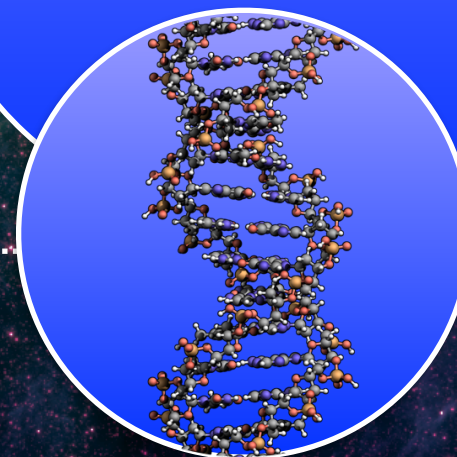
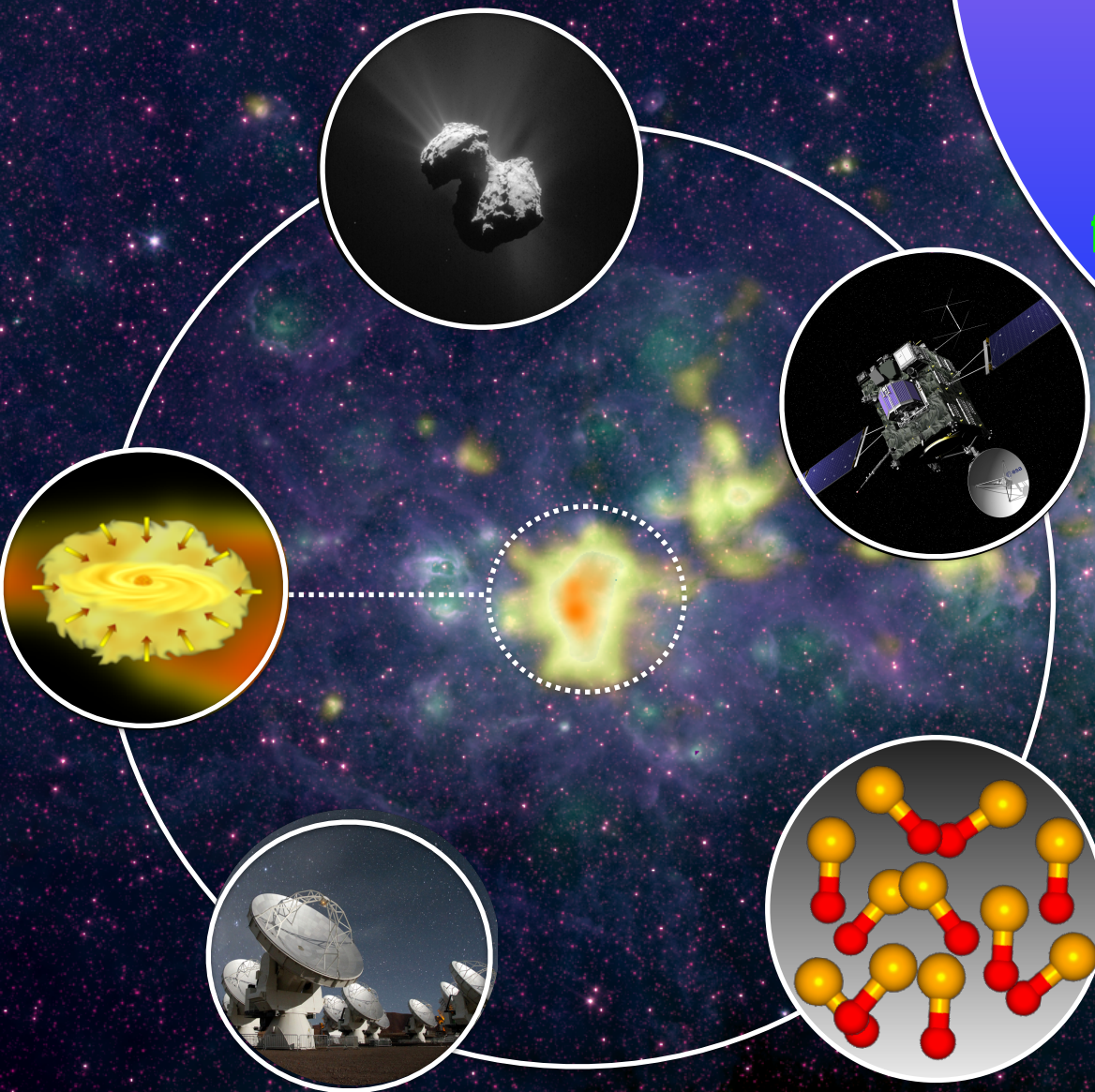


Phosphorus:

the missing prebiotic element...
found in star-forming regions and comets

Víctor M. Rivilla

Marie Skłodowska-Curie Fellow
Osservatorio Astrofisico di Arcetri



Nitrogen

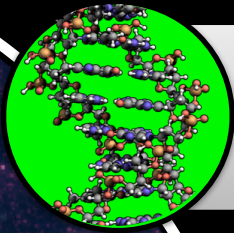
F. Fontani, M. Beltrán, P. Caselli, A. Vasyunin, C. Mininni, J. Martín-Pintado, I. Jiménez-Serra,
R. Cesaroni, M. Drozdovskaya, K. Altwegg and the ROSINA team...and more



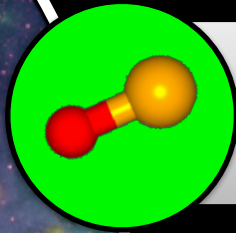
Prebiotic molecules in Space and
Origins of Life on Earth
Bad Honnef, March 19-23 2018



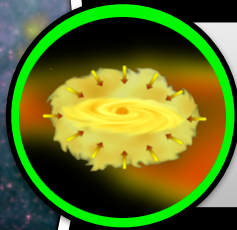
Outline



The prebiotic importance of Phosphorus



P-bearing molecules in the ISM:
a missing element?



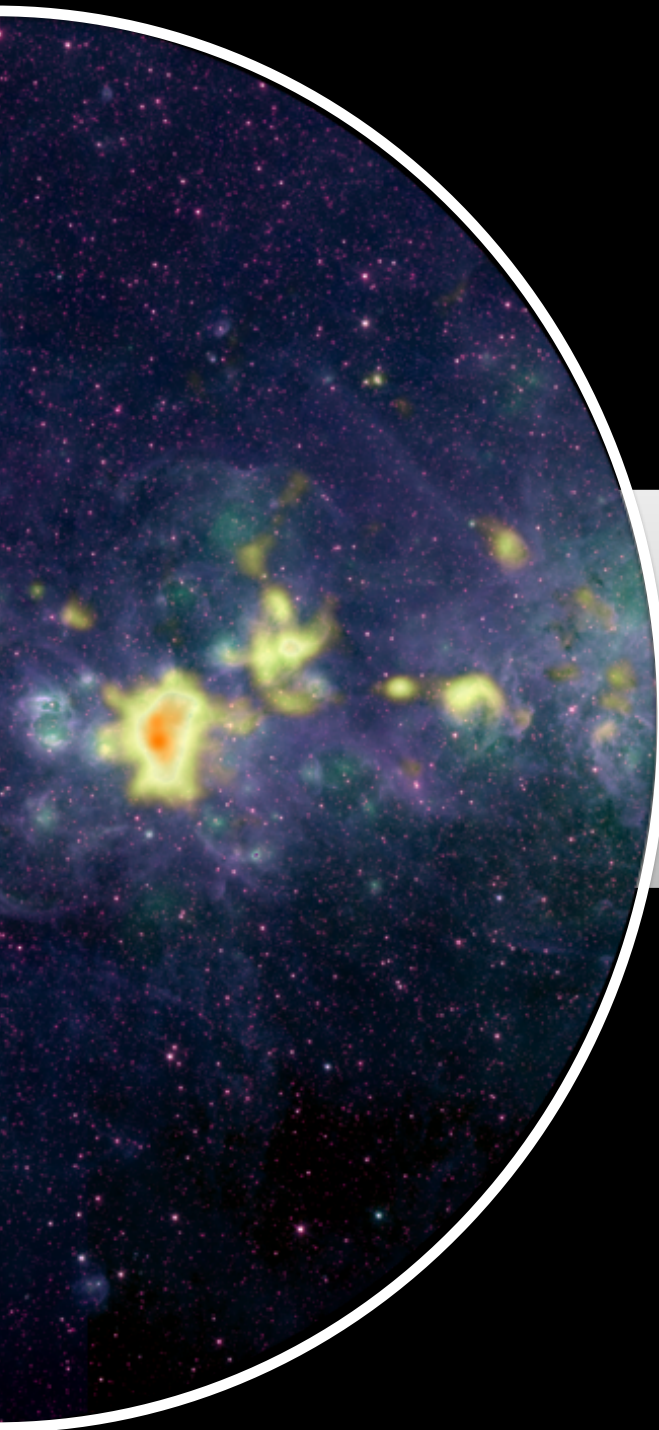
Search for P-bearing molecules in
star-forming regions and the Galactic Center



Phosphorus in the
67P Churyumov-Gerasimenko comet



Conclusions

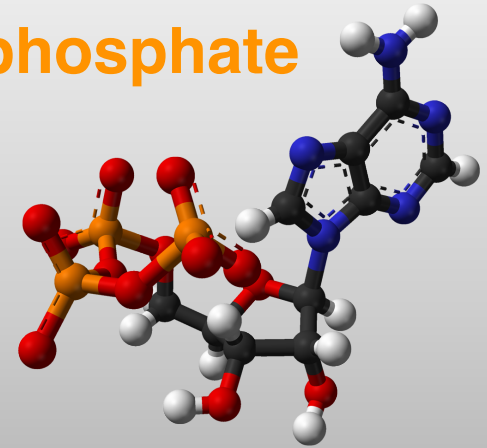
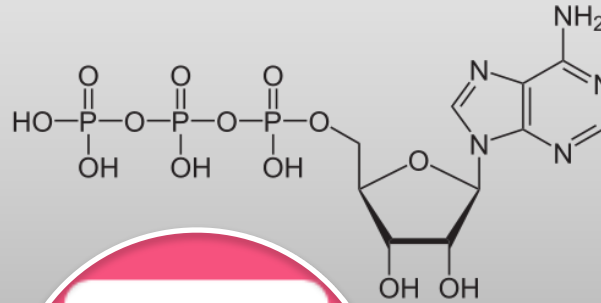


The prebiotic importance of Phosphorus

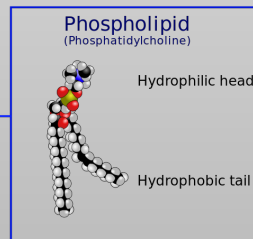
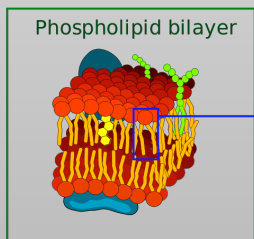
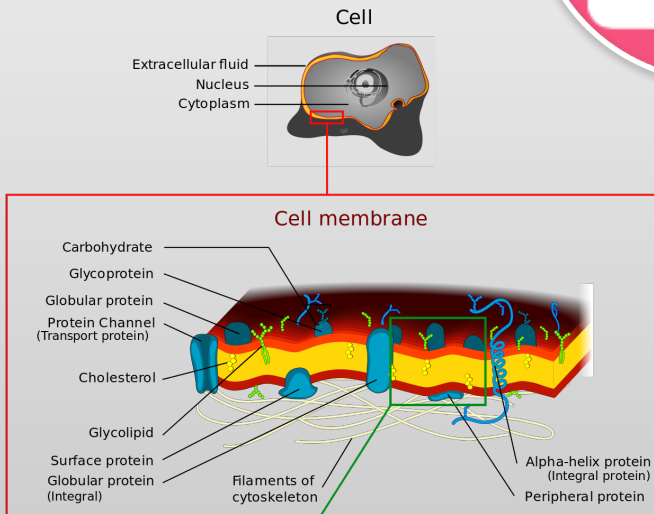
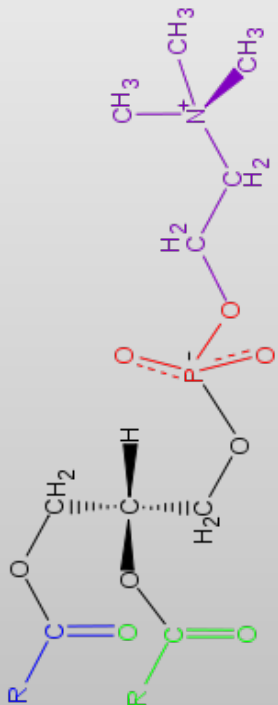
Phosphorus: key to Life

Chemical reactivity
Structural stability

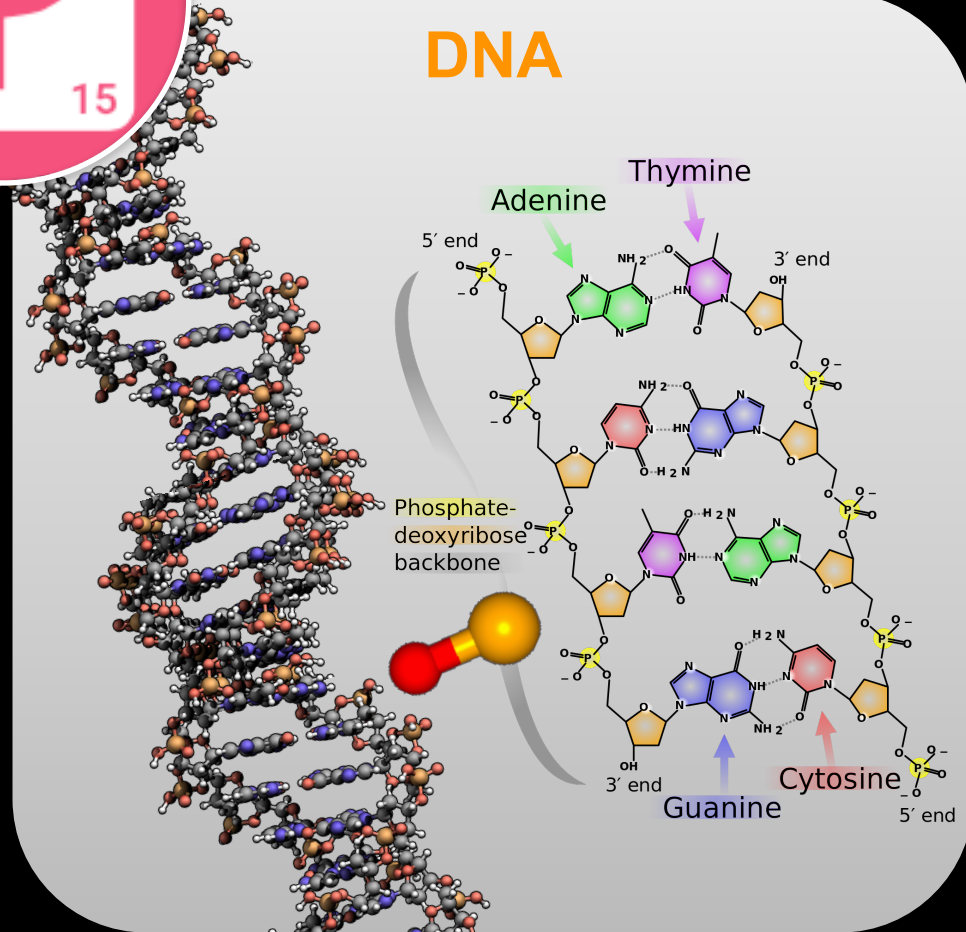
ATP: Adenosine Triphosphate



Phospholipids



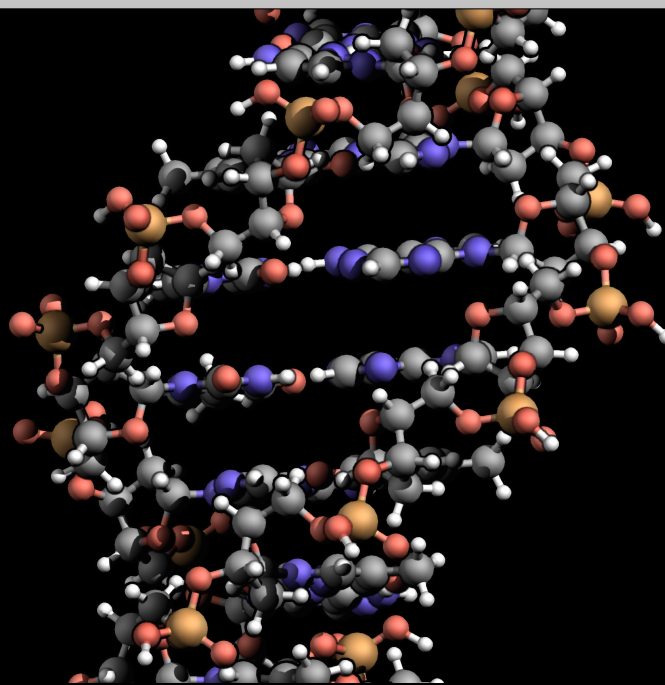
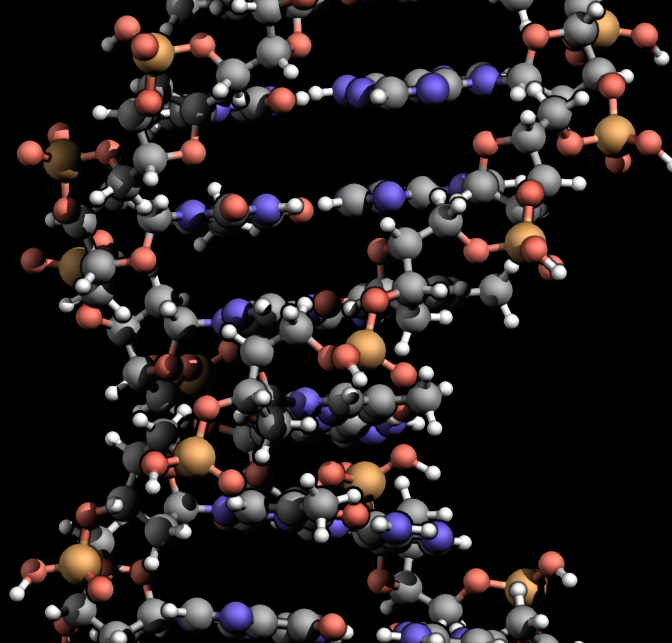
DNA

