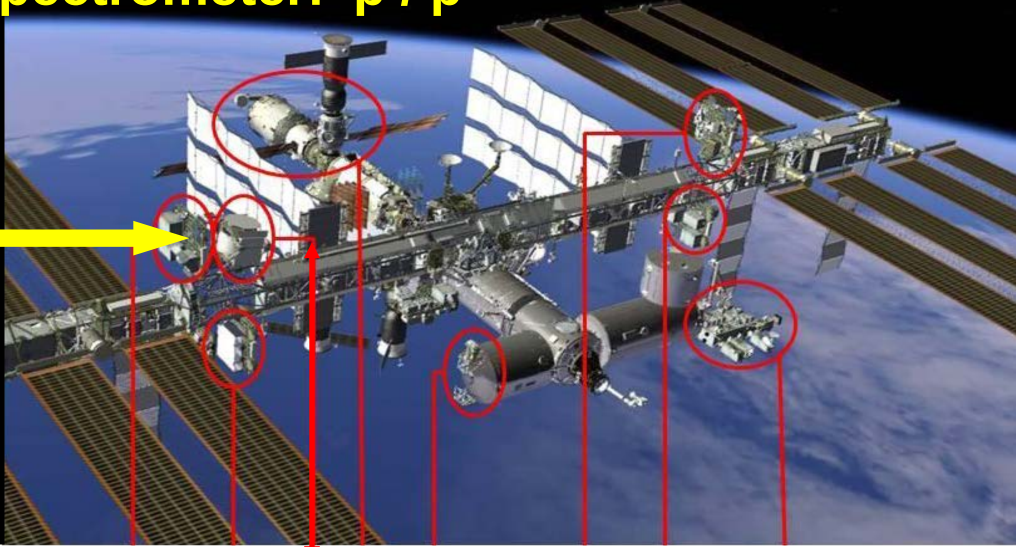
antiproton secondary production

from ordinary cosmic ray collisions

(expected)

Alpha Magnetic Spectrometer: $\bar{p}$ / p



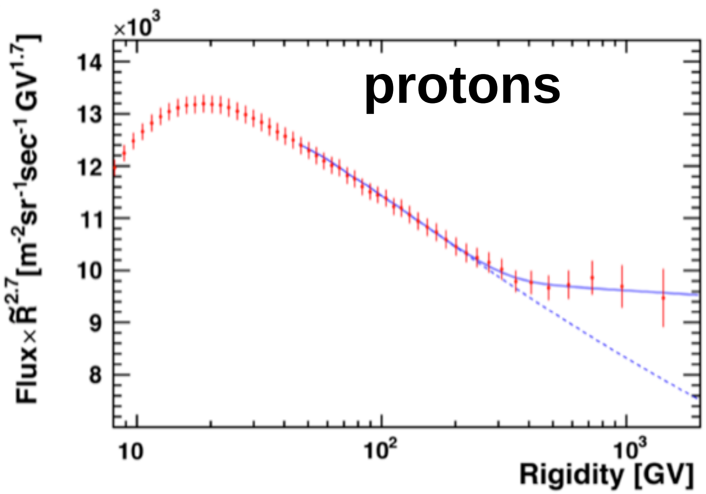


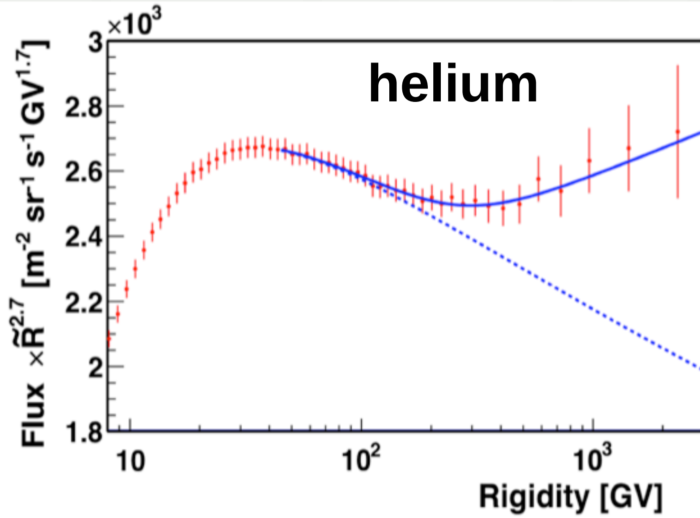
antiproton **proton**

AMS @ Internl. Space Station (ISS)

AMS: 60 billion cosmic ray events after 5 years

b) Mass Spectrometers in Space





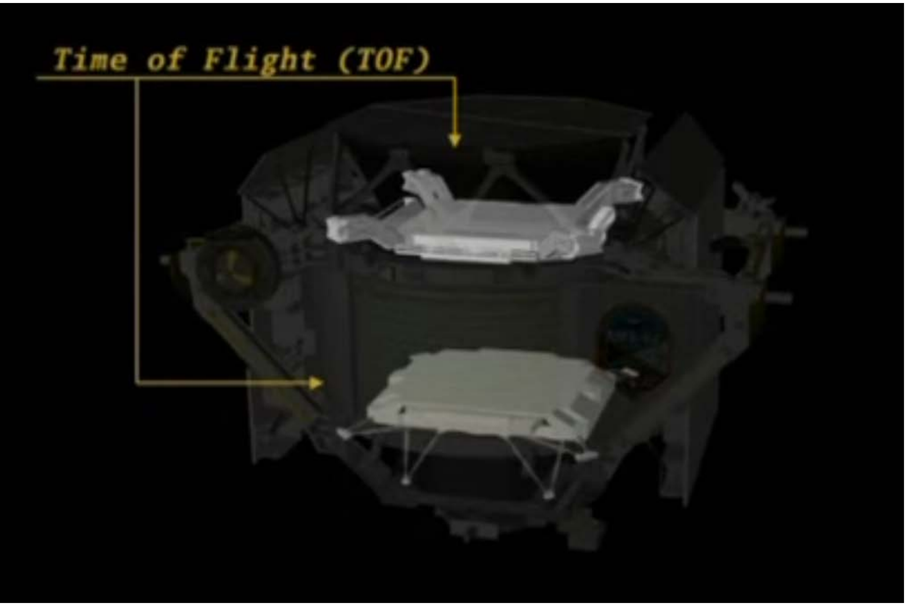
= B r = m v /q

flux

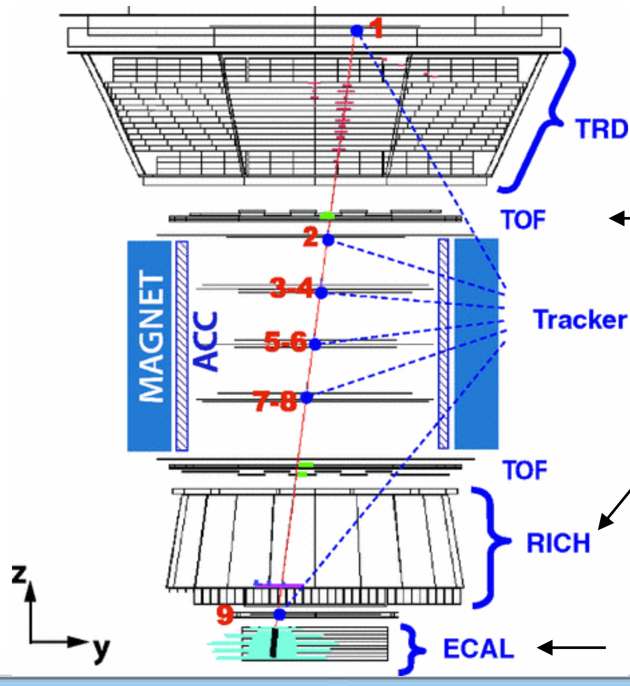
data

higher flux at high energies

prediction



TOF mass spectrometer



PRL 110 (2013)141102

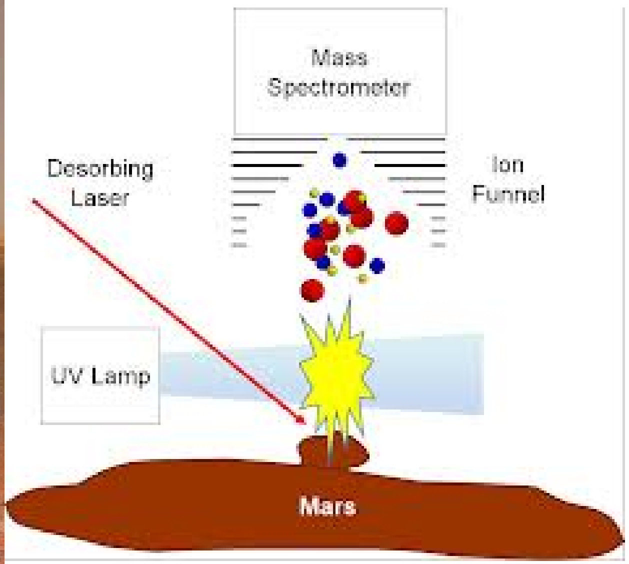
for masses

for trajectories (charges)

energy detector

AMS: a magnetic, TOF and position sensitive spectrometer

b) Mass Spectrometers in Space

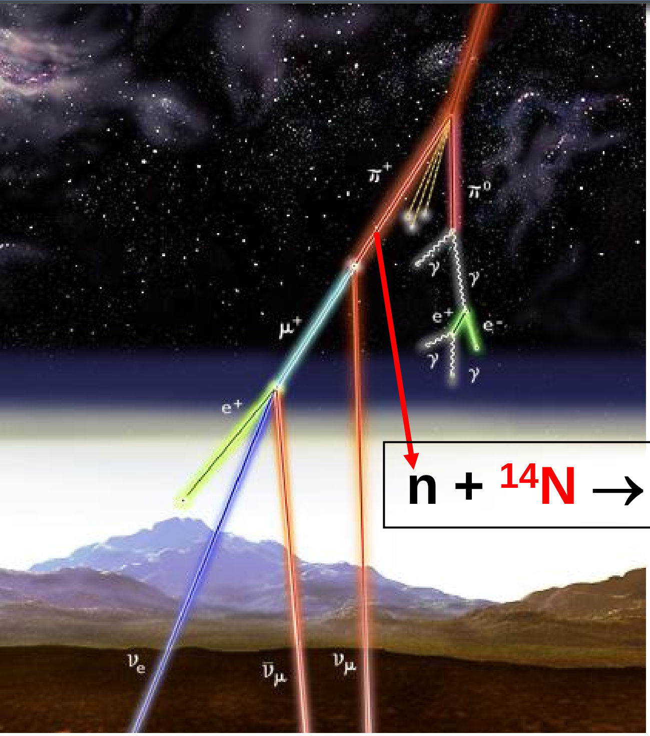


Mars Science Laboratory 2011

Analyzing the surfaces of rocks and other samples directly on Mars' surface.

Laser MS of neutral molecules in Mars soil

c) Cosmogenic materials



$n + {}^{14}N \rightarrow {}^{14}C + p$

$^{14}C \rightarrow {}^{14}N + e^- + \overline{\nu_e}$

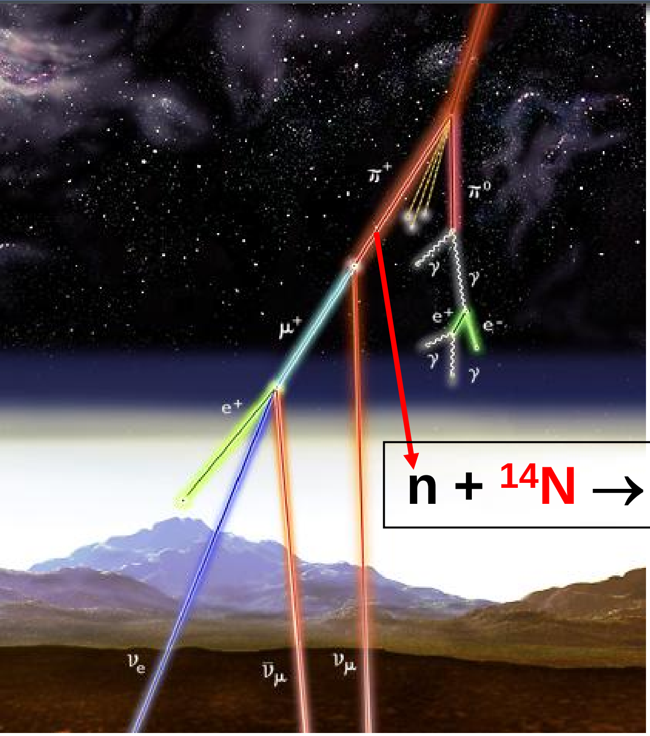
$\tau_{1/2}$ = 5730 years

Beta decay

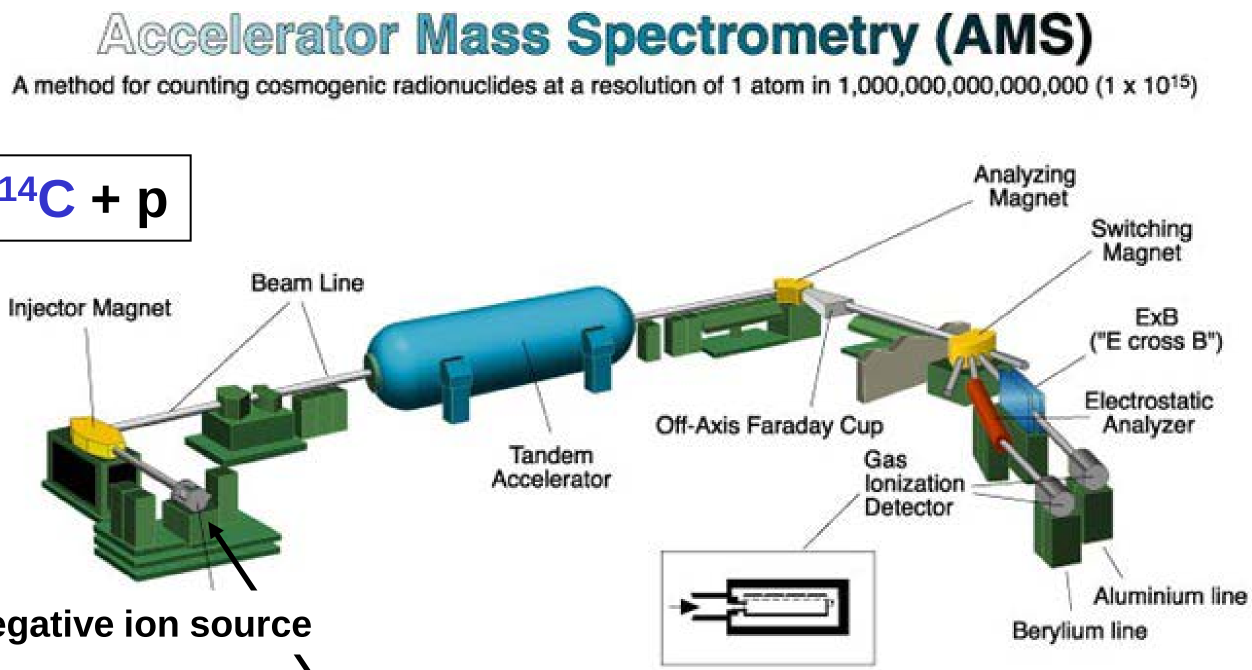
^{14}C & ^{12}C sample

The ^{14}C / ^{12}C ratio gives the sample age

c) Cosmogenic materials



n + ^{14}N → ^{14}C + p



negative ion source

$^{14}C \rightarrow {}^{14}N + e^- + \overline{\nu}_e$

$\tau_{1/2}$ = 5730 years

Beta decay

^{14}C & ^{12}C sample

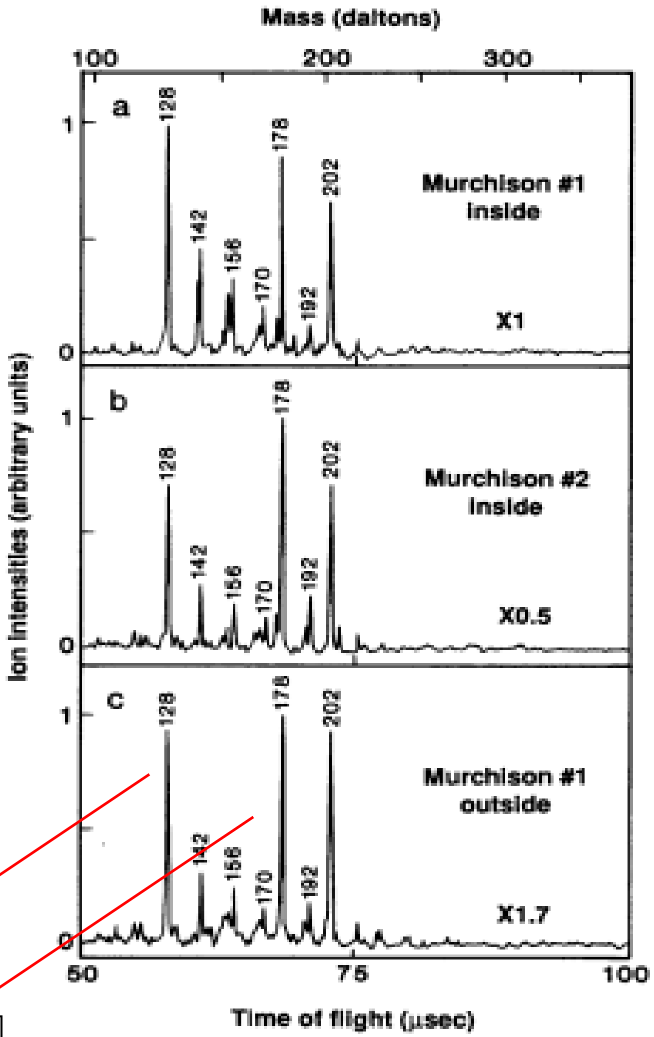
14 {
- **$^{14}N^-$ → instable ion**
- **$^{12}CH_2^-$ → dissociates**
- **$^{14}C^-$ → detected**

The ^{14}C / ^{12}C ratio gives the sample age

d) Cosmic samples

Murchirson meteorite

(Australia – 28 Sep 1969)



mass 128: naphthalene

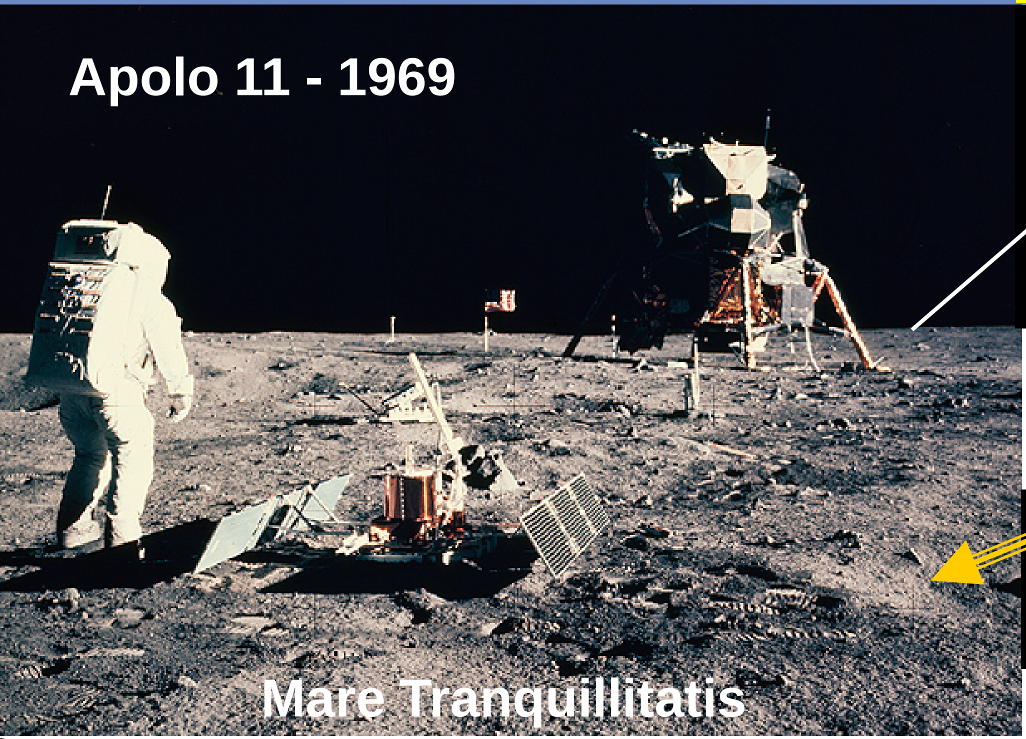
178: phenanthrene / antracene

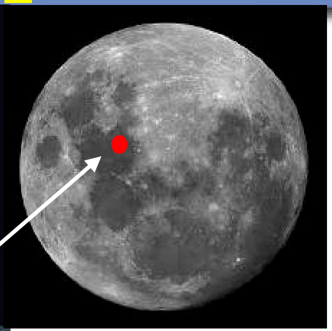
IR + pulsed UV laser MS

(thermal desorption + ionization)

Carbonaceous chondrite type – Hanh et al., Science 239 (1988) 1523

d) Cosmic samples





Regolith

SiO_2 et al.

