稳定同位素技术测定土壤中N_2O的排放贡献

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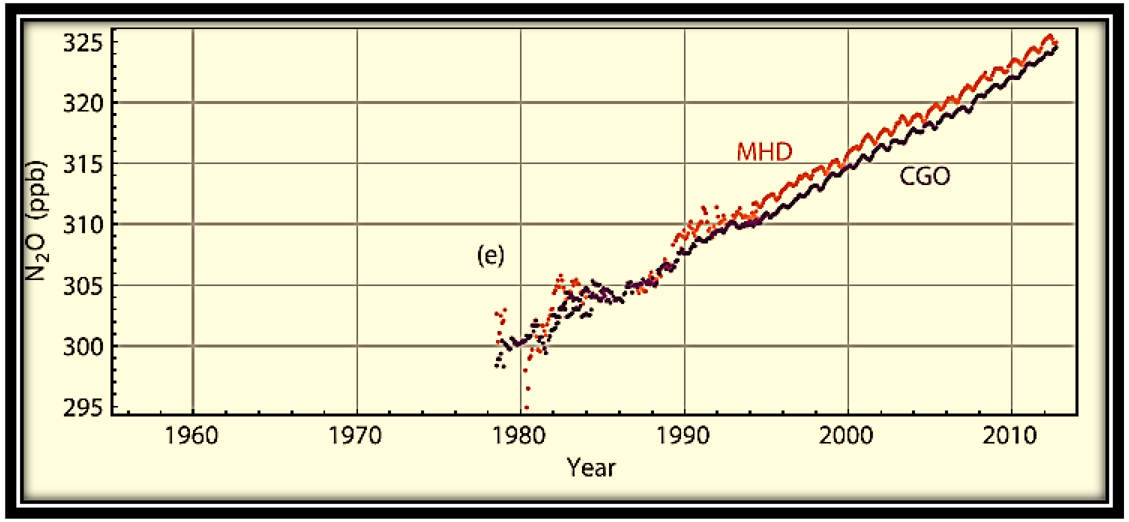
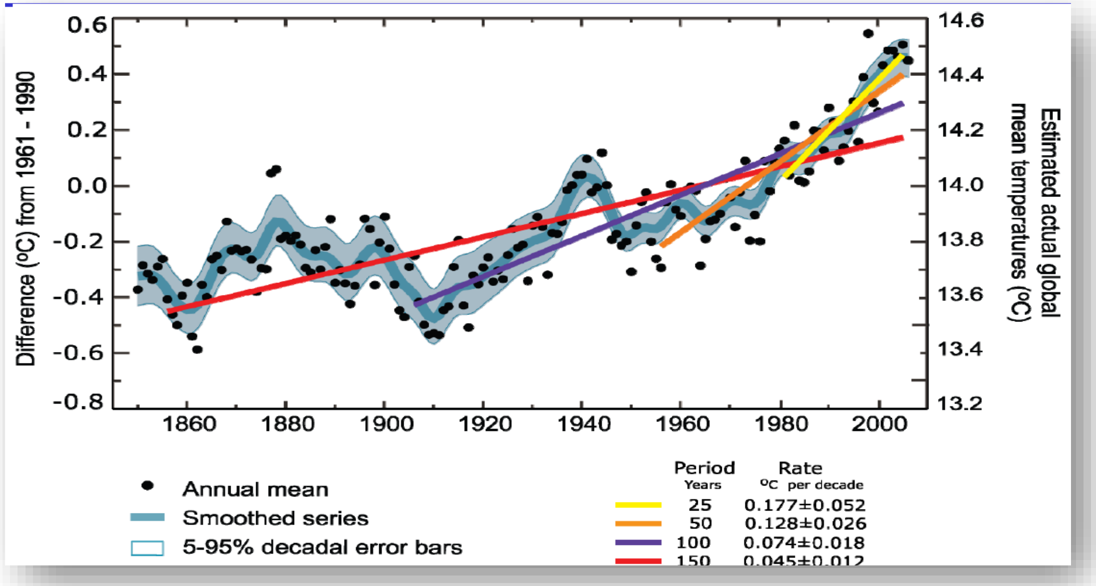
N_2O是一种重要的温室气体