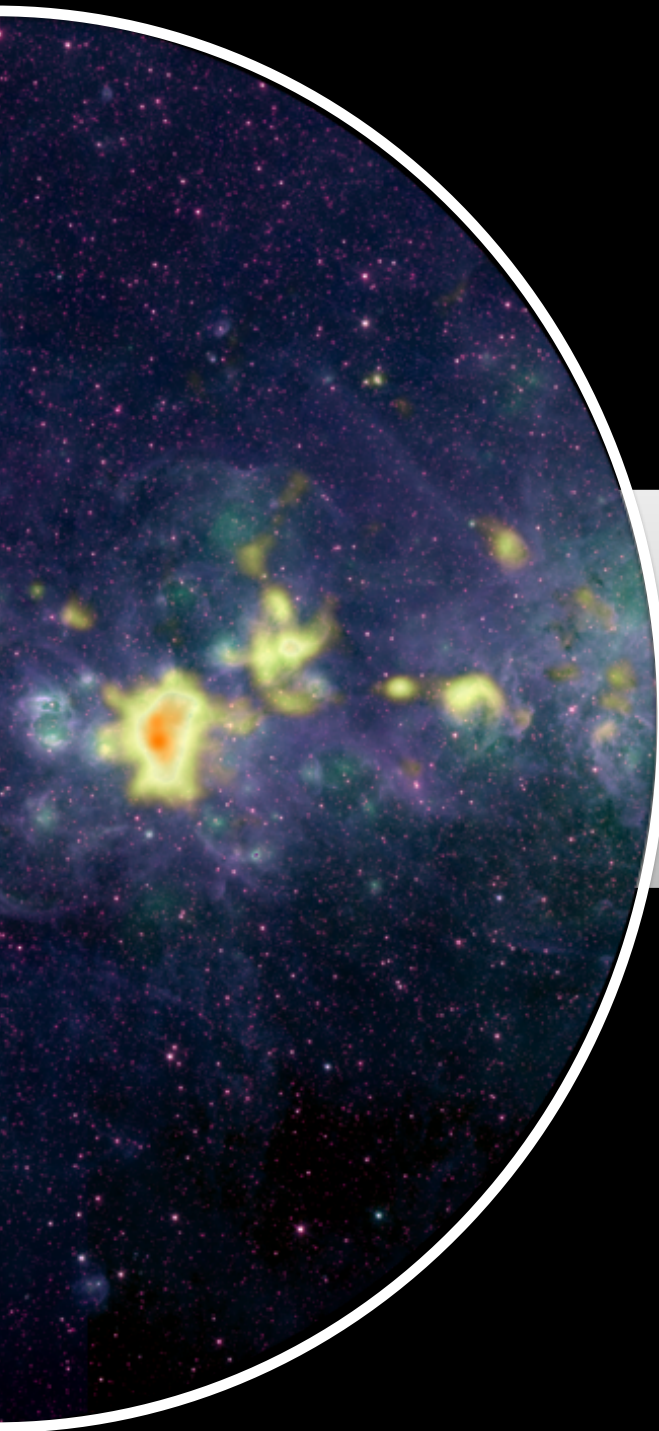




"Where there's life, there's phosphorus

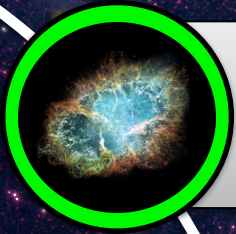
Sir Alexander Todd, Chemistry Nobel Prize, Kyoto Lecture 1982



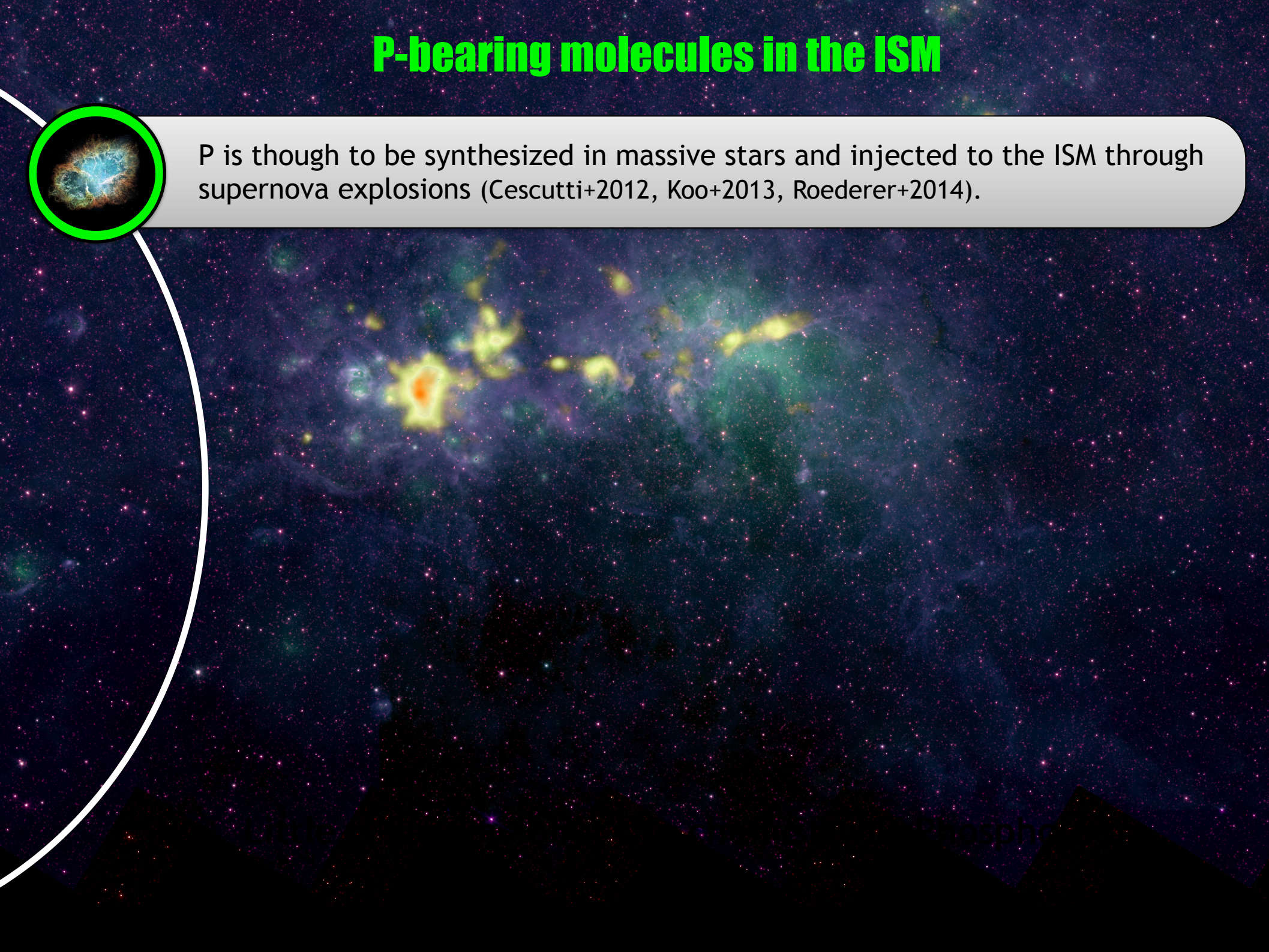


**P-bearing molecules in the ISM:
a missing element?**

P-bearing molecules in the ISM

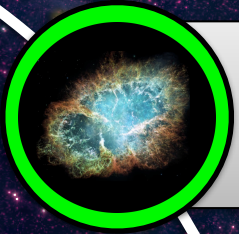


P is thought to be synthesized in massive stars and injected to the ISM through supernova explosions (Cescutti+2012, Koo+2013, Roederer+2014).



Phosphorus

P-bearing molecules in the ISM



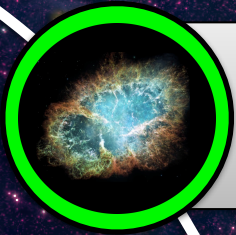
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It is barely detected in space:

- P^+ in several diffuse clouds (Jura & York 1978)
- PN , PO , CP , HCP , C_3P and PH_3 in circumstellar envelopes of evolved stars.
- PH_3 has been observed in the atmospheres of Jupiter and Saturn.

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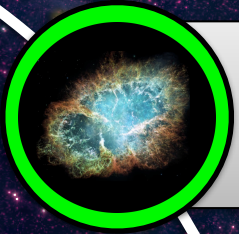


Low cosmic abundance: 3×10^{-7} (Grevesse & Sauval 1998)

Element	Cosmic abundance
C	$\sim 10^{-4}$
O	$\sim 10^{-4}$
N	$\sim 10^{-5}$
P	$\sim 10^{-7}$

Phosphorus

P-bearing molecules in the ISM



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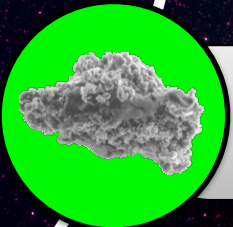


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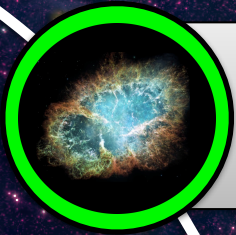


Low cosmic abundance: 3×10^{-7} (Grevesse & Sauval 1998)



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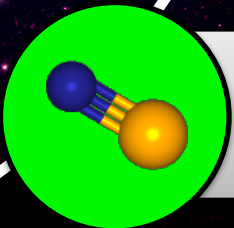
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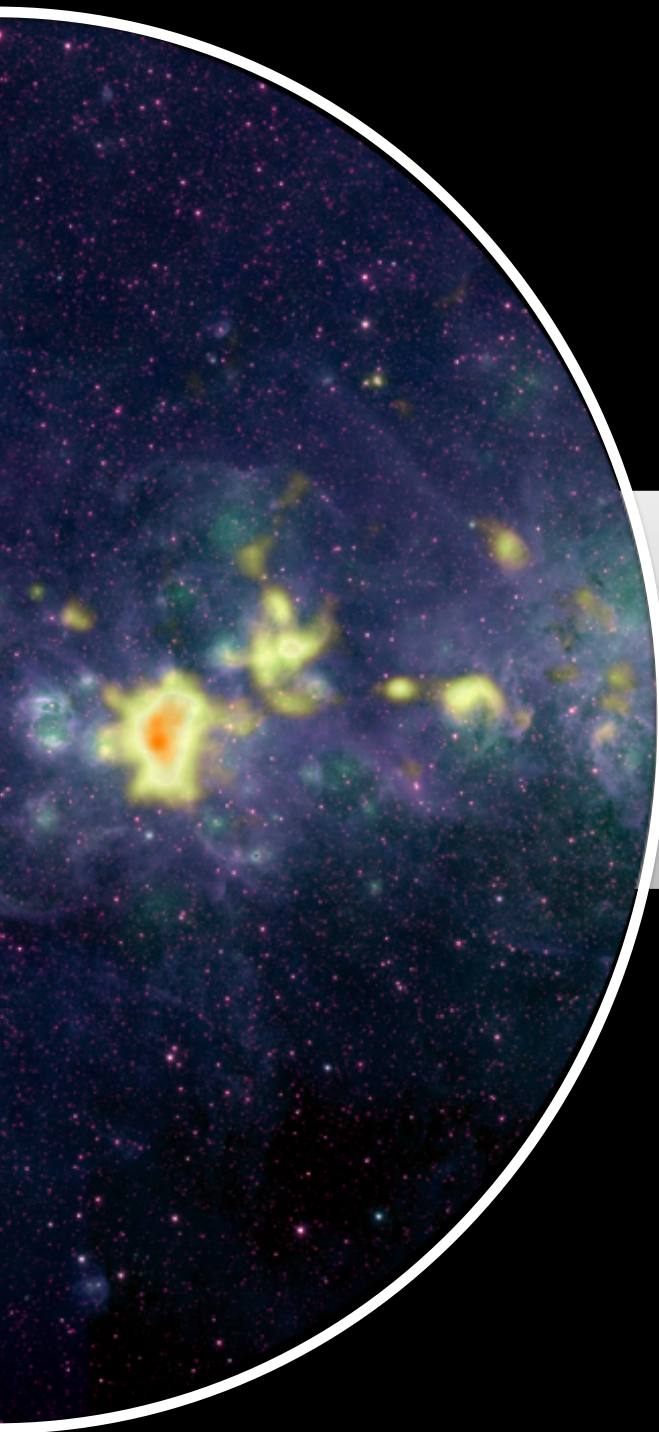
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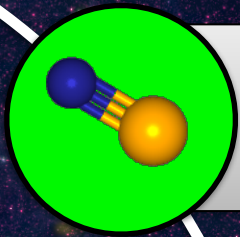


Little is known about the chemistry of Phosphorus

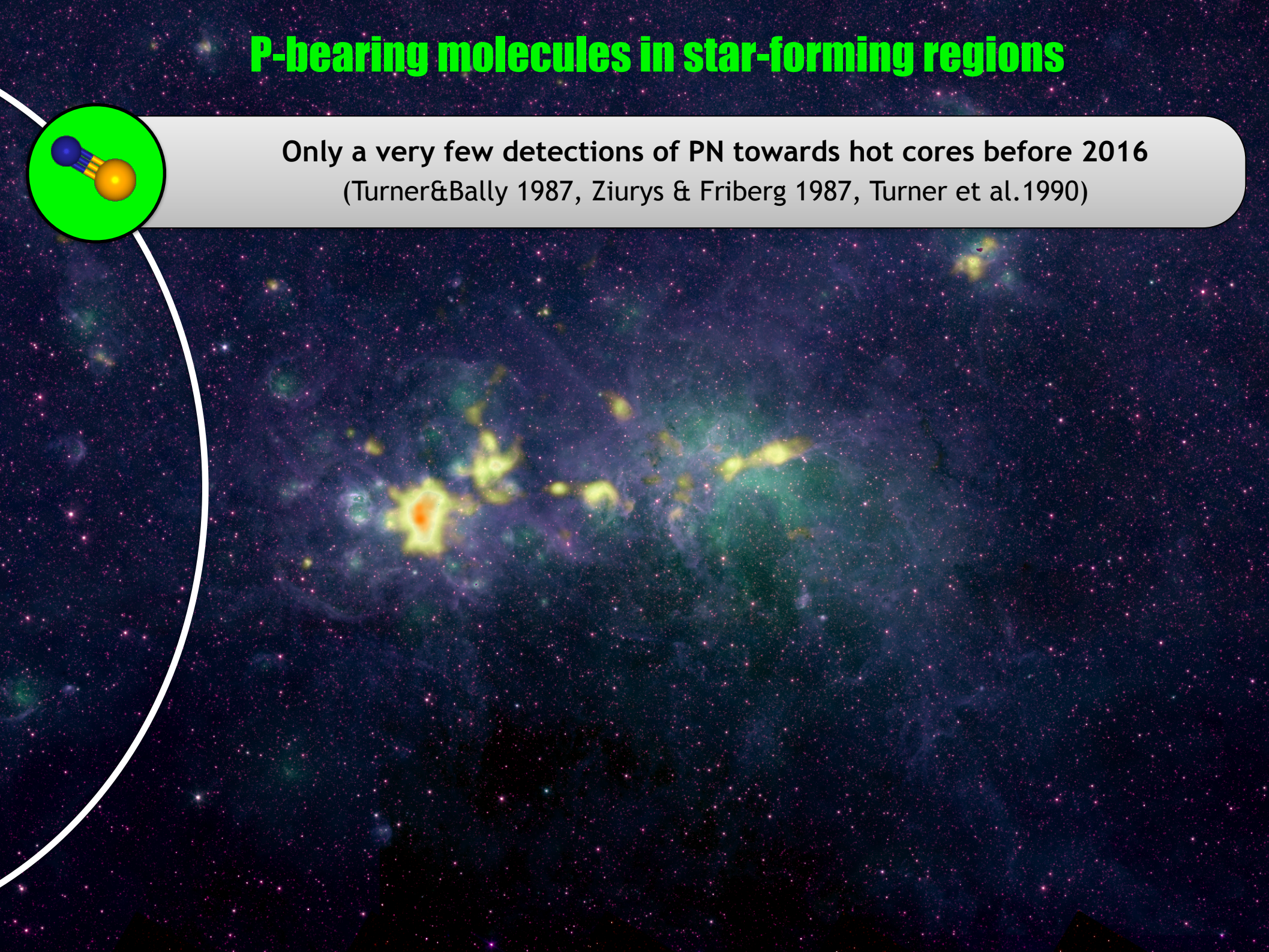


P-bearing molecules in star-forming regions

P-bearing molecules in star-forming regions



Only a very few detections of PN towards hot cores before 2016
(Turner&Bally 1987, Ziurys & Friberg 1987, Turner et al.1990)