Moon rocks

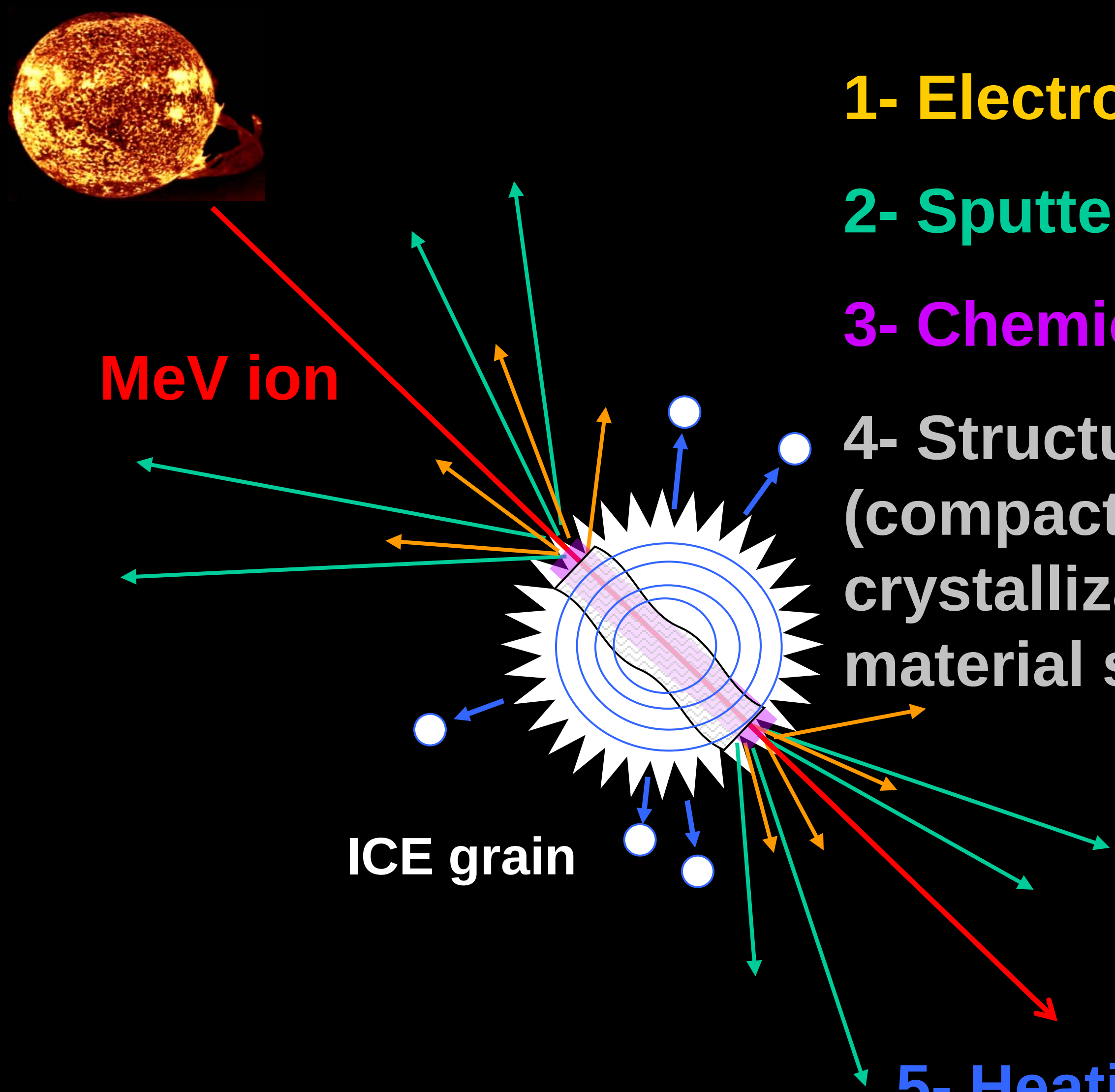
Lunar Mission	Sample Returned	Year
Apollo 11	22 kg	1969
Apollo 12	34 kg	1969
Apollo 14	43 kg	1971
Apollo 15	77 kg	1971
Apollo 16	95 kg	1972
Apollo 17	111 kg	1972
Luna 16	101 g	1970
Luna 20	55 g	1972
Luna 24	170 g	1976

- maria → basaltic lava → olivine $\rho \sim 4\ g/cm^3$
- highlands → anorthosite $\rho \sim 2.6\ g/cm^3$

anorthite

Armstrong's walk on the Moon (on the cat's eye)

main ion-solid mechanisms



1- Electron emission

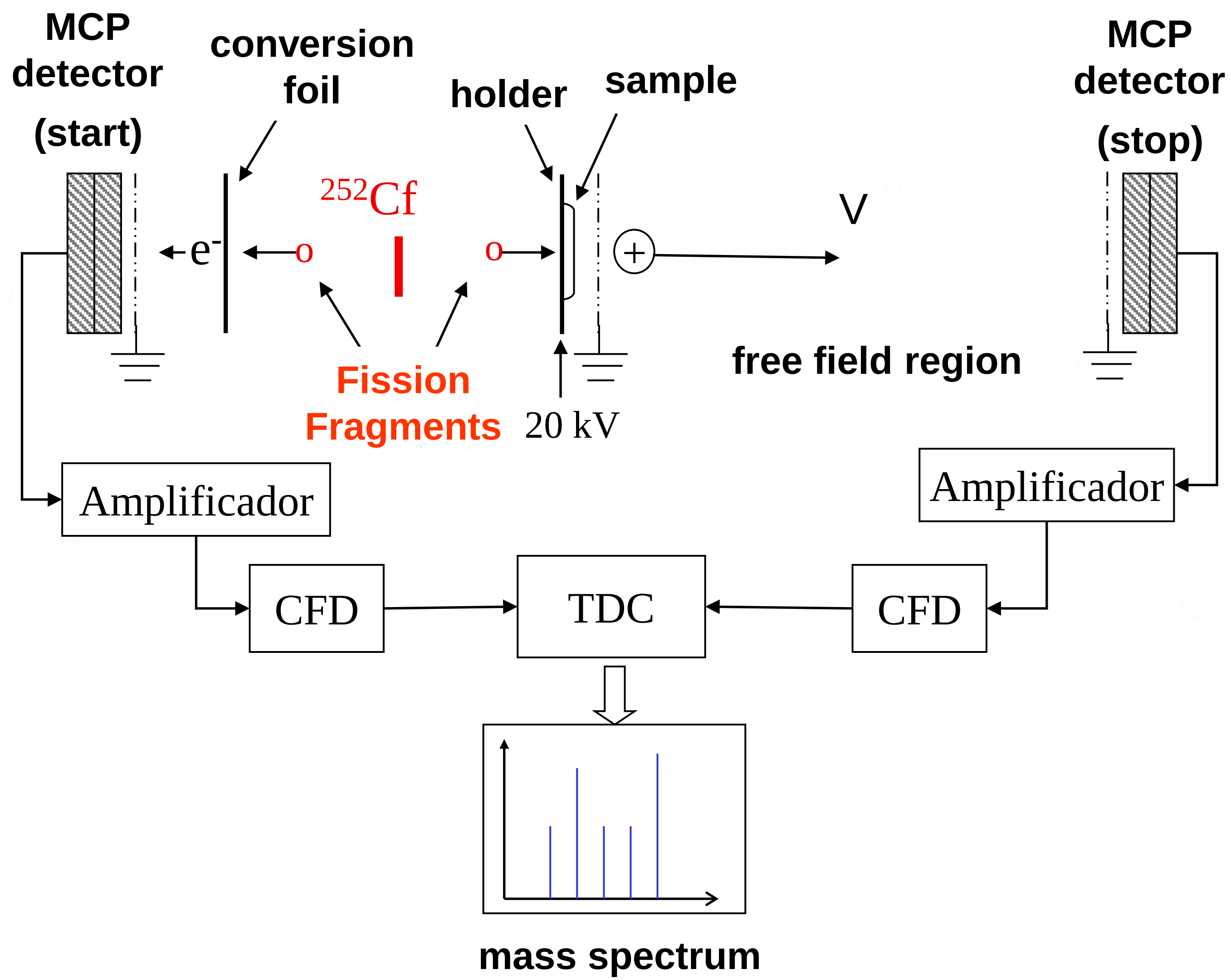
2- Sputtering (neutrals and ions)

3- Chemical reactions

4- Structural modifications (compaction, amorphyzation, crystallization, phase transition, material stress, craters,…)

5- Heating and Sublimation

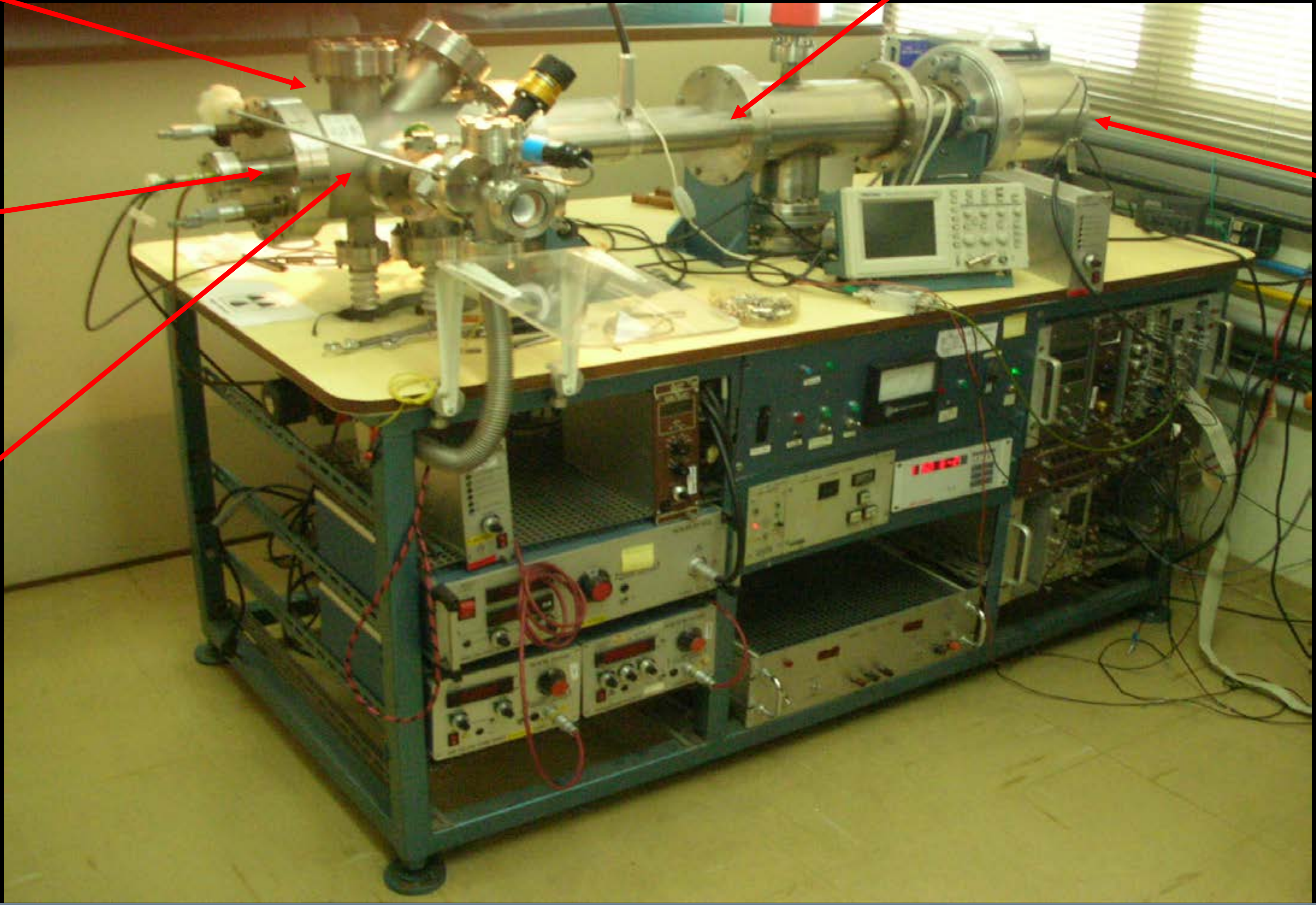
PDMS – Plasma Desorption MS



TOF used in our measurements

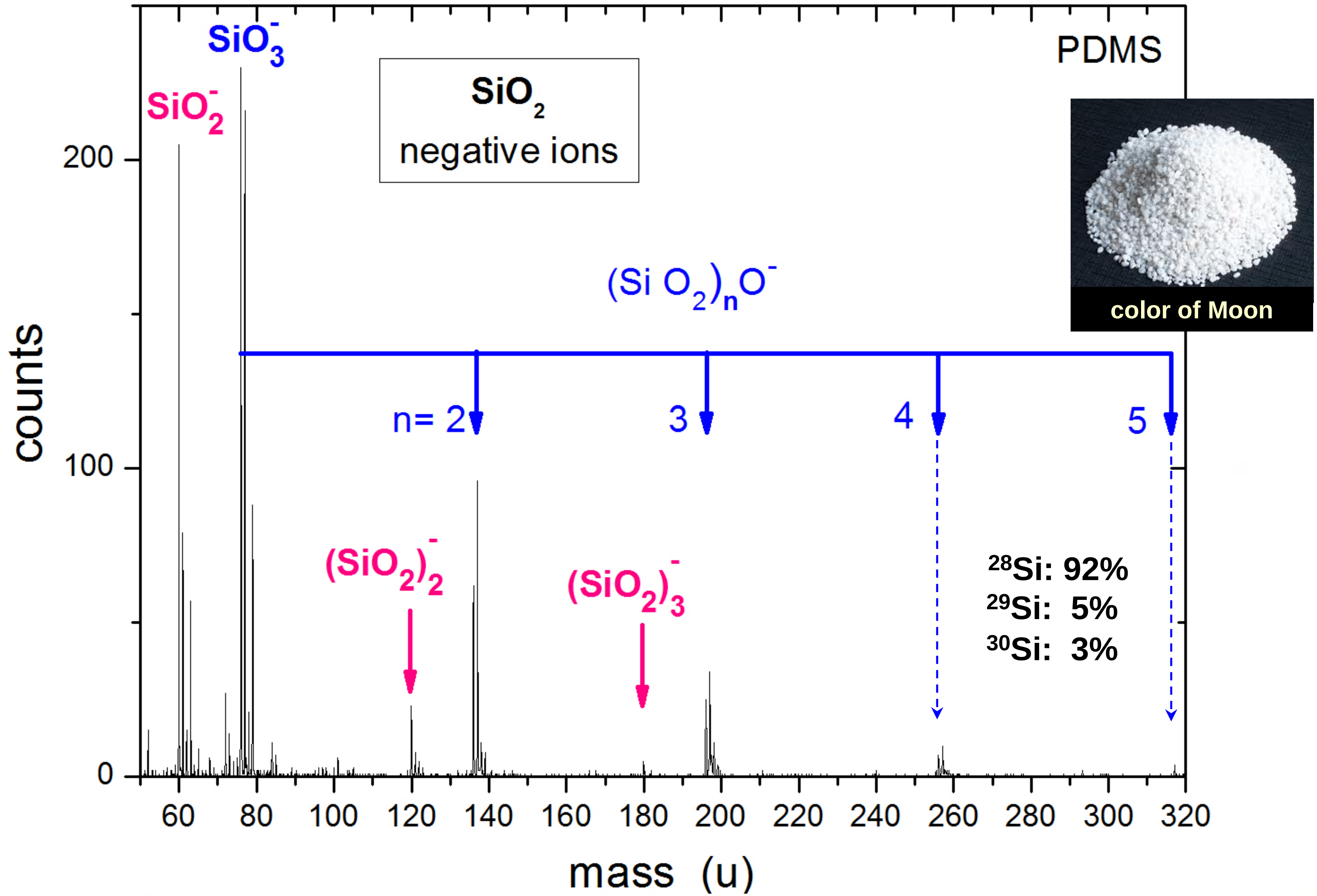
Sputtering of silicates

- Analyzed by TOF mass spectrometer
- At room temperature



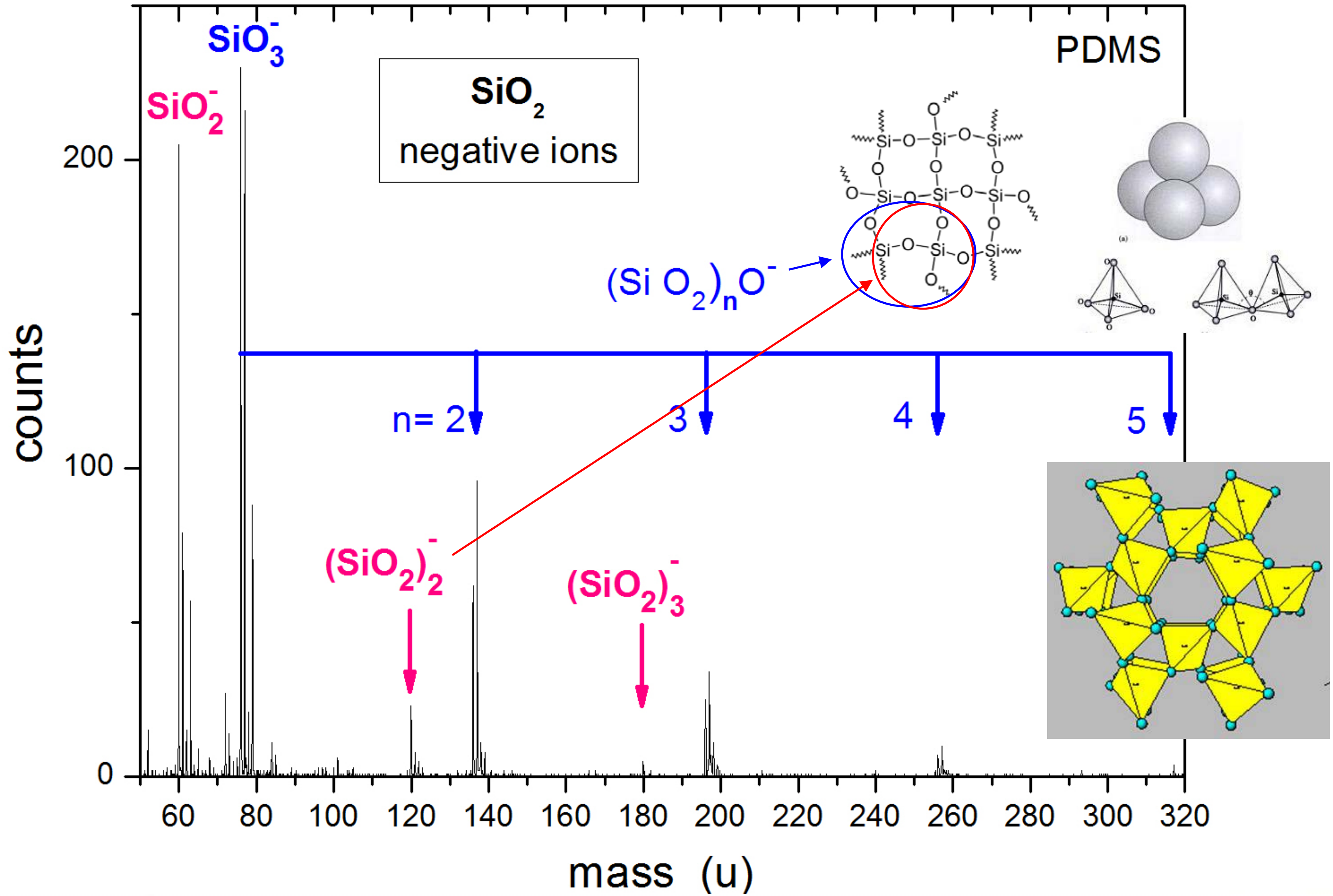
PDMS – Plasma Desorption MS

d) Cosmic samples



Silica / Quartz (from Apollo mission)

d) Cosmic samples



Silica / Quartz (brought by Apollo mission)