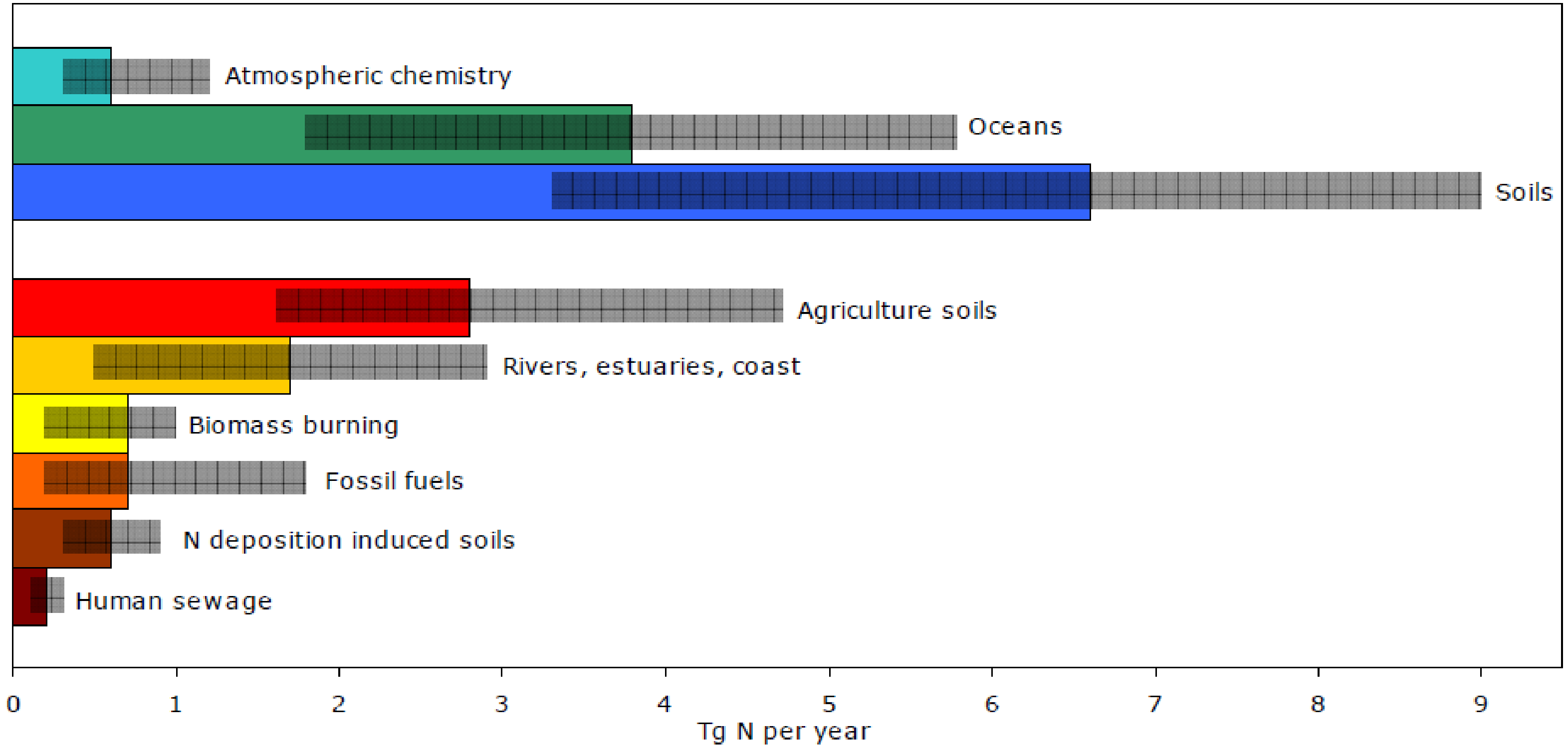
光化学烟雾

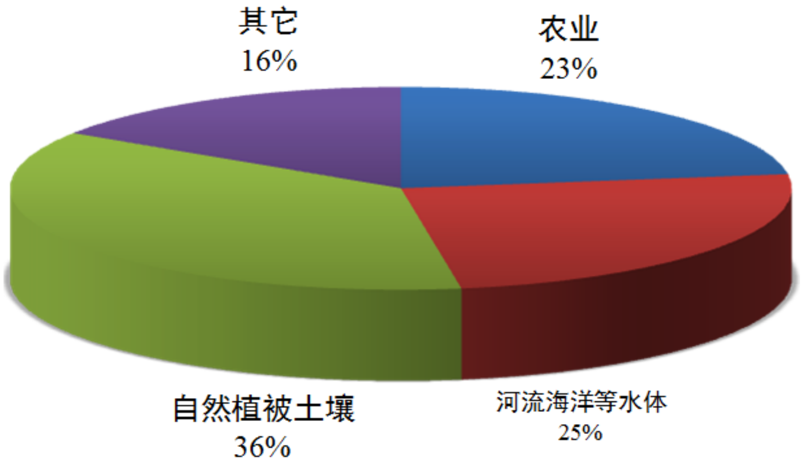
温室效应

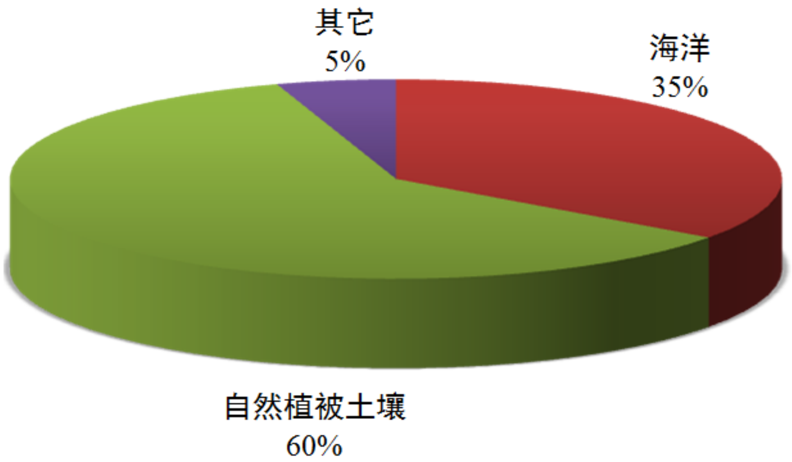
N_2O

破坏臭氧层

酸雨

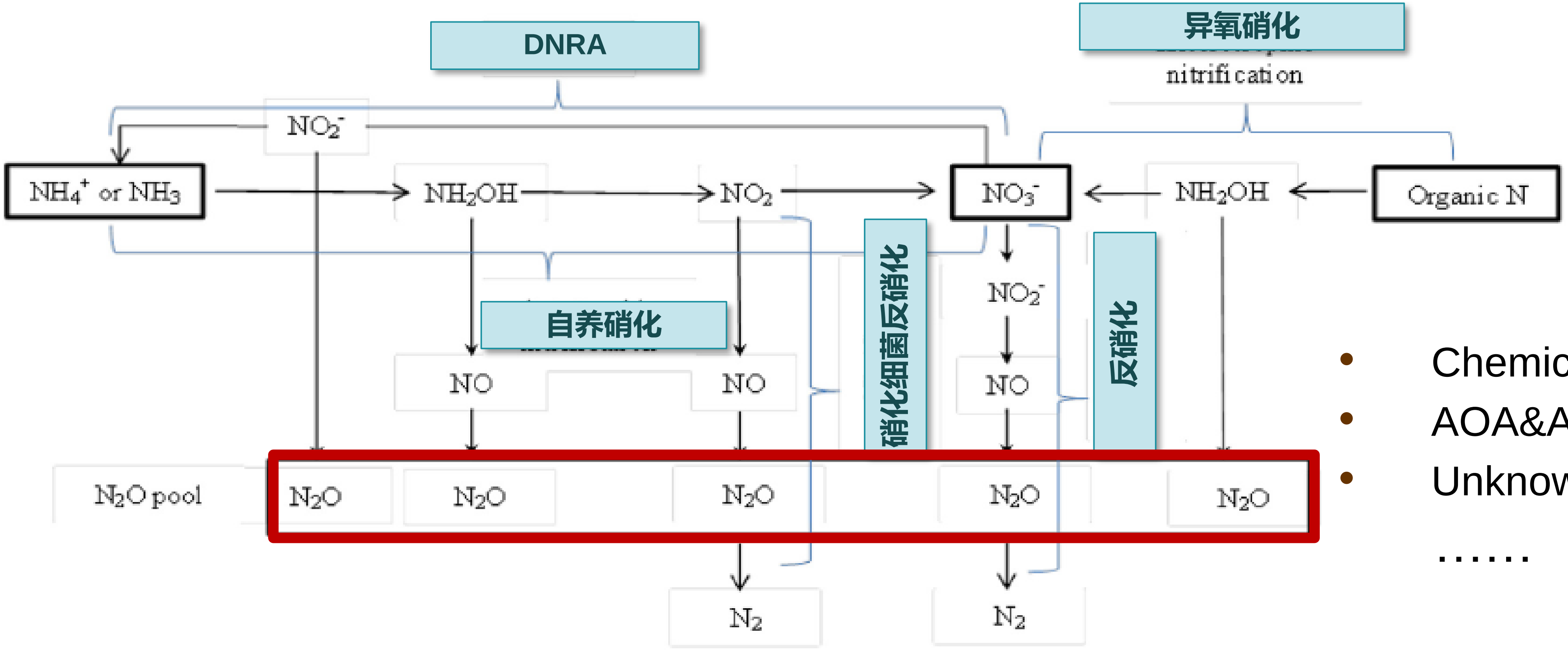






自然植被土壤贡献了N_2O总排放量的36%，N_2O自然源的60%

土壤N_2O主要产生途径



- Chemical denitrification
- AOA&AOB
- Unknown process

……

溯源N_2O产生途径　实现N_2O有效减排

(Wrage et al. 2001; Ostrom et al. 2012; Zhang et al. 2015)

