An Updated Gas/Grain Sulfur Network for Astrochemical Models

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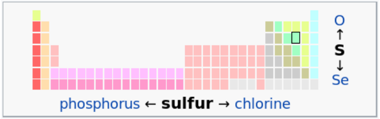
Chemistry of Sulfur

sulfur
16
S
32.065

- Sulfur is heavy, and many important rates $\propto \sqrt{1/mass}$
  - Gas-phase velocity
  - Condensed-phase mobility (migration/reaction/desorption)
- Not quite like oxygen
  - Higher valency → sulfur enjoys company
  - Lower electronegativity → bonds are weaker
  - Many possible oxidation states: **6**, 5, **4**, 3, **2**, 1, −1, **−2**
  - Not a popular laboratory target
- Sulfur has a (relatively) low ionization potential:



Element	Ion. Pot. (eV)
N	14.5
O	13.618
H	13.598
C	11.3
P	10.5
S	**10.4**

Extraterrestrial Sulfur

Species	First Obs.	ISM	Cometary
SH	2012	*	
SH^+	2011	*	
H_2S	1972	*	*
H_2S^+	1984		*
H_3S^+	1990		*
CS	1971	*	*
HCS^+	1981	*	
H_2CS	1973	*	*
NS	1975	*	*
SO	1973	*	*
SO^+	1992	*	
SO_2	1975	*	*
OCS	1971	*	*
S_2	1983		*
S_3	2016		*
S_4	2016		*
C_2S	1987	*	
C_3S	1987	*	
CS_2	2004		*
CH_3SH	1979	*	*
CH_3CH_2SH	2014	* (?)	*
HNCS	1979	*	
HSCN	2009	*	

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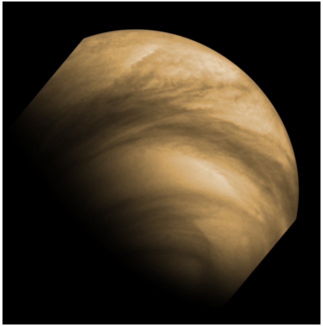


Sulfuric acid (H_2SO_4) on Venus.
Source: *ESA/MPS/DLR/IDA*

Chemical Network - Basics

- Network core is based on Garrod et al. 2008 (i.e. the "OSU gas/grain network")
- $E_{binding}$ for O & NH_3 modified
- Minor updates to thermochemistry via recent *ab initio* calcs
- Important updates/additions to photochemistry for low-A_v
  - Photodesorption (Öberg et al. 2009; Hollenbach et al. 2009)
  - Photodissociation/photoionization cross sections (Heays et al. 2017)

Chemical Network - Sulfur

- Sulfur network greatly updated/expanded via literature
- All interstellar species are now included, except CH_3CH_2SH
- Thermochemistry for allotropes rearranged
- Expanded oxidation routes on grain

Sulfur species*

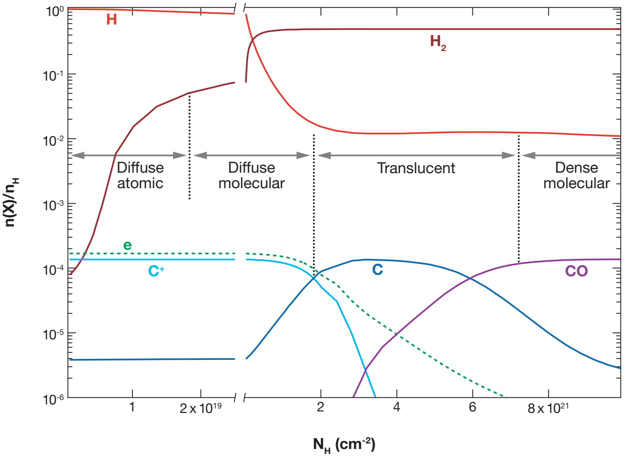
SH	SH^+		
H_2S	H_2S^+	$H_2S(H^+)$	
H_2S_2	$H_2S_2{}^+$	$H_2S_2(H^+)$	
CS	CS^+	HCS	$CS(H^+)$
H_2CS	H_2CS^+	$H_2CS(H^+)$	
C_2S	C_2S^+	**HC_2S**	$C_2S(H^+)$
C_3S	C_3S^+	**HC_3S**	$C_3S(H^+)$
C_4S	C_4S^+	$C_4S(H^+)$	
CH_3SH	**$CH_3SH(H^+)$**	**CH_2SH**	**CH_3S**
CS_2	**$CS_2{}^+$**	**CS_2H**	**$CS_2(H^+)$**
$HCSSH$	**$HCSSH^+$**	**$HCSSH(H^+)$**	
NS	NS^+	$NS(H^+)$	
$HNCS$	**$HNCS(H^+)$**	**$(H^+)HNCS$**	**NH_2CS**
$HSCN$	**$HSCN(H^+)$**		
$HCNS$	**$HCNS(H^+)$**	**$(H^+)HCNS$**	
NH_2CHS	**$NH_2CHS(H^+)$**	**NH_2CH_2SH**	**$NH_3CH_2SH^+$**
SO	SO^+	**HSO**	$SO(H^+)$
SO_2	$SO_2{}^+$	$SO_2(H^+)$	$SO_2(H^+)$
OCS	OCS^+	$OCS(H^+)$	$HOCS(H^+)$
$S_{2\text{-}8}$	S_2H	$S_2(H^+)$	
SiS	SiS^+	$SiS(H^+)$	