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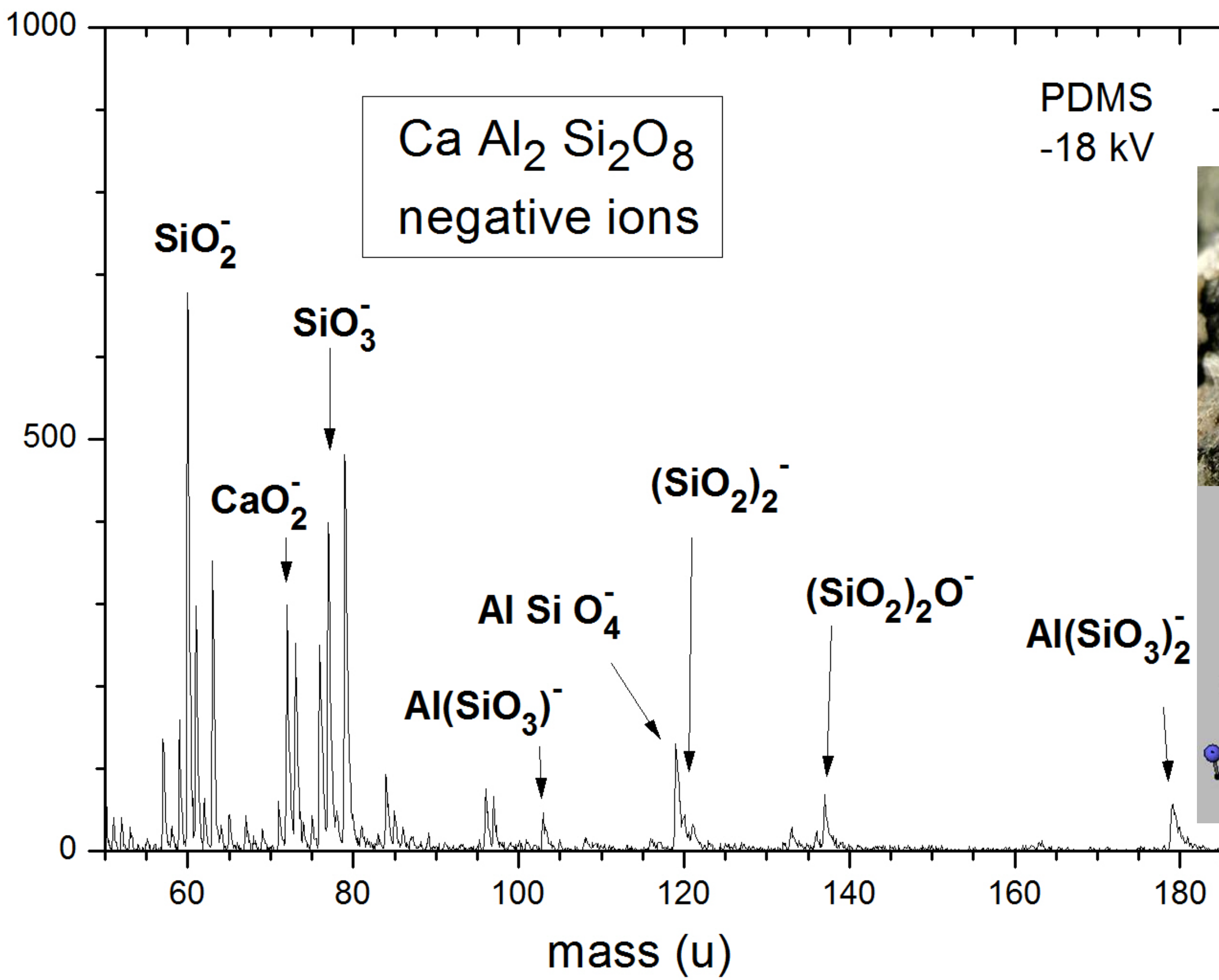
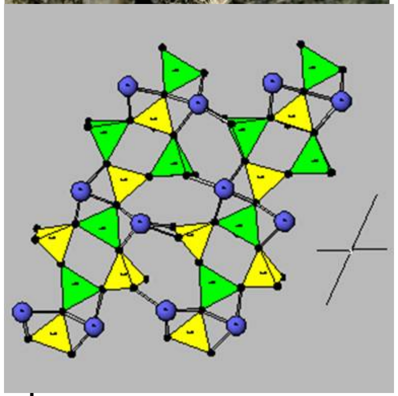
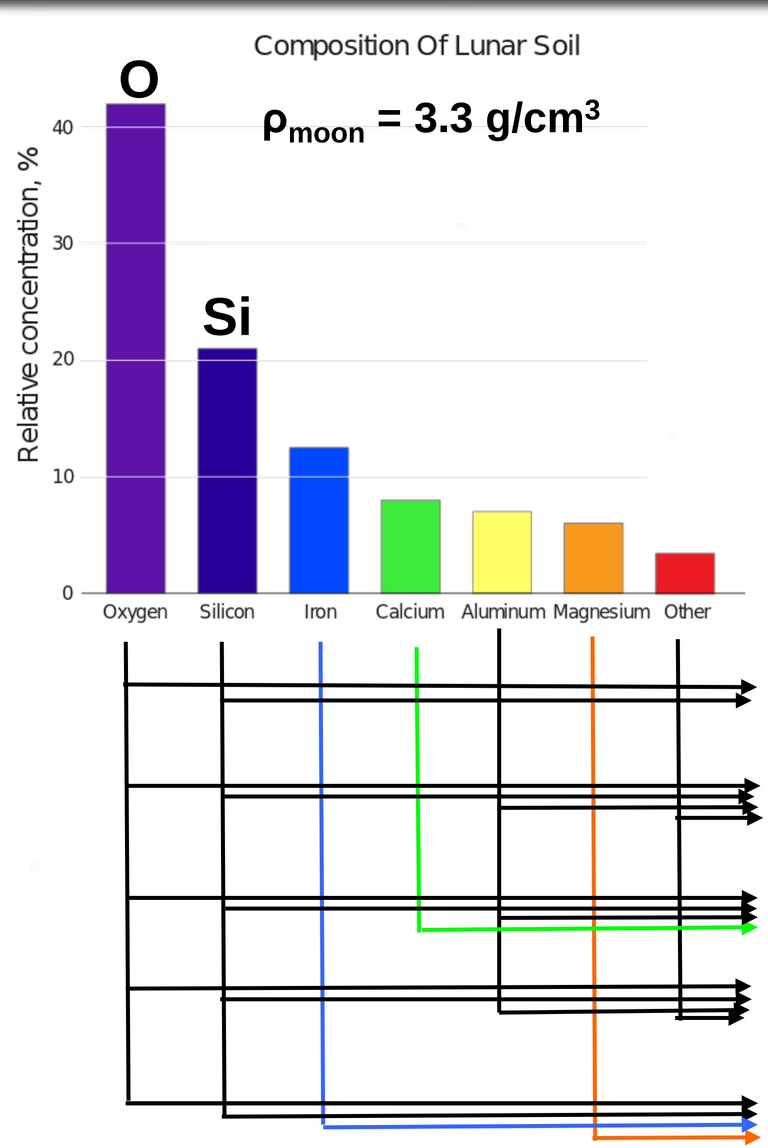
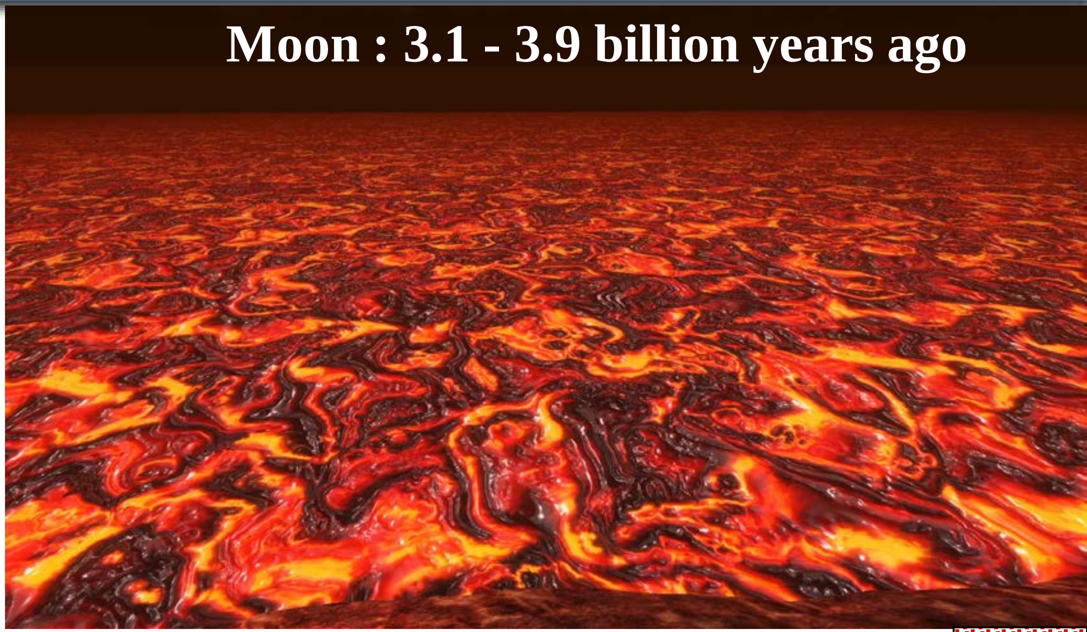




Anorthite (brought by Apollo mission)

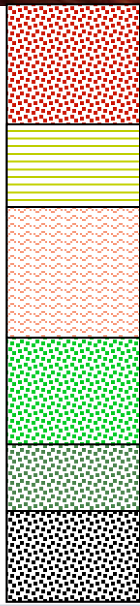
e) Cosmic analogue samples





SiO_2	Silica	2.2
$Na_3KAl_4Si_4O_{16}$	Nepheline	2.6
$CaAlSi_3O_8$	Anorthite	2.7
$NaAlSi_2O_6$	Jadeite	3.3
$(Mg,Fe)_2SiO_4$	Olivine	4.0

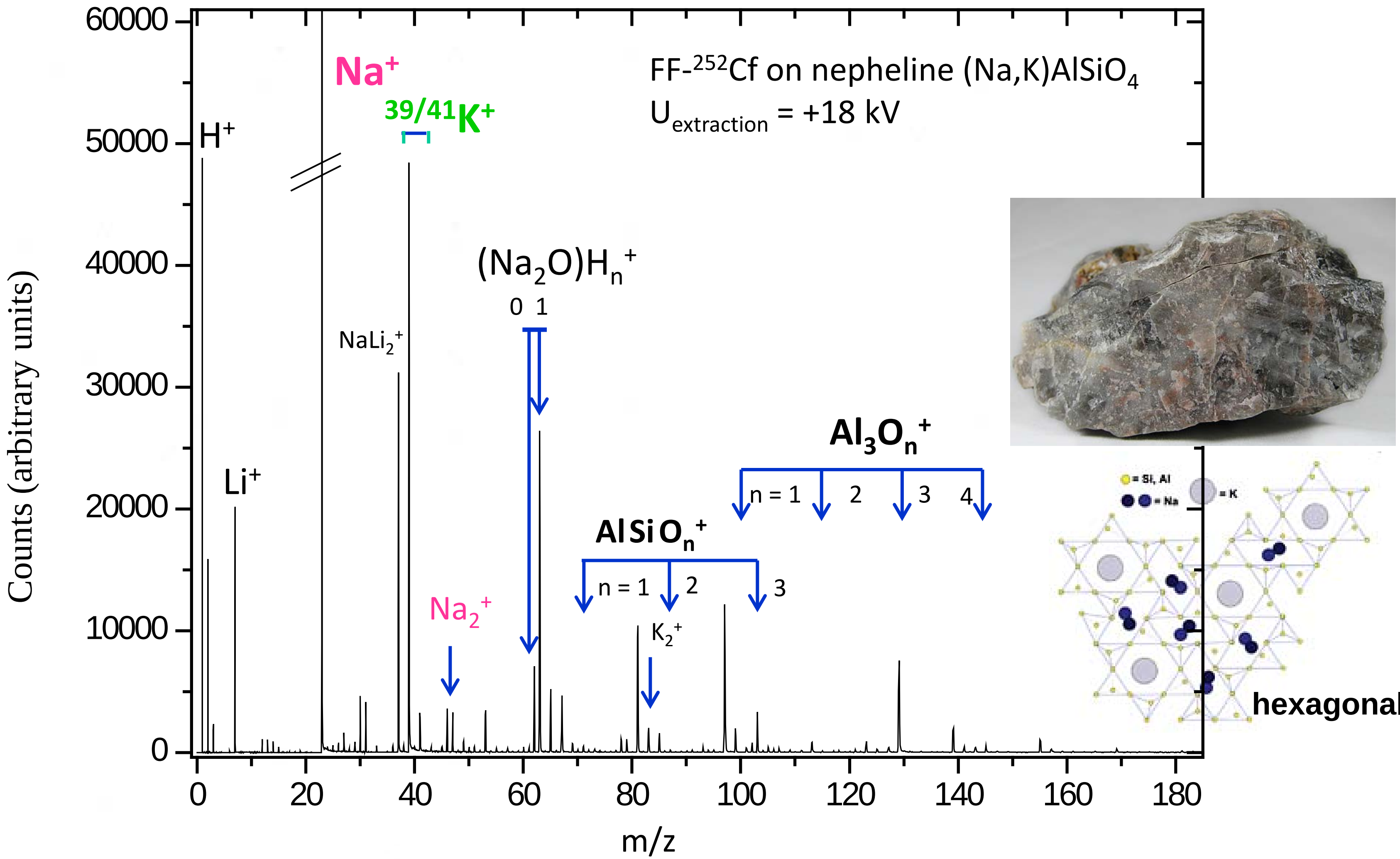
ρ (g/cm^3)



Moon silicates

e) Cosmic analogue samples

nepheline (20 nm) evaporated on a Si wafer (room temperature)