土壤中N_2O排放贡献的区分方法

- 通量法
- 抑制剂法：

  低浓度C_2H_2（between 0.1 and 10 Pa）

- 稳定同位素法：

  （1）富集标记方法——^{15}N成对标记（$^{15}NH_4$、$^{15}NO_3$）

  （2）自然丰度方法

  - ^{15}N、^{18}O
  - ^{15}N—SP，^{18}O—SP

1. 富集标记方法研究土壤N_2O排放贡献

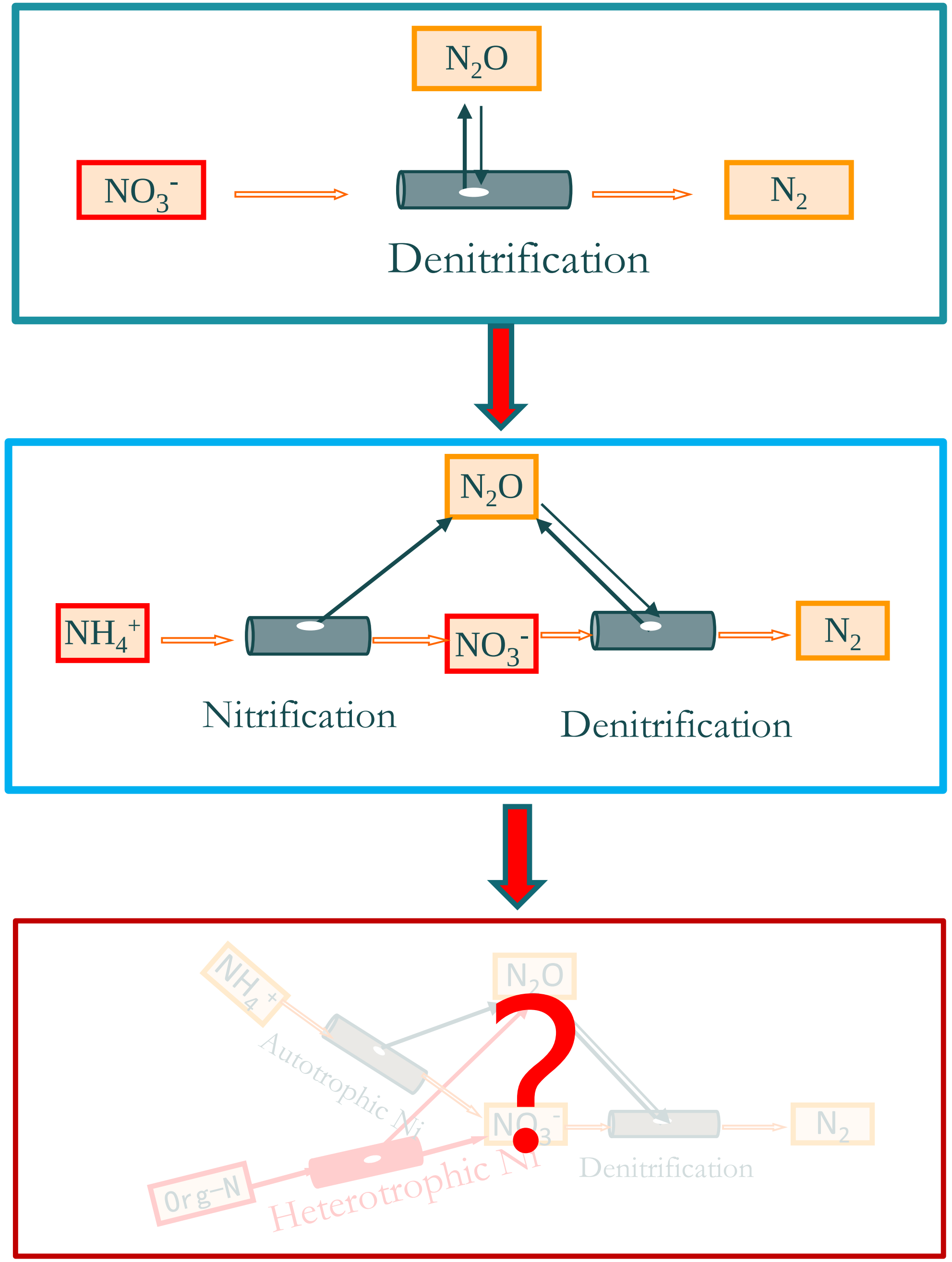
N_2O“管道漏气”概念模型（Hole-in-the-pipe）