*bold entries are new to OSU gas/grain network

Physical Model

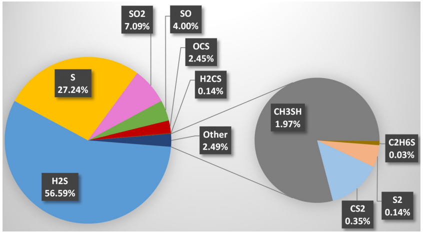
- 3 stages trace cloud history
- Physical conditions are based on Snow & McCall, *Annu. Rev. Astro. Astrophys.*, **2006**

	Stage 1	Stage 2	Stage 3
Classification	Diffuse	Translucent	Dark/Dense
Density (cm^{-3})	100	1000	10^4 – 10^6
A_V	0.5	1.6	10
T_{gas} (K)	100	25	10
T_{dust} (K)	15	15	10
$f_0^n(H_2)$	0.01%	98%	99%
Init. Abund. (K)	Cosmic	–	–
Time (yr)	10^7	10^6	10^6

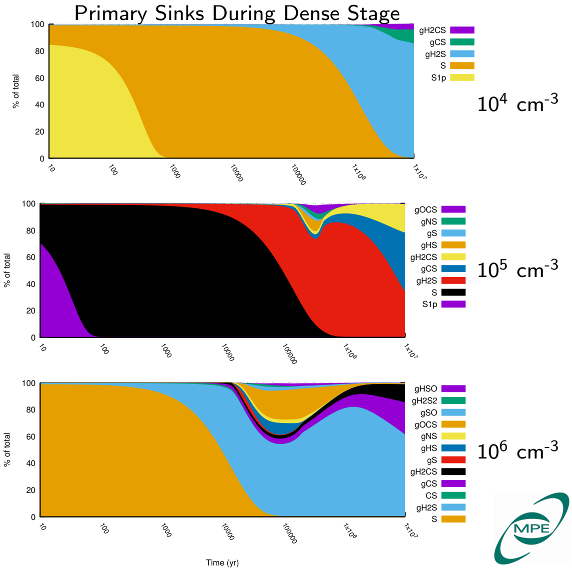


Primary Sulfur Budget

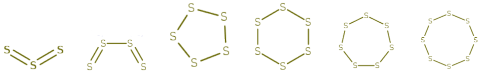
- Sulfur depletes out of gas phase **near free-fall time limit** and at **high densities**
- Majority of the sulfur budget is trapped in ices
- The usual suspects remain top sinks: CS, H_2S, OCS, SO, SO_2



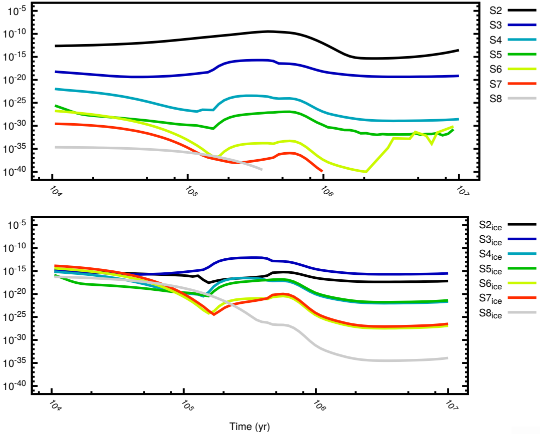
Sulfur budget on comet 67P/Churyumov–Gerasimenko via *Rosetta*/ROSINA. (Calmonte et al. 2016)