P-bearing molecules in star-forming regions

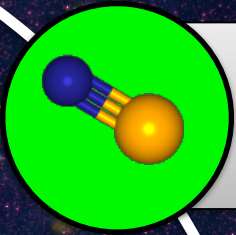


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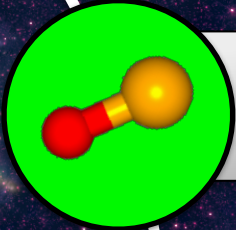


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P-bearing molecules in star-forming regions



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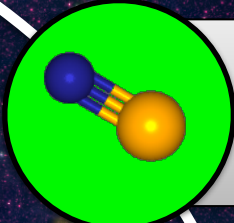


Previous searches of PO were unsuccessful



Our group started several projects to study
P-bearing molecules in star-forming regions

P-bearing molecules in star-forming regions



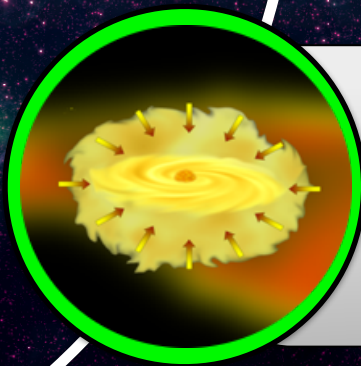
Only a very few detections of PH towards hot cores before 2016
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Previous searches of PO were unsuccessful



Our group started several projects to study
P-bearing molecules in star-forming regions

- 
- **Where:** sample of molecular dense ($n(\text{H}_2) > 10^4 \text{ cm}^{-3}$) clouds with large masses ($> 100 M_{\text{sun}}$) and $T > 20 \text{ K}$.
 - **Why:** they are the birthplaces of most stars, including our Sun (e.g. Adams 2010, Taquet+2016, Drozdovskaya+2018)

PN in a sample of star-forming regions



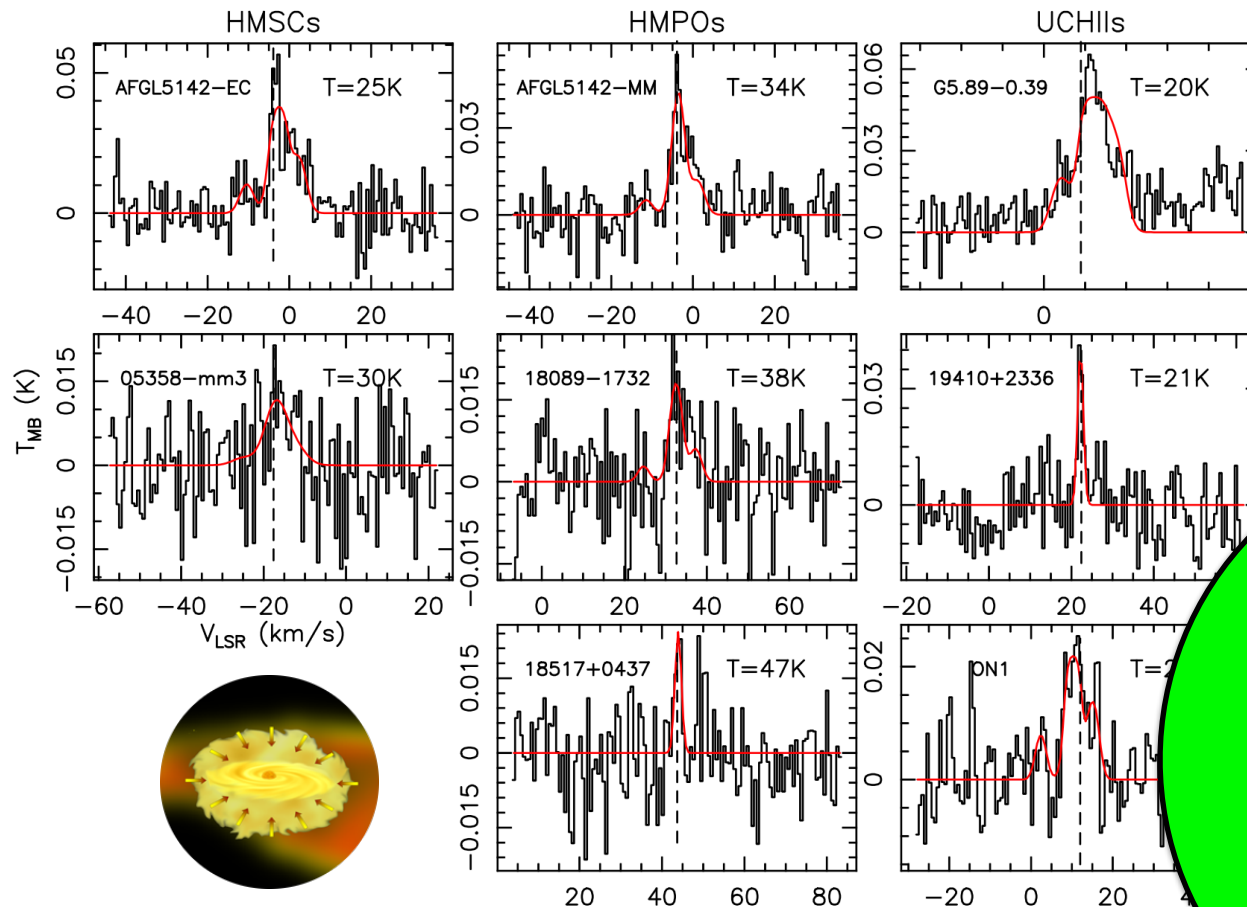
- IRAM 30m telescope (Sierra Nevada, Spain).
- PN(2-1) at 93.9 GHz in a sample of **27 massive dense cores** (Fontani et al. 2011; Fontani et al. 2015; Colzi et al. 2018 - **POSTER 01**)

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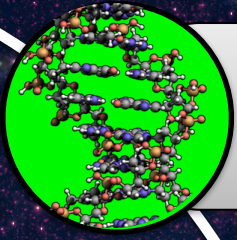


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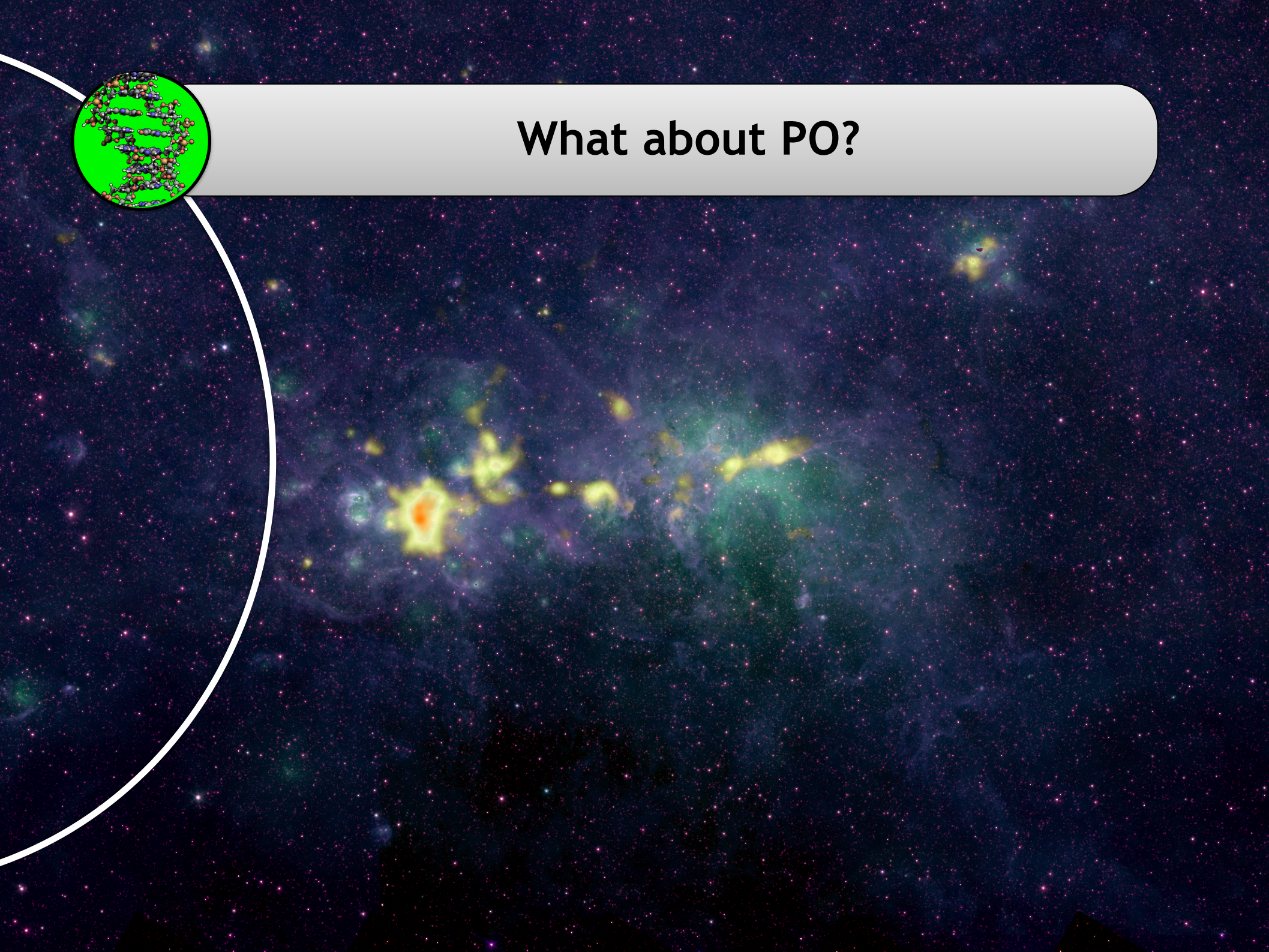
Fontani, Rivilla et al. (2016)

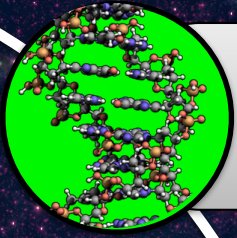


**8 new PN
detections**

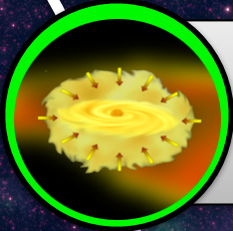


What about PO?

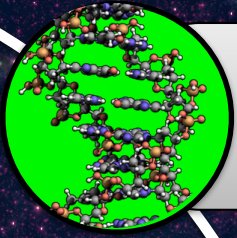




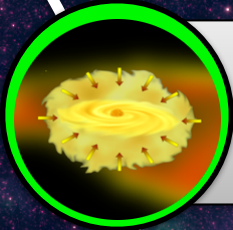
What about PO?



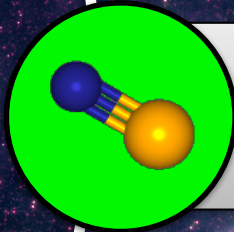
Not detected in any source
Good constraints on upper limits

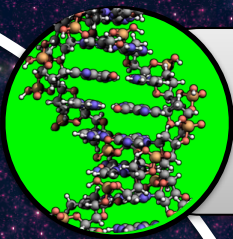


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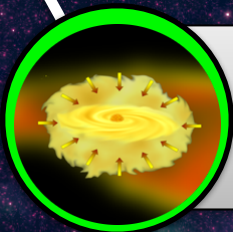


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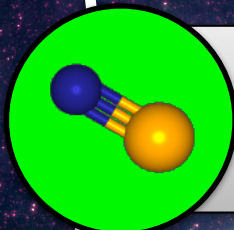

$$N_{\text{PO}}^{\text{upper}} > N_{\text{PN}}$$



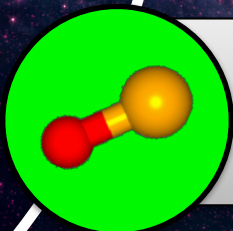
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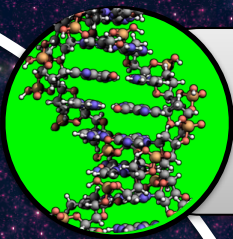
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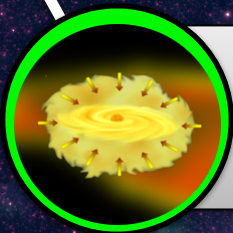
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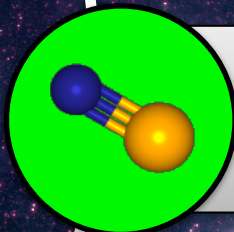
PO could be as abundant as PN



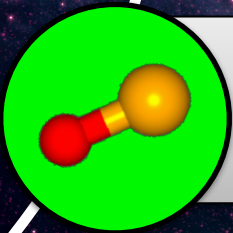
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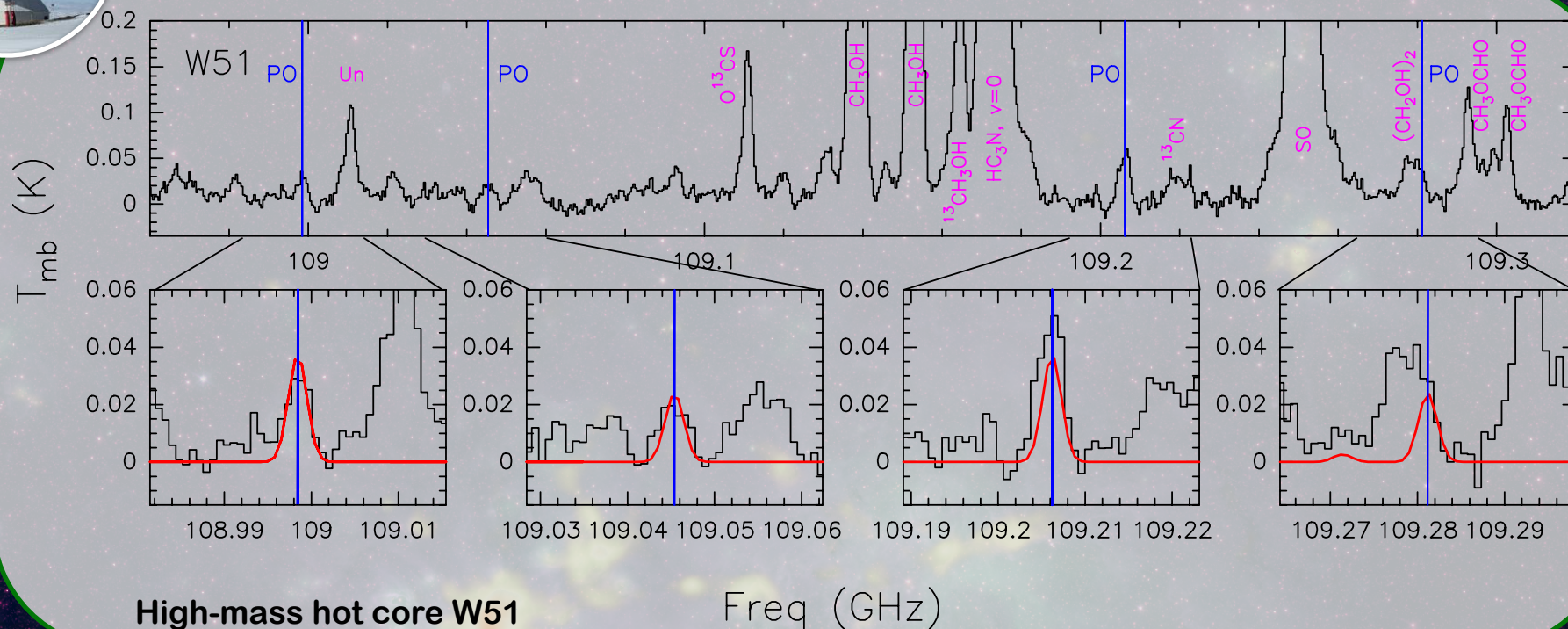
Search in the two brightest cores in PN with the
IRAM 30m telescope

