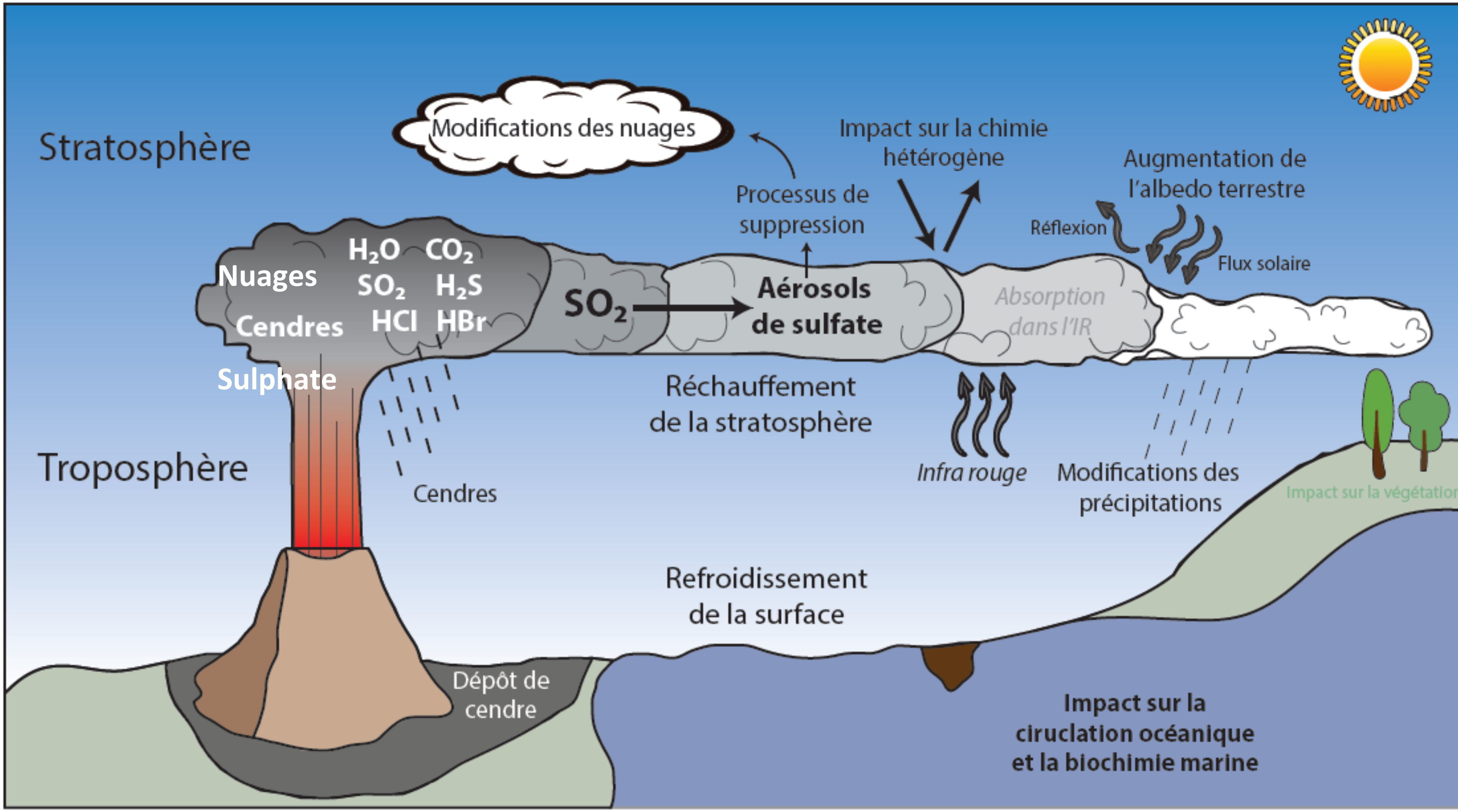
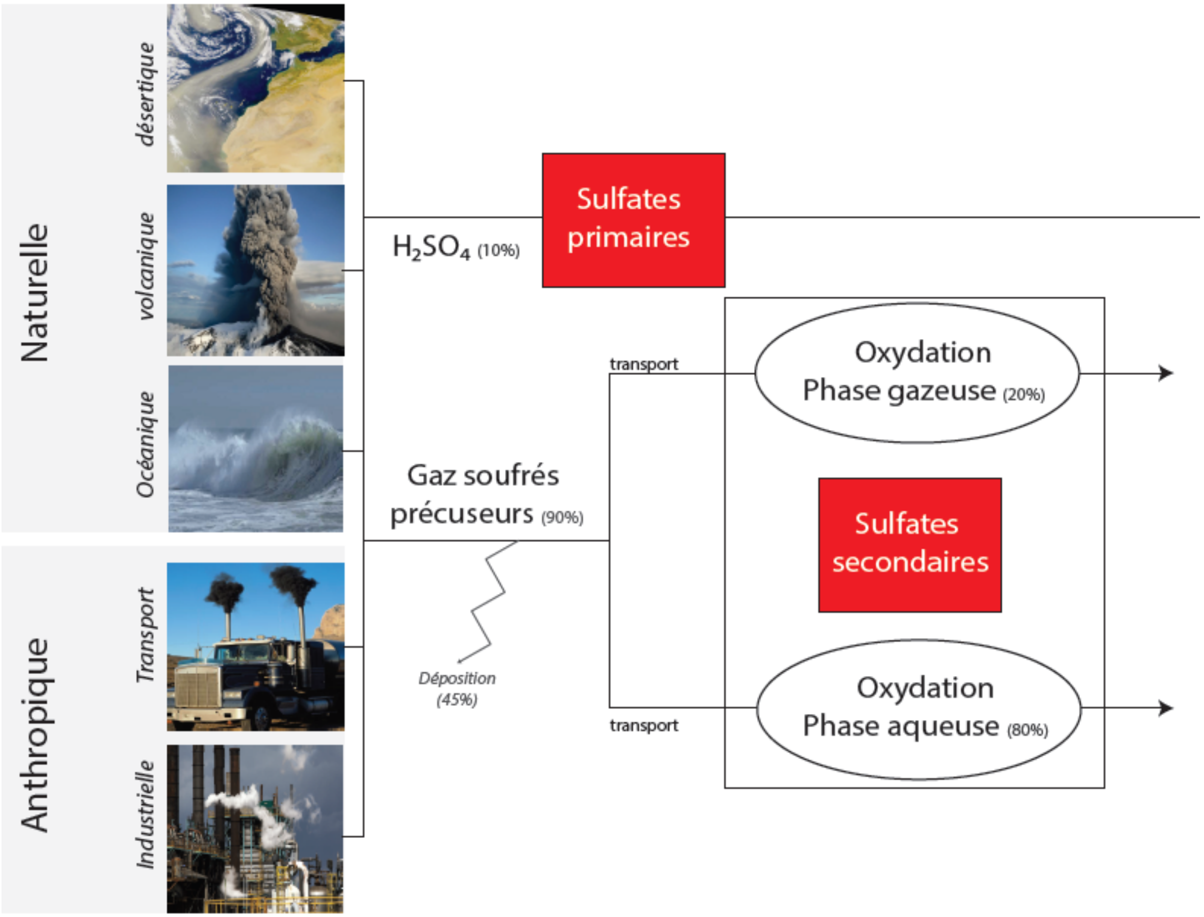
Tommaso Galeazzo

Photochemical box-modelling of volcanic sulphur oxidation: isotopic constraints

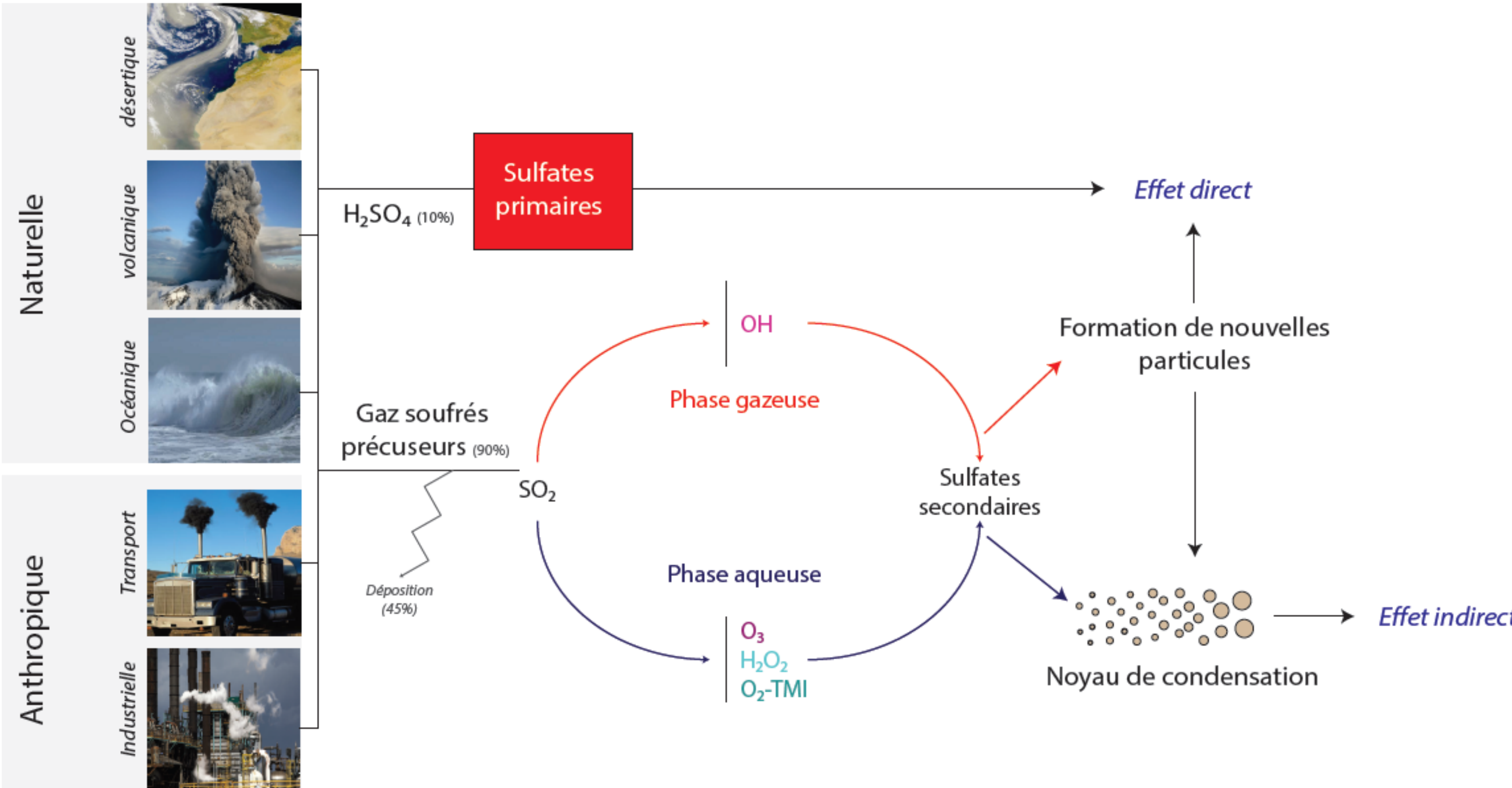
Directeurs de thèse
Slimane Bekki
Erwan Martin


Stratosphère
Modifications des nuages
Impact sur la chimie hétérogène
Augmentation de l'albedo terrestre
Processus de suppression
Réflexion
Flux solaire
Nuages
Cendres
Sulphate
H₂O CO₂ SO₂ H₂S HCl HBr
SO₂
Aérosols de sulfate
Absorption dans l'IR
Réchauffement de la stratosphère
Troposphère
Cendres
Infra rouge
Modifications des précipitations
Impact sur la végétation
Refroidissement de la surface
Dépôt de cendre
Impact sur la ciruclation océanique et la biochimie marine