Sulfur Allotropes (pure chains/rings)



- $S_{2\text{-}4}$ form much faster than $S_{5\text{-}8}$
- $E_{bind} \propto S_n$
  → unfavorable grain rates at 10 K
- Under interstellar conditions, S_2 dominates
  → opposite to terrestrial behavior
- S_2 has magnetic dipole moment



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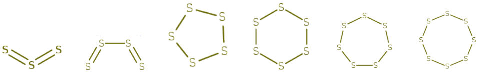

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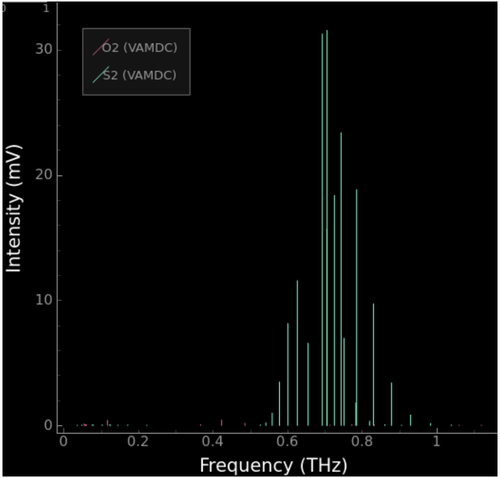
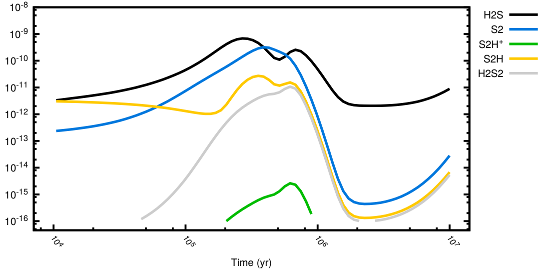


Hydrogenated Species

- Gas-phase abundances are not predicted to be significant
- Upper limits toward IRAS 16293-2422 suggested by Martín-Doménech et al. (2016) are within reasonable agreement



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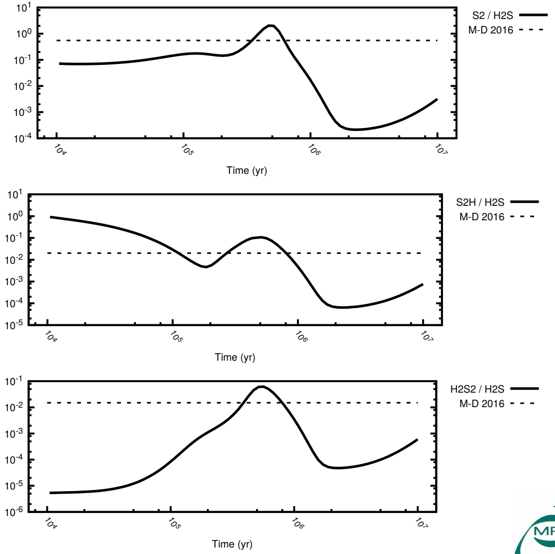

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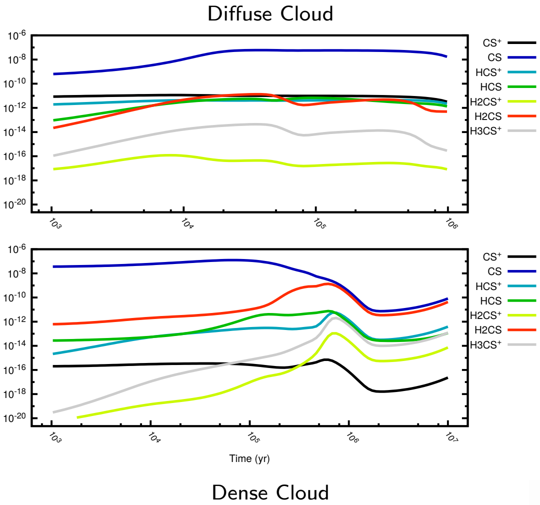
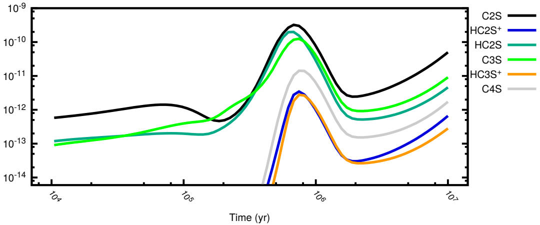
CS, H_2CS & company