First detections of PO in star-forming regions



Rivilla et al. (2016)

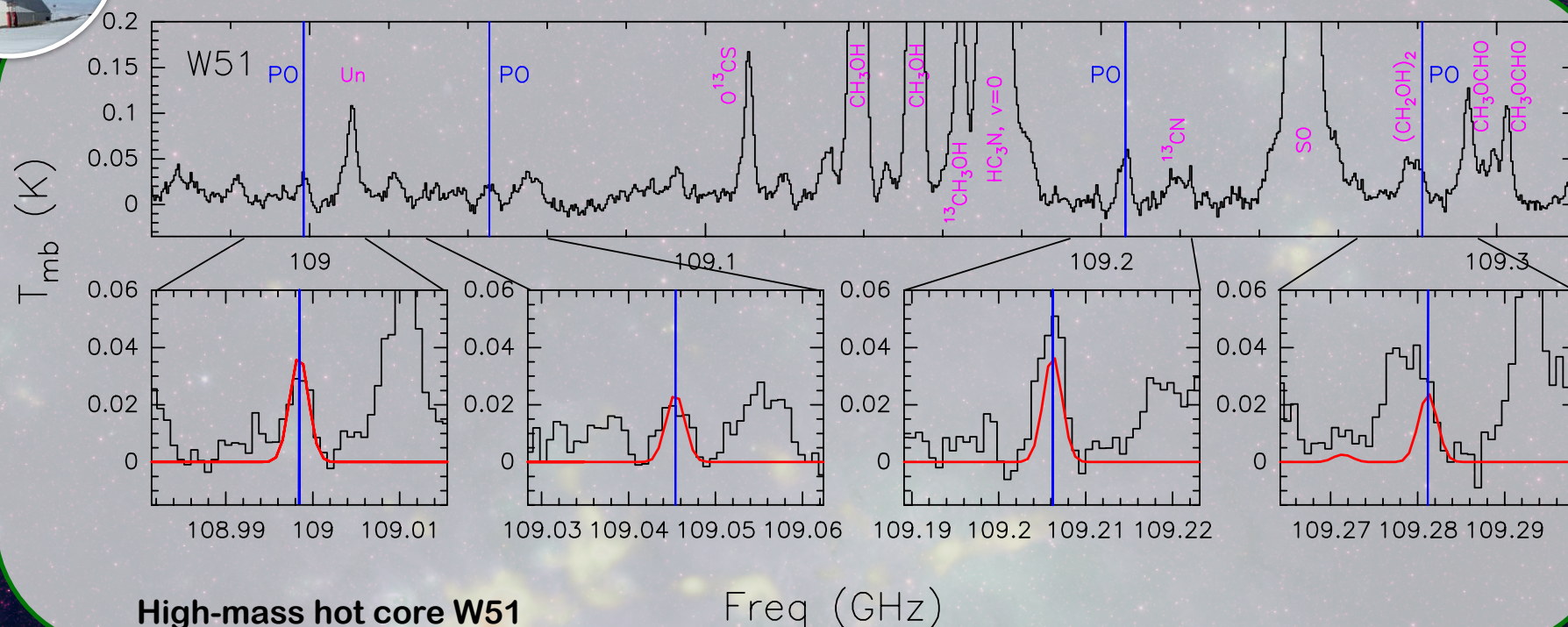
Rivilla et al. 2016



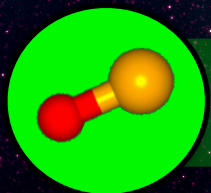
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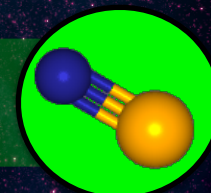
Rivilla et al. 2016



	Abundance (10^{-10})
PN	0.4-1.1
PO	1.2-2.0



PO is a factor 2-3 more abundant than PN !

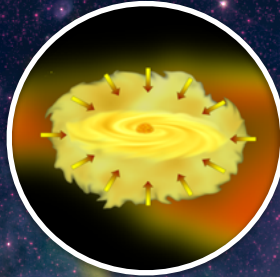




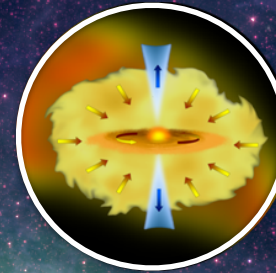
Chemical modeling

- Our theoretical team at MPE (Vasyunin, Caselli) included the chemical network of P in a 2-phase physical model to mimic the evolution of a star-forming region.

Cold starless phase



Warm-up protostellar phase

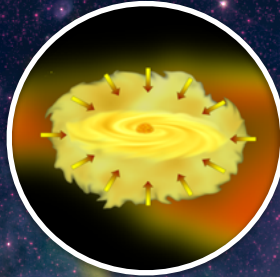




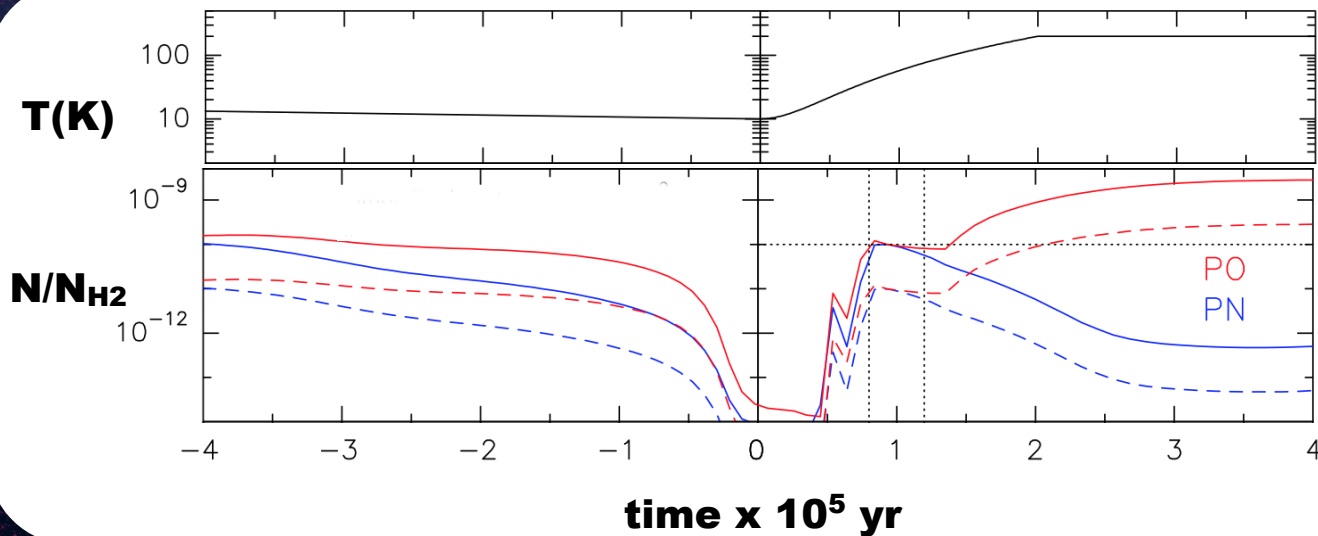
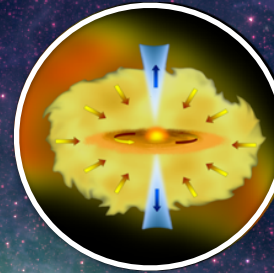
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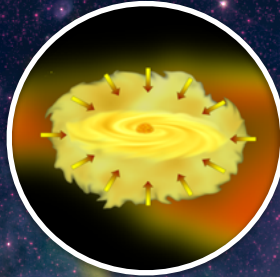




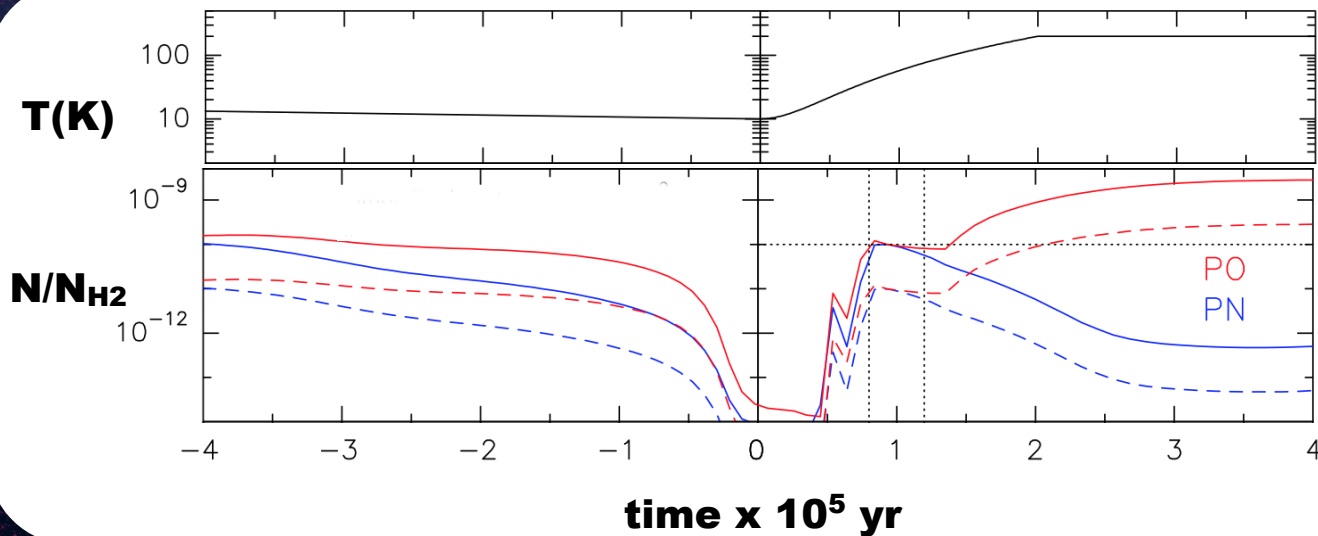
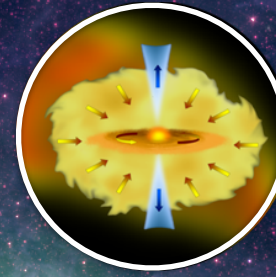
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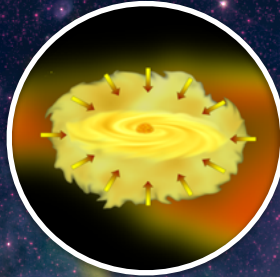
The two P-bearing molecules form in a sequence of **gas-phase ion-molecule** and **neutral-neutral** reactions during the cold collapse phase.



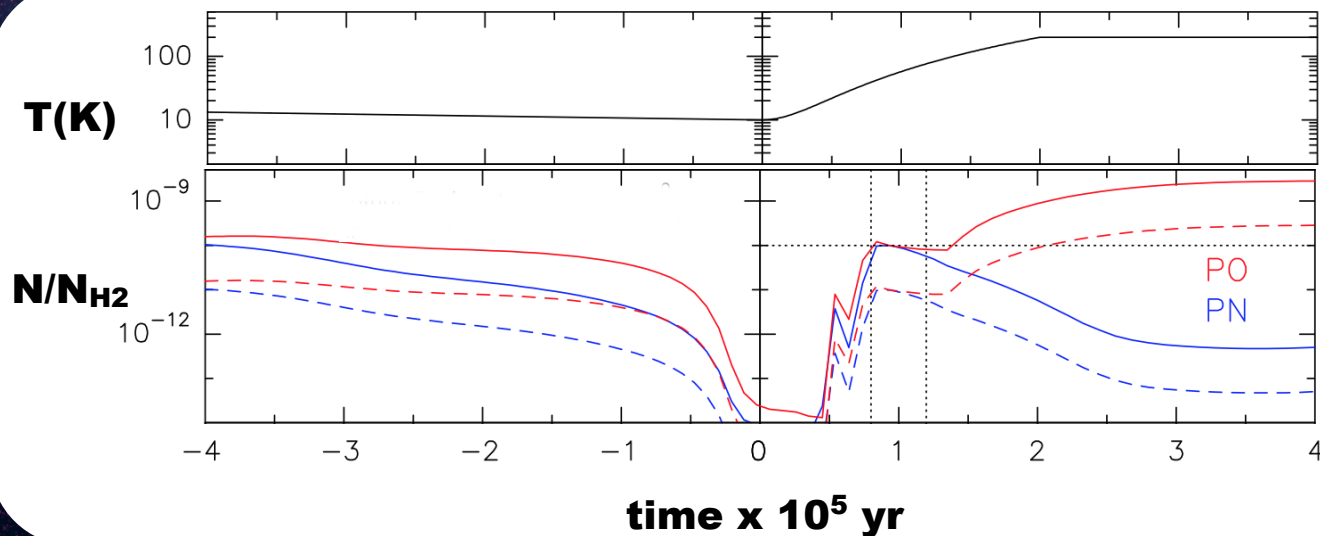
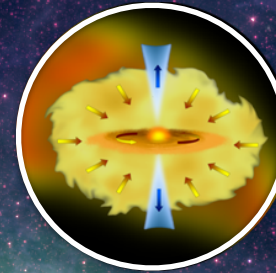
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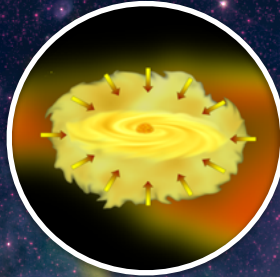
- The heating from the protostar produces the **thermal desorption** of the P-bearing species.
- Hot chemistry** can explain the observed abundances.



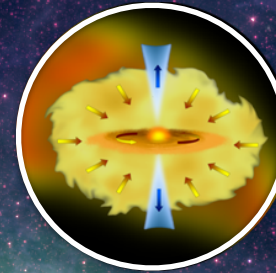
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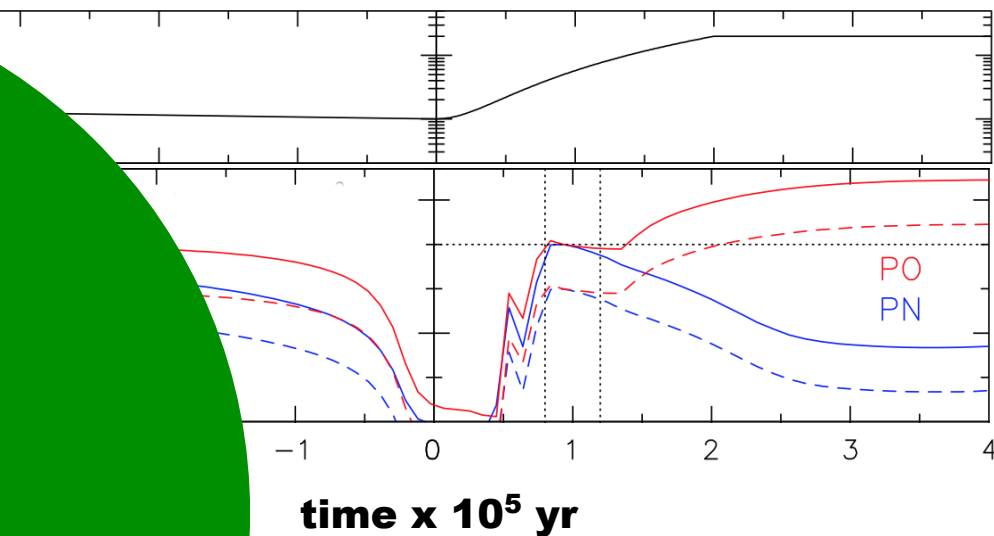
Cold starless phase



Warm-up protostellar phase



P initial abundance = 5×10^{-9}



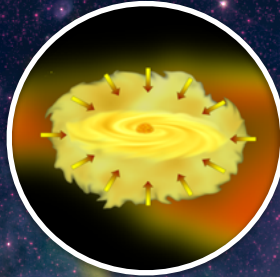
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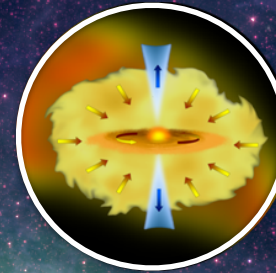
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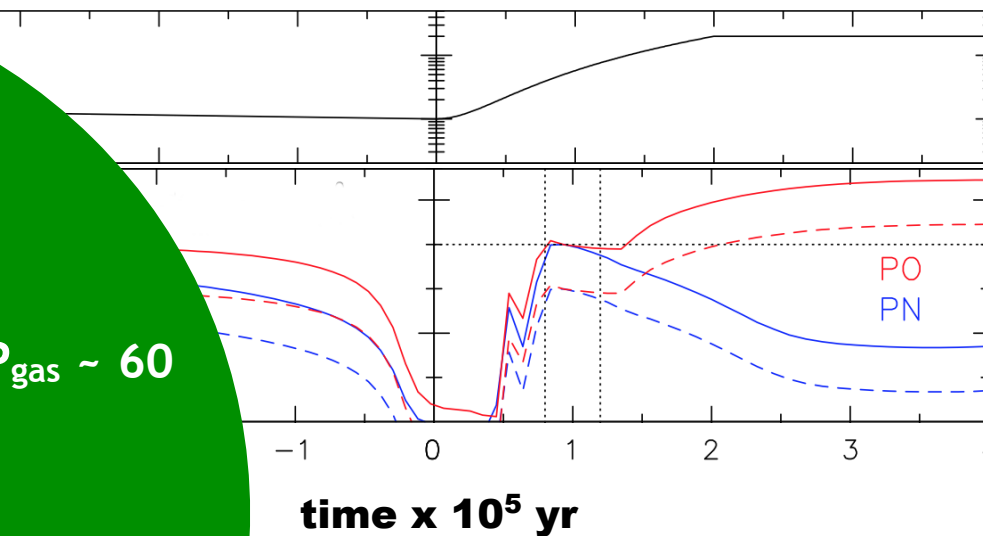
Warm-up protostellar phase



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depletion factor = $P_{\text{cosmic}} / P_{\text{gas}} \sim 60$



m in a
molecule
during

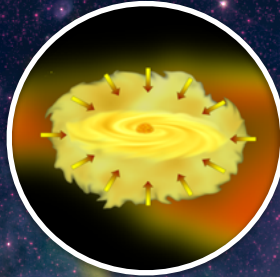
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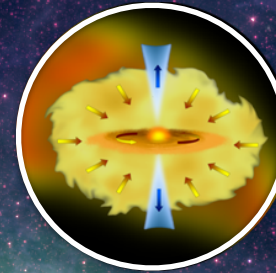
Chemical modeling

- Our theoretical team at MPE (Vasyunin, Caselli) included the chemical network of P in a 2-phase physical model to mimic the evolution of a star-forming region.