Sulfate atmosphériques : Origine & transformations



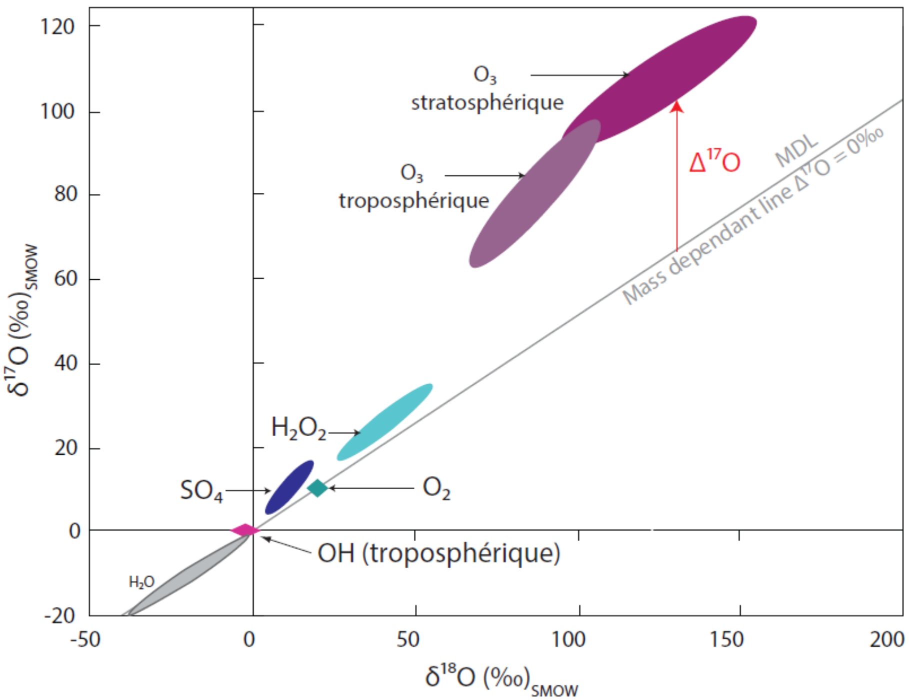
Formation des sulfates secondaires = fonction des oxydants

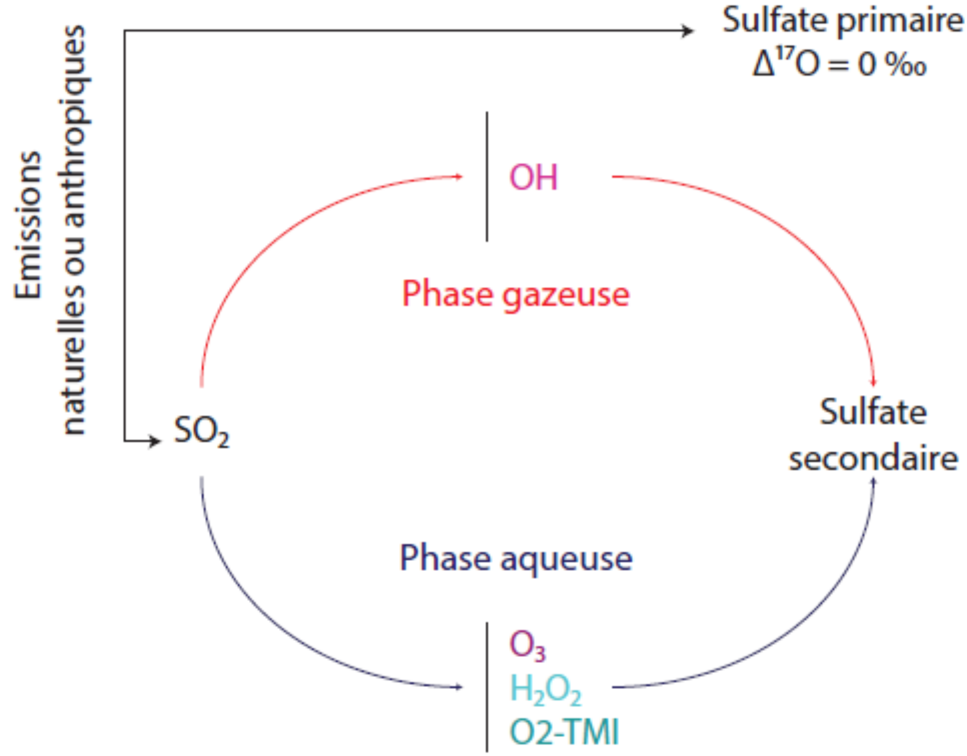


Composition (isotopique!) du sulfate :

- **Sulfates primaires vs sulfates secondaires**
- **Chemins d'oxydation**

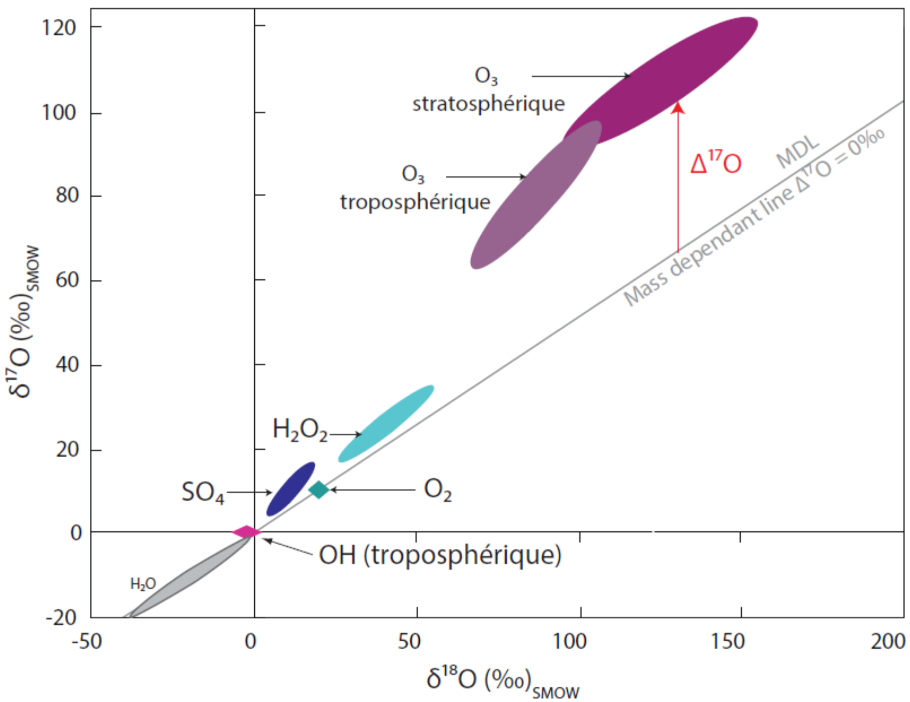
Isotopie : transfert de l'anomalie isotopique

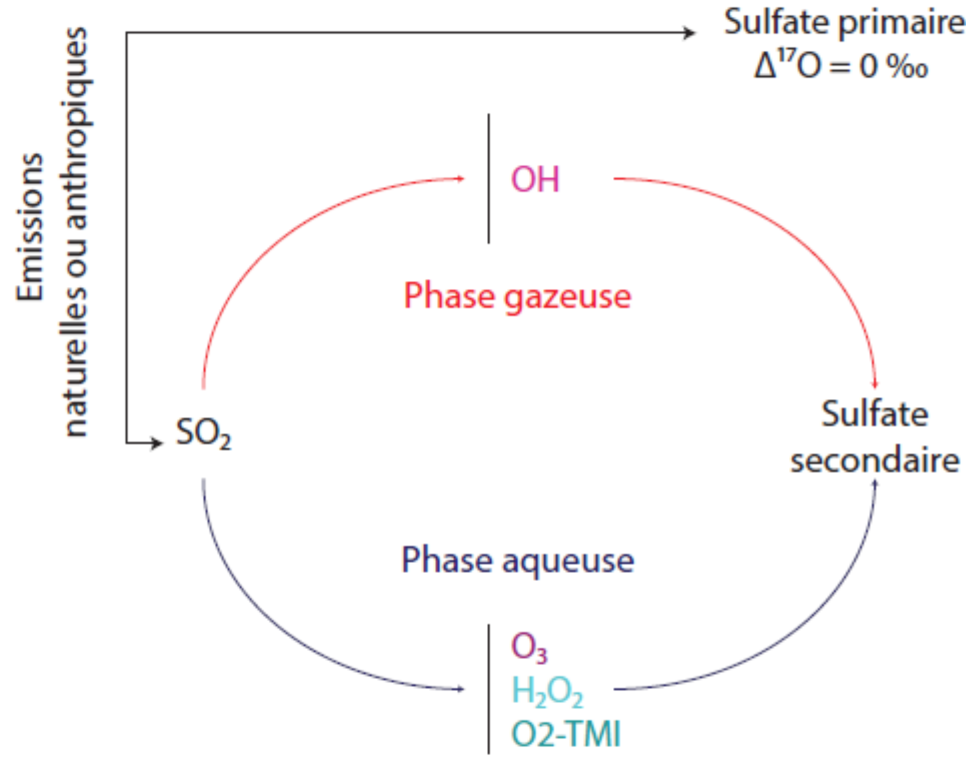




$\Delta^{17}O\ (SO_4^{2-})$	
OH	0 ‰
O_3	8.8 ‰
H_2O_2	0.75 ‰
O_2-TMI	-0.09%

Isotopie : transfert de l'anomalie isotopique



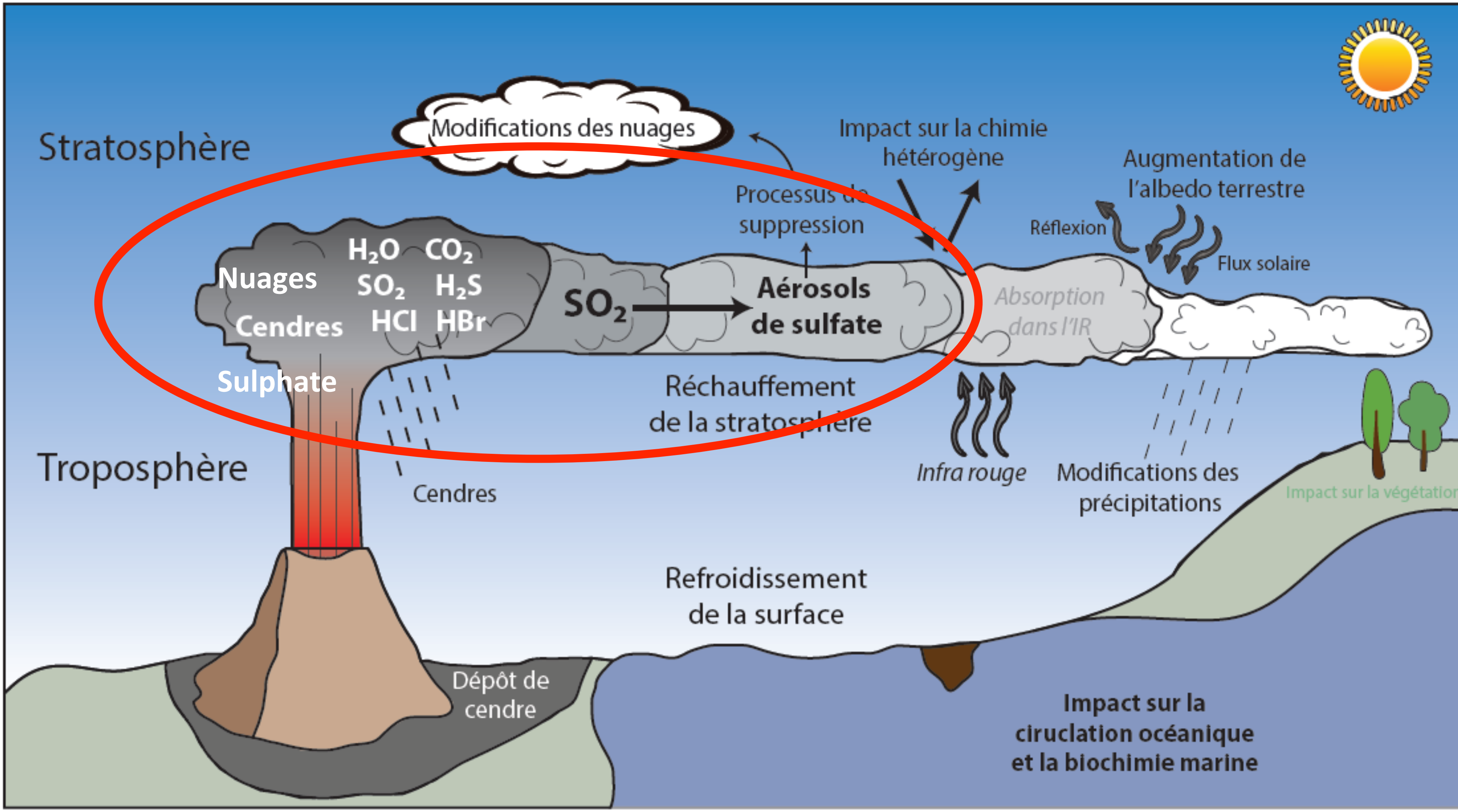


Secondaire:

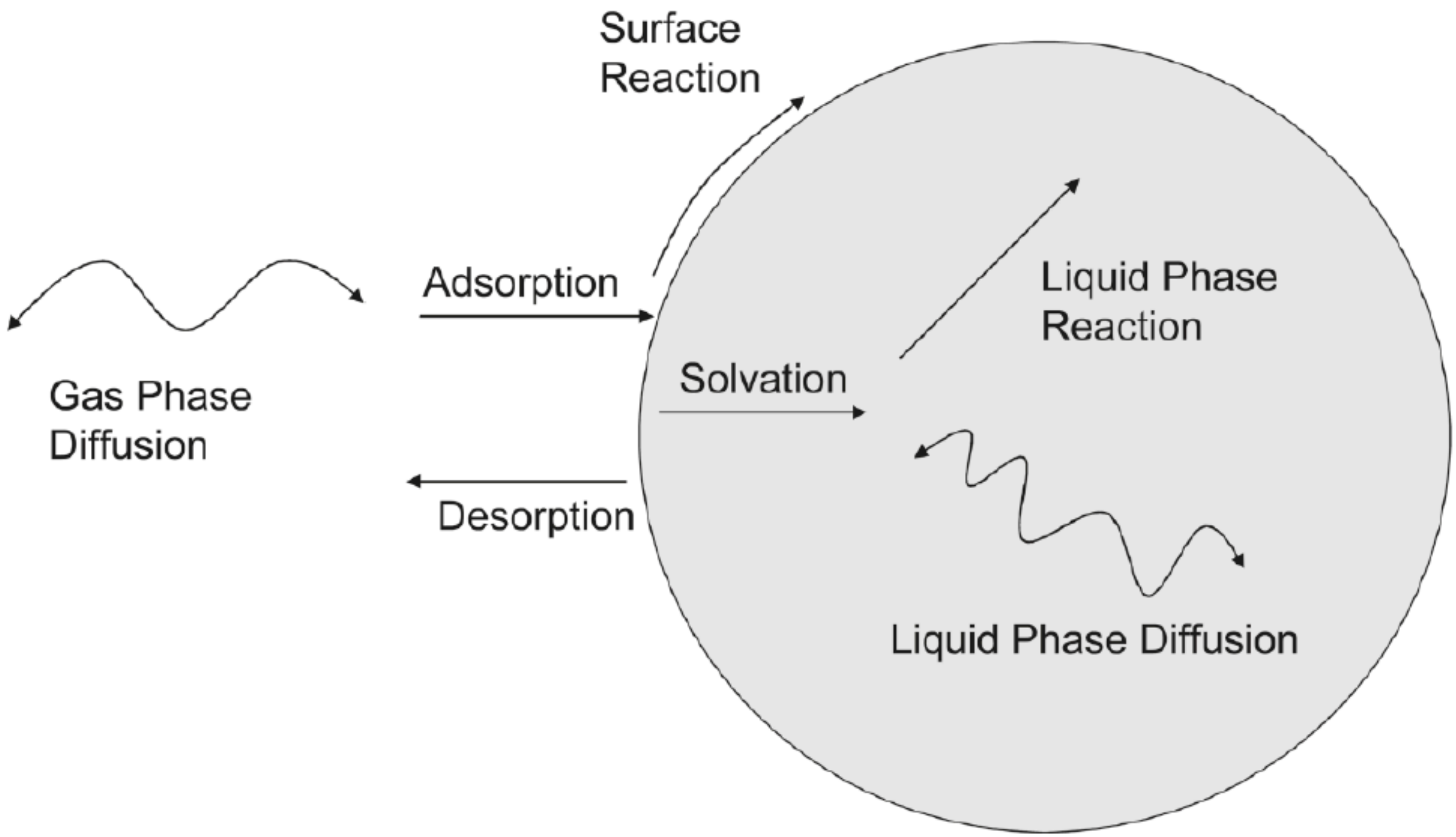
$$\Delta^{17}O\ (\text{sulfate}) = f_{OH} \times \Delta^{17}O_{OH} + f_{H2O2} \times \Delta^{17}O_{H2O2} + f_{O3} \times \Delta^{17}O_{O3} + f_{O2} \times \Delta^{17}O_{O2}$$

	$\Delta^{17}O\ (SO_4^{2-})$
OH	0 ‰
O_3	8.8 ‰
H_2O_2	0.75 ‰
O_2-TMI	-0.09%

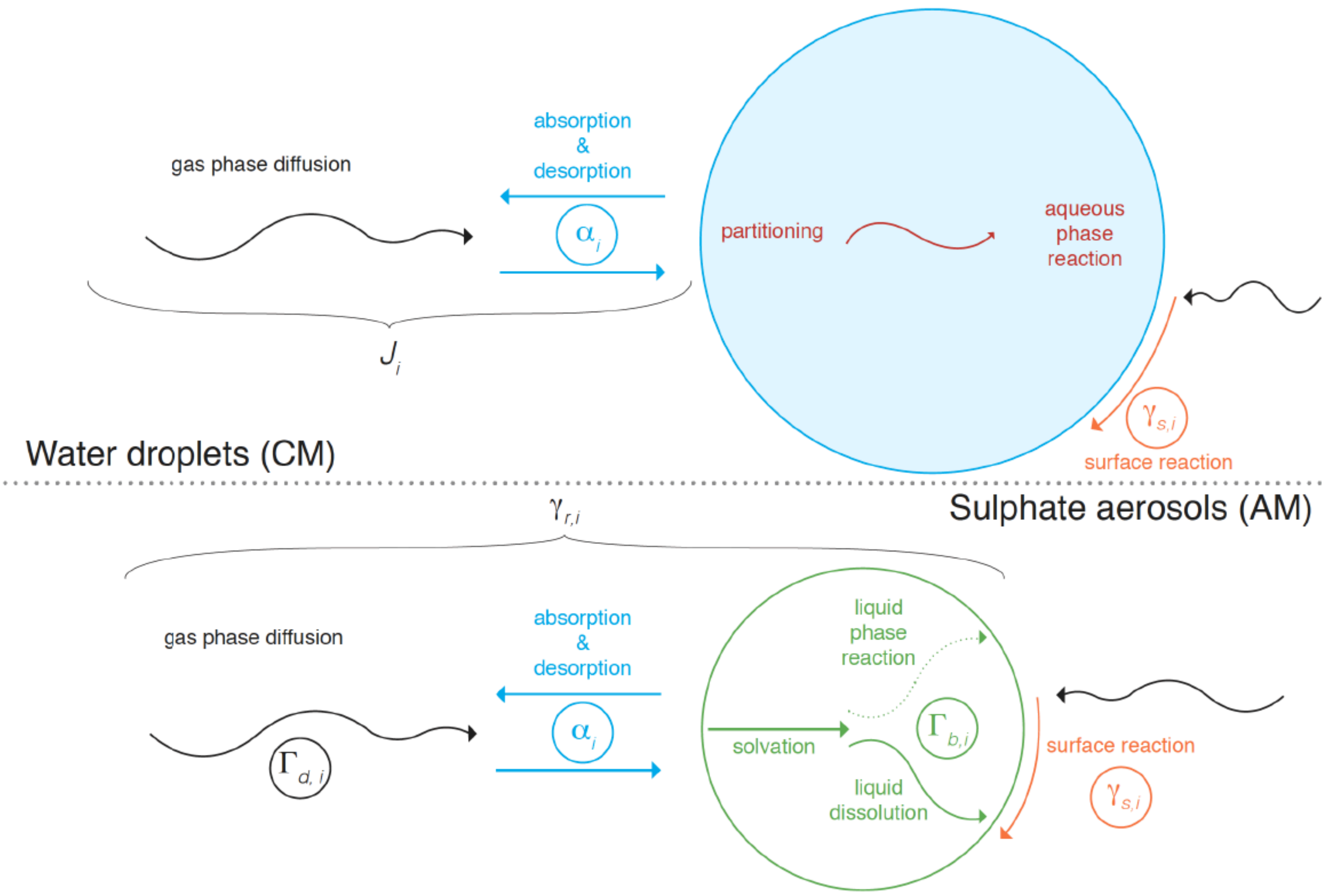
Oxydation du soufre: en phase gazeuse + phases condensées (eau, sulfate)