问题1. 土壤N_2O的来源N库

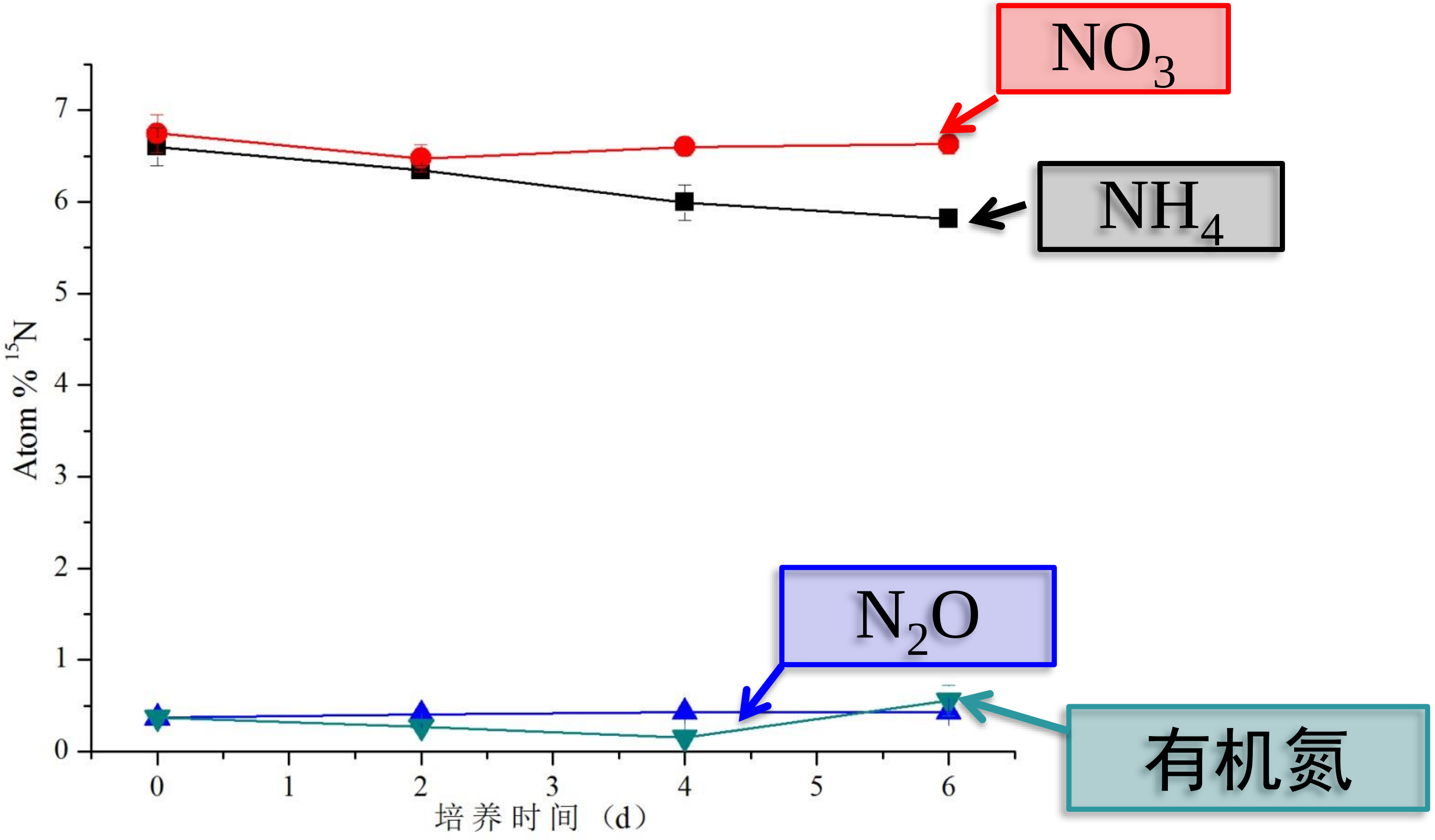
1980年代以前

1980年代以后

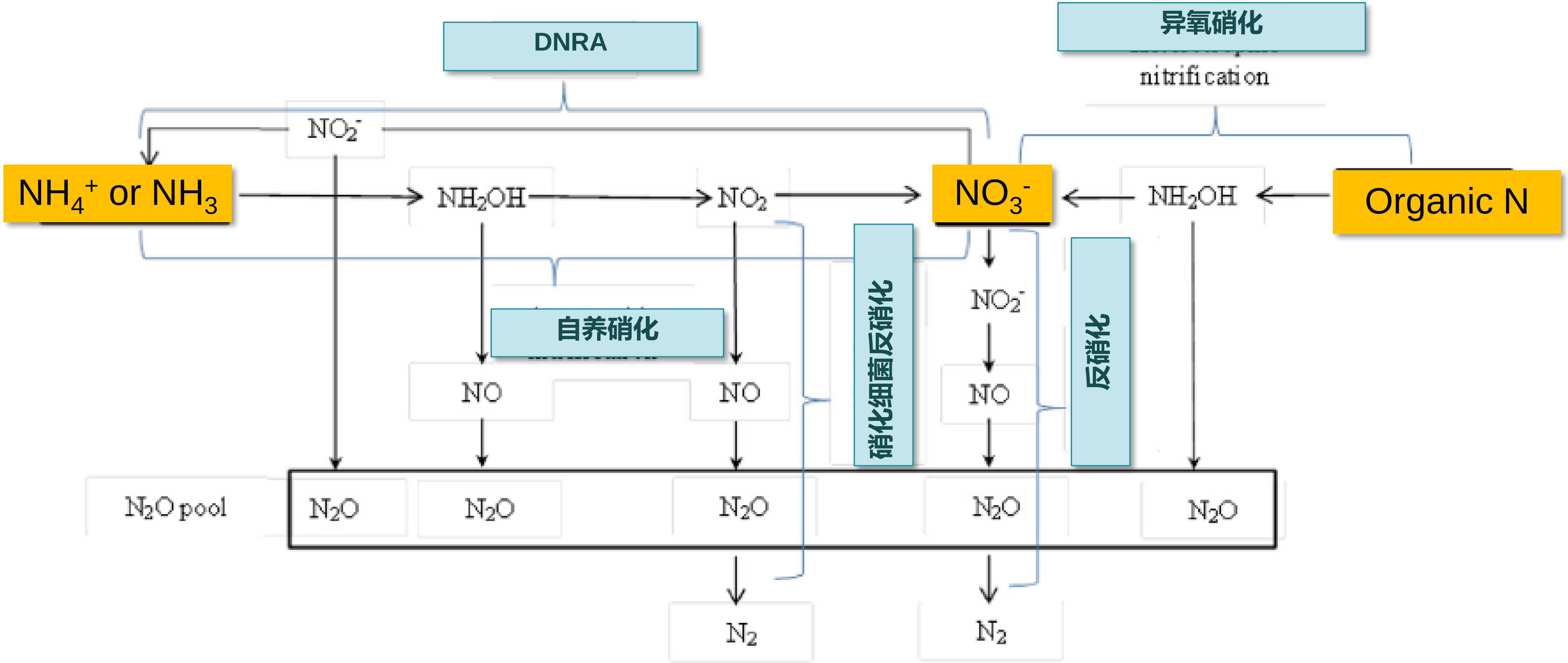
完善N_2O排放模型？



(Firestone and Davidson, 1989)



- 众多^{15}N稳定同位素标记研究结果表明，一些土壤中N_2O主要来源于未标记氮库，而不是NH_4和NO_3 库(Rütting et al., 2010)