Cold starless phase



Warm-up protostellar phase

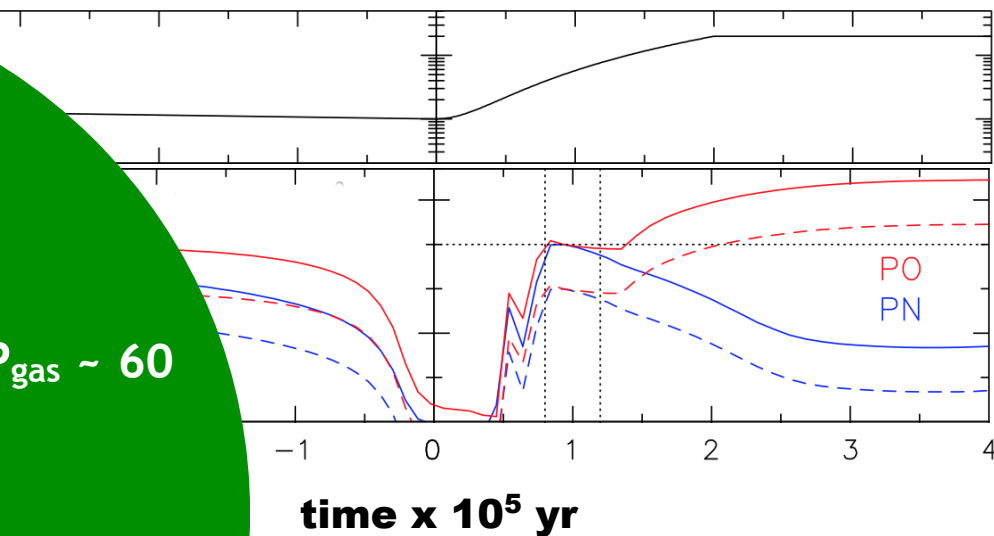


P initial abundance = 5×10^{-9}



depletion factor = $P_{\text{cosmic}} / P_{\text{gas}} \sim 60$

~ 100 (Lefloch et al. 2016)



m in a
molecule
during

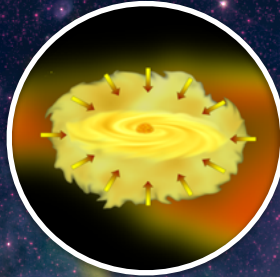
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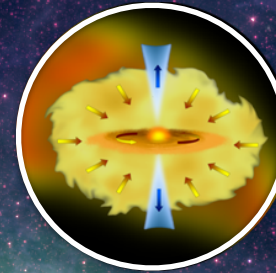
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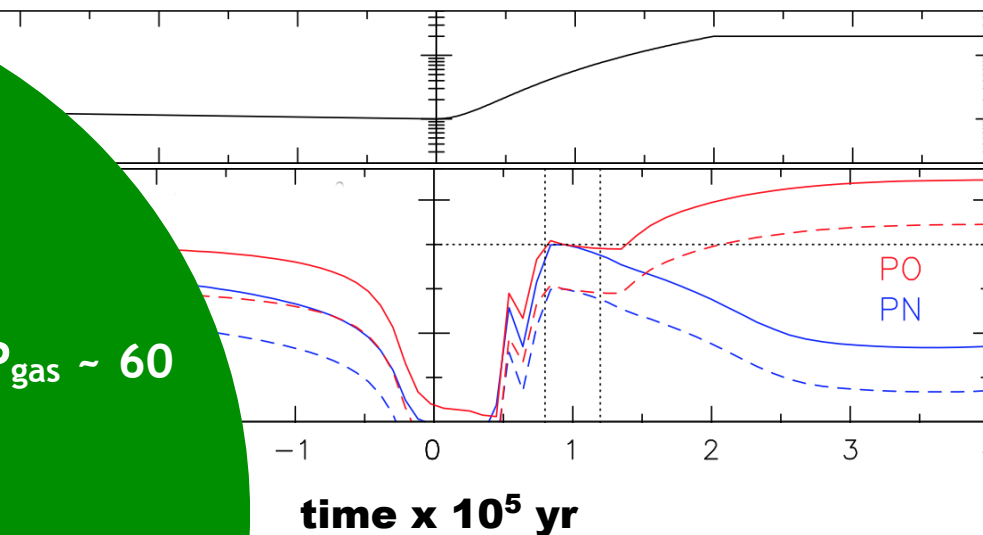
P initial abundance = 5×10^{-9}



depletion factor = $P_{\text{cosmic}} / P_{\text{gas}} \sim 60$

~ 100 (Lefloch et al. 2016)

Significantly lower than the value
previously thought: $600-10^4$
(Turner et al. 1990, Wakelam & Herbst 2008)



m in a
molecule
during

- The heating from the protostar produces the **thermal desorption** of the P-bearing species.
- Hot chemistry** can explain the observed abundances.



Chemical modeling

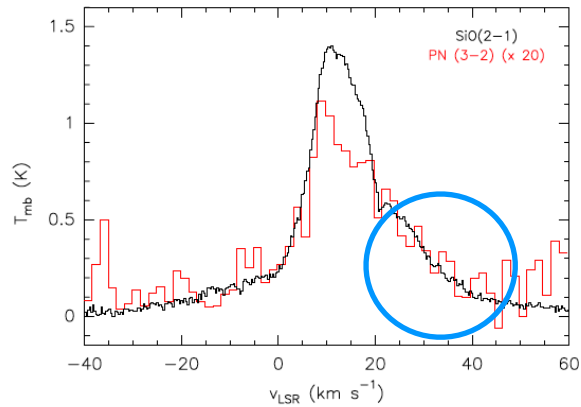
formation in cold phase
+
thermal desorption
+
hot chemistry





Chemical modeling

G5.89-0.39
star-forming region



Mininni et al. (2018)

POSTER 14!

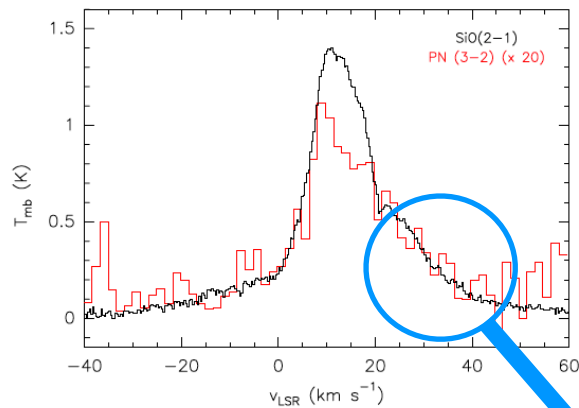
formation in cold phase
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hot chemistry





Chemical modeling

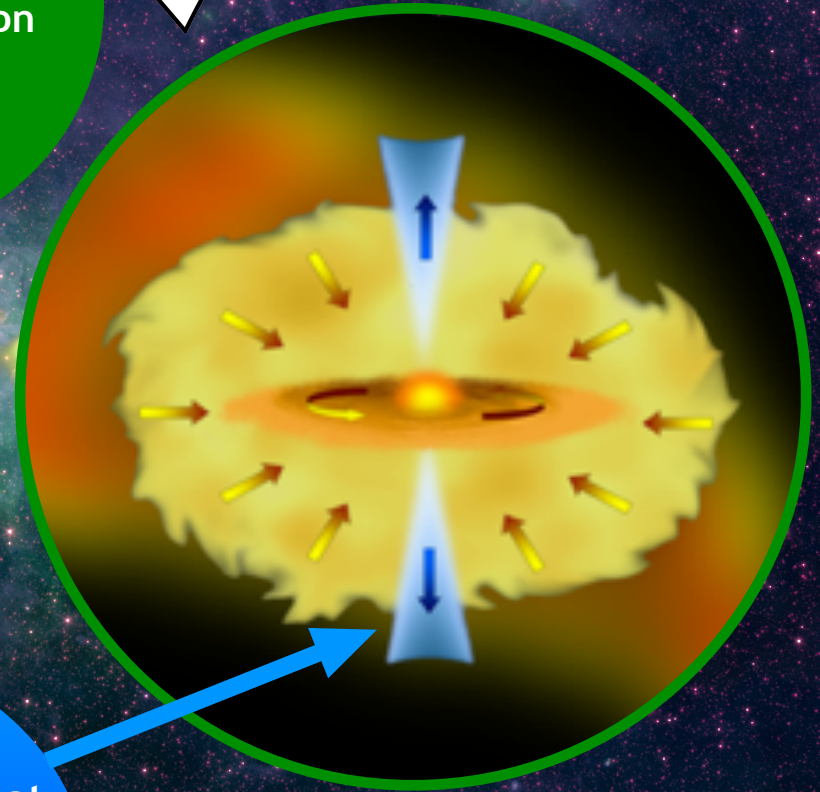
G5.89-0.39 star-forming region



Mininni et al. (2018)

POSTER 14!

formation in cold phase
+
thermal desorption
+
hot chemistry



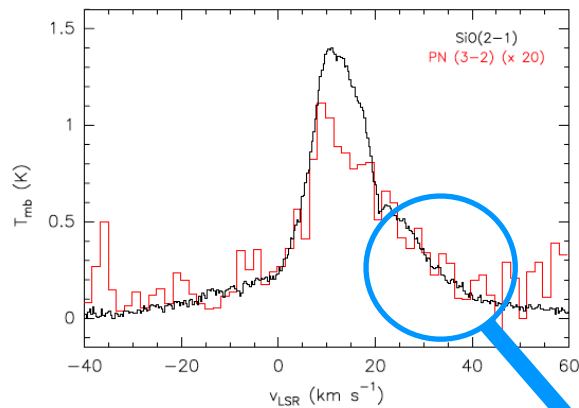
Shocked material at
high velocities



Chemical modeling

formation in cold phase
+
thermal desorption
+
hot chemistry

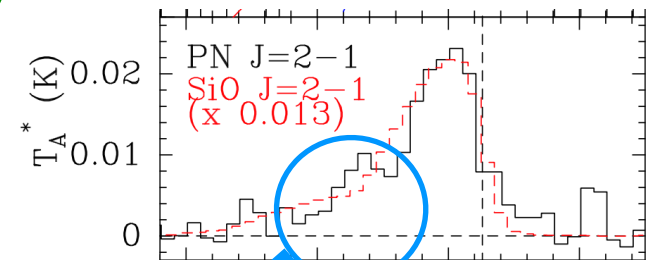
G5.89-0.39 star-forming region



Mininni et al. (2018)

POSTER 14!

L1157-B1 shock



Lefloch et al. (2016)

Talk tomorrow

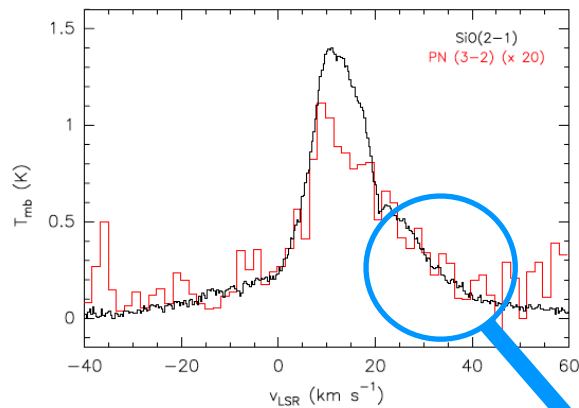
Shocked material at
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Chemical modeling

formation in cold phase
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+
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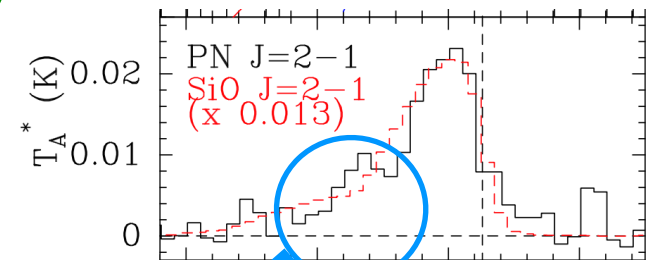
G5.89-0.39 star-forming region



Mininni et al. (2018)

POSTER 14!

L1157-B1 shock



Lefloch et al. (2018)

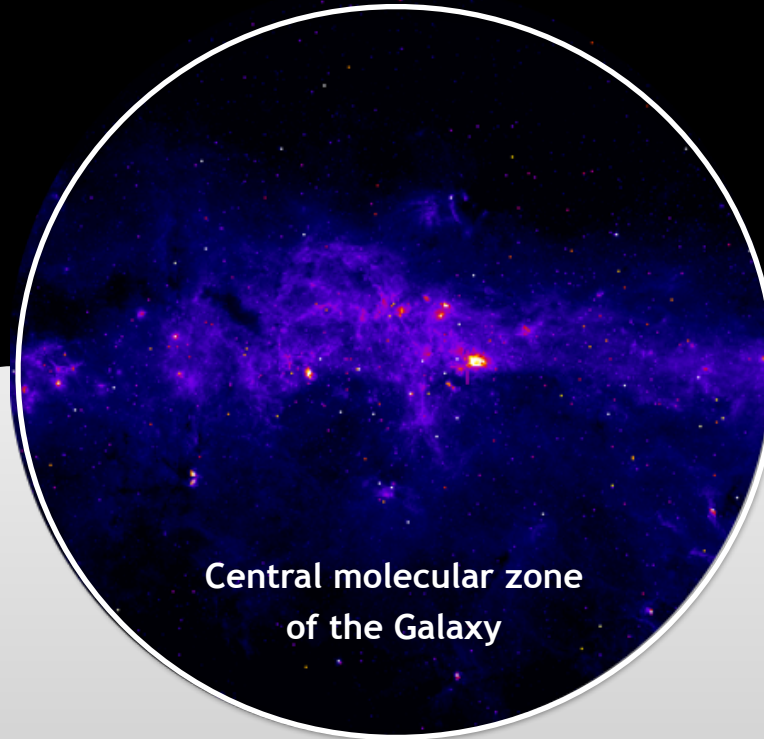
Talk tomorrow

Shocked material at
high velocities

?



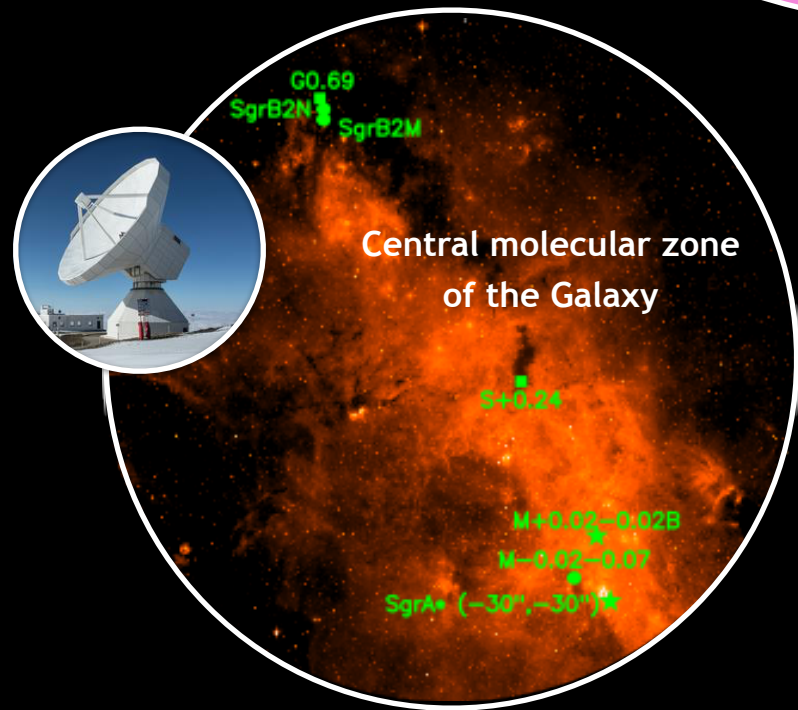
Galactic Center



Central molecular zone
of the Galaxy

- Dust grain sputtering by widespread large-scale low-velocity shocks.