HETEROGENEOUS CHEMISTRY: FRAMEWORK



HETEROGENEOUS (MULTIPHASIC) CHEMISTRY IN A VOLCANIC PLUME



GAS-PHASE DIFFUSION

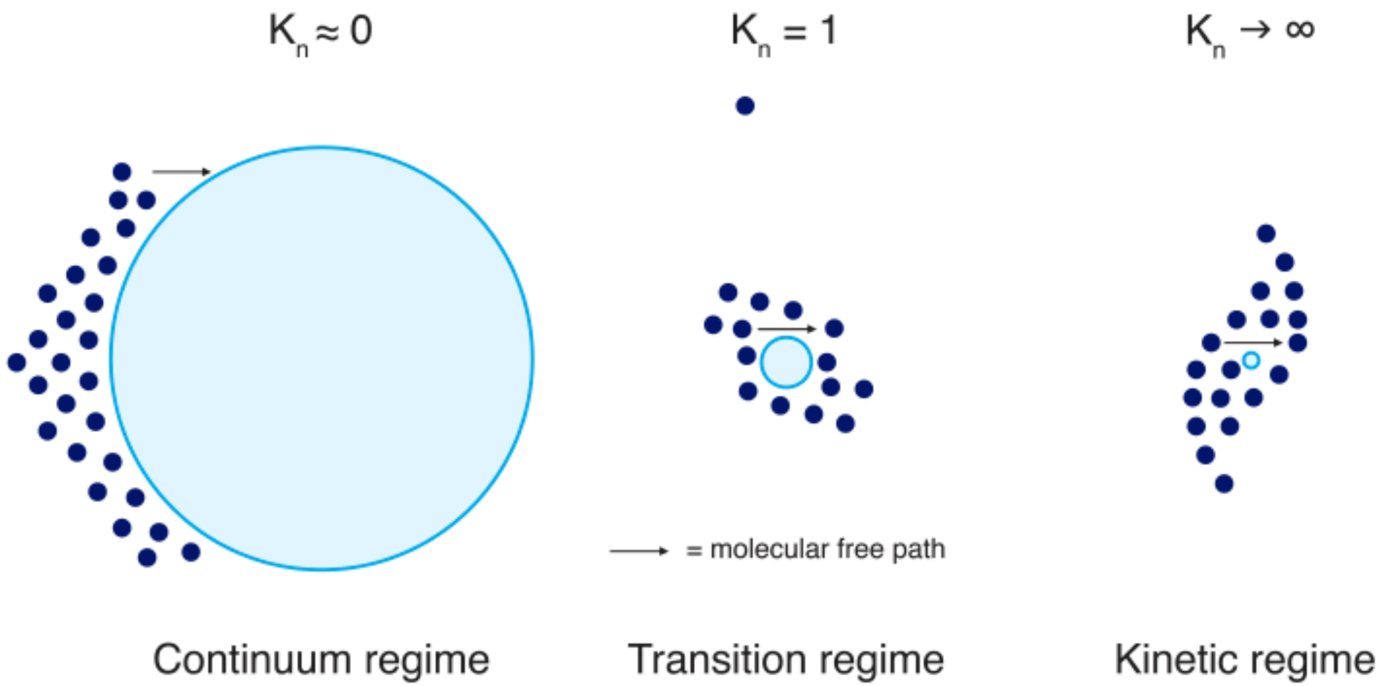


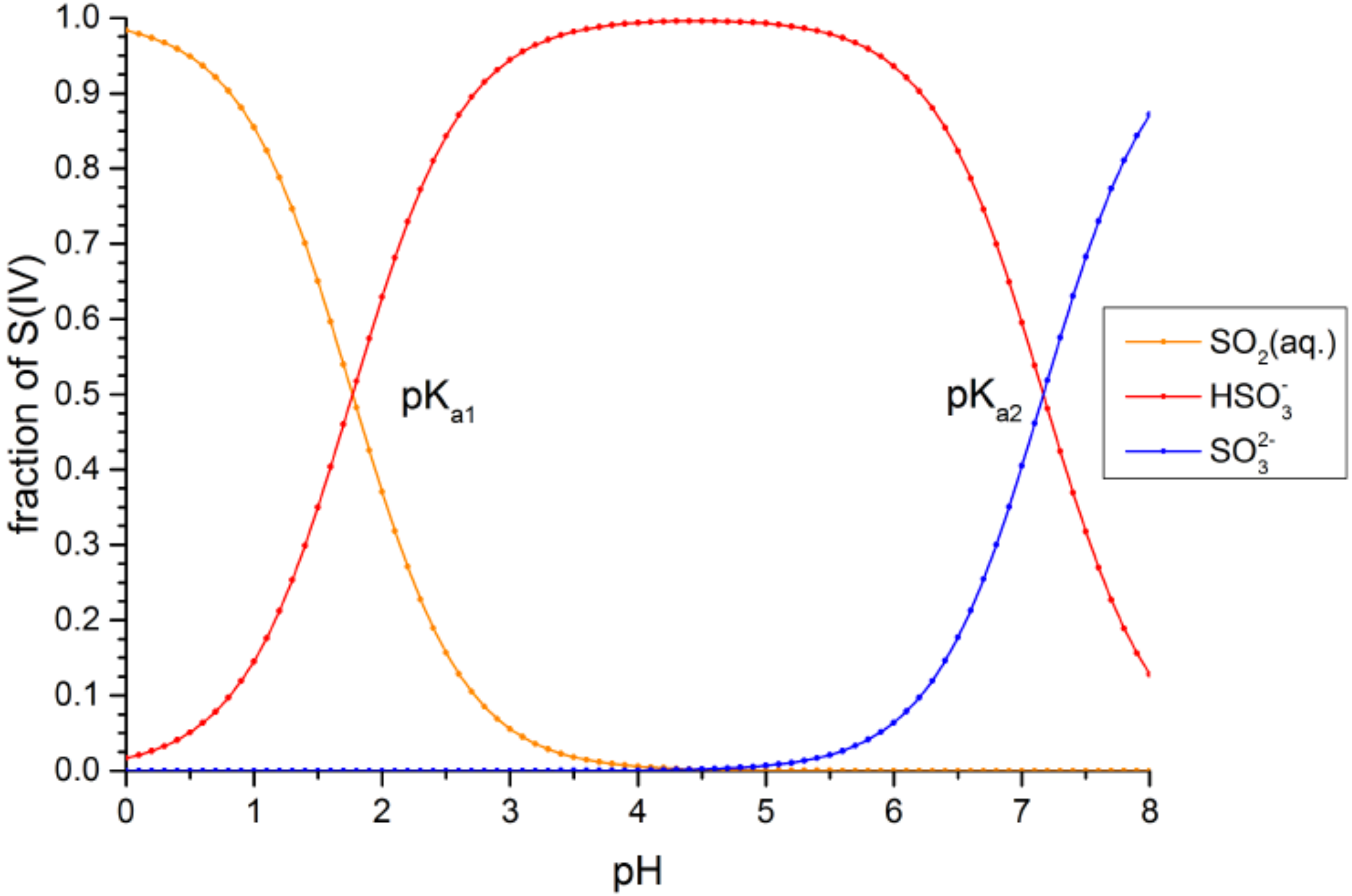
Table 1. Sulfur aqueous equilibria

Equilibrium	K (M^{-1}),	$k_{298(forward)}$ ($M^{-1}s^{-1}$),	E_a/R (K),	$k_{298(back)}$ ($M^{-2}s^{-1}$),
$SO_{2(aq.)} + H_2O \rightleftharpoons HSO_3^- + H_3O^+$	$3.13 \cdot 10^{-4}$	$6.27 \cdot 10^4$	-1940	$2 \cdot 10^8$ [a,c]
$HSO_3^- + H_2O \rightleftharpoons SO_3^{2-} + H_3O^+$	$6.22 \cdot 10^{-8}$	3110	-1960	$5 \cdot 10^{10}$ [a,c]
$H_2SO_4 + H_2O \rightarrow HSO_4^- + H_3O^+$		∞		
$HSO_4^- + H_2O \rightleftharpoons SO_4^{2-} + H_3O^+$	$1.02 \cdot 10^{-2}$	$1.02 \cdot 10^9$	-2700	$1 \cdot 10^{11}$ [b,c]

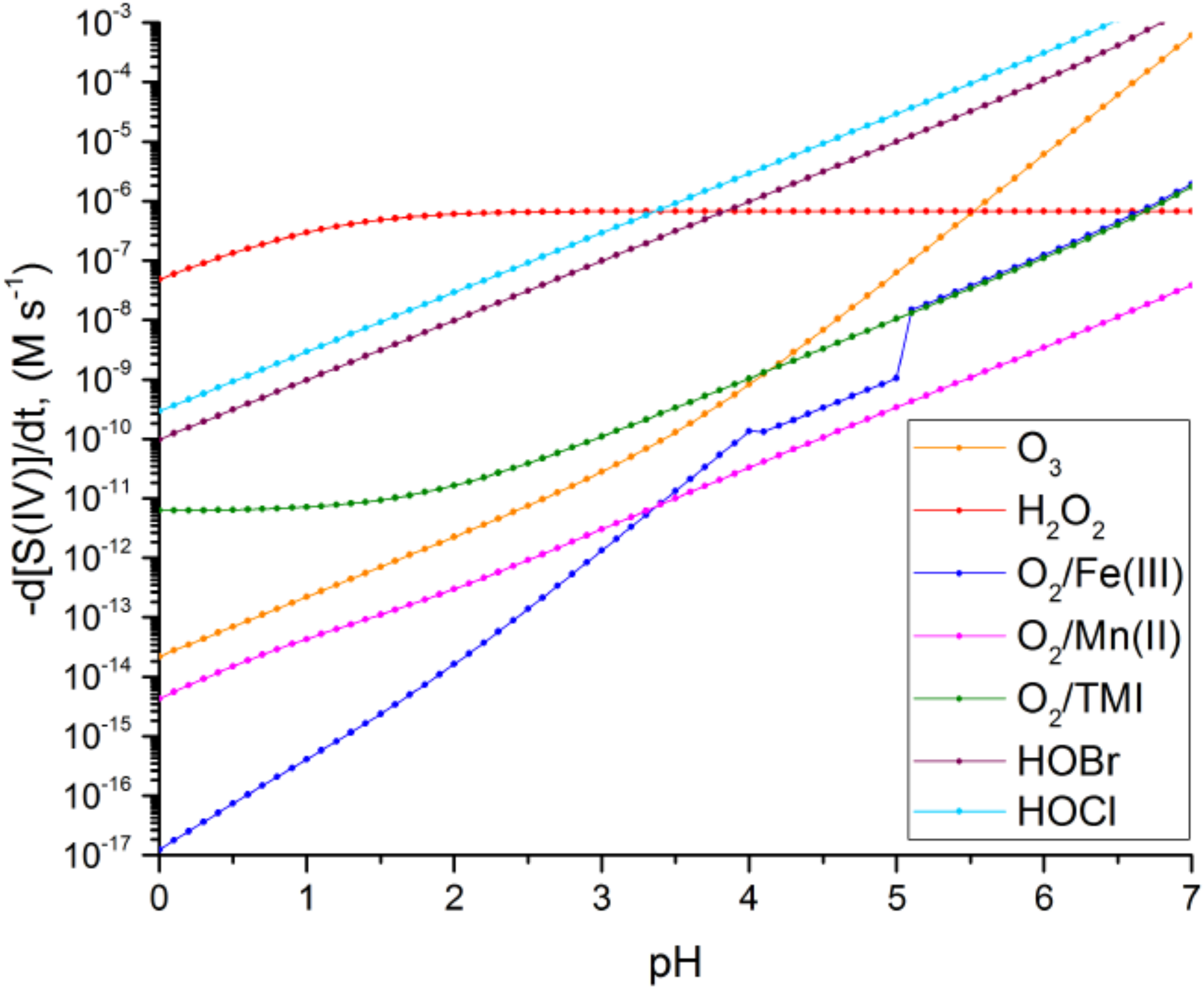
Table 2. Sulfur chemistry scheme

Gaseous reaction	k	units
$SO_2 + OH + M \rightarrow HOSO_2 + M$	$4.62 \cdot 10^{-31} \cdot (T/298.0)^{-3.90}$	$cm^6 molecule^{-2} s^{-1}$ [a]
$HOSO_2 + O_2 \rightarrow HO_2 + SO_3$	$1.30 \cdot 10^{-12} \cdot (-330/T)^{-3.90}$	$cm^3 molecule^{-1} s^{-1}$ [a]
$SO_3 + H_2O \rightarrow H_2SO_4$	$9.10 x 10^{-13}$	$cm^3 molecule^{-1} s^{-1}$ [a]
Aqueous oxidation reaction	**k(aq)**	**units; (T)**
$SO_2 \cdot H_2O + O_3 \rightarrow S(VI) + O_2$	$2.4 x 10^4$	Ms^{-1} [b]
$HSO_3^- + O_3 \rightarrow S(VI) + O_2$	$3.7 x 10^5$	Ms^{-1} [b]
$SO_3^{2-} + O_3 \rightarrow S(VI) + O_2$	$1.5 x 10^9$	Ms^{-1} [b]
$HSO_3^- + H_2O_2 \rightarrow HSO_3^- + H_2O$	$\frac{k_{H_2O_2} \cdot [H^+]}{1 + K_{(eq.)} \cdot [H^+]}$	Ms^{-1} [b]
	with $K_{(eq.)}$ = 13	M^{-1} [b]
	and $k_{H_2O_2}$ = $7.5 x 10^7$	$M^{-2} s^{-1}$ [b]
$S(IV) + \frac{1}{2} O_2 \xrightarrow{TMI} S(VI)$	750 [Mn(II)] + 2600[Fe(III)] + $1.0 x 10^{10}$[Mn(II)][Fe(III)]	s^{-1} [c]

ACIDITY OF WATER DROPLETS: PROGNOSTIC VARIABLE



PH DEPENDENCY OF SULPHUR OXIDATION



SULPHUR OXIDATION BY OH: ISOTOPIC SIGNATURE

$$\Delta^{17}O(OH) = x \cdot \Delta^{17}O(OH^*_{prod.})$$

$$\Delta^{17}O(OH^*_{prod.}) = \frac{1}{2} \cdot \Delta^{17}O(O_3{}^*)$$

~36°%

$$x = \frac{D}{D + k^*_{OH+H_2O} \cdot [H_2O]}$$

$$D = k_{OH+CO} \cdot [CO] + k_{OH+CH_4} \cdot [CH_4] + k_{OH+SO_2} \cdot [SO_2]$$

The mean O-MIF of OH ($\Delta^{17}O(OH)$) is determined by this x variable. If OH chemical loss is much faster than the isotopic exchange, $\Delta^{17}O(OH) = 0.5 \cdot \Delta^{17}O(O_3^*)$. If chemical loss is much slower than the isotopic exchange, $\Delta^{17}O(OH) = 0.0$ ‰.