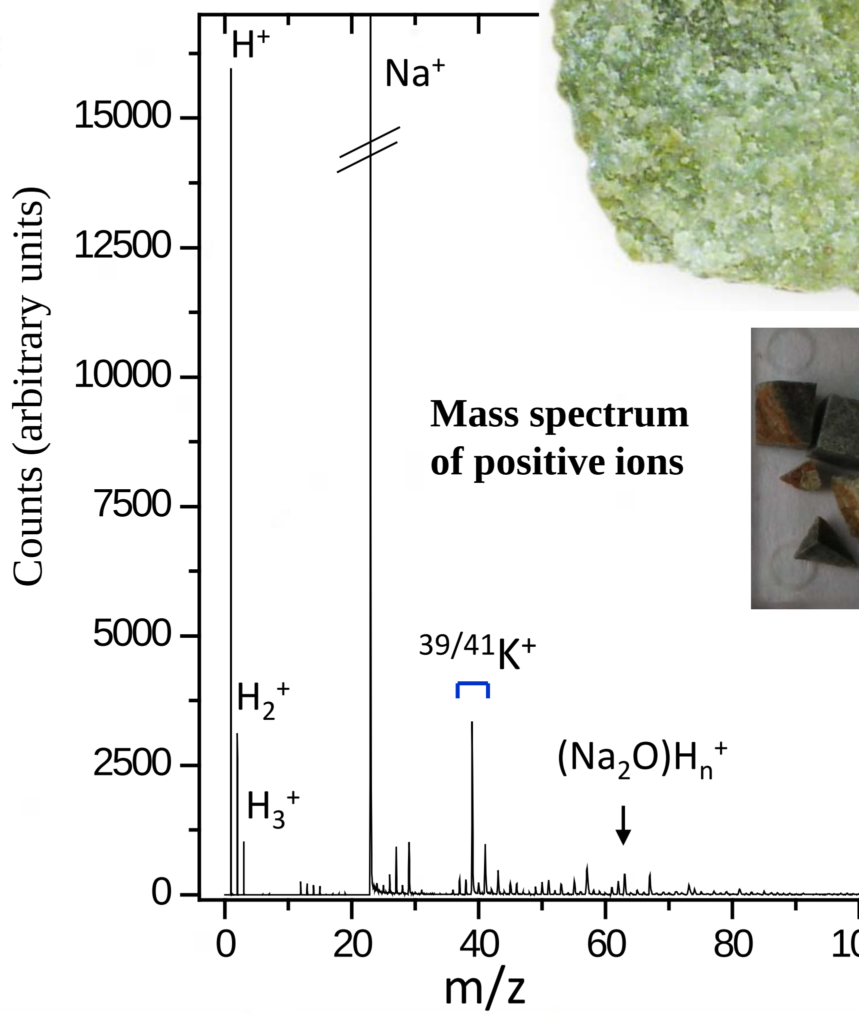


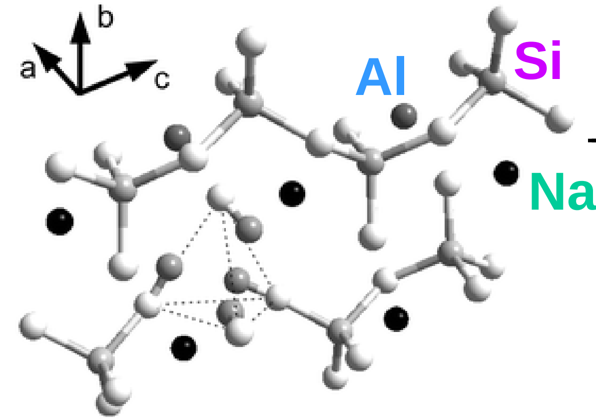
Nepheline

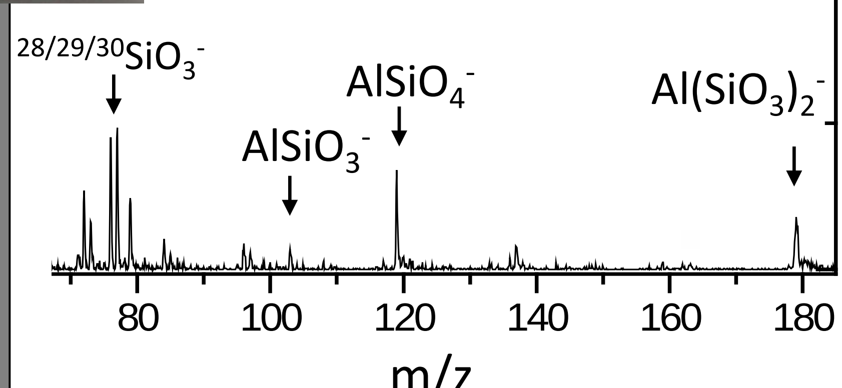
e) Cosmic analogue samples

FF-^{252}Cf on $NaAlSi_2O_6$

$U_{extraction}$ = +18 kV







Jadeite

PDMS Analysis of Meteorites

1. Isna (Egipt, 1970)

    Chondrite: carbonaceous – **CO3**

2. Allende (Mexico, 1969)

    Chondrite: carbonaceous – **CV3**

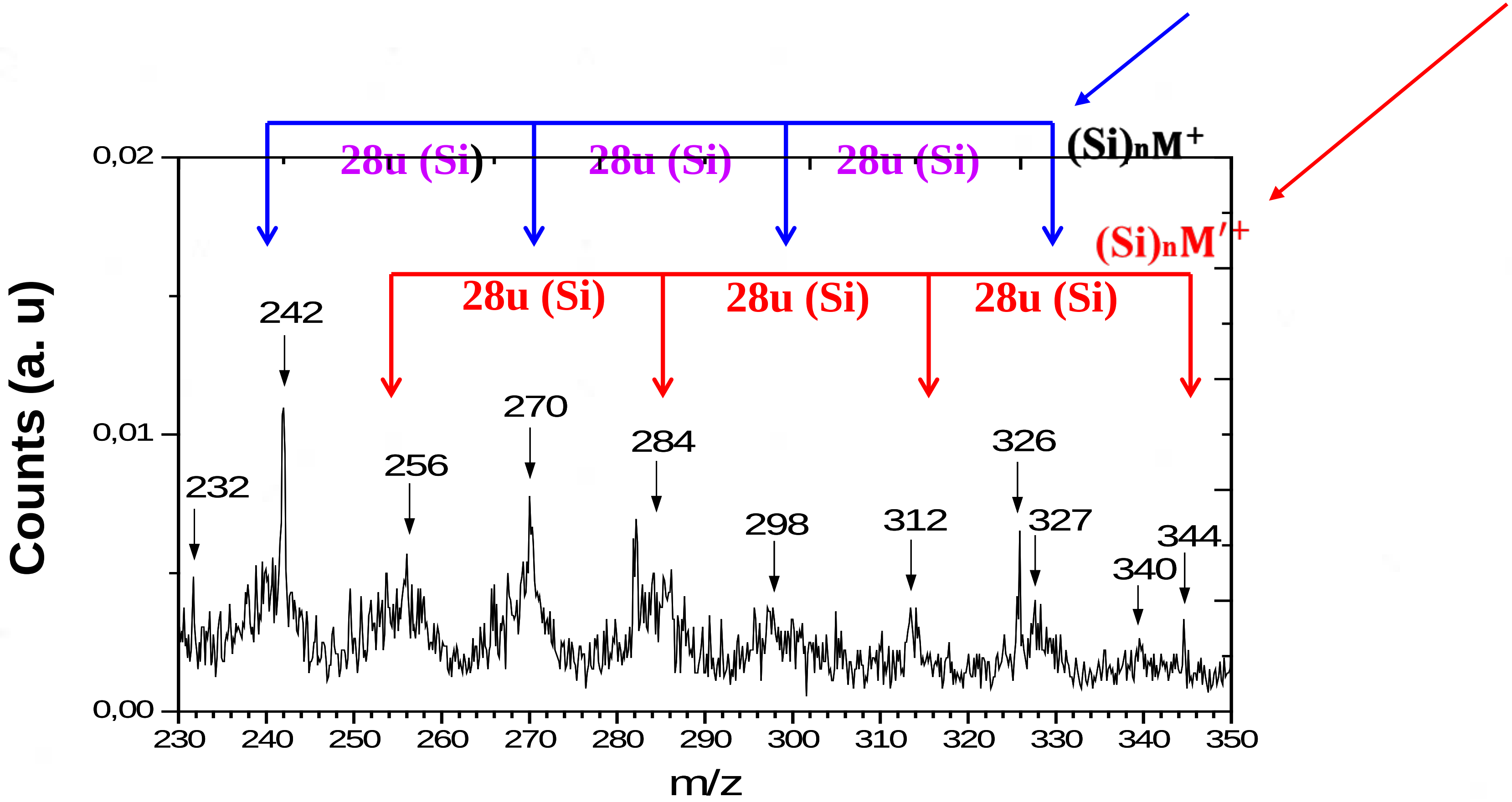
3. Zagami (Nigeria, 1962)

    Acondrite: **Shergotito** (Martian).

PDMS Analysis of Meteorites

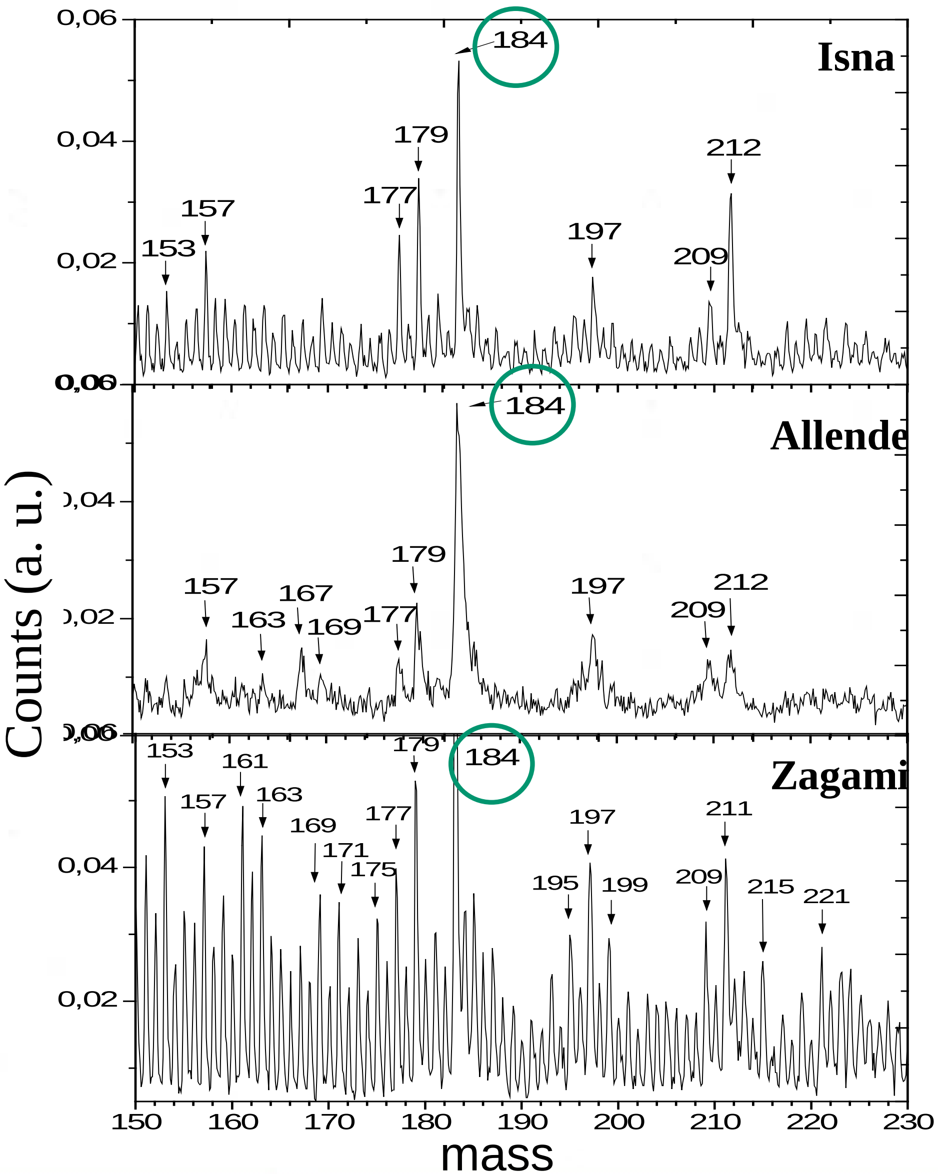
Isna meteorite

Silicon cluster structures

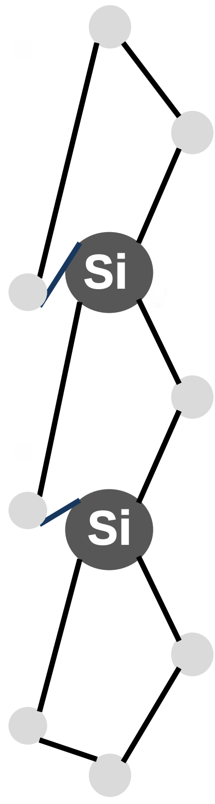


Example : **Positive ion mass spectrum**

PDMS analysis of meteorites: Isna, Allende and Zagami



184 u : a very stable structure



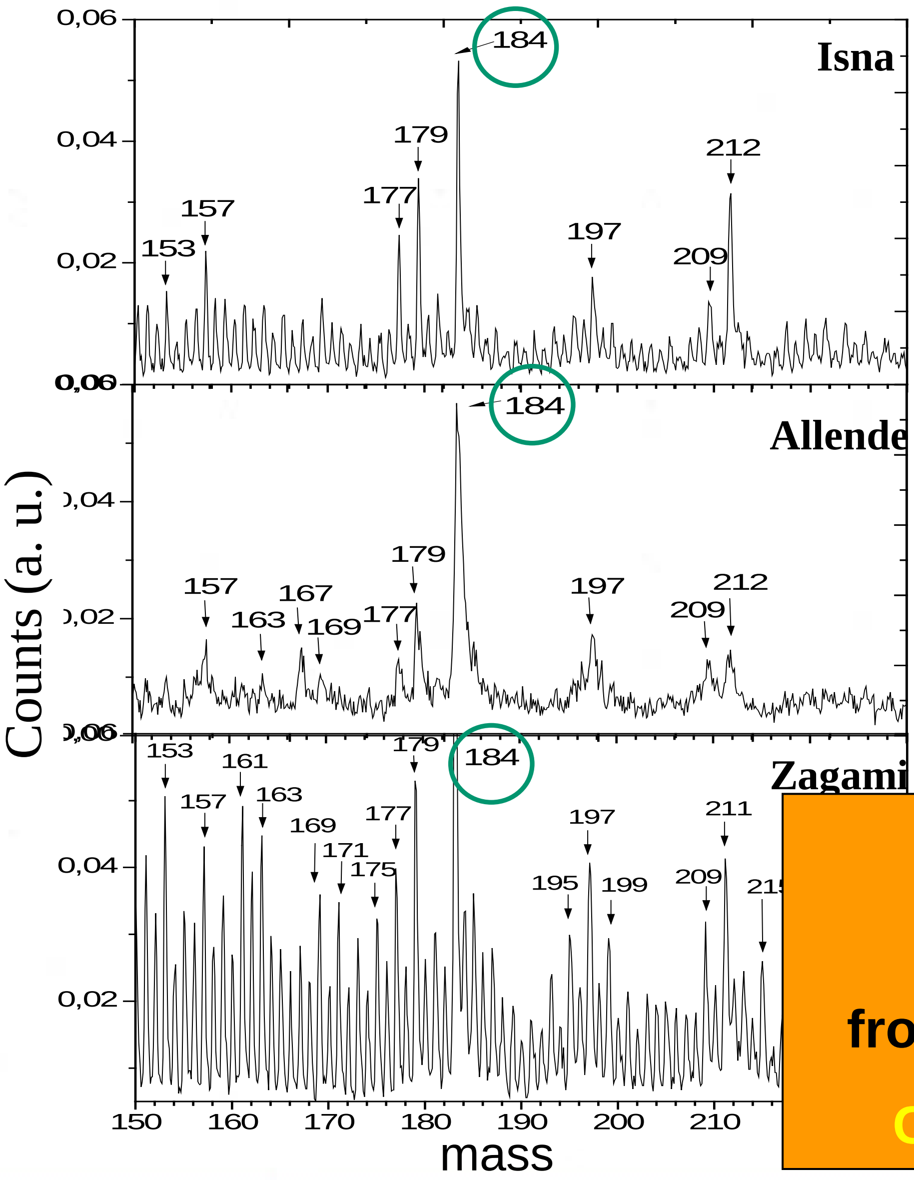
Si_2O_8

184 u

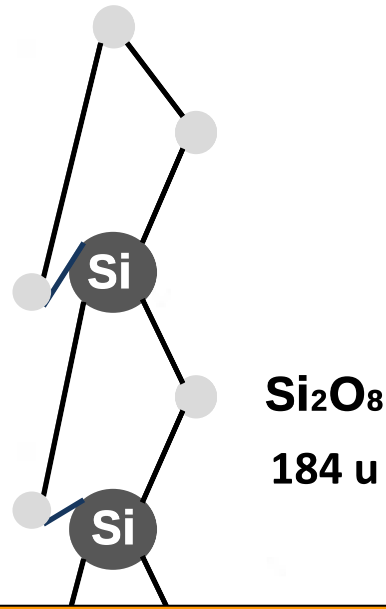
(Yu-Hong and Baoxing, 2014)

Example : **Negative ion mass spectra**

PDMS analysis of meteorites: Isna, Allende and Zagami



184 u : a very stable structure



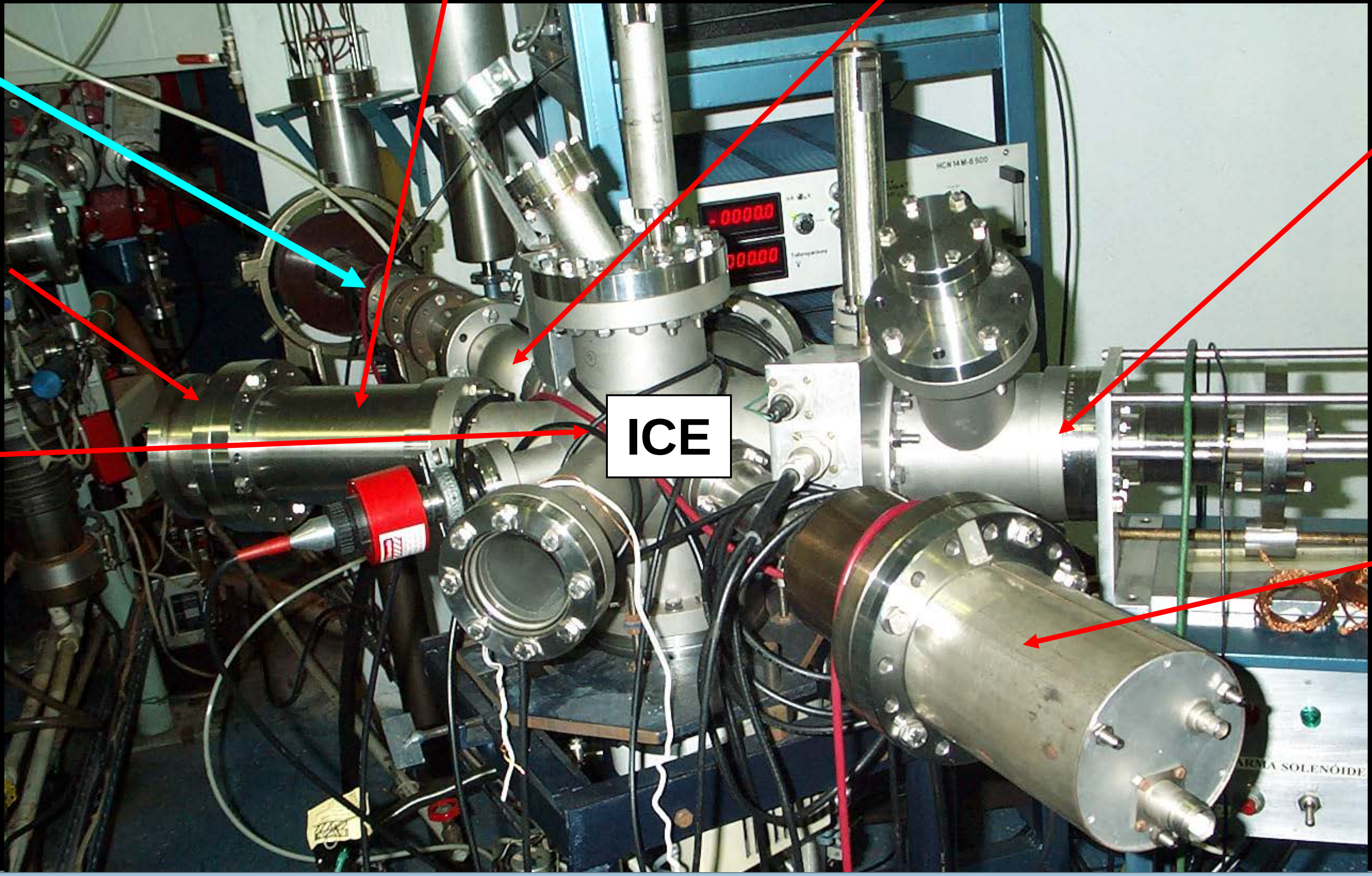
These ion species are actually being "produced" and emitted from interplanetary grains in space:

CR synthesis in *ONE* impact !!!