DNRA

异氧硝化

nitrification

NO_2^-

NH_4^+ or NH_3

NH_2OH

NO_2

NO_3^-

NH_2OH

Organic N

自养硝化

硝化细菌反硝化

NO_2^-

反硝化

NO

NO

NO

N_2O pool

N_2O

N_2O

N_2O

N_2O

N_2O

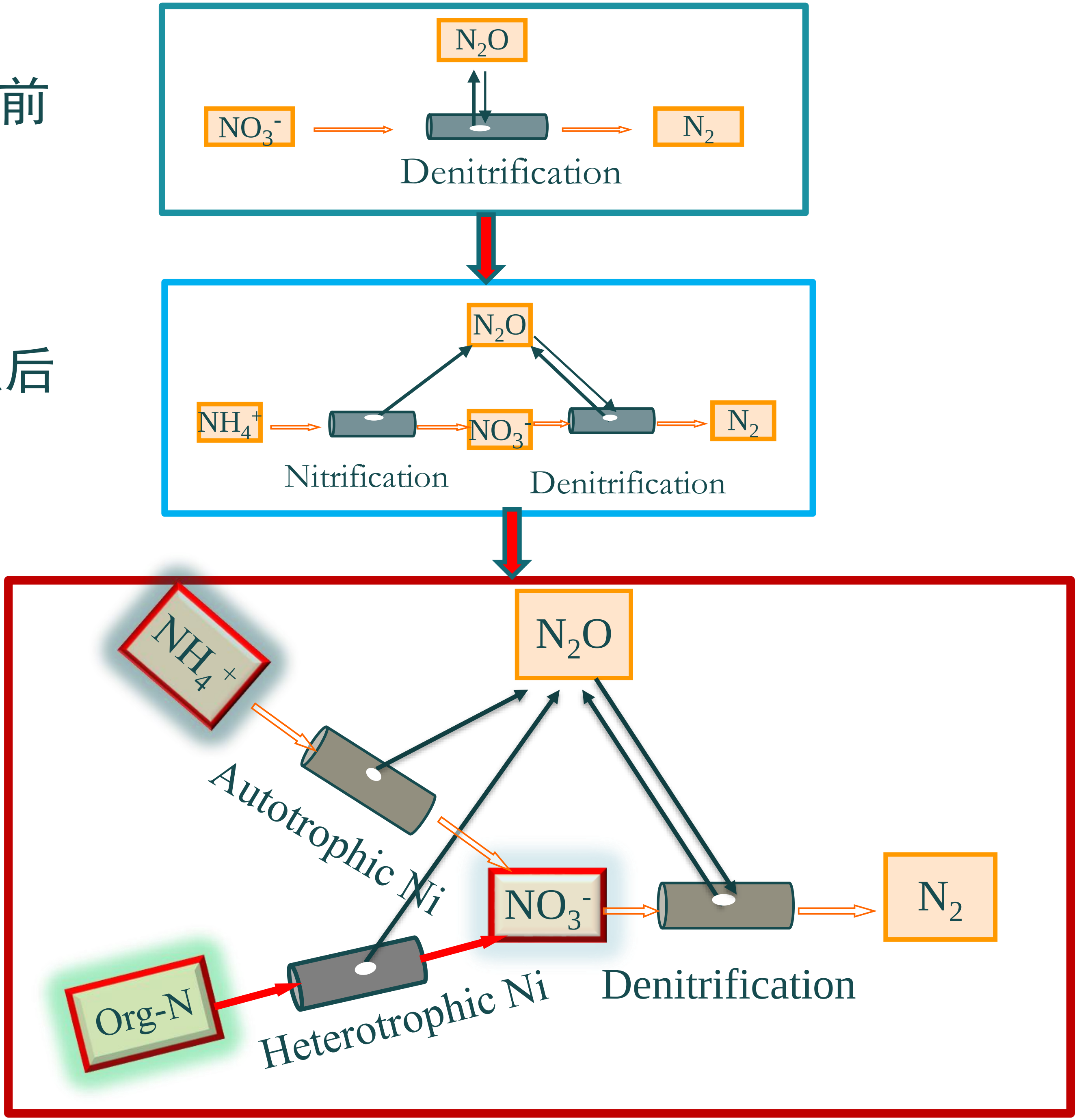
N_2

N_2

1980年代以前

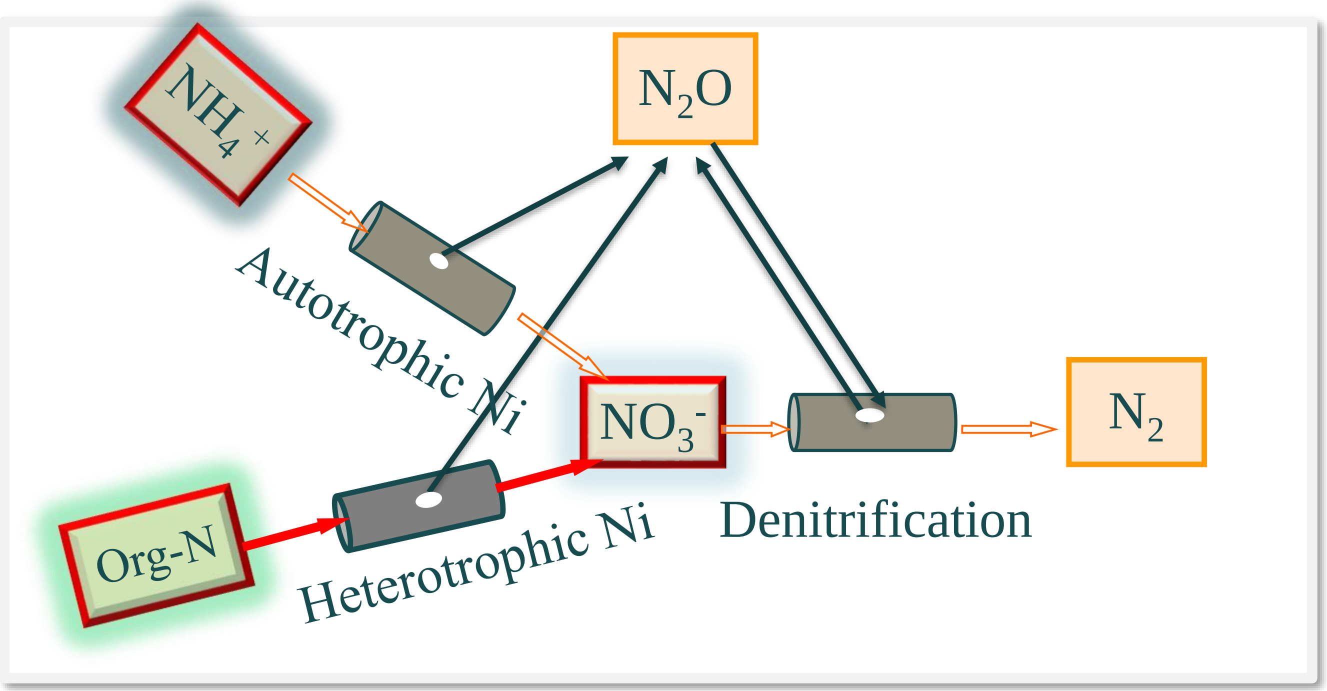
1980年代以后

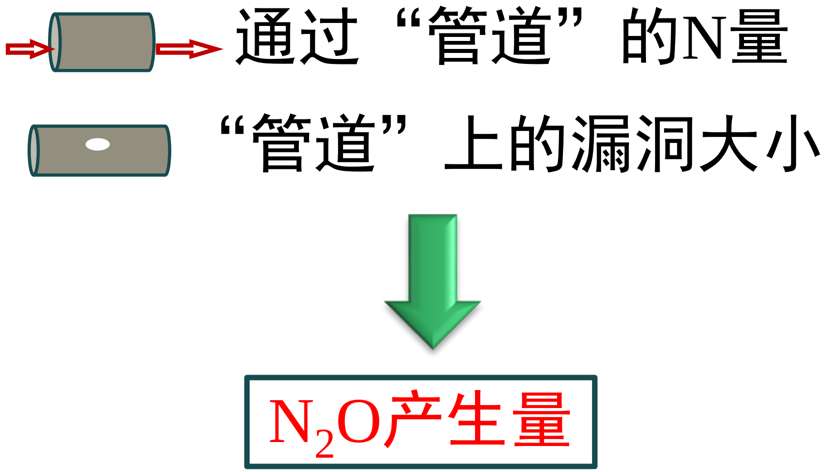
完善N_2O排放的管道漏气模型



Zhang et al. 201

问题2. 定量化





通过“管道”的N量

“管道”上的漏洞大小

N_2O产生量

① 通过管道的总氮量？

② 各“管道”对N_2O排放的贡献率？(N_2O的产生途径)

③ 各“管道”的N_2O产生量？

④ 各“管道”的N_2O产生率？ (漏洞大小)