ΔOH = de 0 à 18°%

S OXIDATION BY OZONE, H2O2 AND O2/TMI: ISOTOPIC SIGNATURE

$$\Delta^{17}O(S(VI))_{O_3+SO_2} = \frac{1}{4} \cdot \Delta^{17}O(O_3^*)$$

△O3 ~ 9°%

$$\Delta^{17}O(S(VI))_{H_2O_2+SO_2} = \frac{1}{2} \cdot \Delta^{17}O(H_2O_2)$$

△H2O2 ~ 0.9 °%

tropospheric H_2O_2 range between 1.30 and 2.20 ‰ with a mean O-MIF of 1.70 ‰

ed by the H_2O_2 oxidation is assumed to carry a $\Delta^{17}O(S(VI))_{H_2O_2+SO_2} = 0.87$ ‰

$$\Delta^{17}O(S(VI))_{O_2+SO_2} = \frac{1}{4} \cdot \Delta^{17}O(O_2)$$

$\Delta^{17}O\ (O_2)$ being taken as -0.340 ‰ (see above)

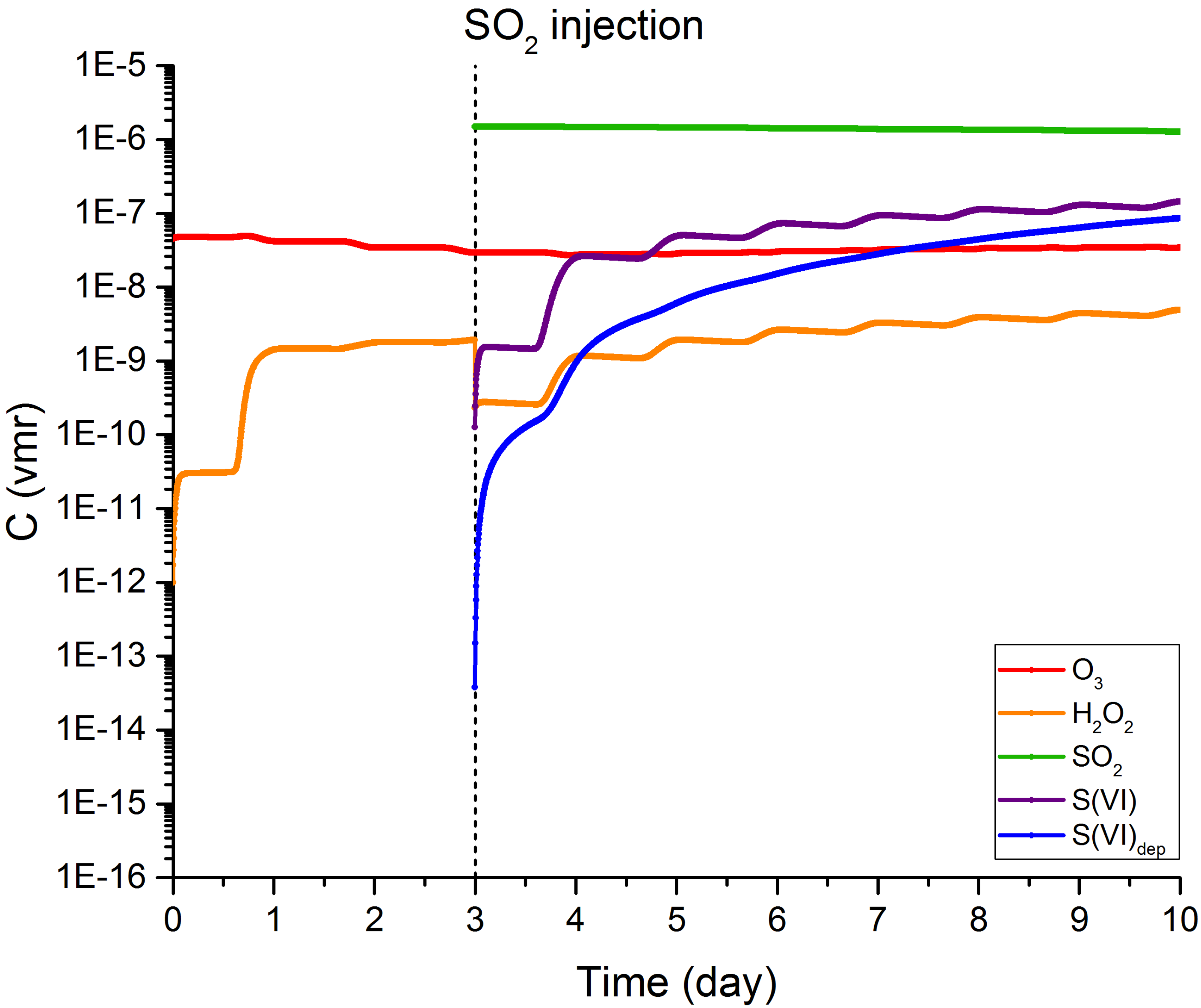
△O2/TMI ~ -0.1°%

almost null, of about -0.09 ‰ (?).

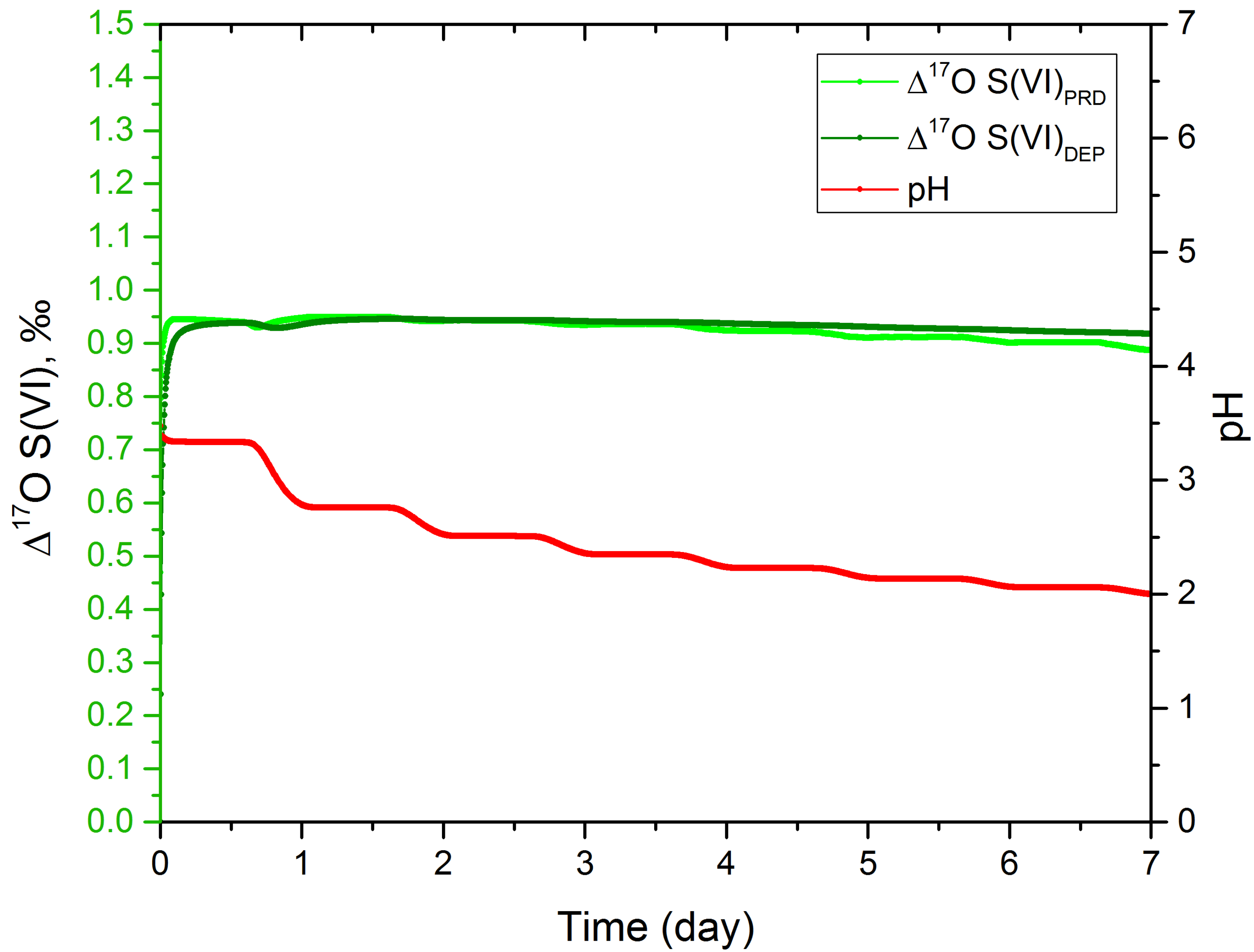
Table 3. Ranges of SO_2, LWC and TMI explored in the sensitivity studies