- CS has a significant abundances (ice & gas) in translucent & dense clouds
- HCS & H_2CS only become important in denser phase



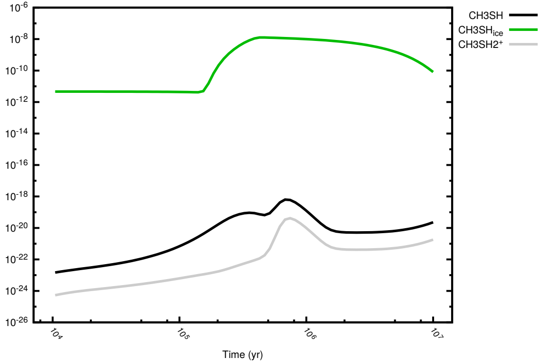
C_nS Chains

- C_2S & HC_2S^+ reach non-negligible gas-phase abundances
- Hydrogenated species are **good targets for lab + obs** (even the cations)



CH_3SH

- Formation routes are similar to methanol (CH_3OH)
  - gas-phase (ineffi105cient):
    $CH_3^+ + H_2S \longrightarrow CH_3SH(H^+) + h\nu$
    $CH_3SH(H^+) + e^- \longrightarrow CH_3SH + H$
  - grain surface:
    $S + CH_3 \longrightarrow CH_3S$
    $SH + CH_2 \longrightarrow CH_2SH$
    $CH_3S/CH_2SH + H \longrightarrow CH_3SH$
- Gas-phase abundances are negligble
- Model predicts near-cometary abundances



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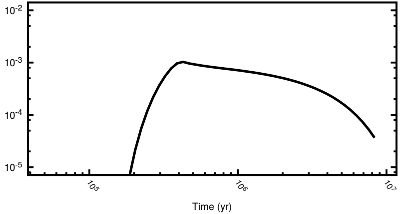
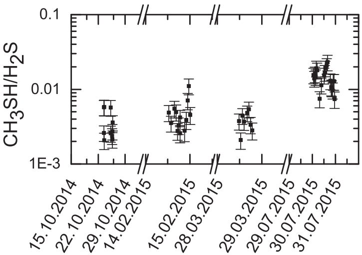
Dense cloud CH_3SH / H_2S ratio



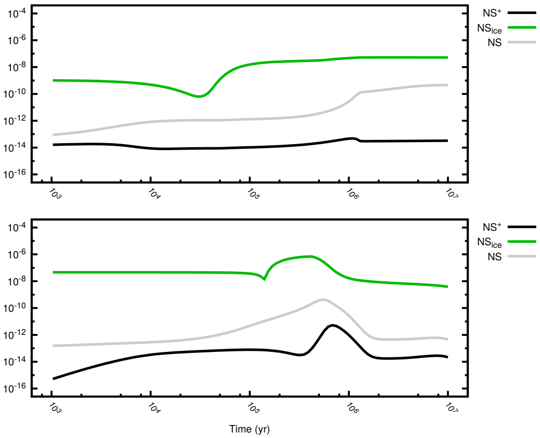


Multiple epochs of 67P (Calmonte et al. 2016)

N-bearing Species

- NS_{ice} is nearly constant during/after translucent stage
- NS^+ is closed-shell cation $\rightarrow$ **good target for lab + obs**
- HCNS isomeric family is not yet finished
- NH_xCH_yS do not reach appreciable abundances

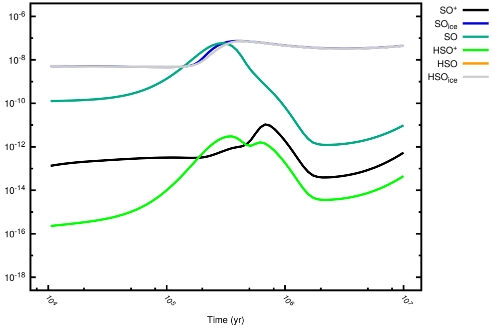
Diffuse Cloud



Dense Cloud

Oxygenated Species

- SO is important in both gas & ice, in translucent & dense clouds
- SO_2 is important in both phases in dense clouds
  - gas-phase:
    $O + SO \longrightarrow SO_2 + h\nu$
  - grain:
    $O_2 + SO \longrightarrow O + SO_2$
- OCS is most important O-bearing species in dense ice
  - gas-phase:
    $S + HCO \longrightarrow H + OCS$
    $O + HCS \longrightarrow OCS + H$
    $OH + CS \longrightarrow H + OCS$
  - grain:
    $S + gCO \longrightarrow gOCS$
    $CS + gO_2 \longrightarrow gOCS + gO$