⑤ 影响因素？

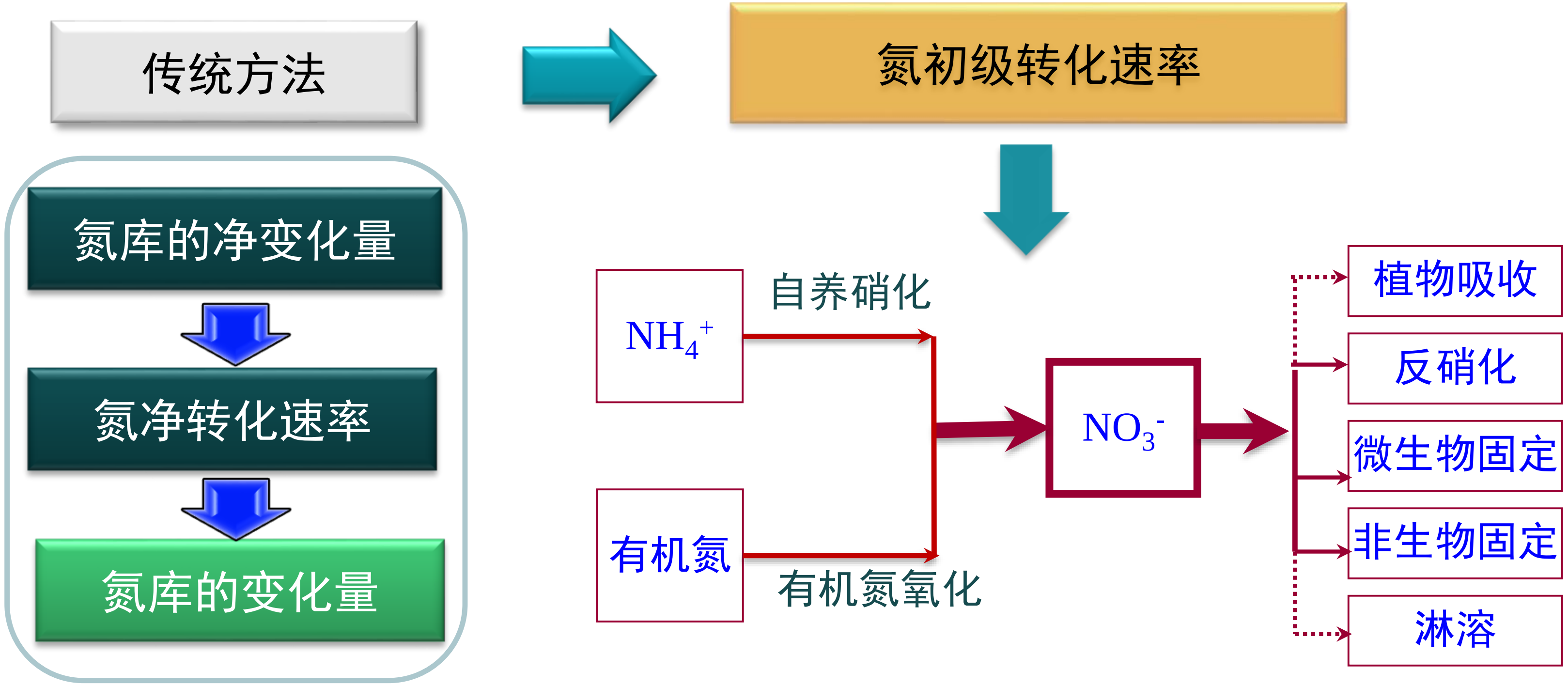
氮转化速率

- **净转化速率(Net transformation rate)**

  通过测定单位时间内氮含量净变化。

- **初级转化速率(Gross transformation rate)**

  土壤氮从一种形态转化为另一种形态的实际转化率。



传统方法

氮库的净变化量

氮净转化速率

氮库的变化量

氮初级转化速率

氮转化速率研究方法

传统方法

- 氮库的净变化量
- 氮净转化速率
- 氮库的变化量

算术方法

- 同位素稀释法
- 氮初级转化速率
- 途径数量有限

数值方法

- 同位素成对标记
- 数值模型分析
- 氮转化复杂过程

^{15}N标记方法+MCMC方法计算土壤氮总转化速率

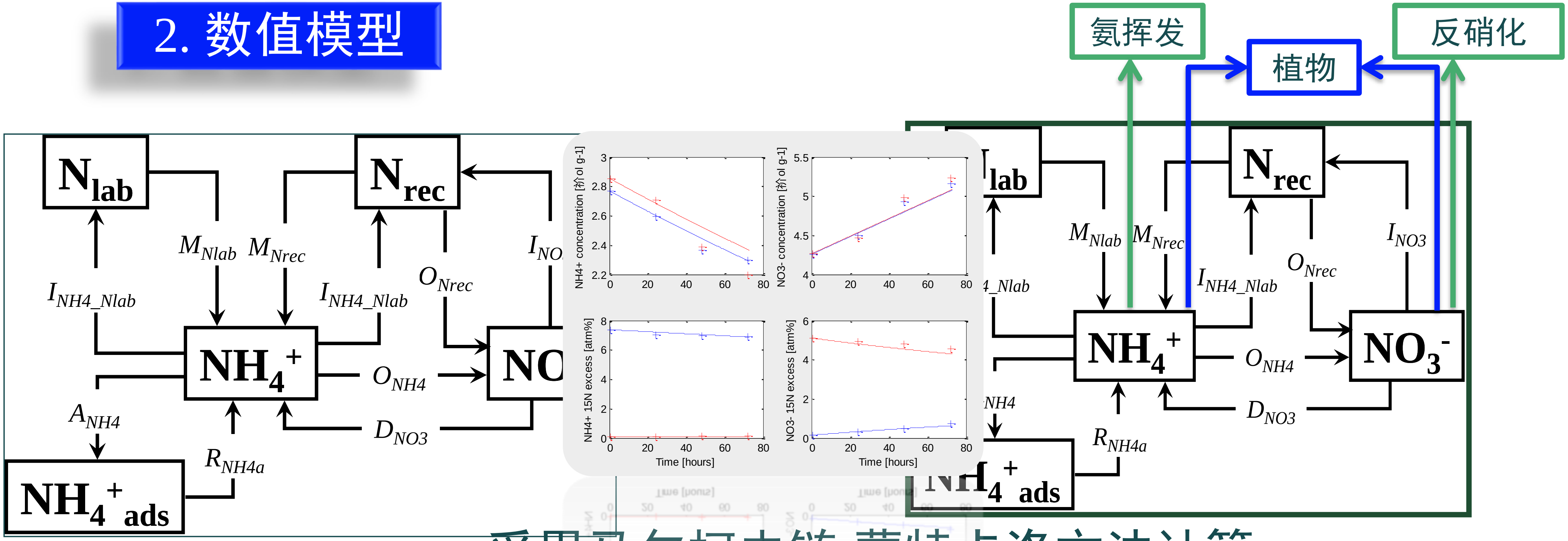
1. 成对标记

$^{15}NH_4NO_3$

$NH_4{}^{15}NO_3$

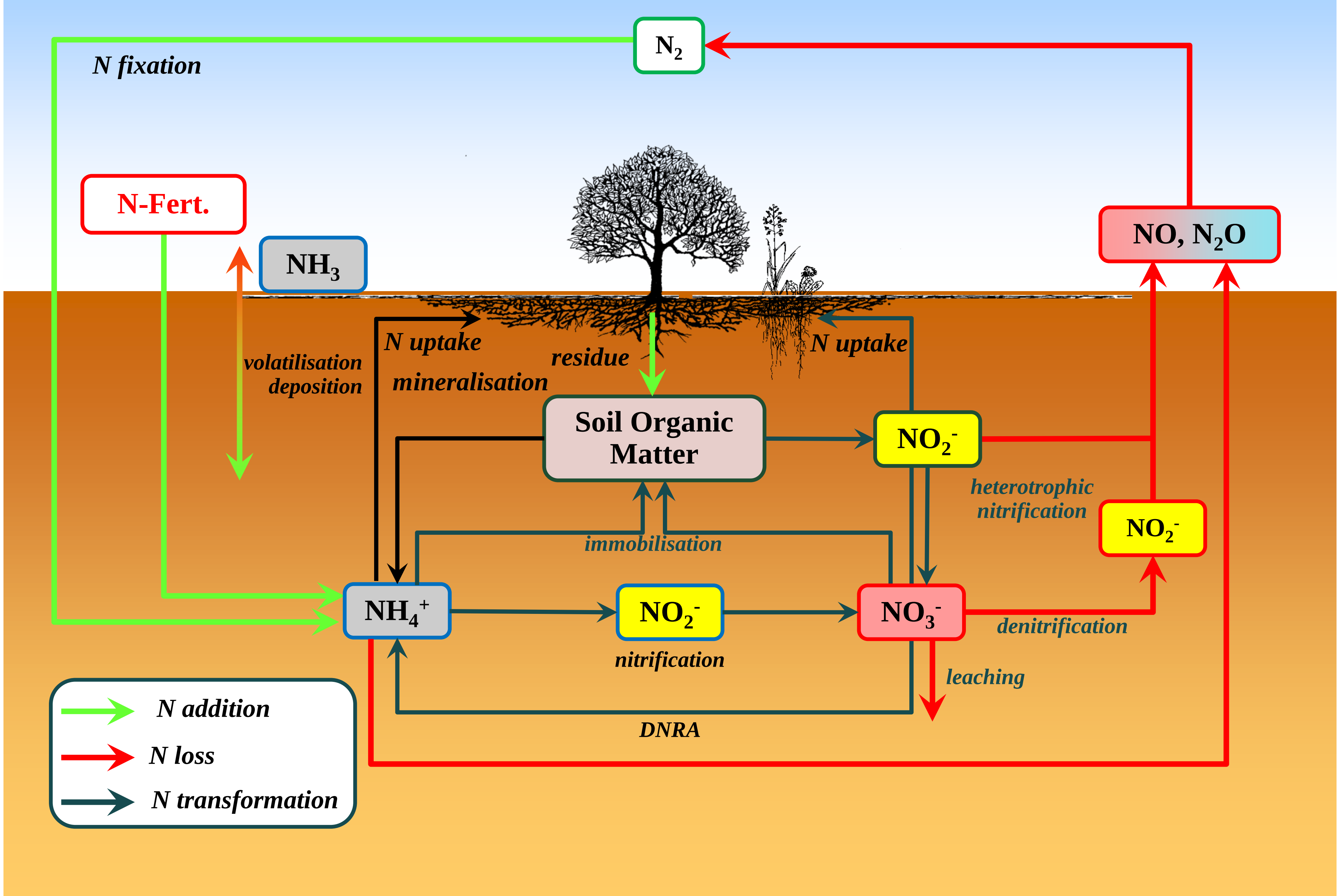
→ NH_4，NO_3，土壤有机氮 含量和丰度

2. 数值模型



采用马尔柯夫链-蒙特卡洛方法计算

氮循环



N_2

N fixation

N-Fert.

NH_3

volatilisation
deposition

N uptake

residue

mineralisation

N uptake

Soil Organic Matter