Example : **Negative ion mass spectra**

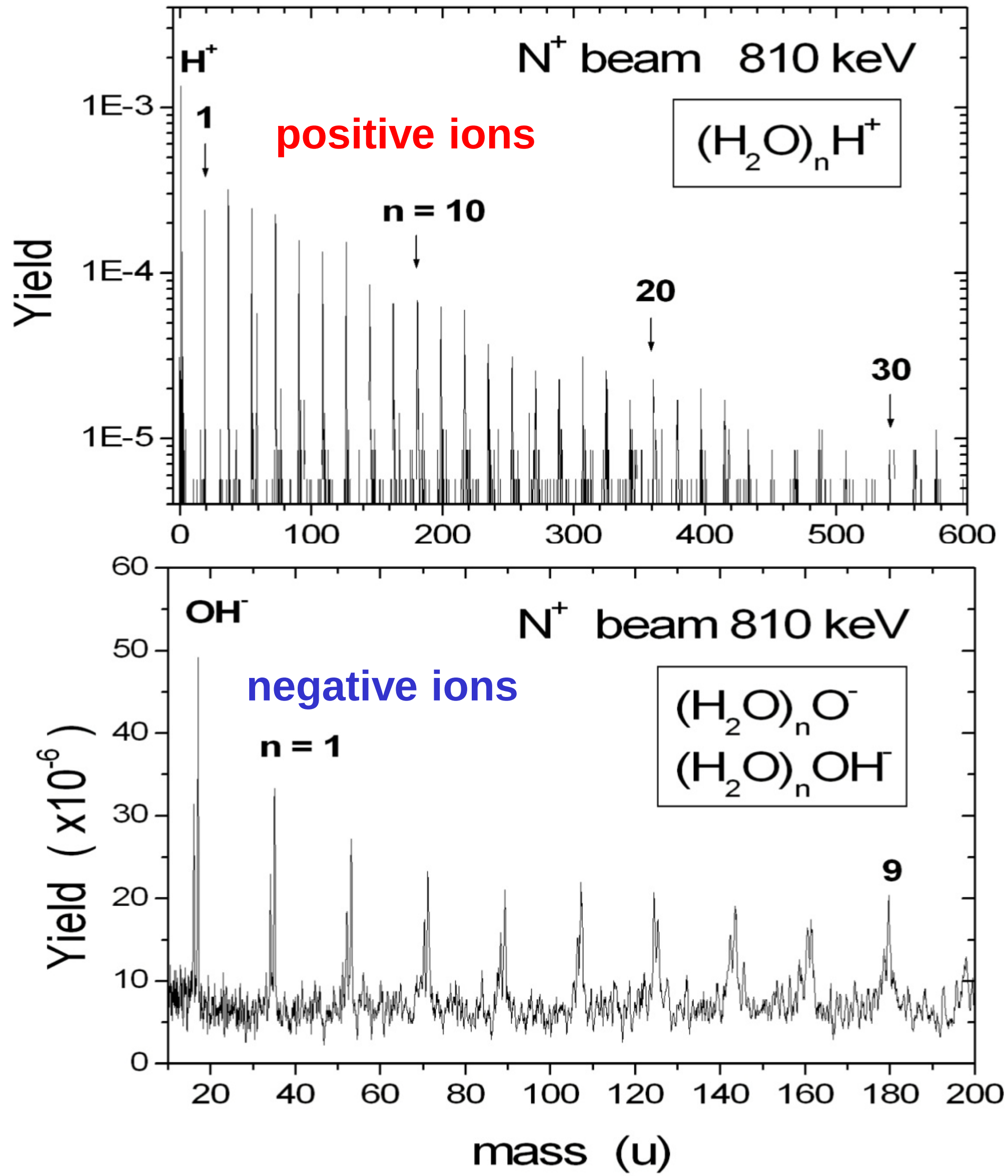
Sputtering of ices

- Analyzed by TOF mass spectrometer
- At cryogenic temperatures



Van de Graaff Accelerator – PDMS sputtering analysis line

Water - H_2O



most abundant emitted ions :

H^+ , H_3O^+

H^- , O^-, OH^-

Hydrogen bridges:

H_2O ice ejects

intense series of

ionic clusters

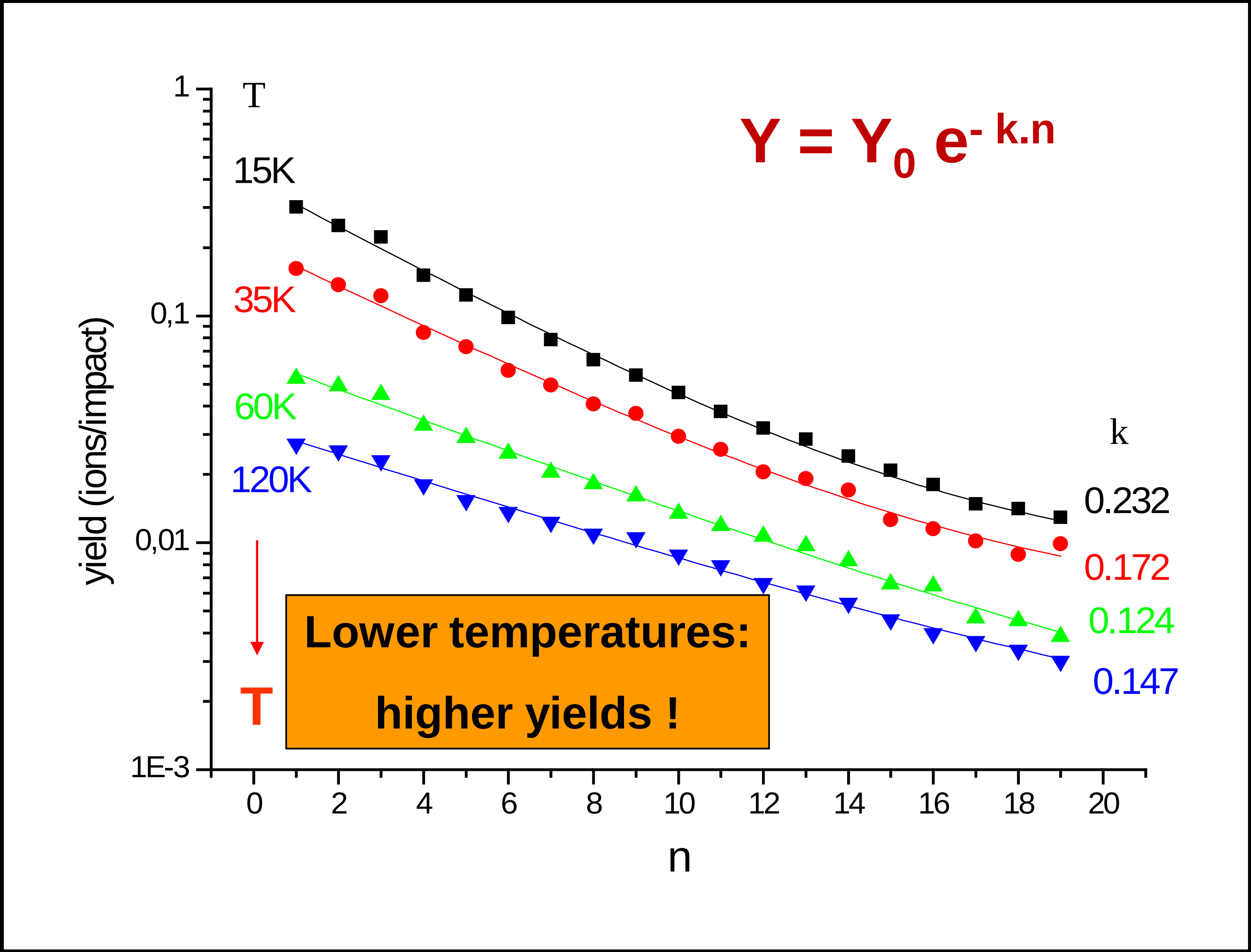
main series :

$(H_2O)_nH_2O^+$

$(H_2O)_nO^-$, $(H2O)_nOH^-$

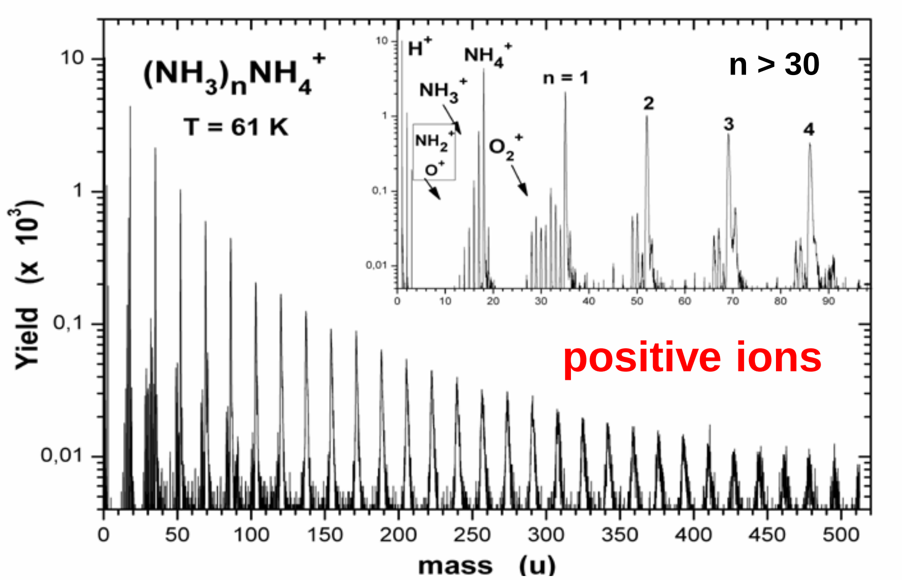
n > 60

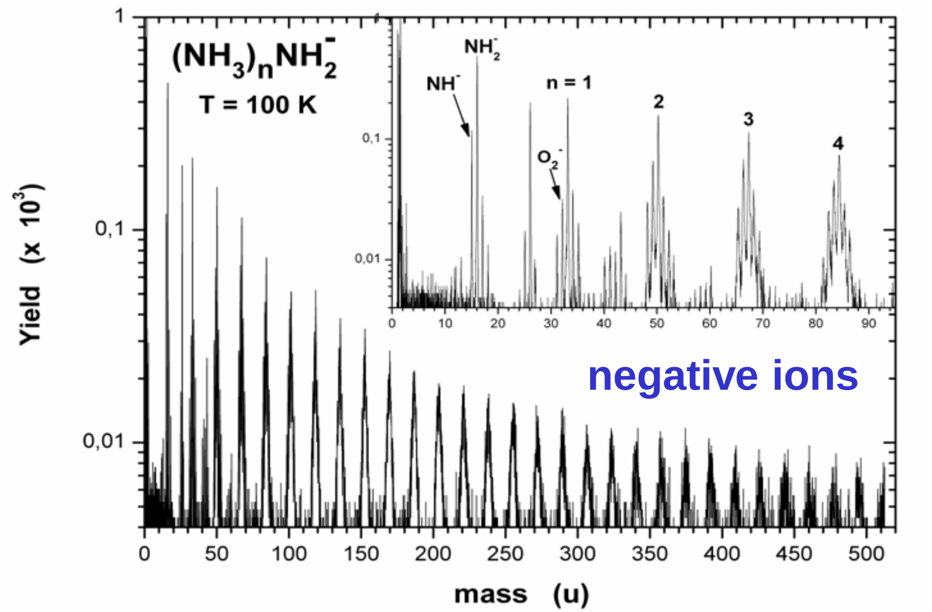
$(H_2O)_n H_3O^+$ emission decreases as the temperature increases!

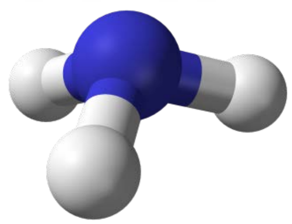


N – 1.5 MeV beam **k – decay parameter**

Ammonia - NH_3







most abundant emitted ions :

H^+, NH_4^+, NH_3^+

H^-, NH_2^-, NH^-

Hydrogen bridges:

H_2O e NH_3 eject

intense series of

ionic clusters

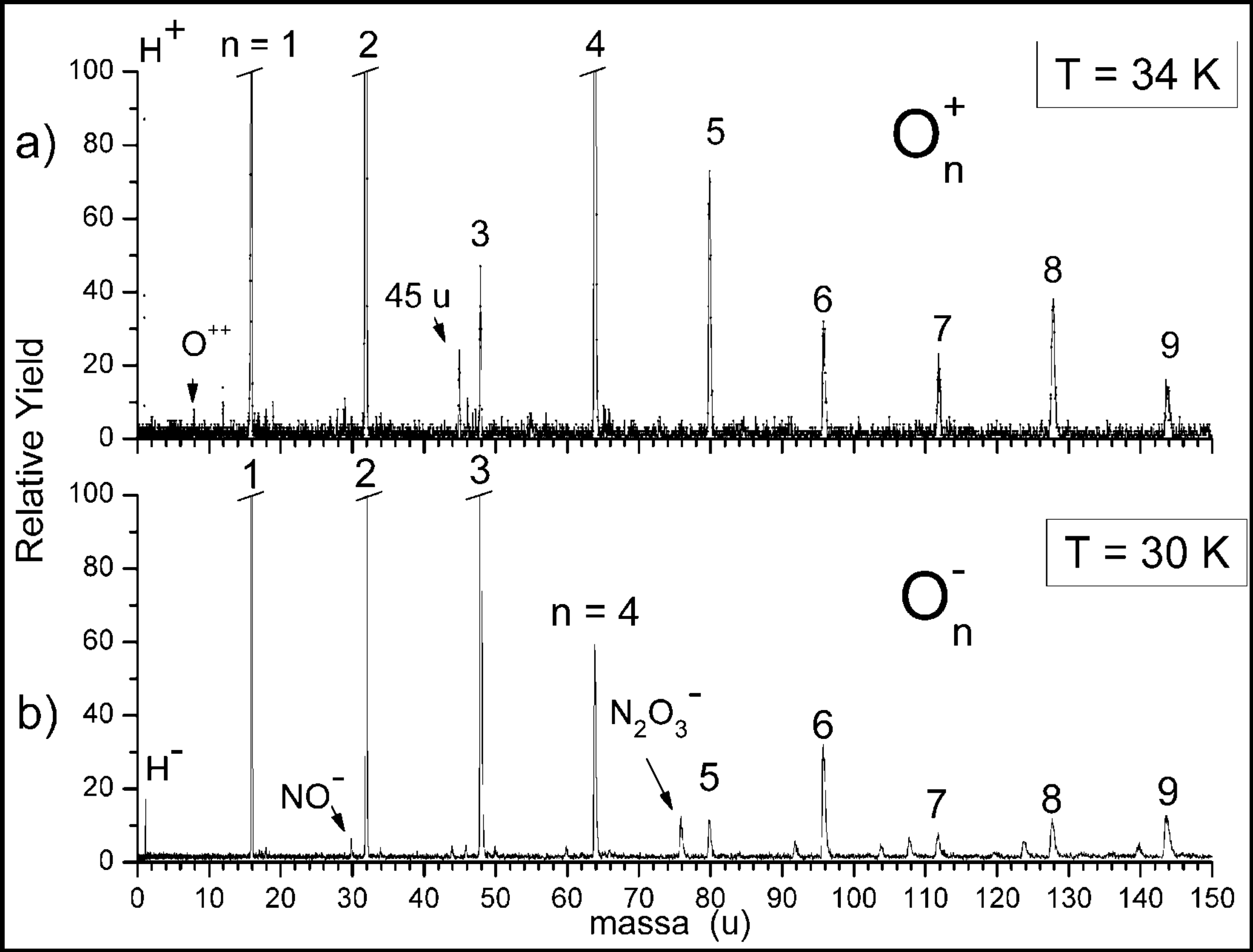
main series :

$(NH_3)_nNH_4^+$

$(NH_3)_nNH_2^-$

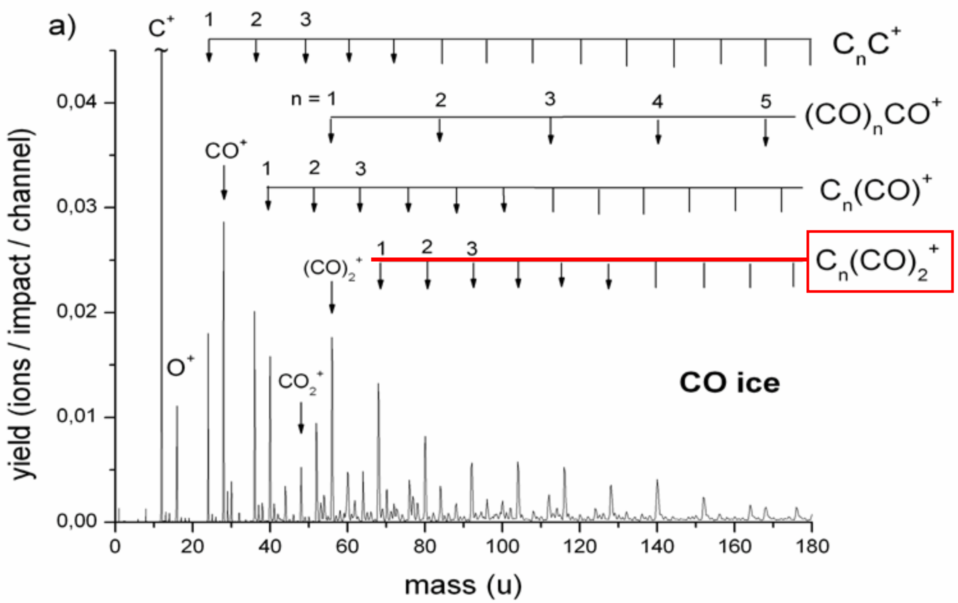
Ices without H : Oxygen

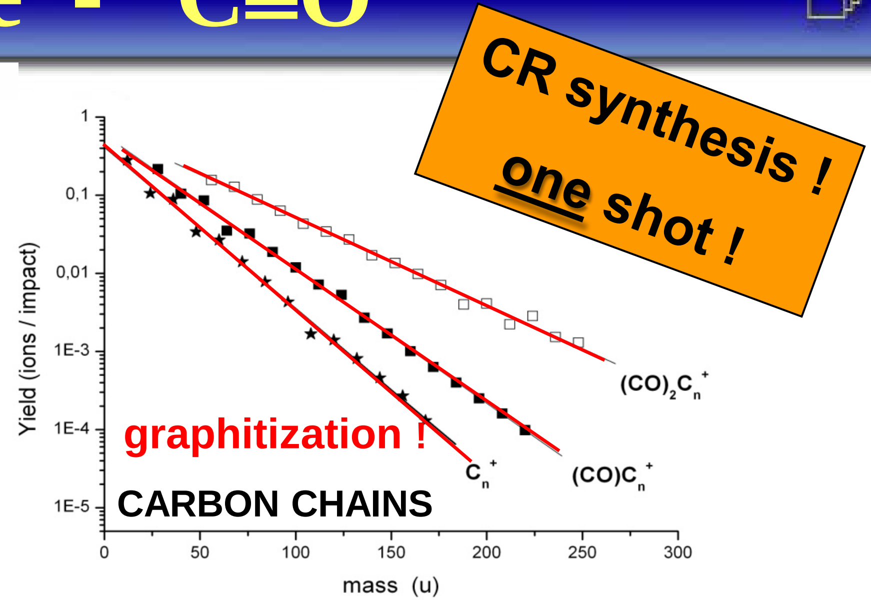
~ 65 MeV ^{252}Cf fission fragments

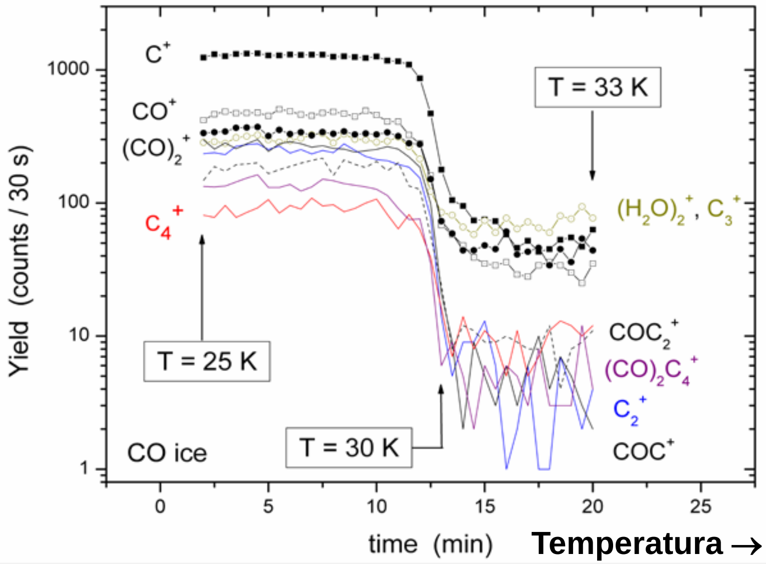


Molecular clusters are ejected into the gas phase → Radio telescopes ?