Galactic Center



THE SAMPLE

Shock-dominated
regions

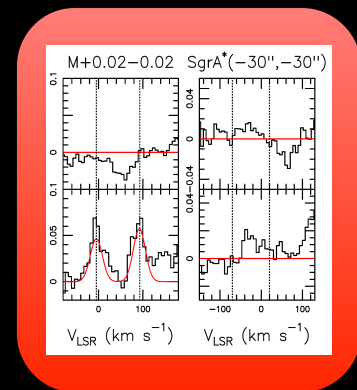
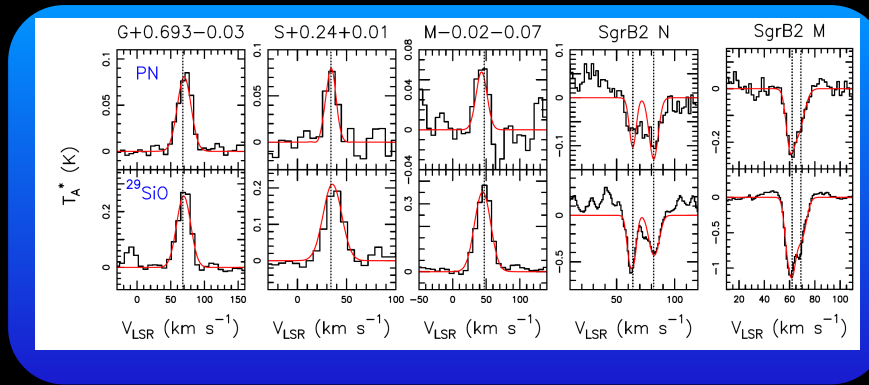
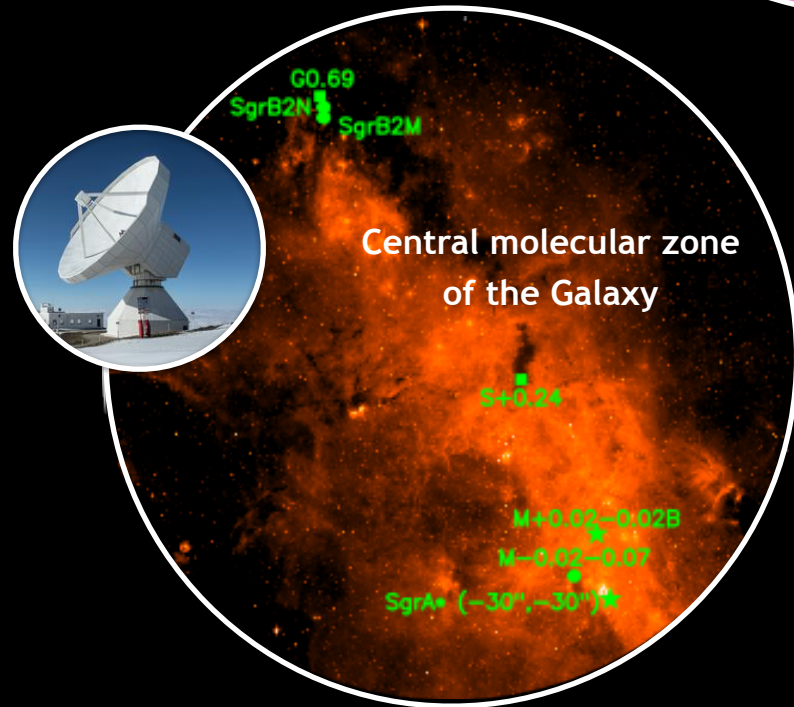
COMs-rich

Radiation-dominated
regions

Cosmic rays
X-rays
UV

Rivilla et al. (2018)

Galactic Center



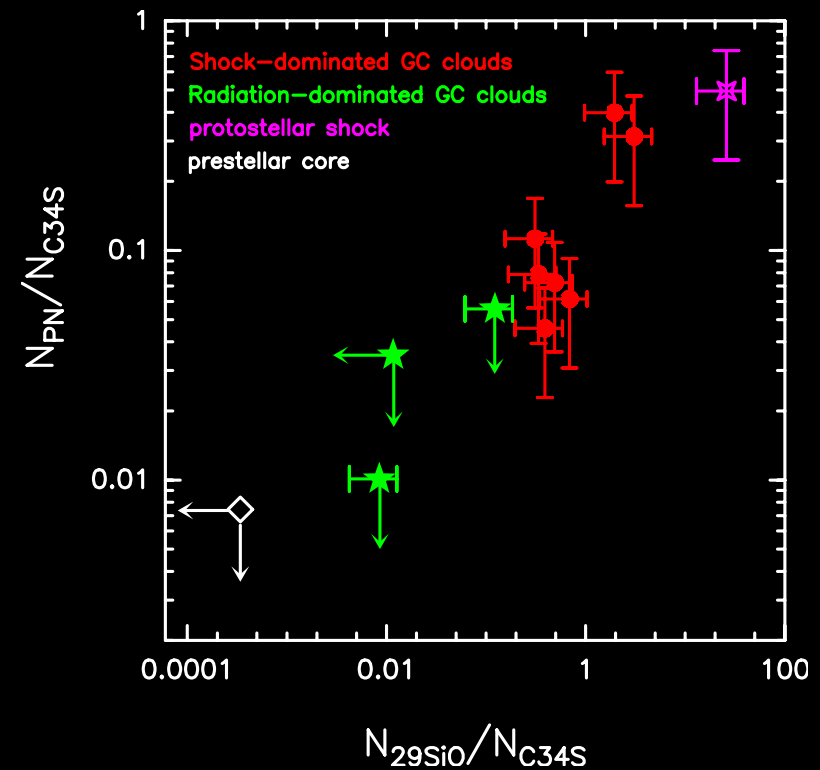
THE SAMPLE

Shock-dominated regions

COMs-rich

Radiation-dominated regions

Cosmic rays
X-rays
UV



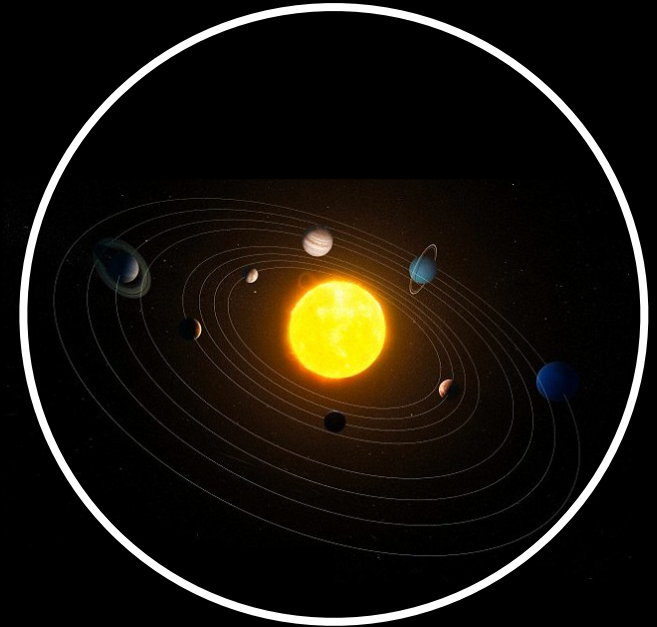
Rivilla et al. (2018)



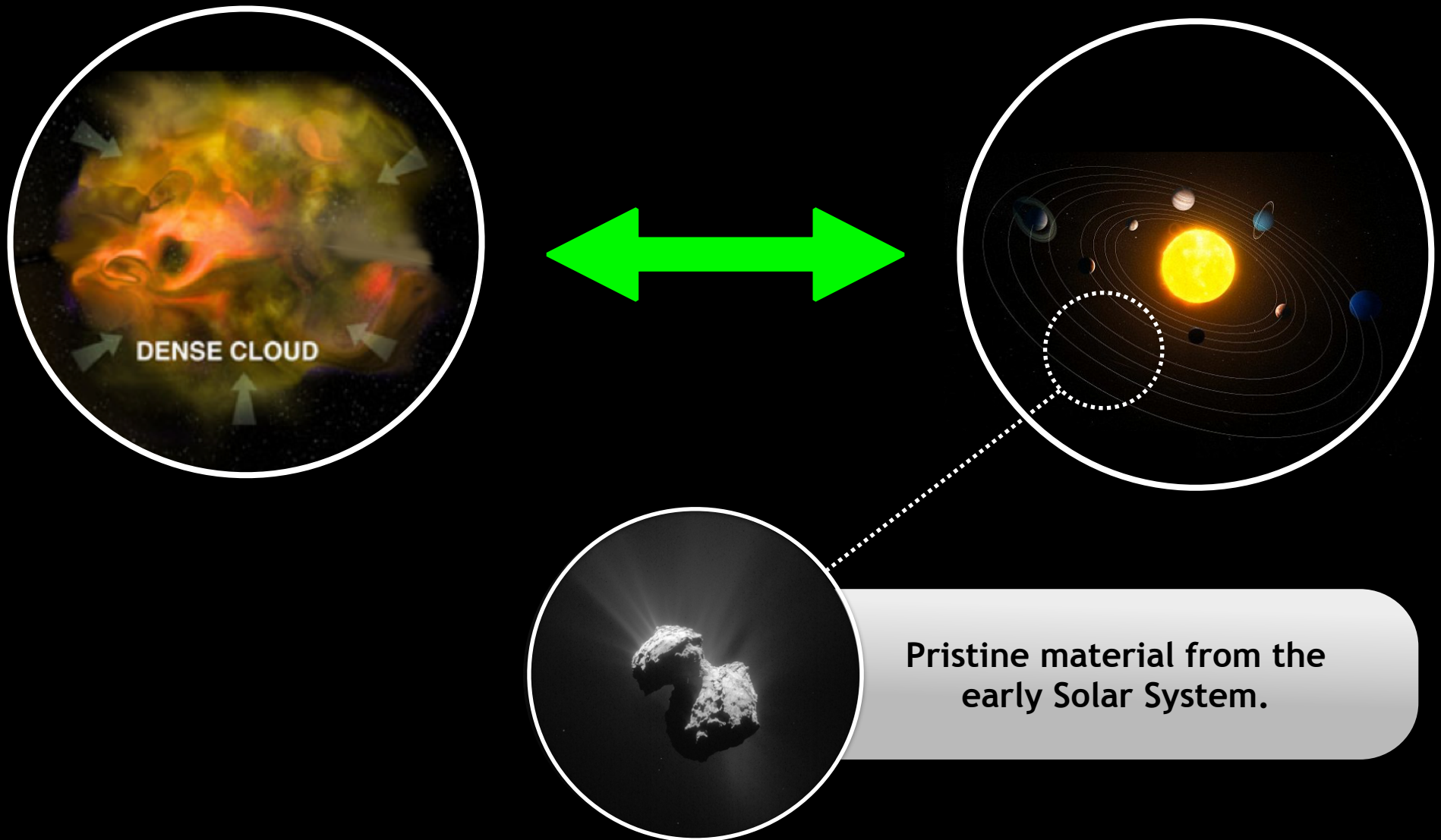
Phosphorus in the 67P Churyumov-Gerasimenko comet

**Collaboration with Maria Drozdozvsкая,
Kathrin Altwegg, and the ROSINA team**

The Phosphorus connection between protostars and comets

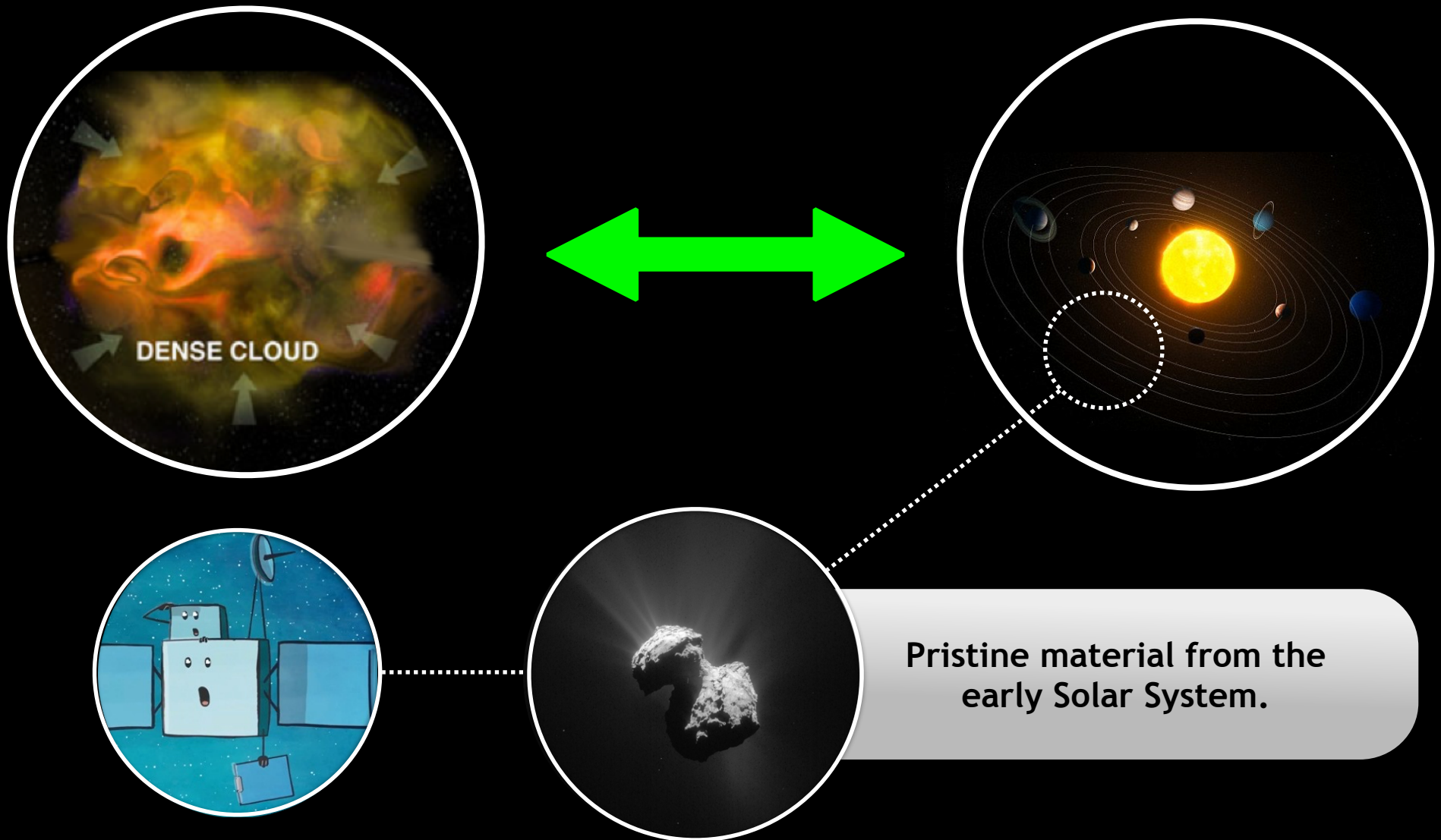


The Phosphorus connection between protostars and comets



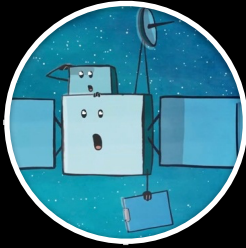
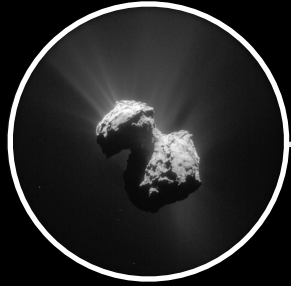
67P Churyumov-Gerasimenko comet