NO_2^-

heterotrophic nitrification

NO, N_2O

NO_2^-

immobilisation

NH_4^+

NO_2^-

NO_3^-

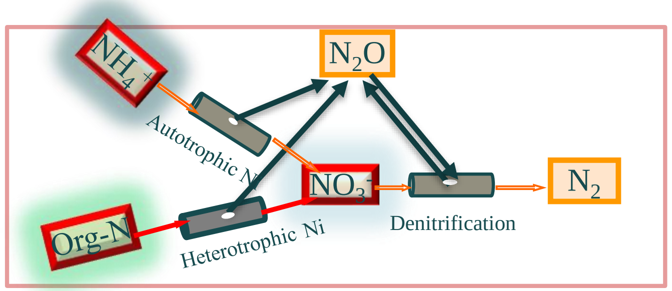
nitrification

denitrification

leaching

DNRA

→ *N addition*
→ *N loss*
→ *N transformation*



定量方法

□ 通过“管道”的N量 ← 初级转化速率

- 算术方法
- 数值方法

□ “管道”上漏洞的大小 ← N_2O产生量/总转化N量

N_2O产生速率*时间/初级转化速率*时间

➢ N_2O产生速率/初级转化速率

□ 各“管道”对N_2O排放的贡献率

- 来源分析法
- 反向标记法
- 示踪模型法

“管道漏气模型”的定量化

- $^{15}NH_4NO_3$和$NH_4{}^{15}NO_3$成对标记或增加$^{15}NH_4{}^{15}NO_3$
- 测定NH_4^+(a_{NH4})、NO_3^-(a_{NO3-})、有机氮(a_{org}) 和N_2O（a_{N2O}）^{15}N丰度。

□ 各“管道”对N_2O排放的贡献率

$$a_{N2O} = da_{NO3} + na_{NH4} + ha_{org}$$

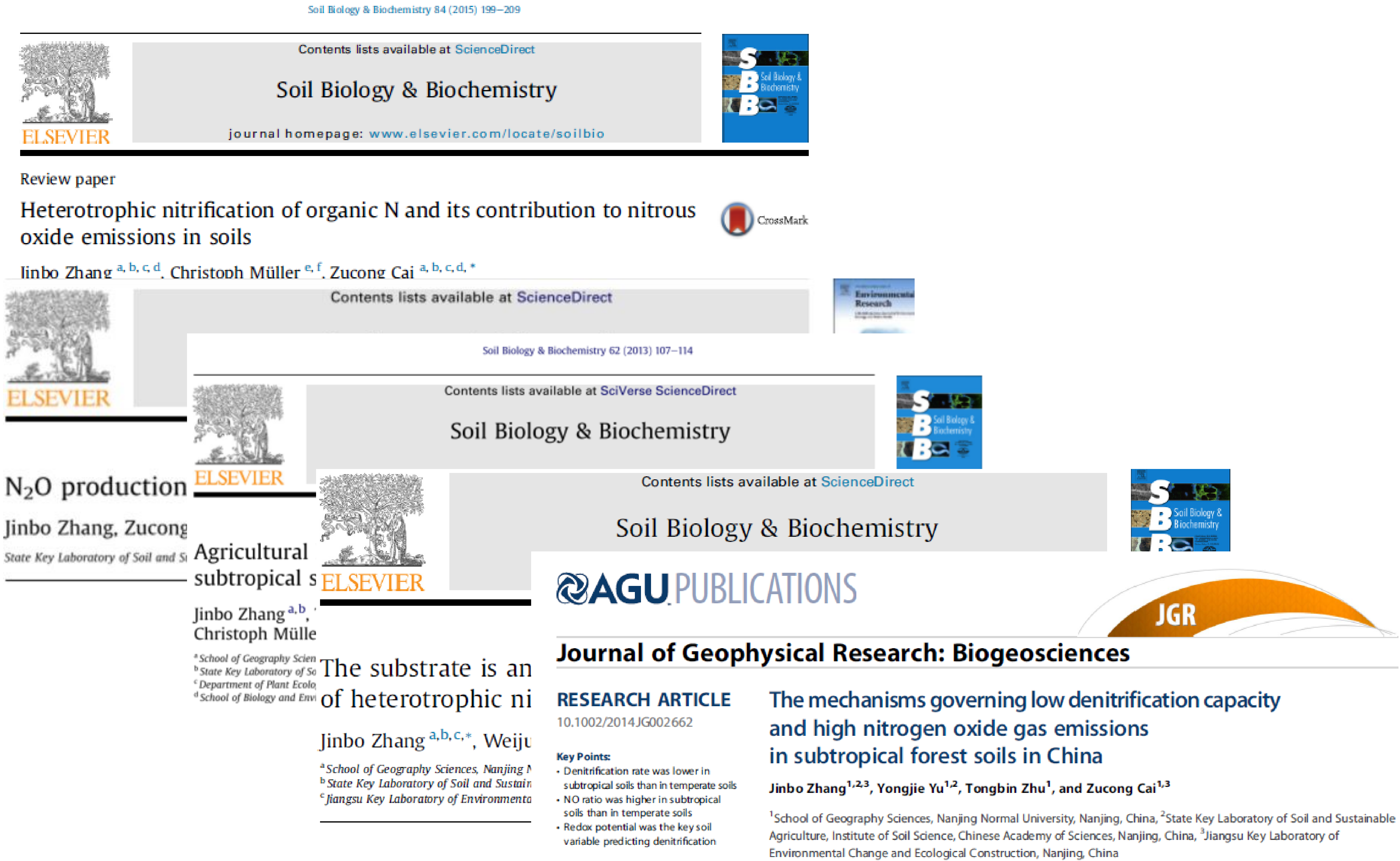
(其中：$d + n + h = 1$)