Carbon Monoxide - C≡O







abundants:

C^+, CO^+, O^+, CO_2^+

O^-, C^-, C_2^-

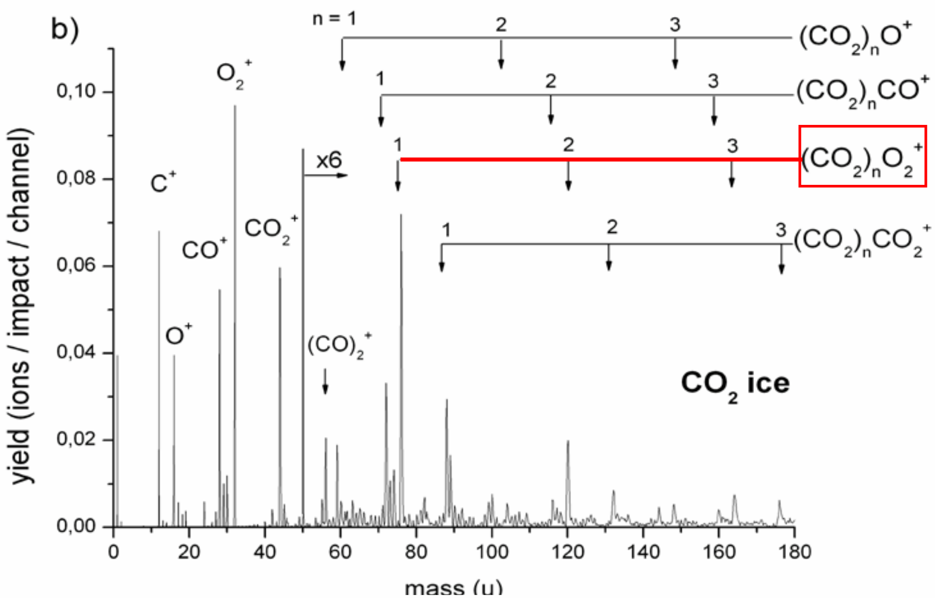
dominants:

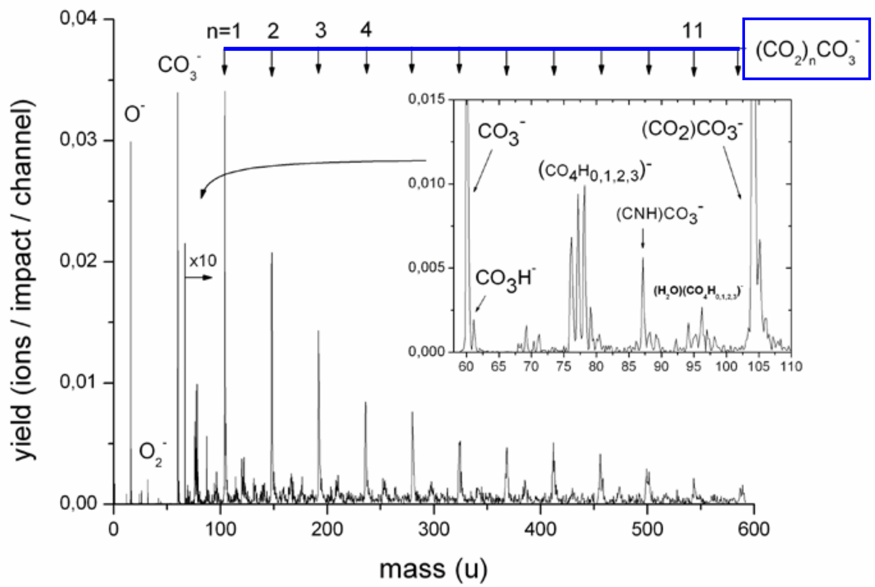
$C_n(CO)_2^+$, $C_n(CO)^+$, C_n^+

C_n^-, O_n^-

Synthesization : CO_3^-, $C_2O_3^-$

Carbon Dioxide - O=C=O





abundants:

O_2^+, CO_2^+, C^+, CO^+

CO_3^-, O^-

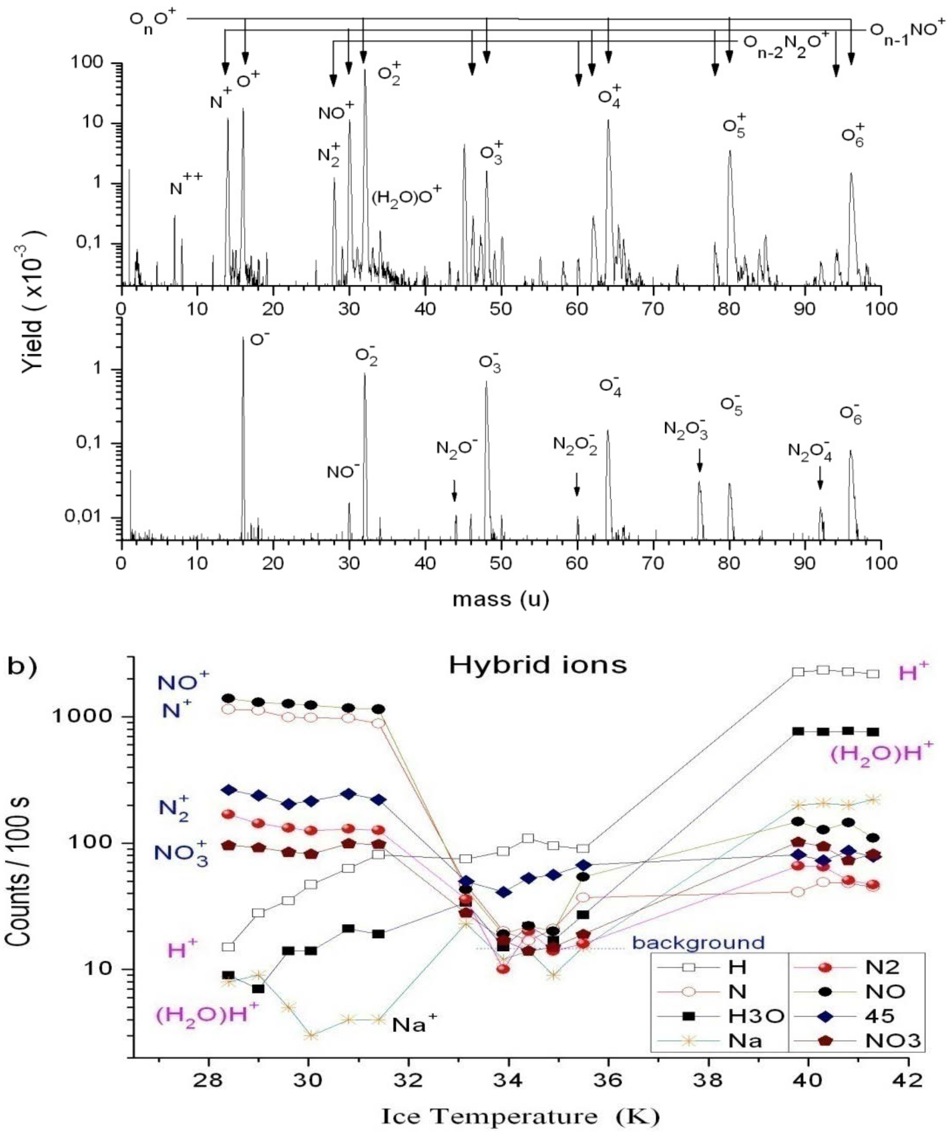
dominants:

$(CO_2)_nO_2^+$

$(CO_2)_nCO_3^-$

J. Am. Soc. Mass Spectrom. 17 (2006) 1120-1128

Mixture $O_2 + N_2$



abundants:

O_2^+, O^+, O_3^+,

N_2^+, N^+, N_3^+, NO^+

O^-, O_2^- (no N^-)

Main series:

$(O_2)_nO_2^+$, $(O_2)_nO^+$, $(O_2)_nO_3^+$

$(N_2)_nN_2^+$, $(N_2)_nN^+$

O_n^-, $O_nN_2^-$

Synthesis of:

NO^+, NO_3^+, O_nNO^+, $O_nN_2^+$

NO^-, N_2O^-

H_2O ice Sputtering Yield

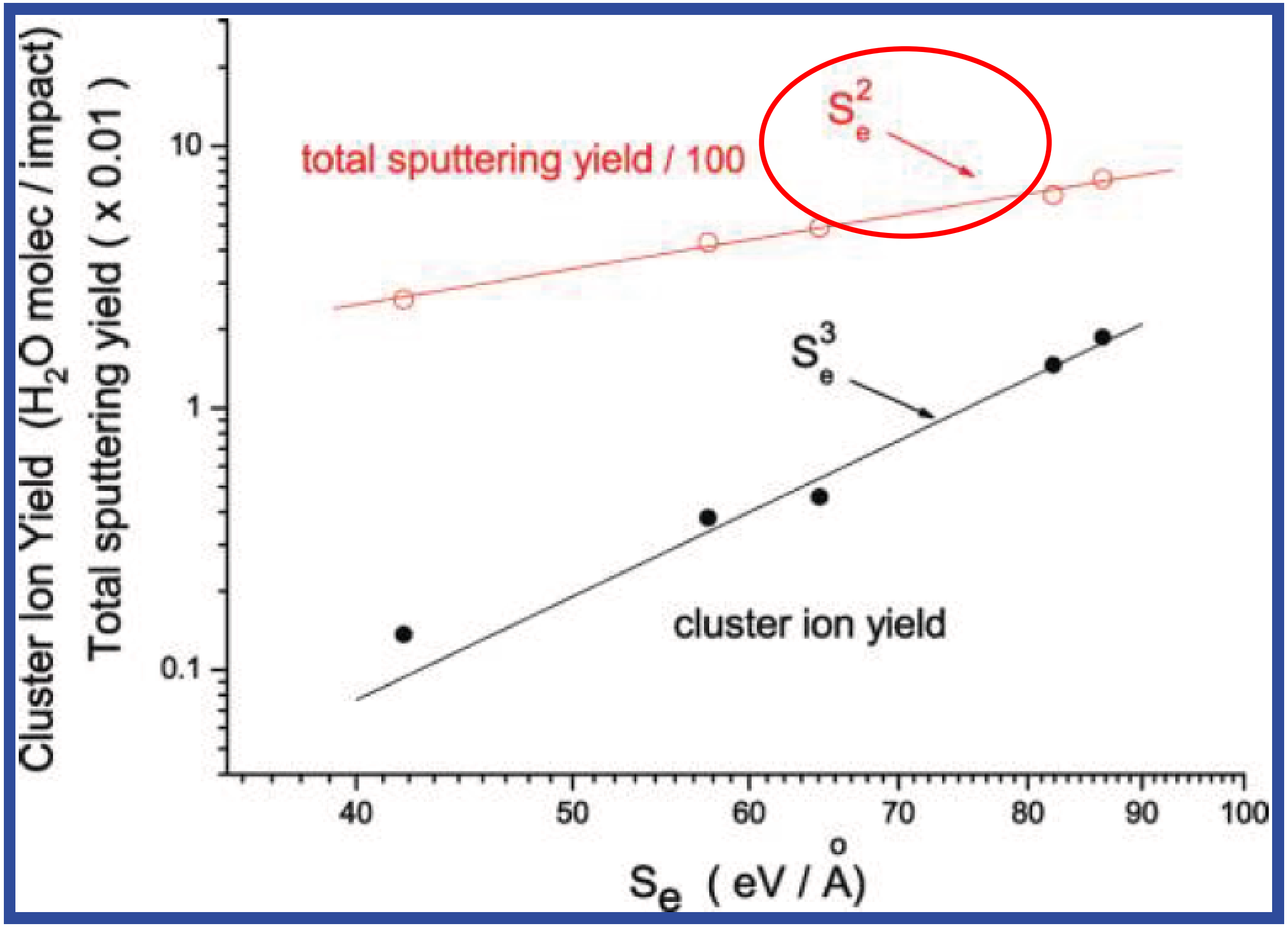
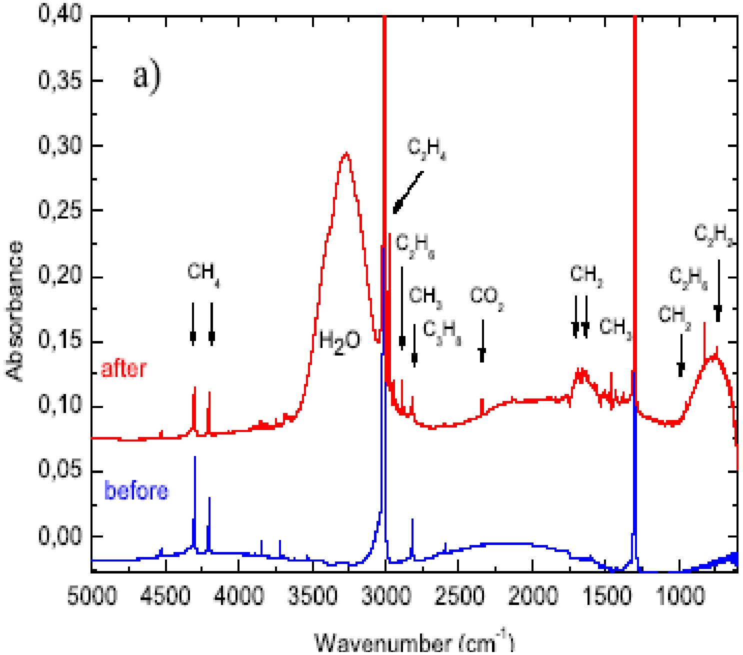
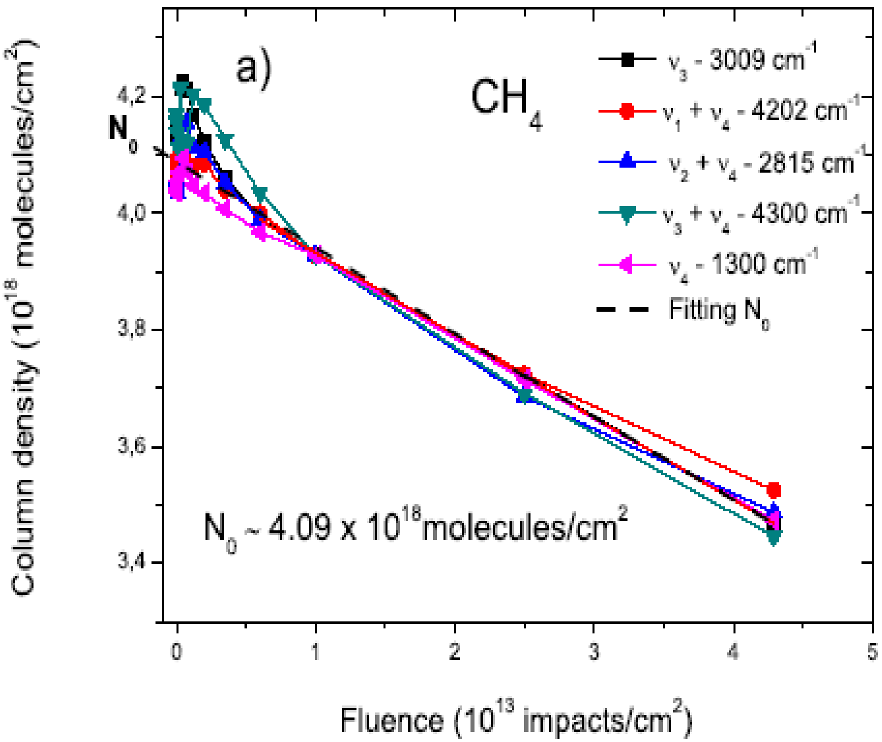
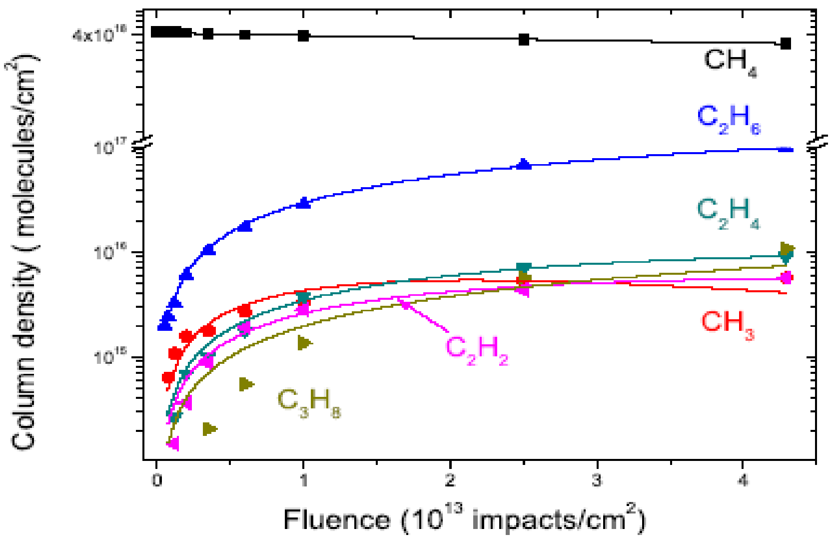


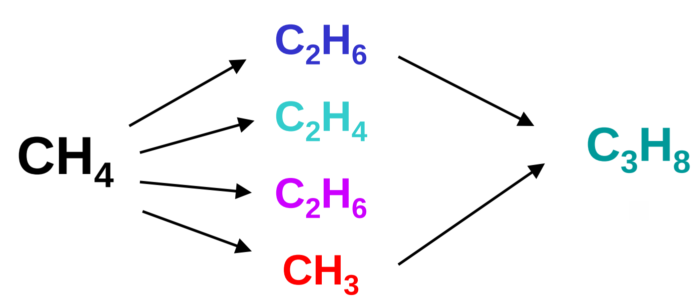
Figure 5. Comparison between total sputtering[8] and ion yields of water clusters corresponding to bombardment of MeV N ions on water ice at a temperature of 80 K.

CH_4 Radiolysis : FTIR vs MS



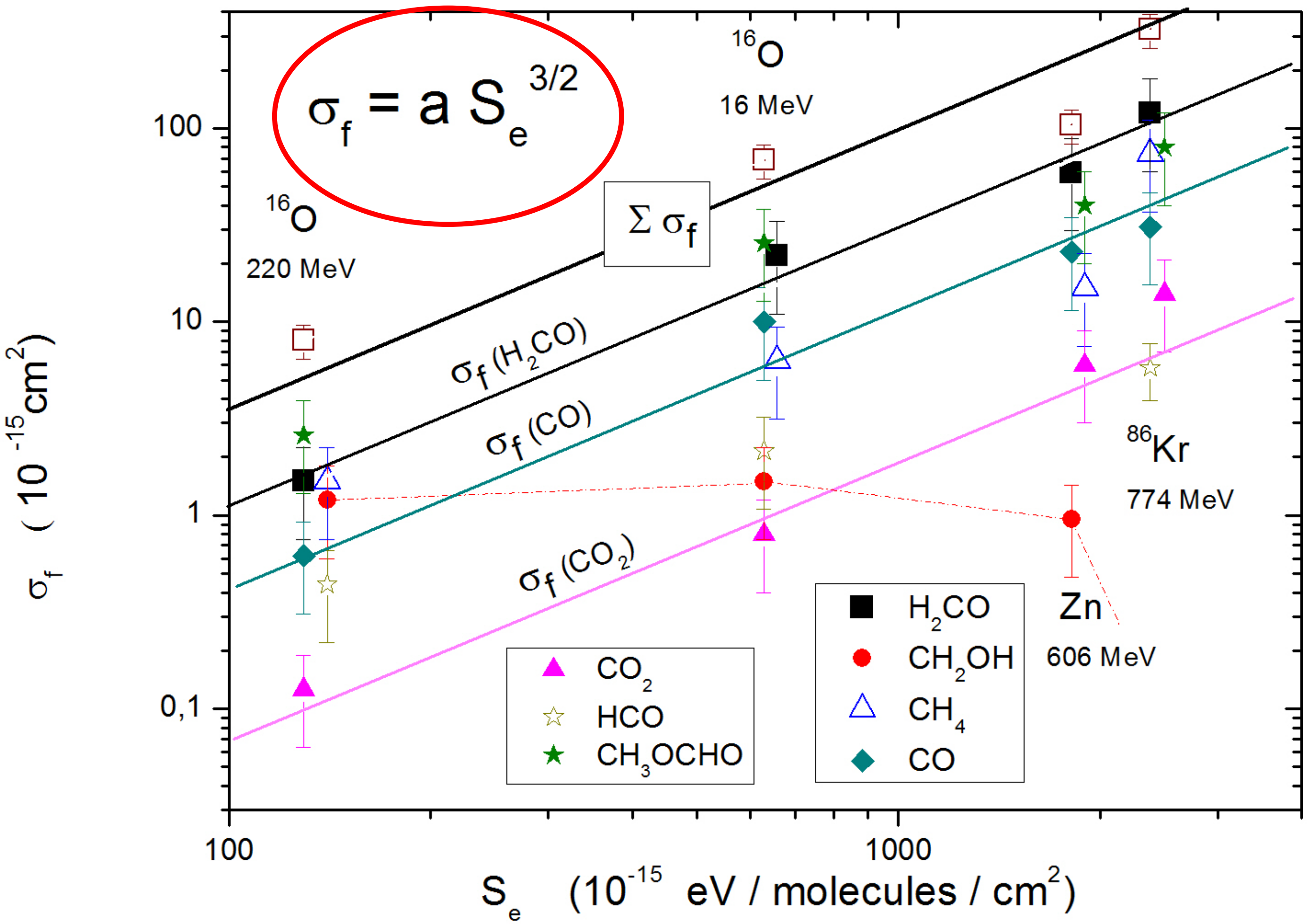






CH_3OH Radiolysis - FTIR

Formation cross section σ_f



CR impacts : Qualitative Results

Chemistry:

- Hot chemistry (10^4 K) in very cold material (10 - 100 K)

  RT → 1/40 eV ; keV → 4000 K

- Fast chemistry (ps) in solids

  No thermodynamical equilibrium

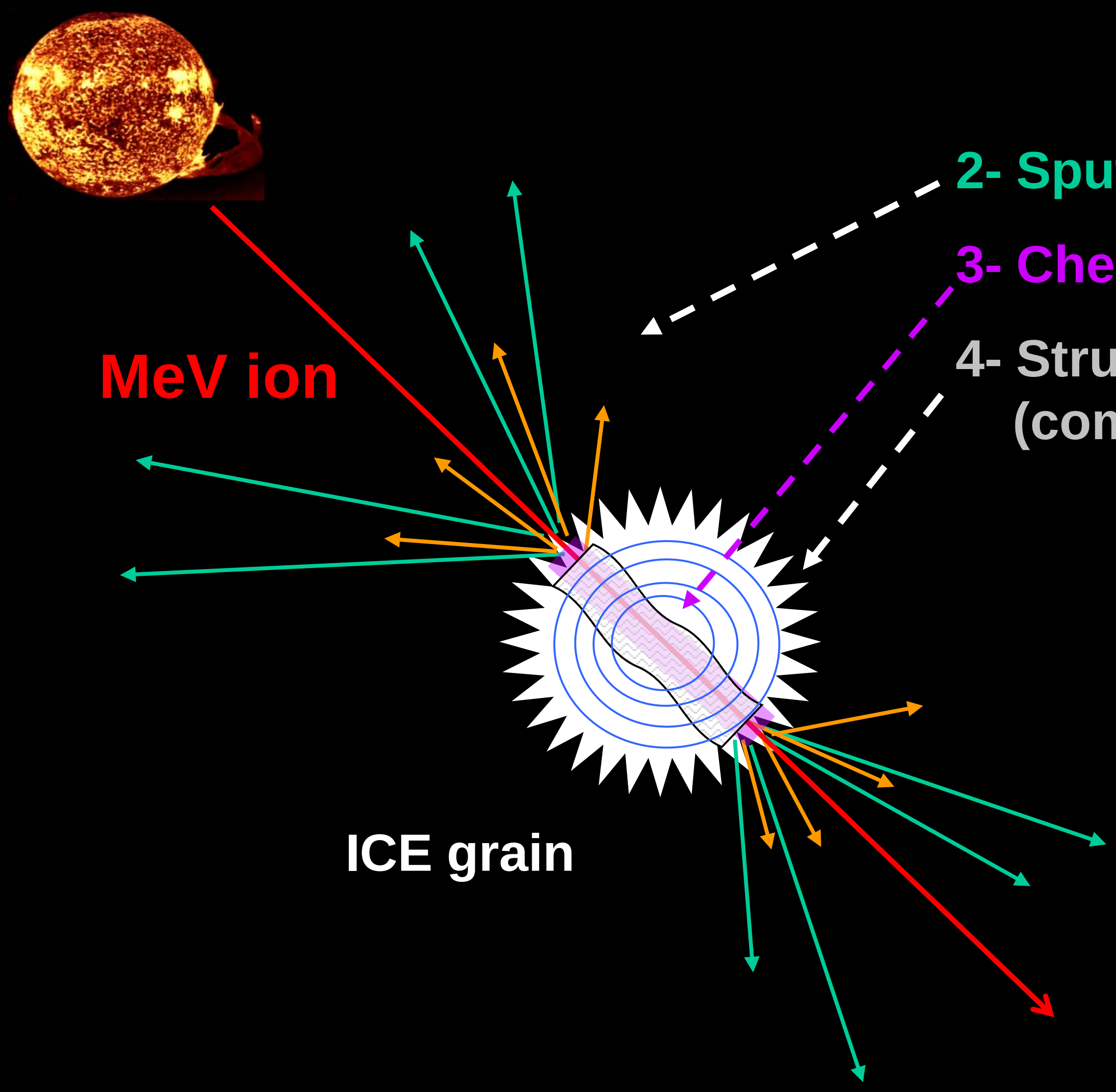
- New pathways for Organic Chemistry:

  The bombardment of CO by ions has an interesting and relevant property: the formation of carbon chains

Biochemistry

"Strategical" molecules for the prebiotic synthesis, like HCN and OCN, are easily formed by fast ion impact.

main ion-solid mechanisms



2- Sputtering (neutrals and ions)

3- Chemical reactions

4- Structural modifications (compaction)

Reminder:
the 3 relevant mechanisms for synthesis

Final comments : dependence on S

From the sputtering and radiolysis experiments:

1- Ion beams interact with matter and transfer energy with a characteristic rate called Stopping Power (S).

2- Three main phenomena : dependence on S

a) Sputtering (removal of surface material): $Y \sim S^2$

b) Chemical reactions: σ_f or $\sigma_d \sim S^n$ $2/3 < n < 3/2$

c) Compaction (structural modification): $\sigma_c \sim S^2$

Synthesis / sputtering: $\sigma / Y \sim S^n / S^2 = 1/S^{2-n}$ ↘ $2 - n > 0$

Final comments : dependence on S

From the sputtering and radiolysis experiments:

1- Ion beams interact with matter and transfer energy with a characteristic rate called Stopping Power (S).

2- Three main phenomena : dependence on S

a) Sputtering (removal of surface material): $Y \sim S^2$

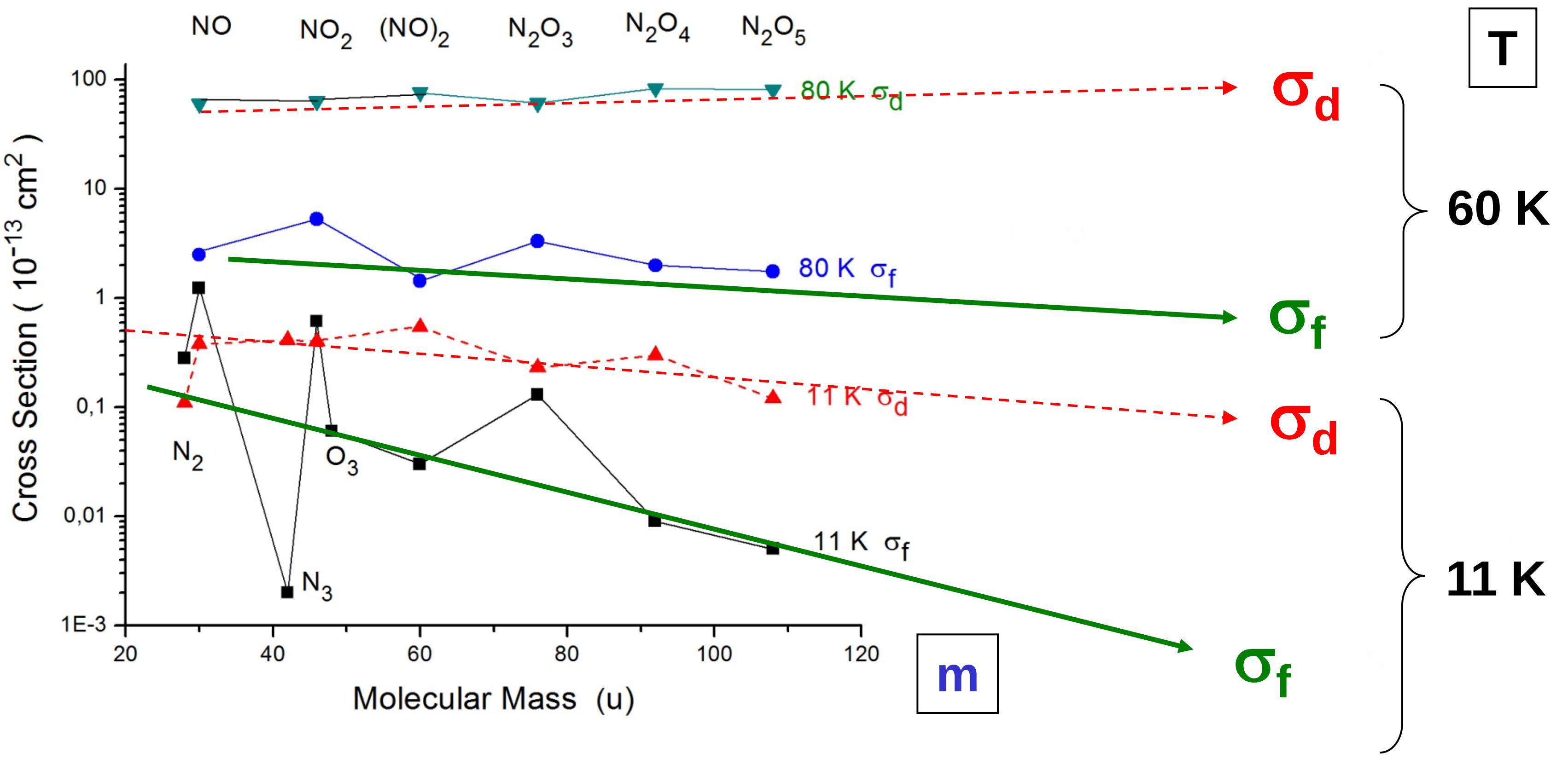
b) Chemical reactions: σ_f or $\sigma_d \sim S^n$

c) Compaction (structural modification): $\sigma_c \sim S^2$

Conclusion:
Heavy ions are much more efficient than protons for radiolysis AND sputtering

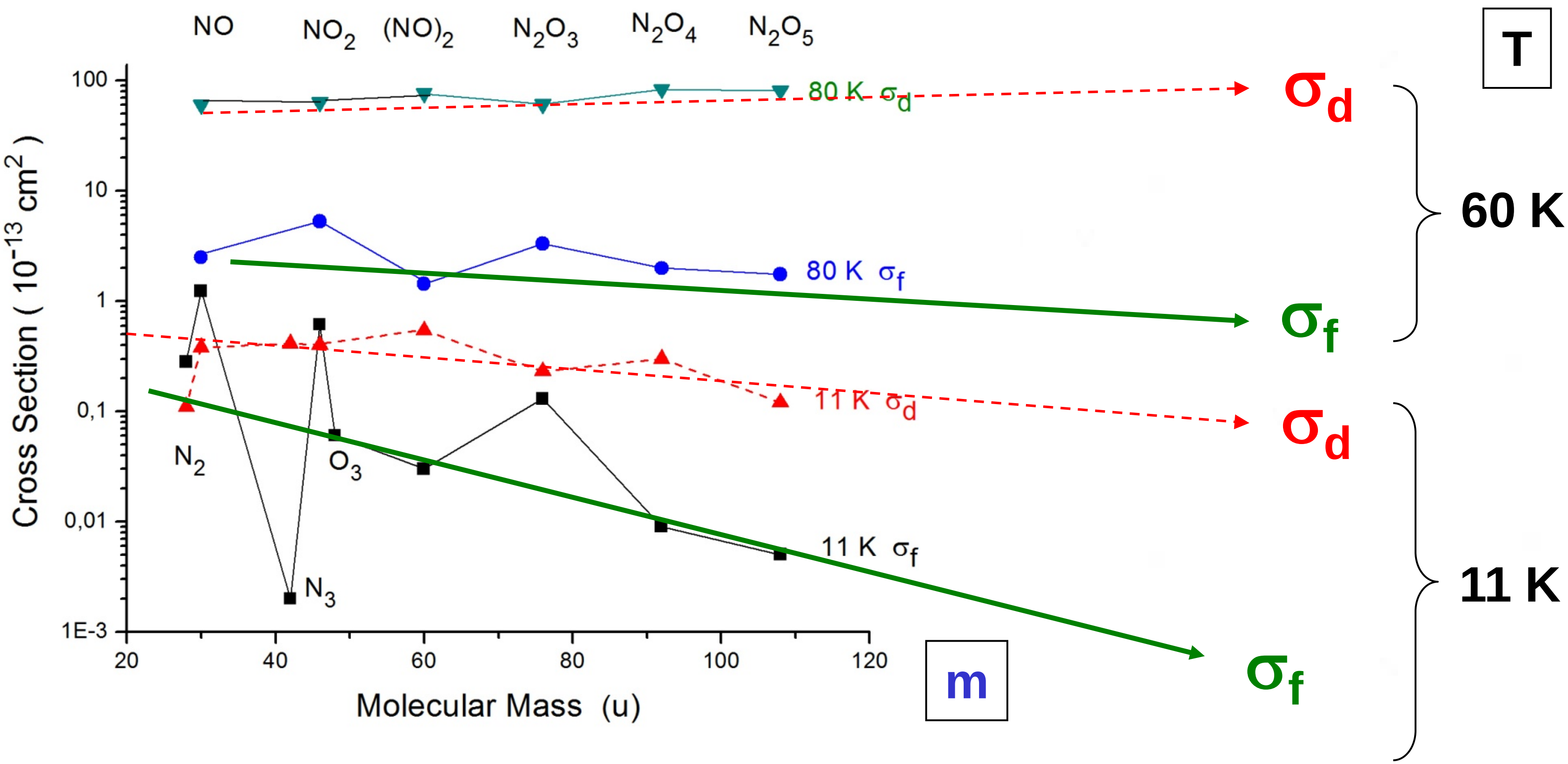
This is :
- good – large molecules are formed faster by heavy ions
- bad - they destroy the target before processing it enough

Final comments : dependence on m and T



N_2O radiolysis (only 2 elements)

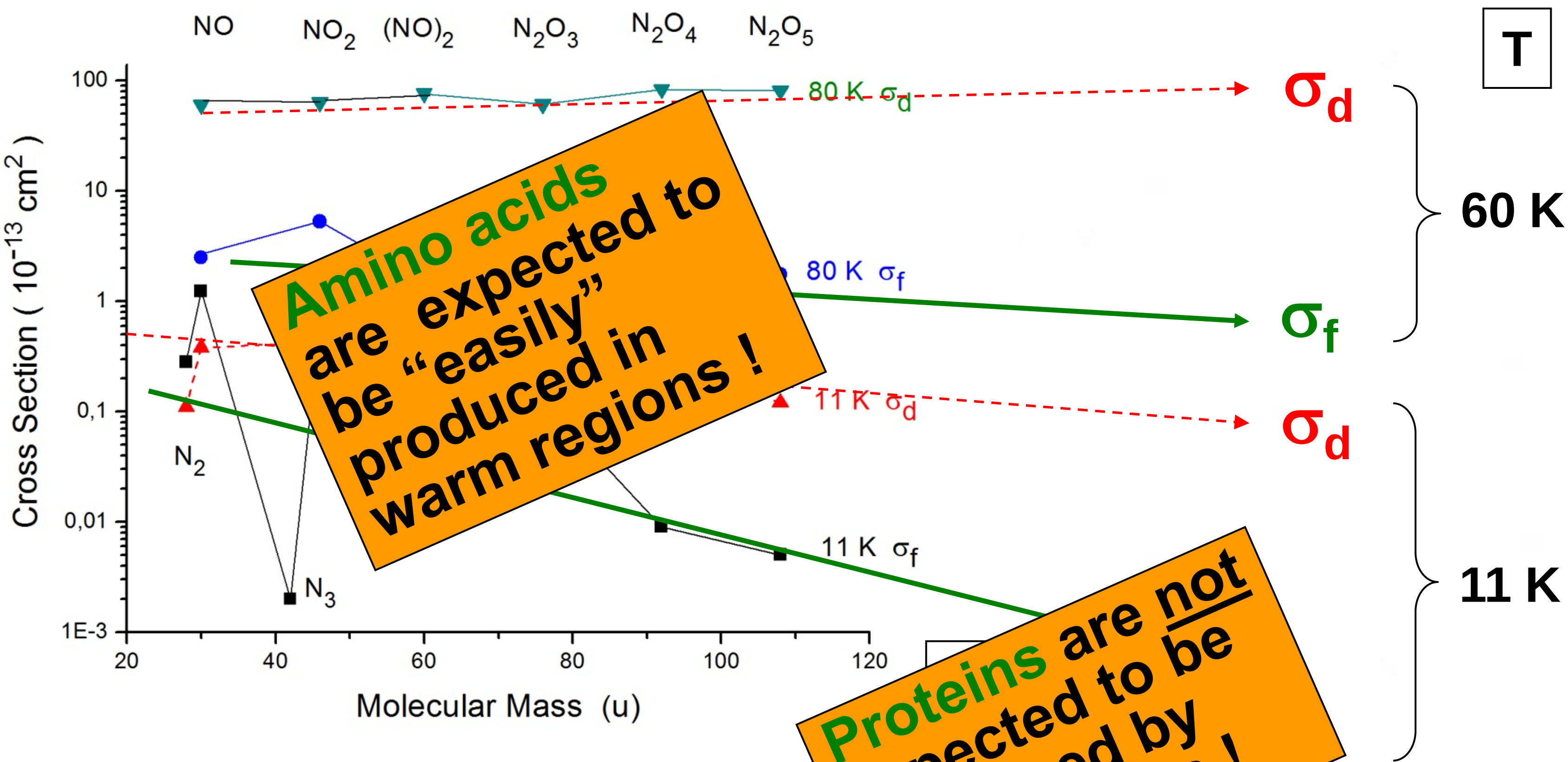
Final comments : dependence on m and T



as m increases:

	σ_f	σ_d	σ_f / σ_d	synthesis
low T	↘	↘	↘	very bad
high T	↘	↗	↘	bad

Final comments : dependence on m and T



as m increases

	σ_f	σ_d	σ_d	synthesis
low T	↘	↘	↘	very bad
high T	↘	↗	↘	bad

(If the N_2O results can be generalized)

CREDITS (lunar rocks & analogues)

CIMAP/GANIL (France): T. Langlinay, P. Boduch, H. Rothard

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PUC-Rio: C. Ponciano,

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CREDITS (ions + ices)

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UFSC: L. Farenzena

Nitriles:

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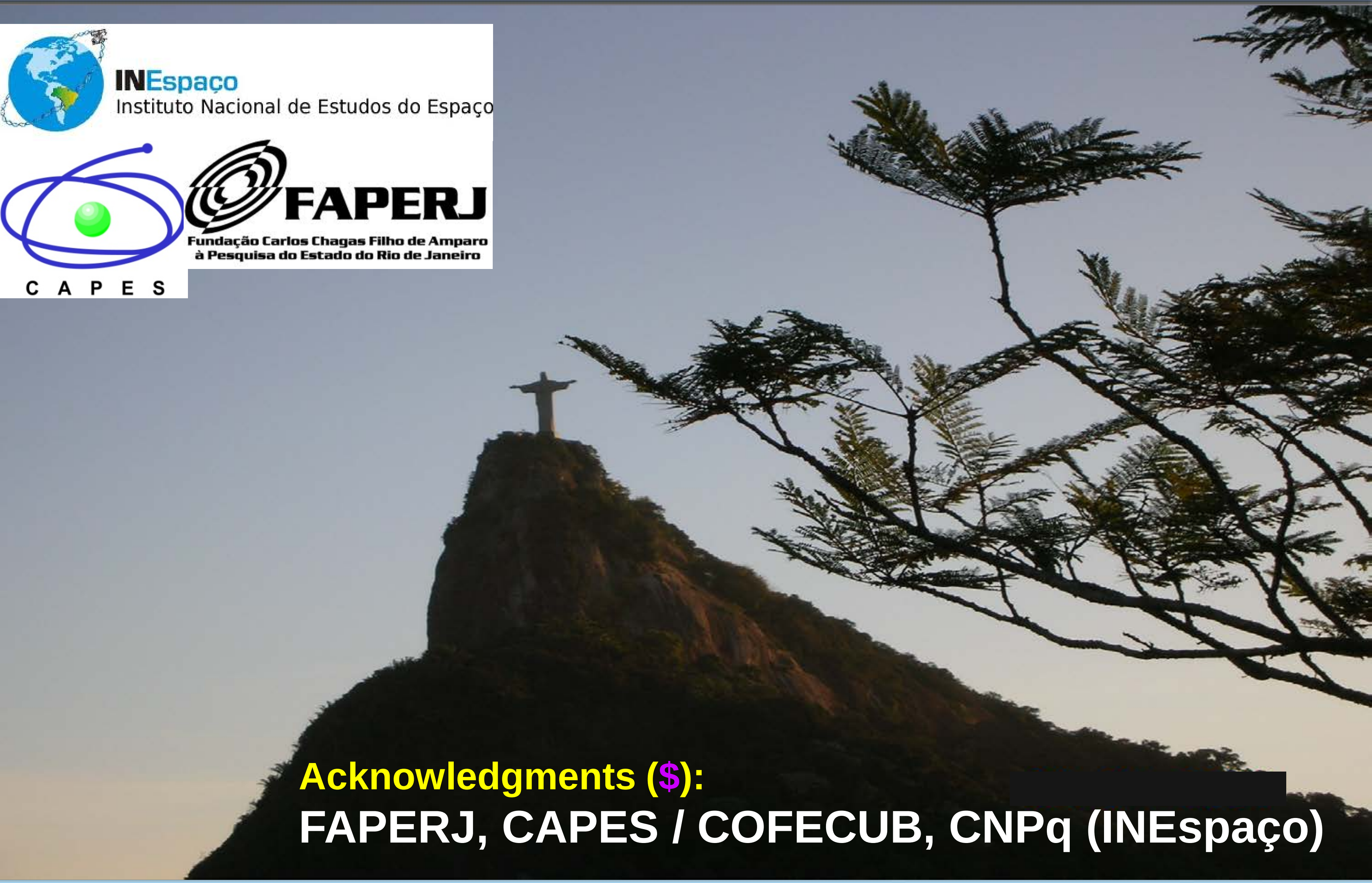
Thank you for the attention !