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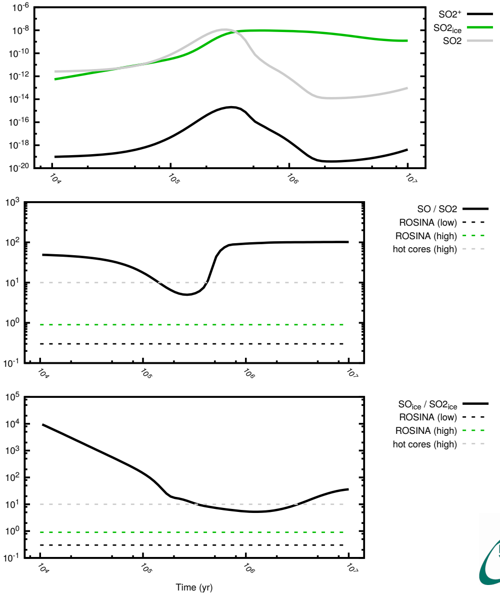

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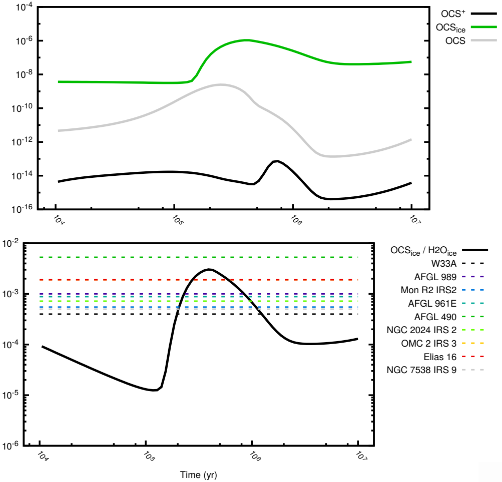
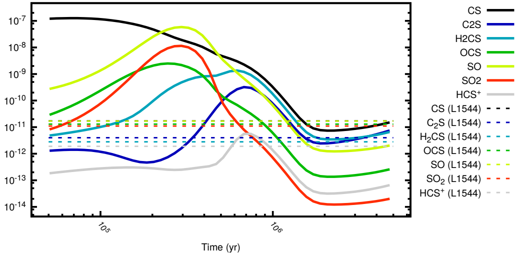
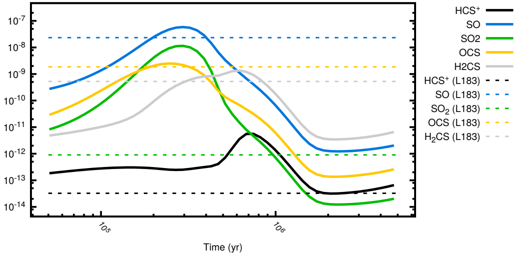


Is there hope?

L1544 vs model (Spezzano, *priv. comm.*)



L183 vs model (Lattanzi, *priv. comm.*) (**WF06**)



- Some environments are not consistent
- Modeling non-equilibrium chemistry proves challenging. . .

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- Observers:
  Silvia Spezzano
  Valerio Lattanzi (**WF06**)
- Modeling:
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  Anton Vasyunin
- Lab Spec:
  Domenico Prudenzano (**TF04**)

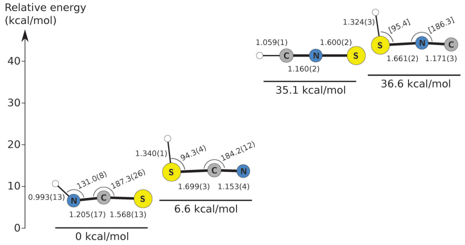
Mike McCarthy (CfA)

Maria Palumbo (INAF, Catania)

Thanks!

HCNS Isomeric Family

- Thermodynamic stabilities not sig. wrt. ice kinetics
  $CH_2 + NS \longrightarrow HCNS + H$
  $N + HCS \longrightarrow HNCS/HSCN$
- HSCN missing efficient gas formation
  $S + H_2CN \longrightarrow H + HCNS$
  $NH_2 + CS \longrightarrow HNCS + H$
  $H_2S^+ + HNC \longrightarrow HNCSH^+$
  $HNCSH^+ + e^- \longrightarrow HSCN + H$



Relative energies of HNCS isomers. (McGuire et al. 2016)