SO_2	0.1 – 10.0 ppmv
LWC	0.1 – 2.5 gr m^{-3}
TMI	0.1 – 3.0 µM

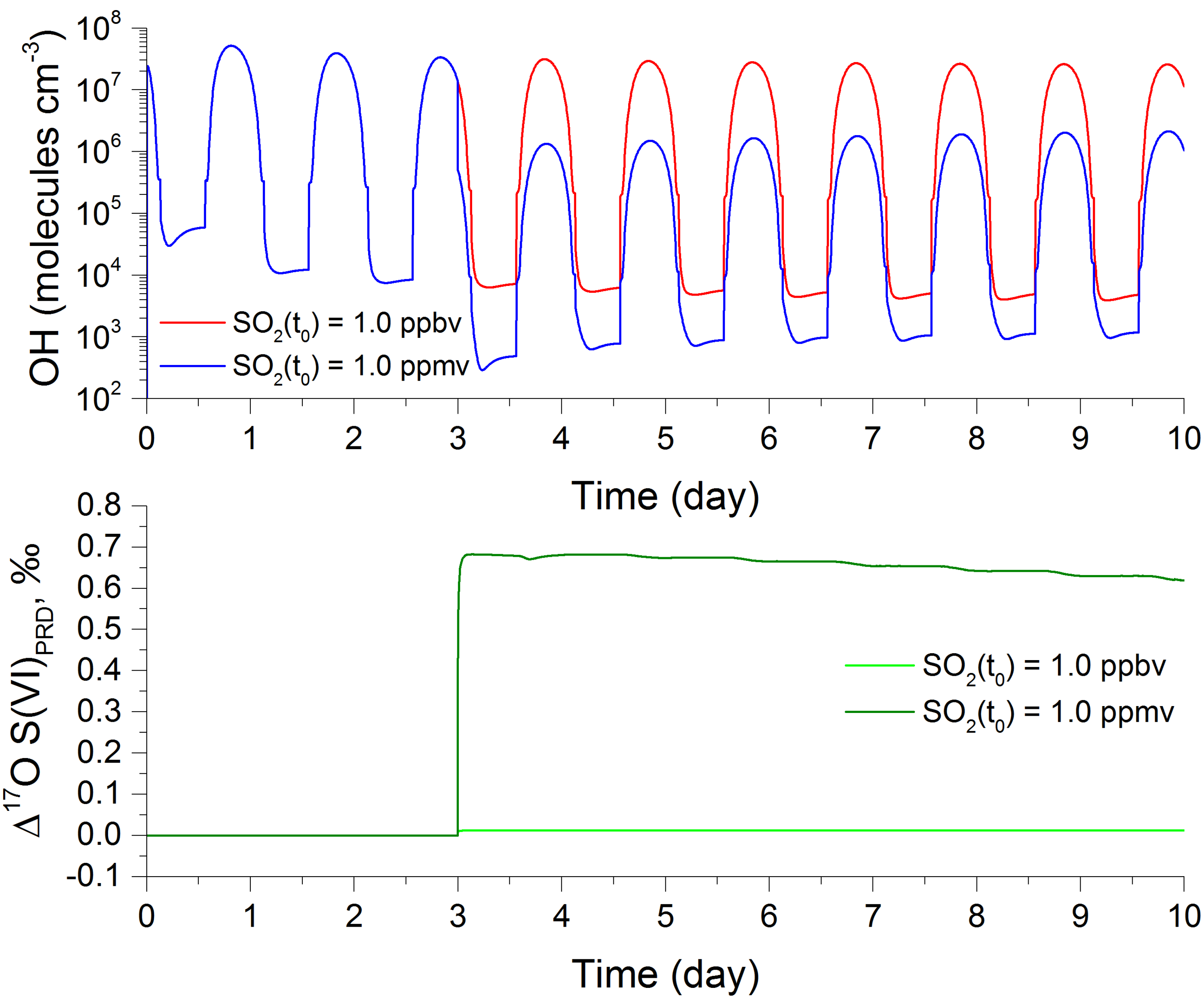
GAS-PHASE OXIDATION ONLY



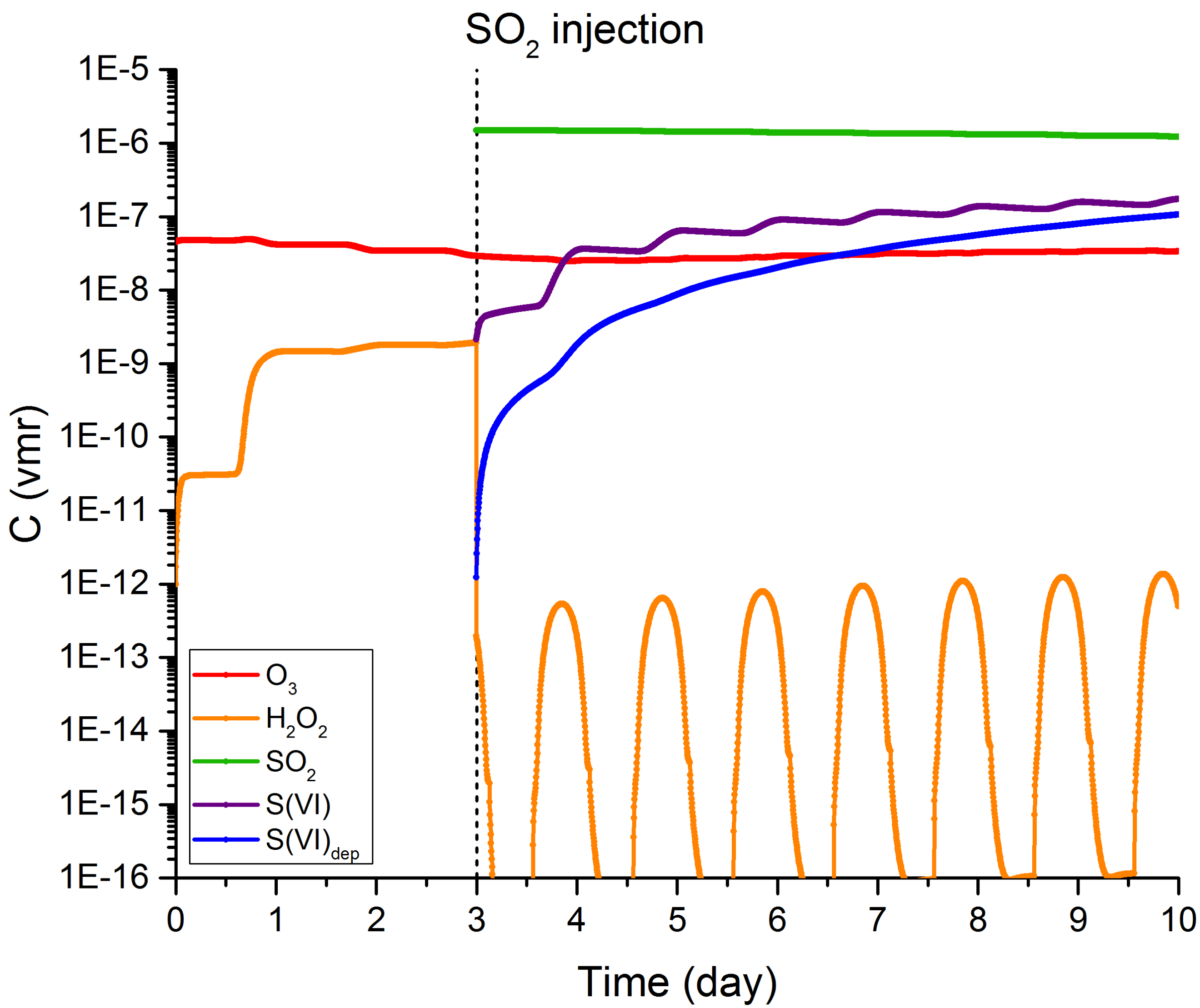
GAS-PHASE OXIDATION ONLY



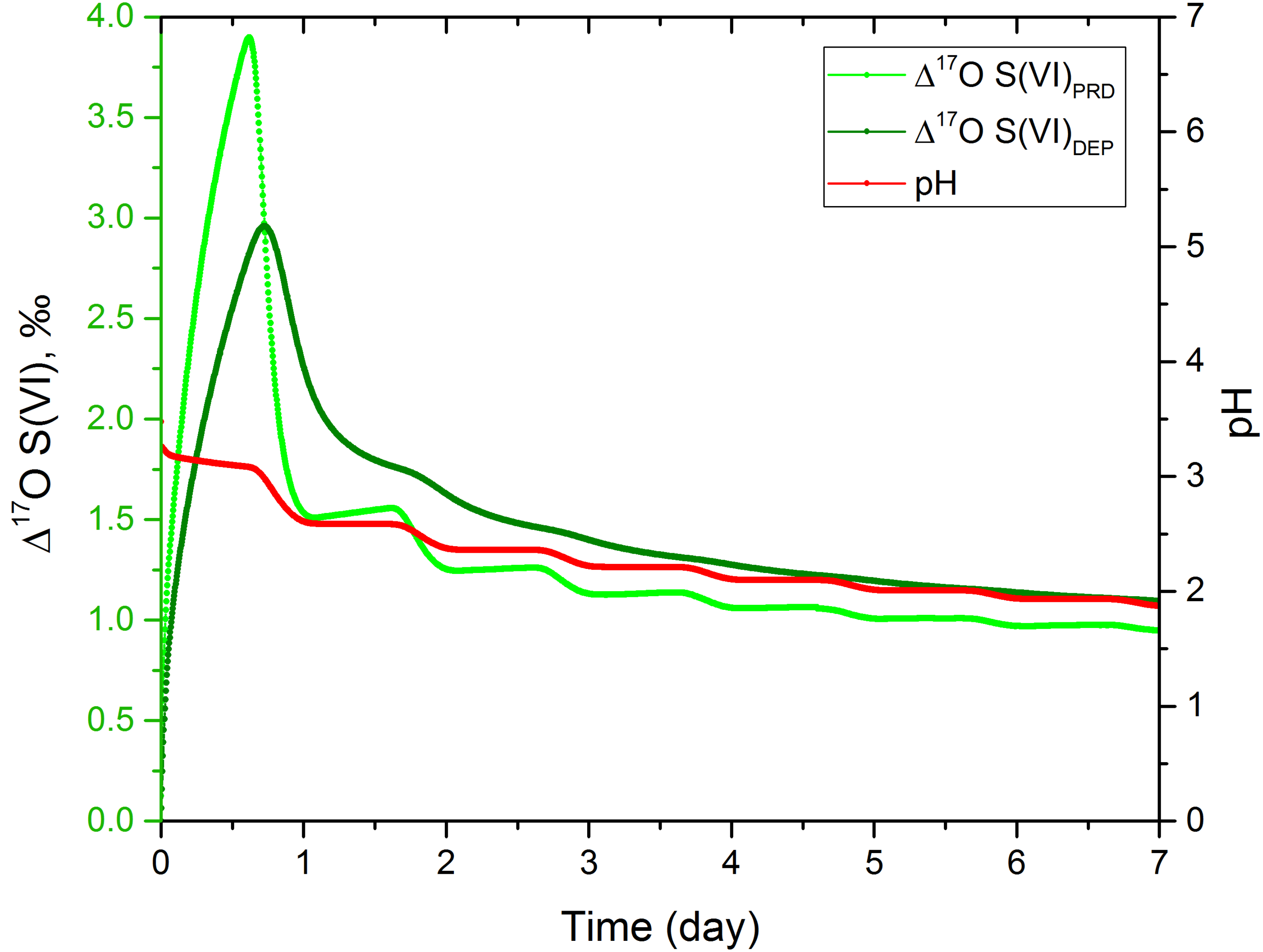
GAS-PHASE OXIDATION ONLY



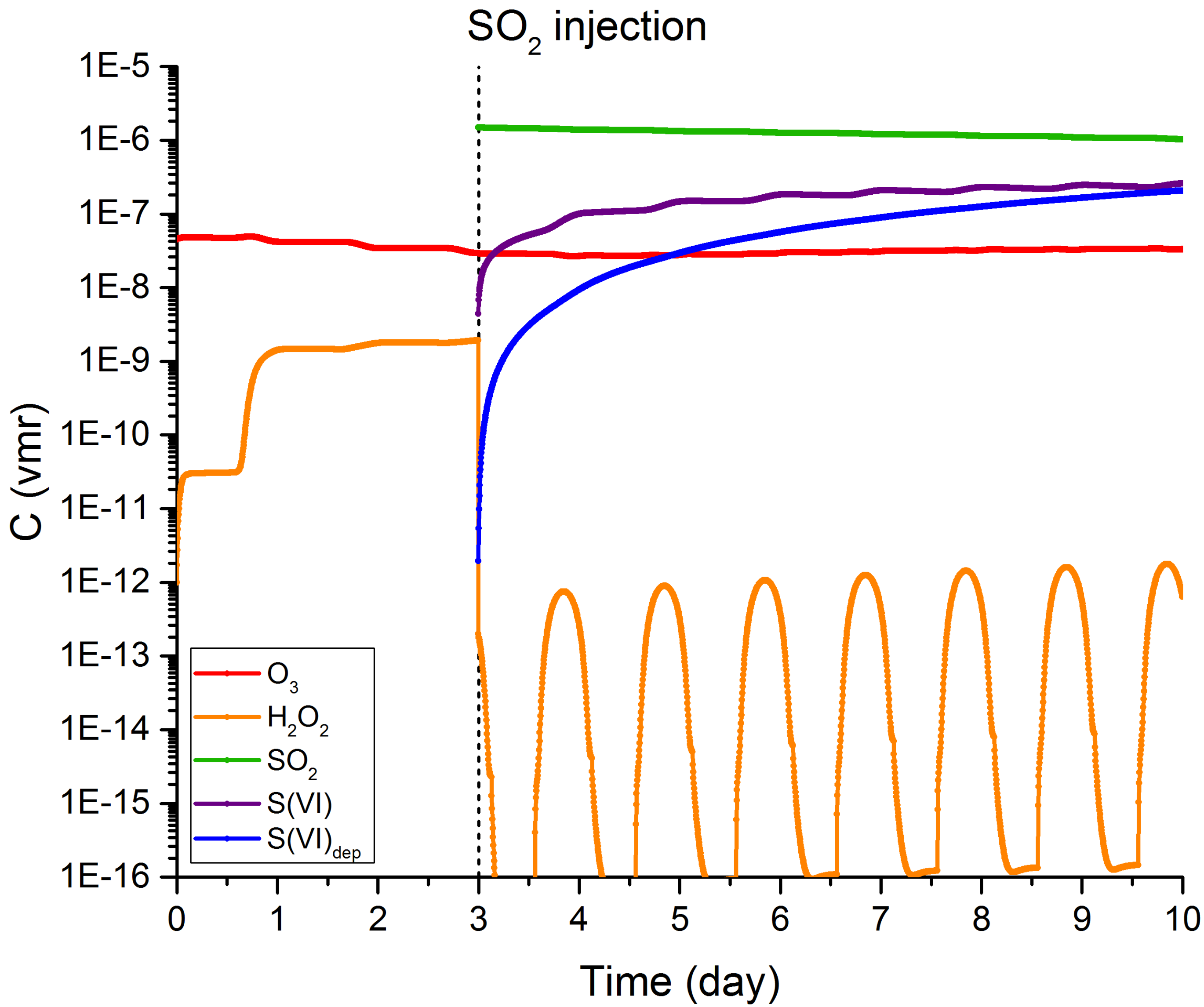
GAS-PHASE + AQUEOUS (O3, H2O2) OXIDATION