Thanks for the attention !



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Mass Spectrometry in Astrophysics

SUMMARY

MS has been used to analyze ions coming from the outer space and arriving in Earth, Moon and in orbiting spacecrafts

→ Meteorites, lunar rocks, Mars surface, etc are extensively examined by standard MS techniques

Isotope ratios and isotope dating (e.g. ^{238}U - ^{206}Pb or ^{14}C) give very useful information on the sample origin

→ Cosmic analogue samples have been produced in laboratory and analyzed by MS

Such experiments show in particular what to expect from *in situ* measurements

a) What Cosmic Rays are ?

- Primary Cosmic Rays are very energetic (10^3 to 10^{22} eV) charged particles that traverse outer space

- Basically, they are:

  - light ions: protons + deuterons (87%) and α particles (11%)

  - heavy 4n ions : ^{12}C, ^{16}O, ^{20}Ne, ^{24}Mg, ^{28}Si, ^{32}S, ^{40}Ar, ^{40}Ca and ^{56}Fe (Ni)

  - electrons (~1%)

  [unstable ions or neutrals are excluded: neutrons, neutrinos, X-rays, γ rays]

- After collision with interstellar matter and atmosphere,

  Secondary Cosmic Rays are formed. They are constituted by:

  - Li, Be, B, neutrons (formed by spallation)

  - pions, kaons, mesons, positrons and γ rays

Solar Neutrinos in Earth : 6×10^{10} / cm^2 s

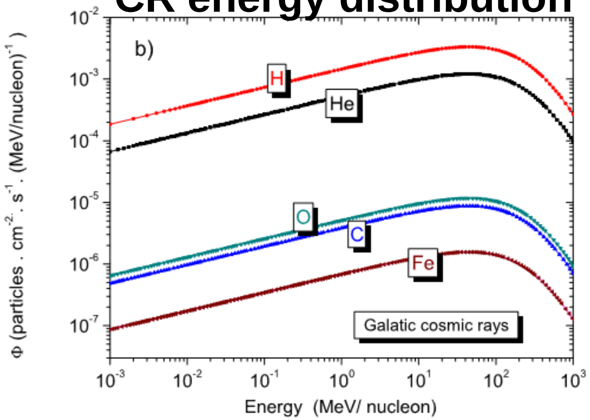
^{14}C is a produced nuclide

What for?

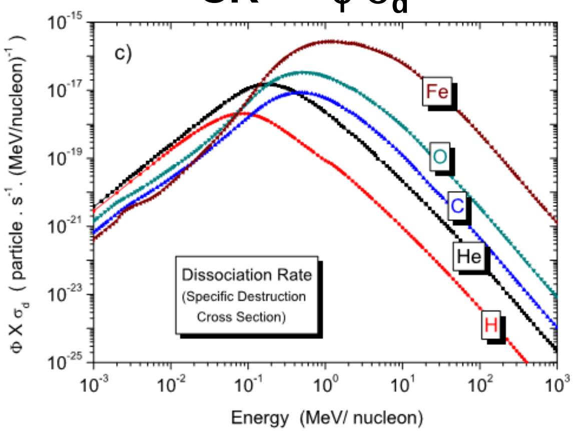
Astronomy:

- To predict mean-liv

CR energy distribution

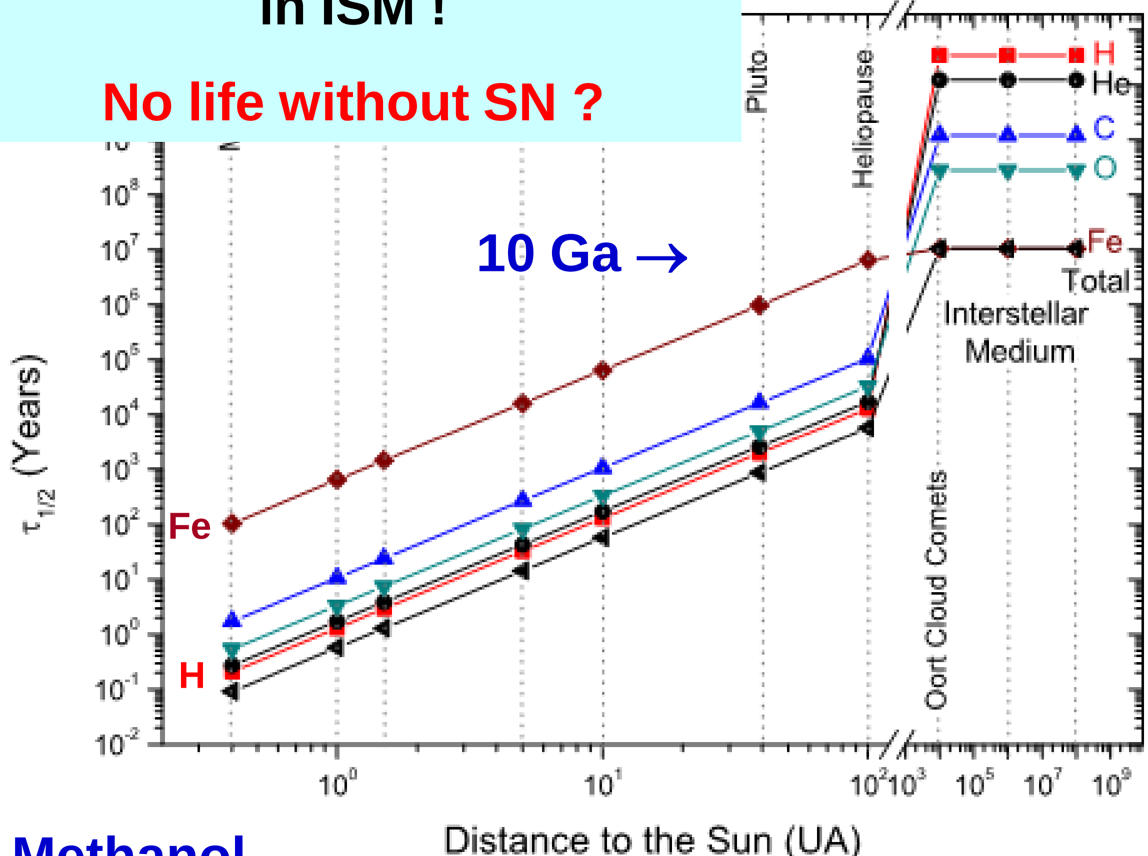


CR $\phi\ \sigma_d$



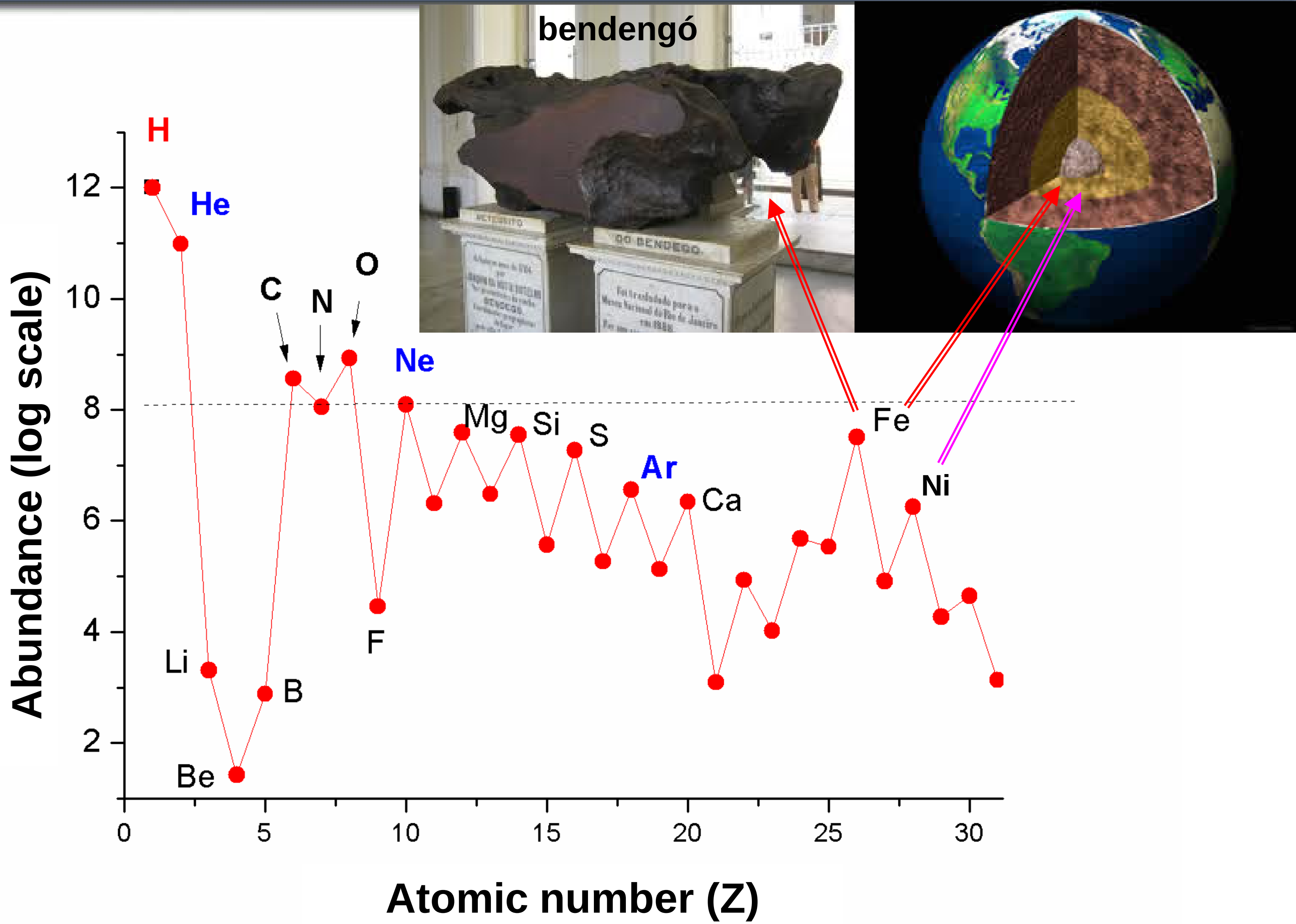
This means that iron beam (and not protons or alphas) is responsible for chemistry in ISM !

No life without SN ?



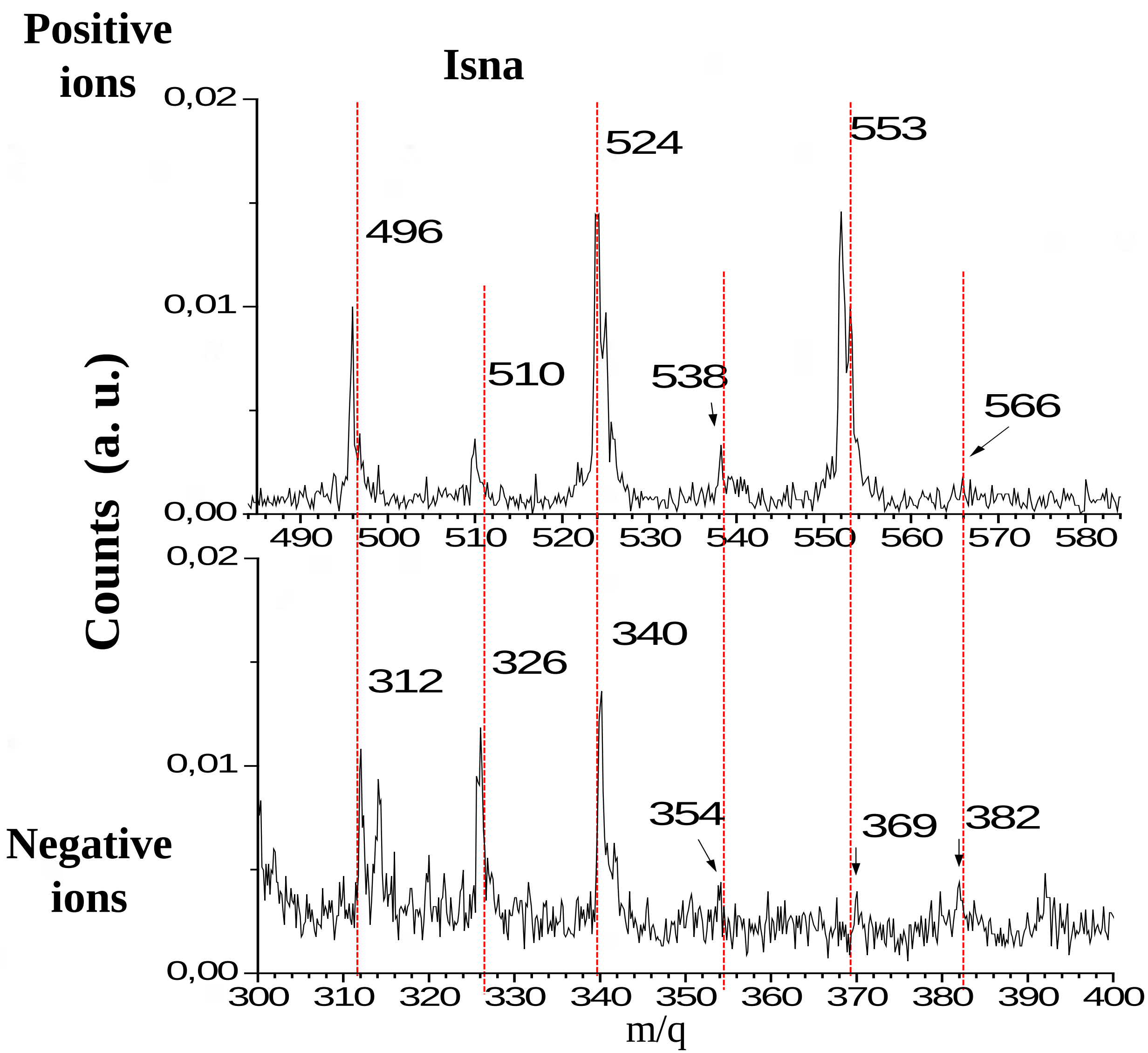
Methanol

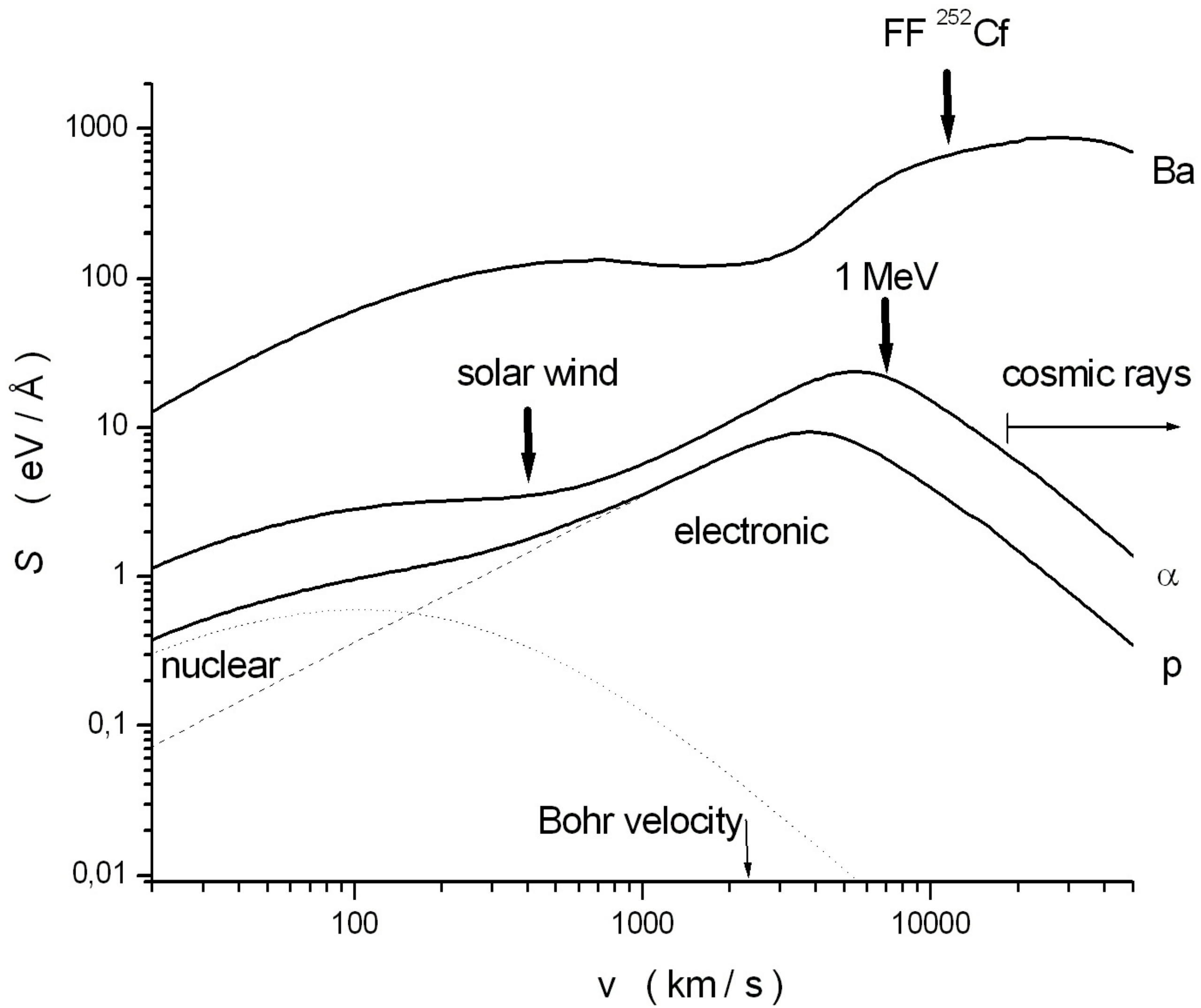
Genesis of the Fe-Ni meteorites (6%)



Fe and Ni are abundant in planet cores

PDMS Analysis of Meteorites





FF 252Cf
1000
100
10
1
0,1
0,01
S (eV / Å)
Ba
1 MeV
solar wind
cosmic rays
electronic
α
nuclear
p
Bohr velocity
100
1000
10000
v (km / s)