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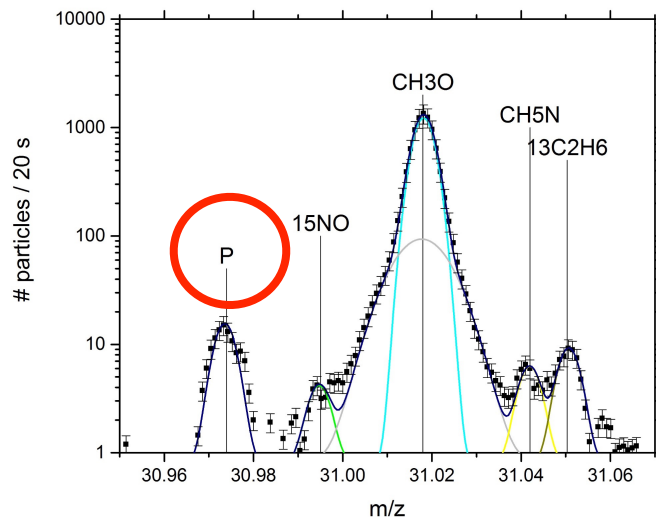


67P Churyumov-Gerasimenko comet

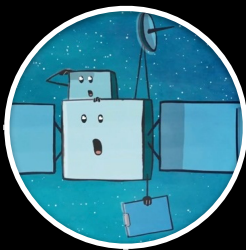
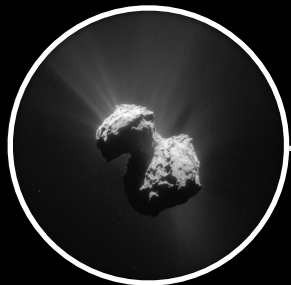
Phosphorus in 67 P



Altwegg et al. (2016)

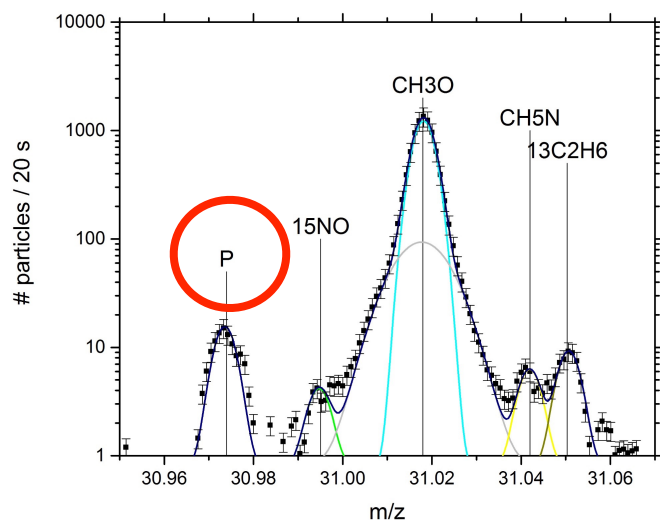


Clear mass peak at the
location of P (30.9737 Da)



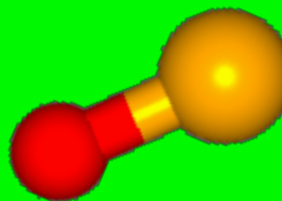
Phosphorus in 67 P

Altwegg et al. (2016)

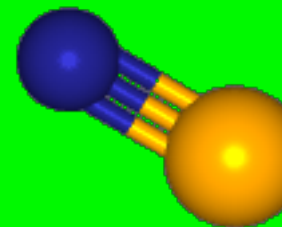


Clear mass peak at the
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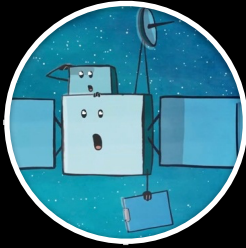
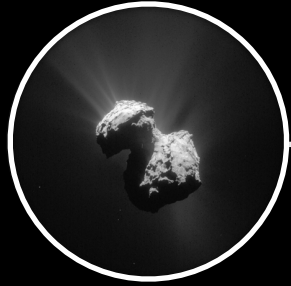
PO



PN

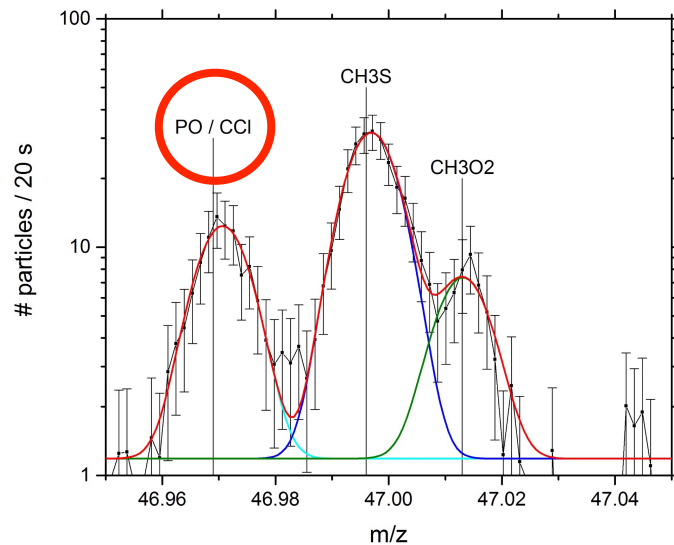


?

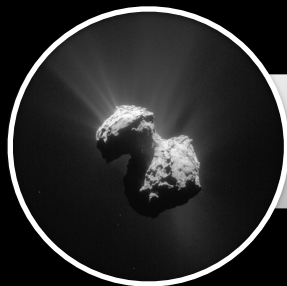


Phosphorus in 67 P

Rivilla et al. (in prep.)



- Clear mass peak at the location of **PO** (mass 46.9681 Da).
- Possible contamination from **CCI** (same mass).

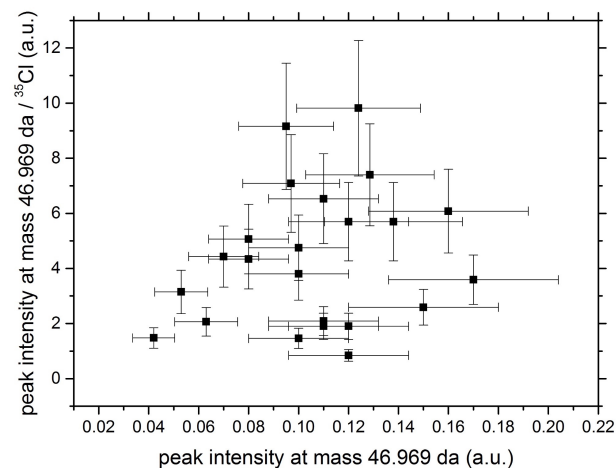


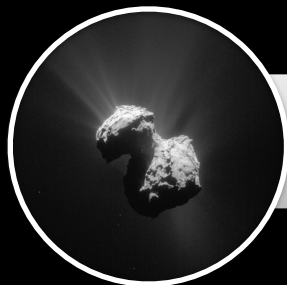
Correlation between the peak at 46.969 and the P peak (mass 31) and ^{35}Cl (mass 35)

Rivilla et al. (in prep.)

CCI?

No Correlation with ^{35}Cl peak



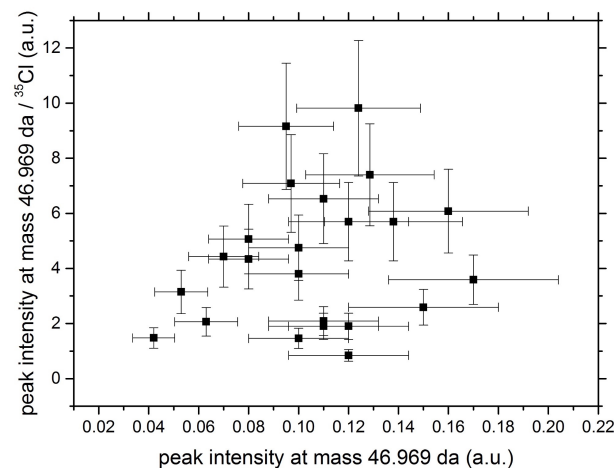


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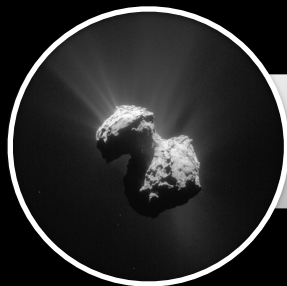
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CH_3Cl (possible precursor of CCl) not detected at that measurement period

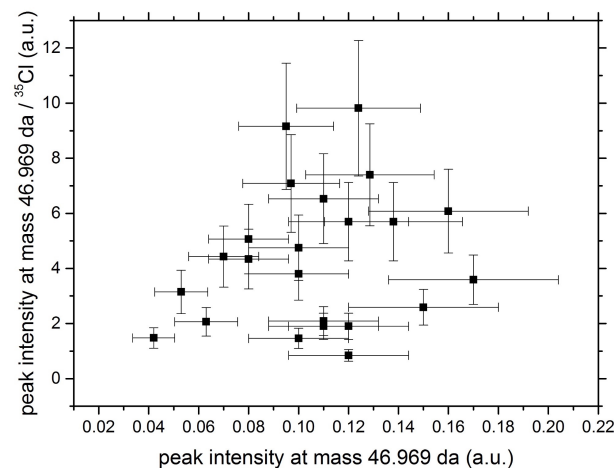


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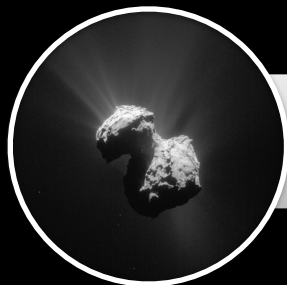
Rivilla et al. (in prep.)

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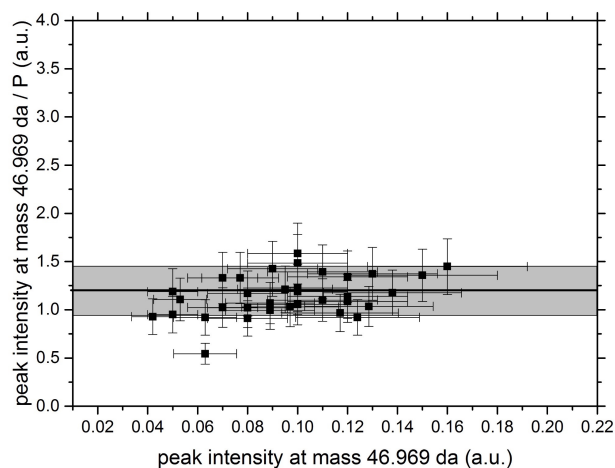


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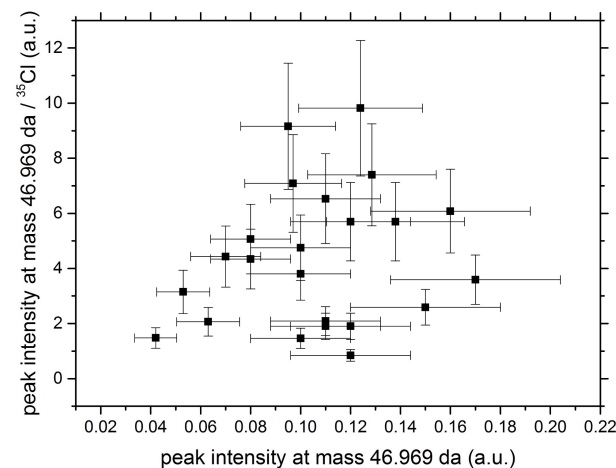
PO?

Correlation with P peak

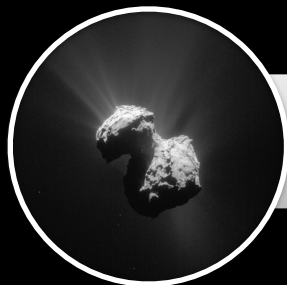


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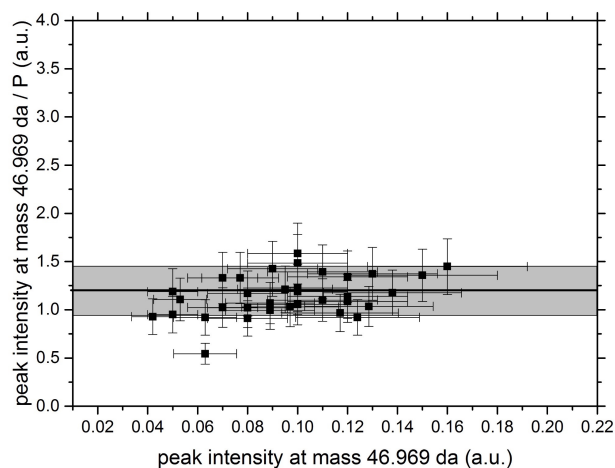


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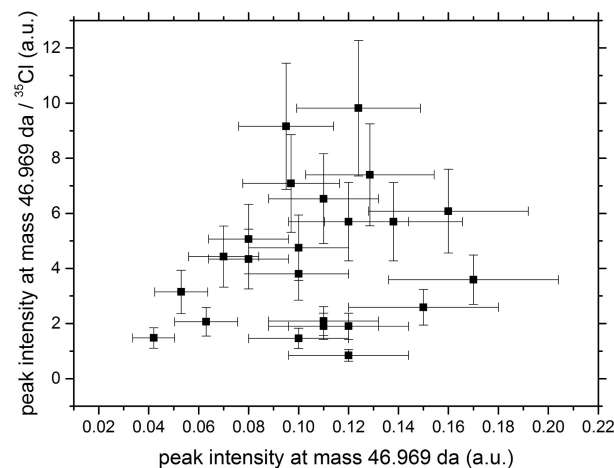
PO?

Correlation with P peak



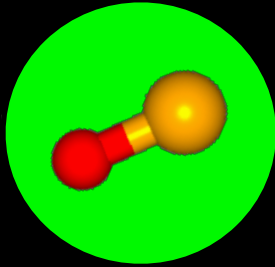
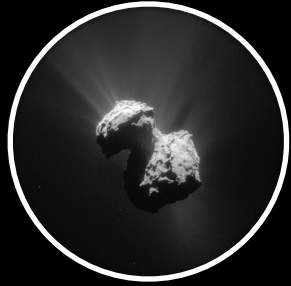
CCI?

No Correlation with ^{35}Cl peak

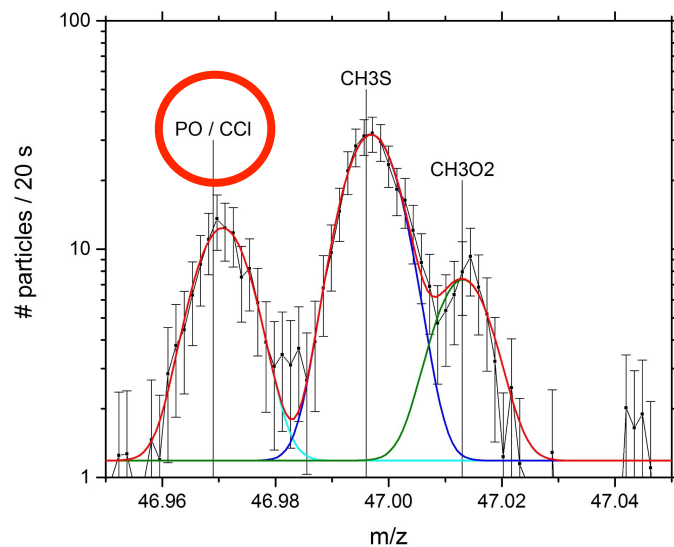


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Phosphorus in 67 P

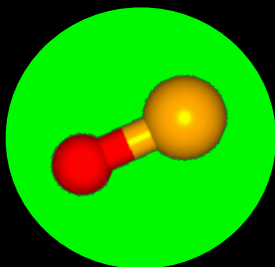
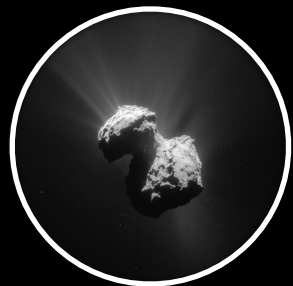


Rivilla et al. (in prep.)

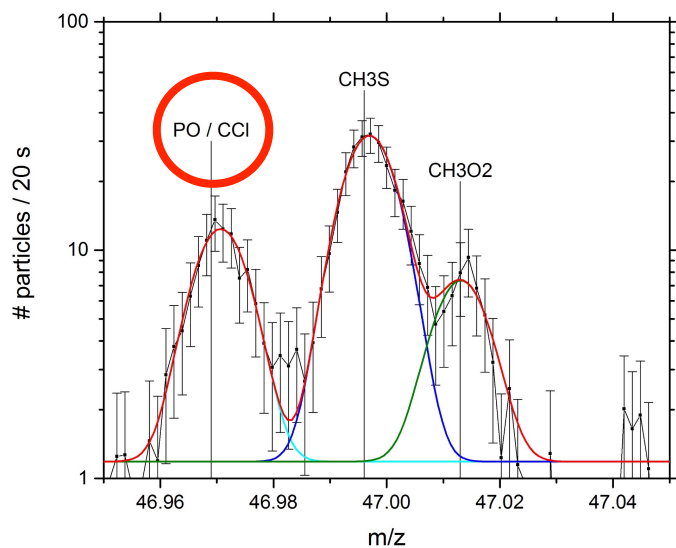


PO is present in the comet.