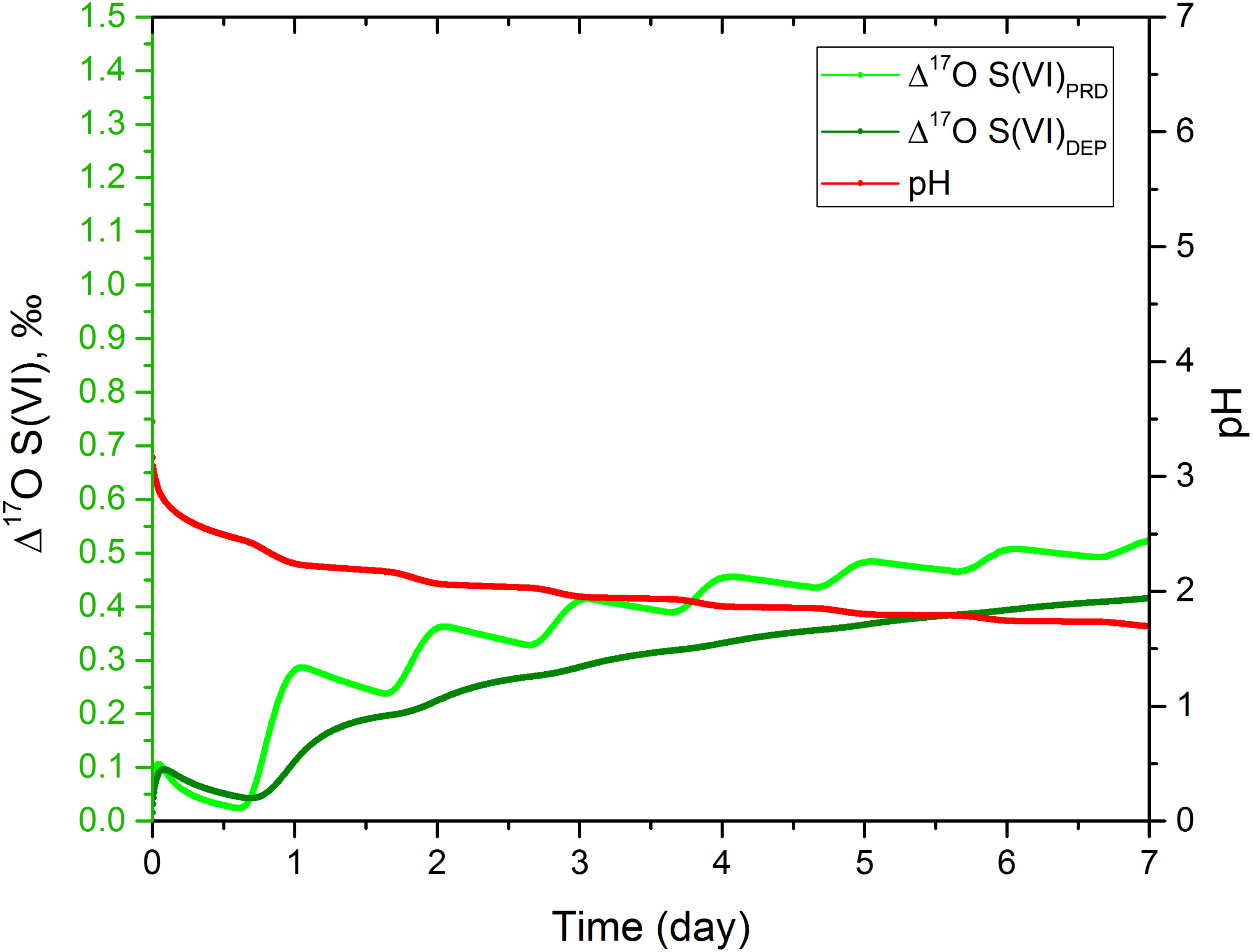
GAS-PHASE + AQUEOUS (O3, H2O2) OXIDATION



GAS-PHASE + AQUEOUS (O3, H2O2, O2/TIM) OXIDATION



GAS-PHASE + AQUEOUS (O3, H2O2, O2/TIM) OXIDATION



GAS-PHASE + AQUEOUS (O3, H2O2, O2/TIM) OXIDATION

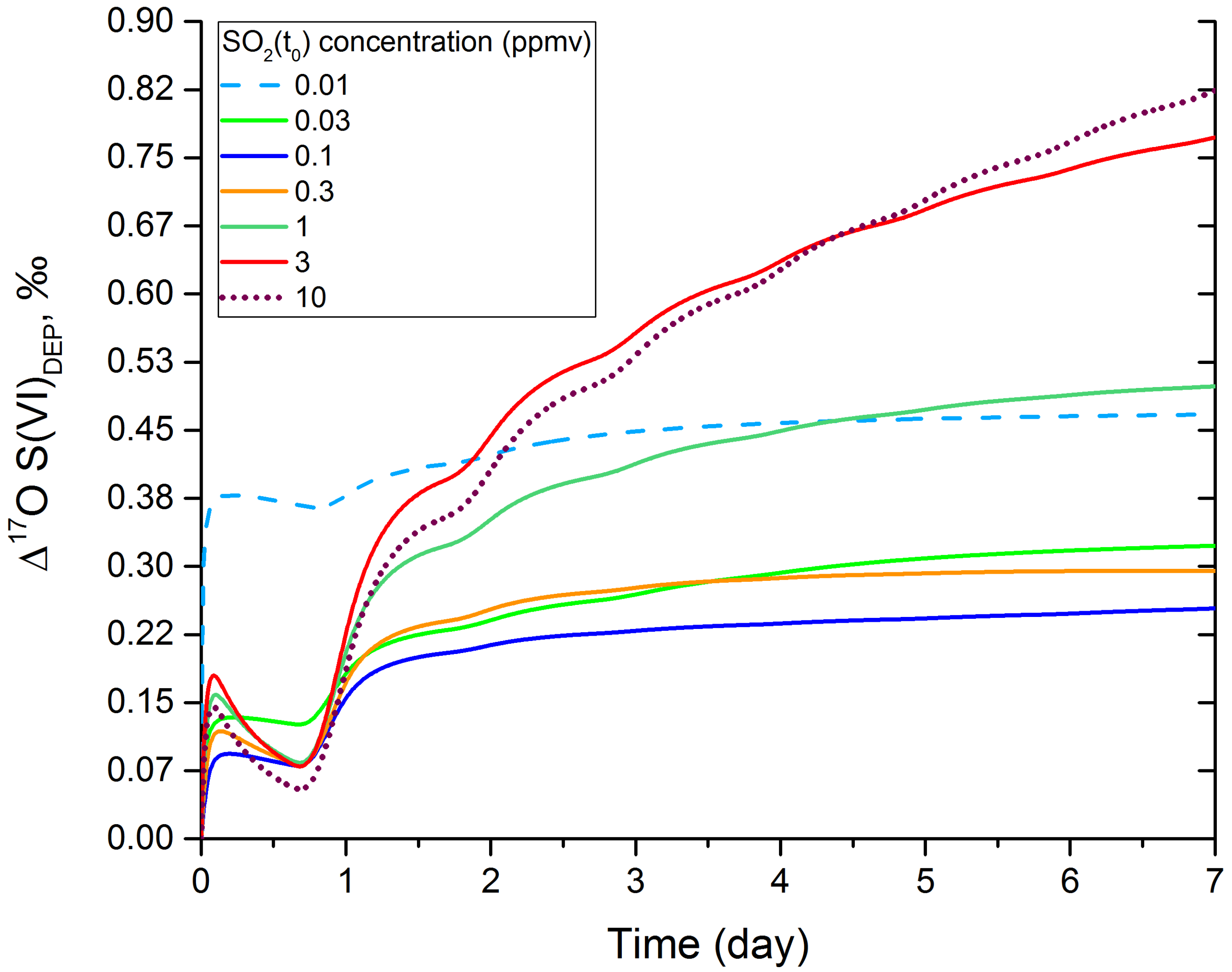
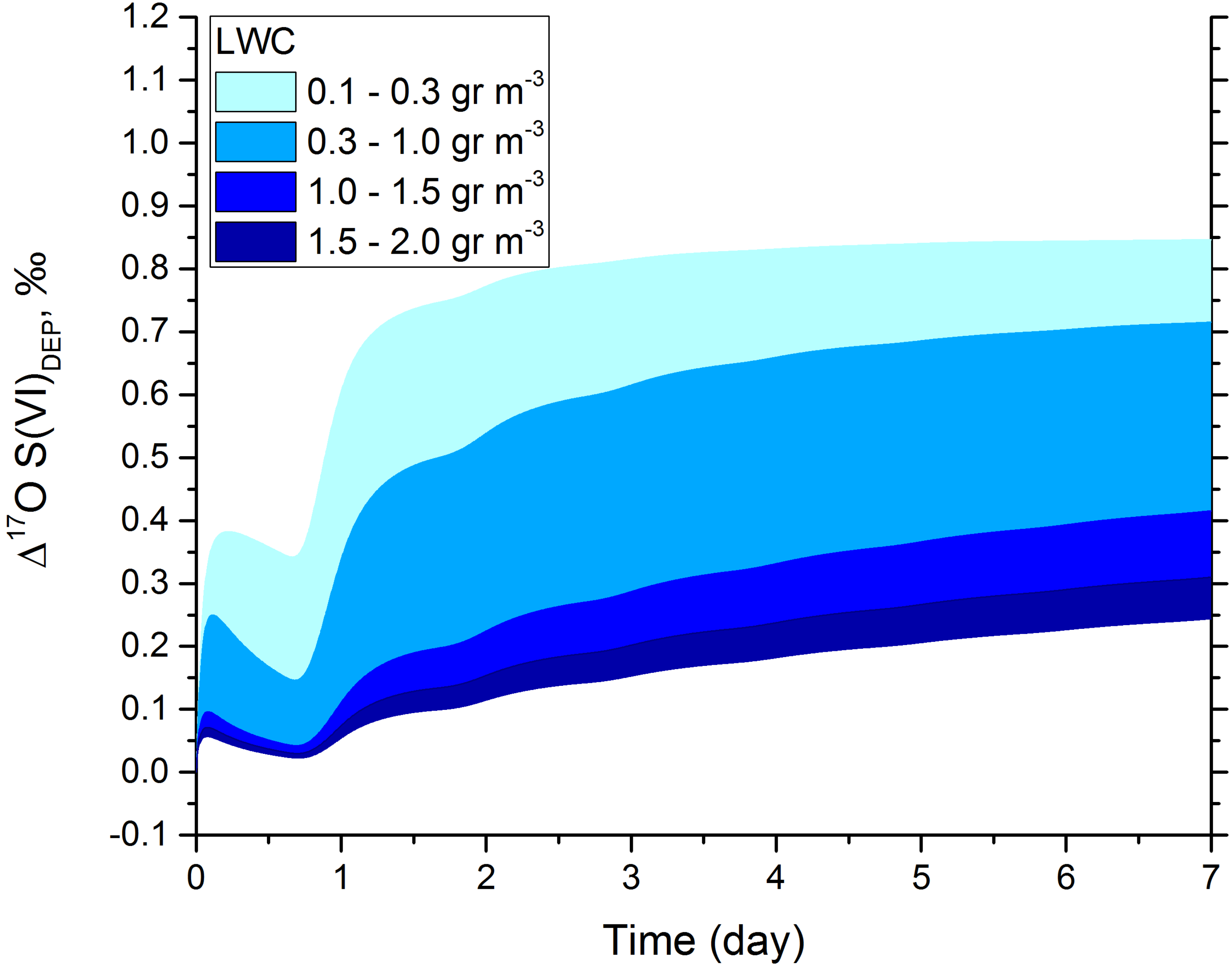