Phosphorus in 67 P



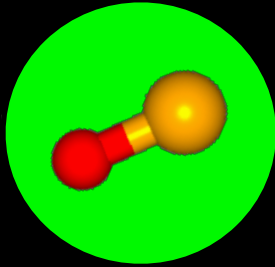
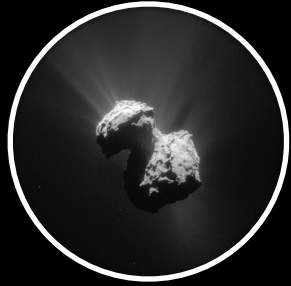
Rivilla et al. (in prep.)



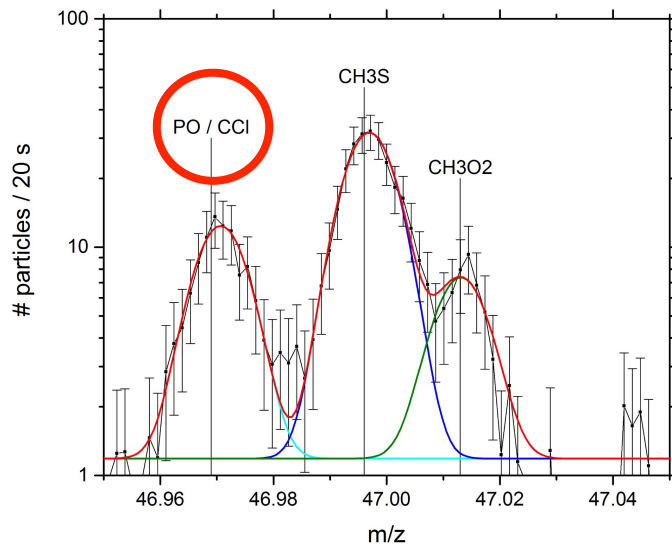
PO is present in the comet.

- Upper limits for PN, PH₃ and CP.

Phosphorus in 67 P



Rivilla et al. (in prep.)

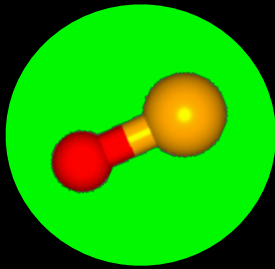
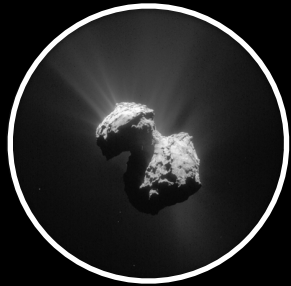


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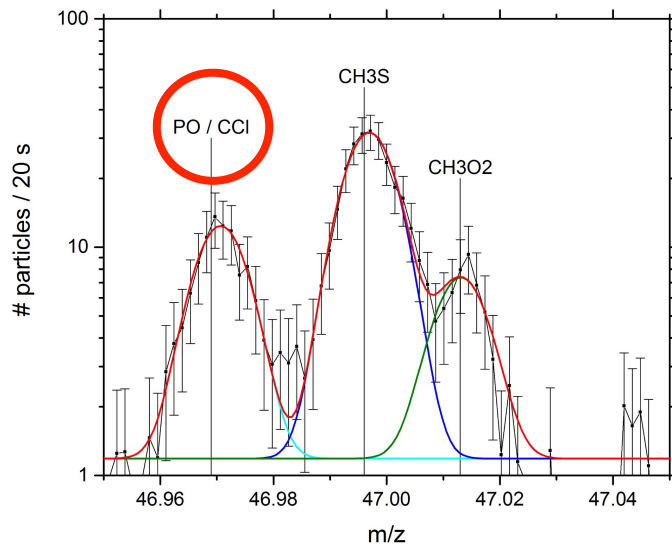
- Upper limits for PN, PH₃ and CP.

$[PO/PN] > 10$

Phosphorus in 67 P



Rivilla et al. (in prep.)



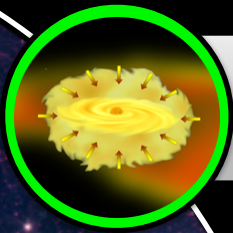
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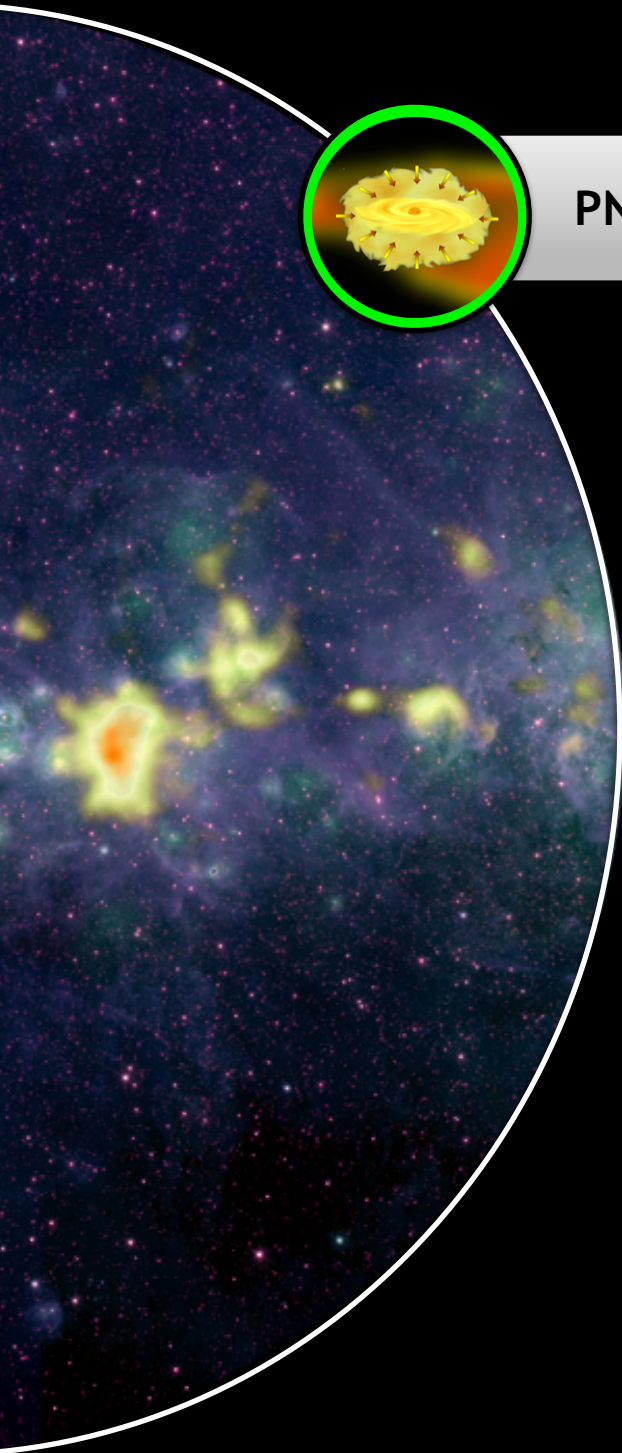
[PO/PN] > 10

PO is more abundant than PN both in star-forming regions and the comet.

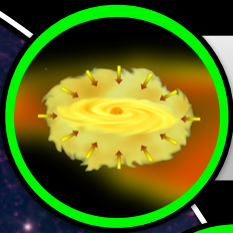
Conclusions



PN detected in a sample of massive dense star-forming cores



Conclusions

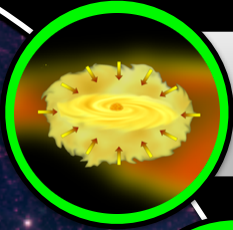


PN detected in a sample of massive dense star-forming cores

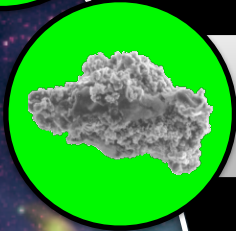


P is less depleted in SF regions than previously thought.

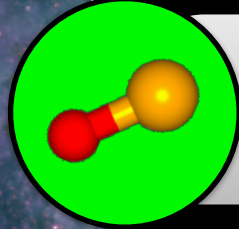
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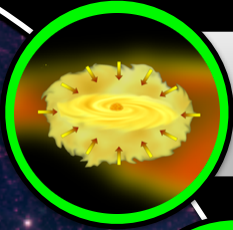


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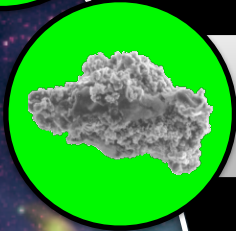


PO detected for the first time in 3 star-forming regions and in a quiescent cloud in the Galactic Center.

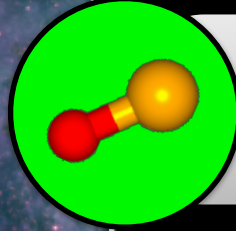
Conclusions



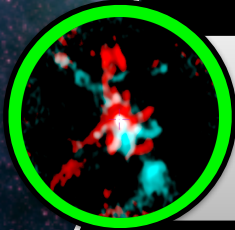
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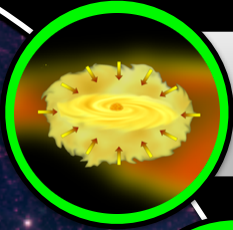


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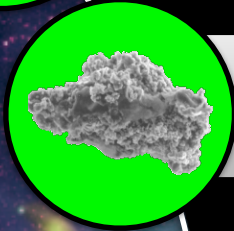


Several observations point towards a shocked origin of P-bearing molecules.

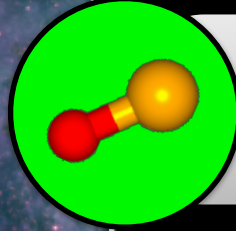
Conclusions



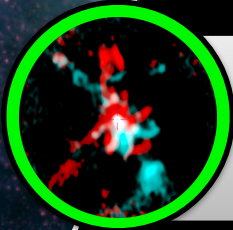
PN detected in a sample of massive dense star-forming cores



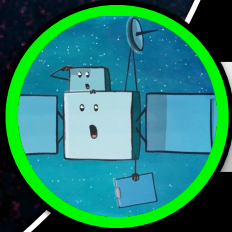
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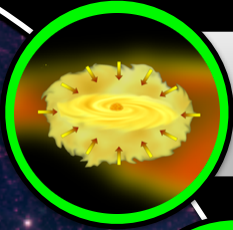


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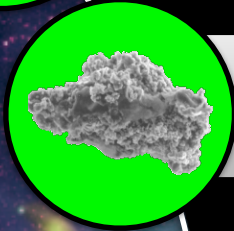


Confirmation of PO in the comet 67-P.

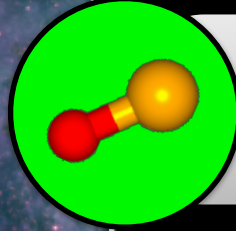
Conclusions



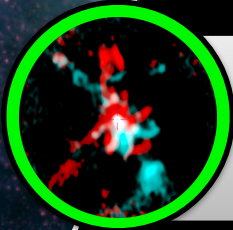
PN detected in a sample of massive dense star-forming cores



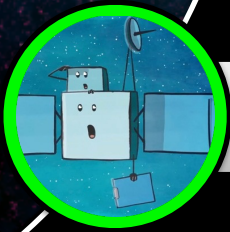
P is less depleted in SF regions than previously thought.



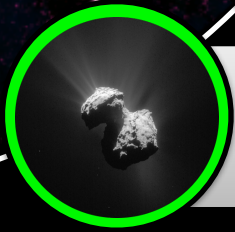
PO detected for the first time in 3 star-forming regions and in a quiescent cloud in the Galactic Center.



Several observations point towards a shocked origin of P-bearing molecules.



Confirmation of PO in the comet 67-P.



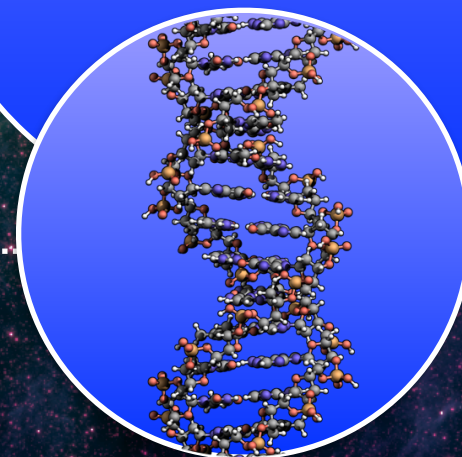
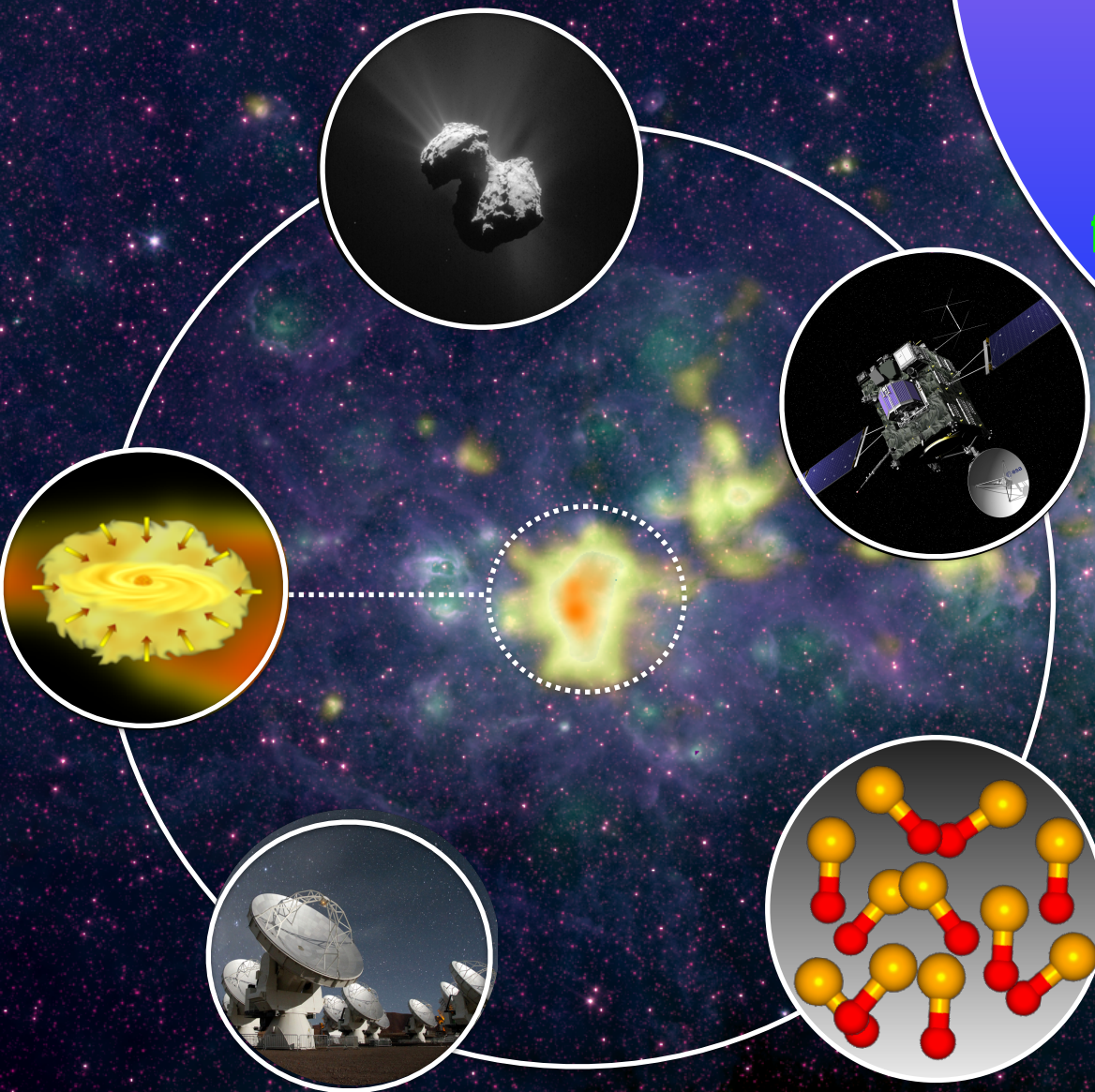
Chemical connection between SF regions and comet:
PO is always more abundant than PN.

Phosphorus:

the missing prebiotic element...
found in star-forming regions and comets

Víctor M. Rivilla

Marie Skłodowska-Curie Fellow
Osservatorio Astrofisico di Arcetri



Nitrogen

F. Fontani, M. Beltrán, P. Caselli, A. Vasyunin, C. Mininni, J. Martín-Pintado, I. Jiménez-Serra, R. Cesaroni, M. Drozdovskaya, K. Altwegg and the ROSINA team...and more



Prebiotic molecules in Space and
Origins of Life on Earth
Bad Honnef, March 19-23 2018