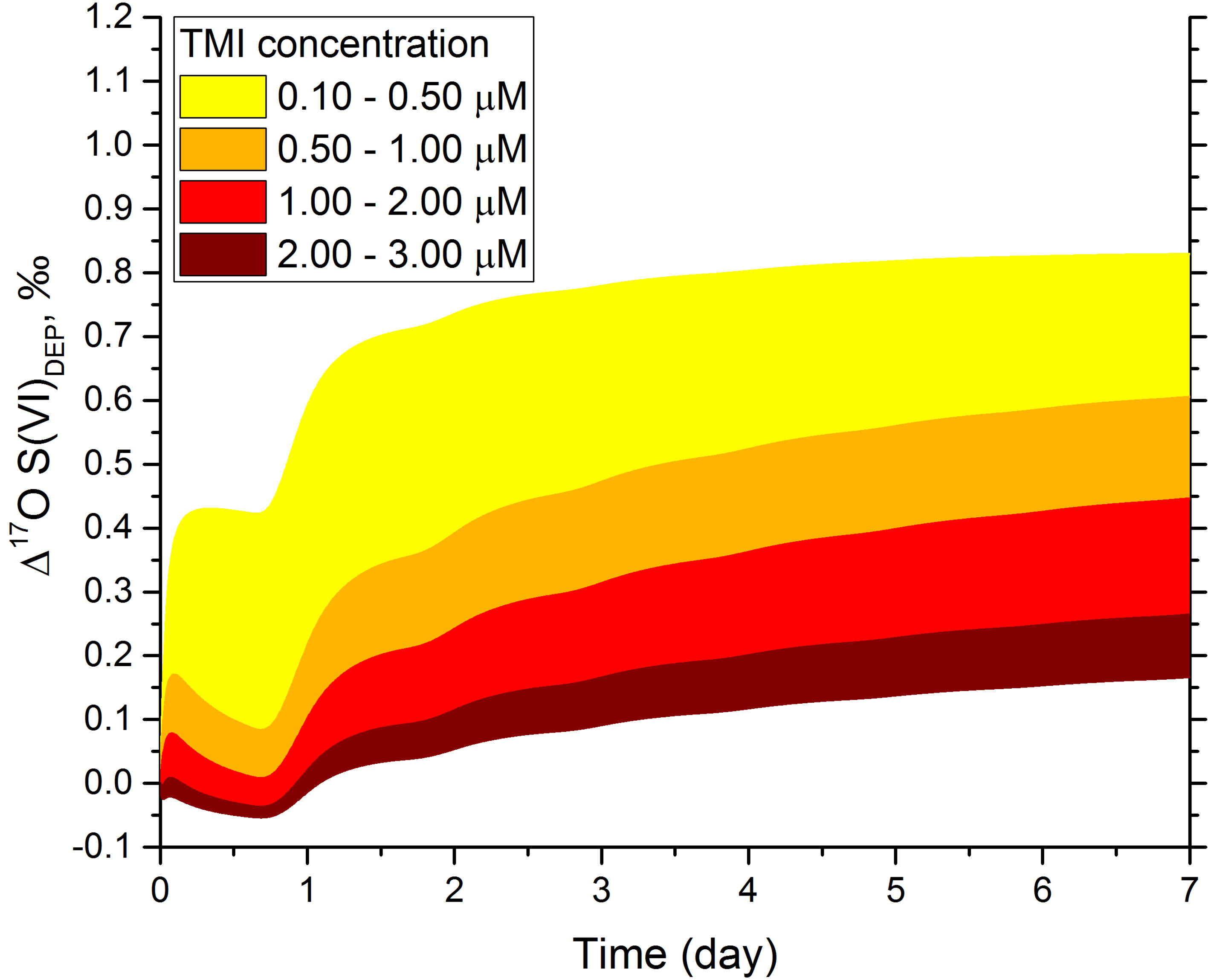
Table 4. Contribution of different pathways of oxidation to sulfate production at varying initial concentration of SO_2

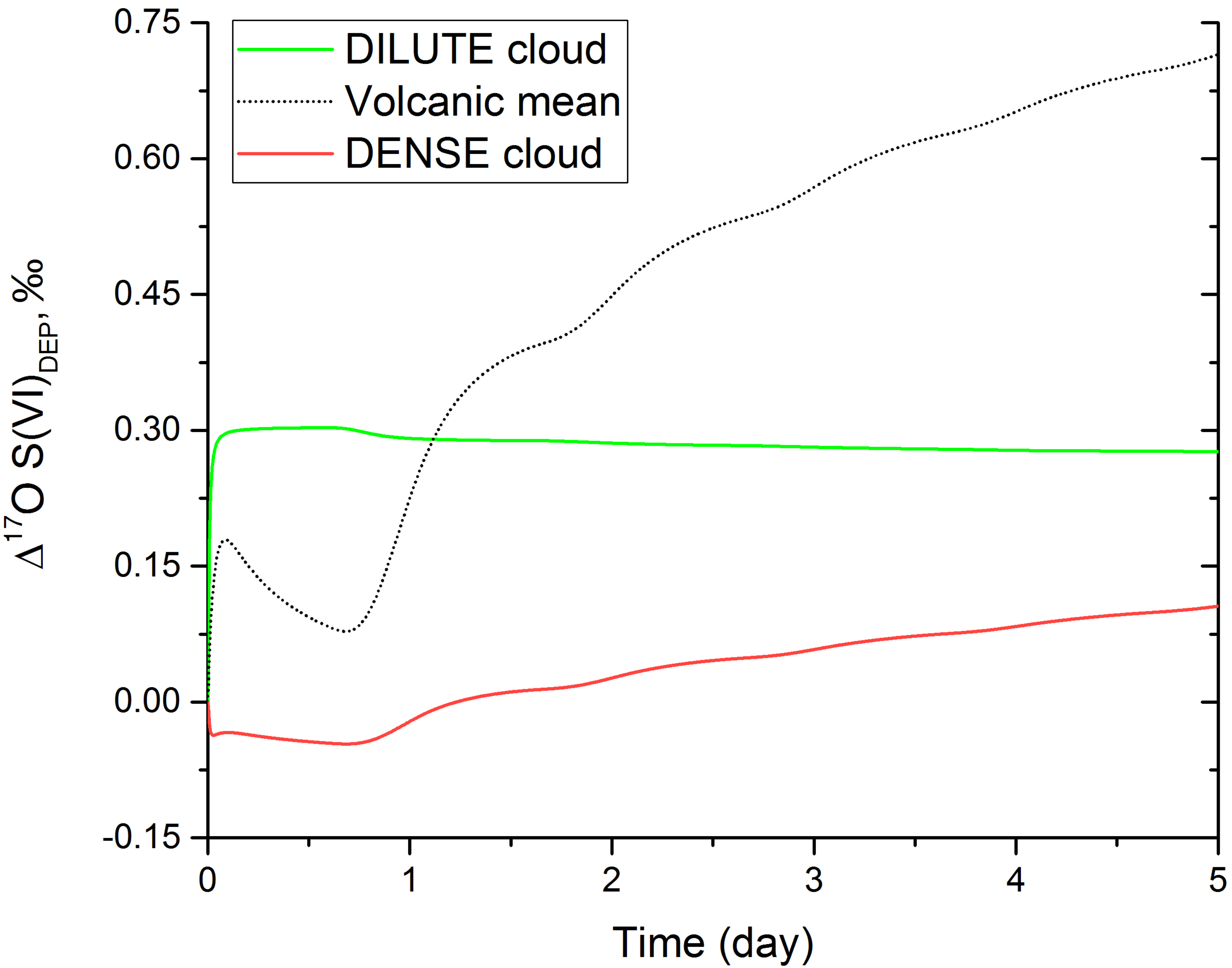
C_0, SO_2 (ppmv)	t (day)	OH (%)	O_3 (%)	H_2O_2 (%)	O_2/TMI (%)	$\Delta^{17}O(S(VI), dep.)_f$ (‰)
0.01	0	4	0	96	5	-
	1	39	0	55	6	0.38
	7	35	0	60	5	0.47
0.03	0	19	0	77	4	-
	1	60	0	30	10	0.18
	7	54	0	40	6	0.32
0.1	0	57	0	21	22	-
	1	63	0	22	15	0.15
	7	66	0	28	6	0.32
0.3	0	44	0	15	41	-
	1	56	0	19	25	0.17
	7	69	0	22	9	0.29
1.0	0	24	1	8	67	-
	1	43	0	15	42	0.20
	7	62	0	19	19	0.50
3.0	0	11	1	4	85	-
	1	30	0	10	60	0.23
	7	51	0	14	35	0.77
10	0	4	1	1	94	-
	1	17	0	5	77	0.19
	7	33	0	9	58	0.82

GAS-PHASE + AQUEOUS (O3, H2O2, O2/TIM) OXIDATION



GAS-PHASE + AQUEOUS (O3, H2O2, O2/TIM) OXIDATION





DILUTE cloud
Volcanic mean
DENSE cloud
$\Delta^{17}O$ S(VI)$_{DEP}$, ‰
Time (day)
0.75
0.60
0.45
0.30
0.15
0.00
-0.15
0
1
2
3
4
5

- **Signature isotopique de OH**
- **Contribution de H_2O_2 est negligeable**
- **O_2/TIM important**

Impact des émissions d’ halogens (en cours)