□ 各“管道”的N_2O排放量

$$N_2O_n = n \times N_2O_T$$
$$N_2O_h = h \times N_2O_T$$
$$N_2O_d = d \times N_2O_T$$

□ 各“管道”的N_2O产生率

$$R_h = N_2O_h / O_{Nrec}$$
$$R_n = N_2O_n / O_{NH4}$$
$$R_d = N_2O_d / Den$$



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Review paper

Heterotrophic nitrification of organic N and its contribution to nitrous oxide emissions in soils

Jinbo Zhang [a, b, c, d], Christoph Müller [e, f], Zucong Cai [a, b, c, d, *]

Contents lists available at ScienceDirect

N_2O production

Jinbo Zhang, Zucong

State Key Laboratory of Soil and S

Soil Biology & Biochemistry 62 (2013) 107–114

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Soil Biology & Biochemistry

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AGU PUBLICATIONS

Journal of Geophysical Research: Biogeosciences

RESEARCH ARTICLE

10.1002/2014JG002662

Key Points:

- Denitrification rate was lower in subtropical soils than in temperate soils
- NO ratio was higher in subtropical soils than in temperate soils
- Redox potential was the key soil variable predicting denitrification

The mechanisms governing low denitrification capacity and high nitrogen oxide gas emissions in subtropical forest soils in China

Jinbo Zhang[1,2,3], Yongjie Yu[1,2], Tongbin Zhu[1], and Zucong Cai[1,3]

[1] School of Geography Sciences, Nanjing Normal University, Nanjing, China, [2] State Key Laboratory of Soil and Sustainable Agriculture, Institute of Soil Science, Chinese Academy of Sciences, Nanjing, China, [3] Jiangsu Key Laboratory of Environmental Change and Ecological Construction, Nanjing, China

2. N_2O同位素异位体的质谱测定及应用

同位素异位体（Isotopomer/Isotopologue)

- **定义：**化合物分子的一个位点被稳定同位素所代替，某种化合物的同位素异位体的数目取决于构成化合物元素的种类、每种元素的同位素数量和分子结构的对称性

- **N_2O：**N-N-O 三原子不对称的直线型结构

  N（^{14}N、^{15}N），O（^{16}O、^{17}O、^{18}O）

  理论上共有 12种 同位素异位体（2*2*3=12）

  只有5种具有明显的自然丰度

  8种可被常规三杯配置的IRMS测定

Isotopologue	Abundance (mole fraction)	m/z
$^{14}N^{14}N^{16}O$	0.99032	44
$^{14}N^{15}N^{16}O$	0.00362	45
$^{15}N^{14}N^{16}O$	0.00362	45
$^{14}N^{14}N^{18}O$	0.00204	46
$^{14}N^{14}N^{17}O$	0.00038	45
$^{15}N^{15}N^{16}O$	1.32E-5	46
$^{14}N^{15}N^{18}O$	7.43E-6	
$^{15}N^{14}N^{18}O$	7.43E-6	
$^{14}N^{15}N^{17}O$	1.38E-6	46
$^{15}N^{14}N^{17}O$	1.38E-6	46
$^{15}N^{15}N^{18}O$	2.72E-8	
$^{15}N^{15}N^{17}O$	5.03E-9	

^{15}N在中间位（α位）　$^{14}N^{15}N^{16}O$

^{15}N在末端位（β位）　$^{15}N^{14}N^{16}O$

Isotopologue	Abundance (mole fraction)	m/z
$^{14}N^{14}N^{16}O$	0.99032	44
$^{14}N^{15}N^{16}O$	0.00362	45
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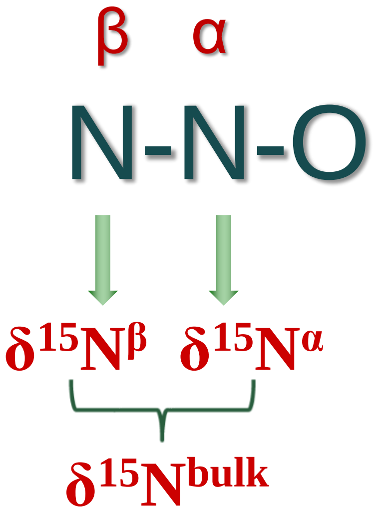
$^{14}N^{14}N^{18}O$	0.00204	46
$^{14}N^{14}N^{17}O$	0.00038	45



α position or 2 position：中间位

β position or 1 position：末端位

$$\delta^{15}N^{bulk} = (\delta^{15}N^{\alpha} + \delta^{15}N^{\beta}) / 2$$

$$\text{SP(位点优势值)} = \delta^{15}N^{\alpha} - \delta^{15}N^{\beta}$$

-SP：site preference

常规IRMS测定N_2O的方法：

（1）**化学法**： $N_2O \rightarrow N_2+CO_2$，分别测定$\delta^{15}N_{Air}$和$\delta^{18}O_{SMOW}$

（2）**直接测定法**：需配备痕量气体预浓缩装置

Precon(Thermo Scientific Inc.)

配有m/z 44, 45, 46三杯，直接同时测定N_2O的$\delta^{15}N_{Air}$和$\delta^{18}O_{SMOW}$

$\delta^{15}N^{bulk}$

~~$\delta^{15}N^{\alpha}$~~

~~$\delta^{15}N^{\beta}$~~

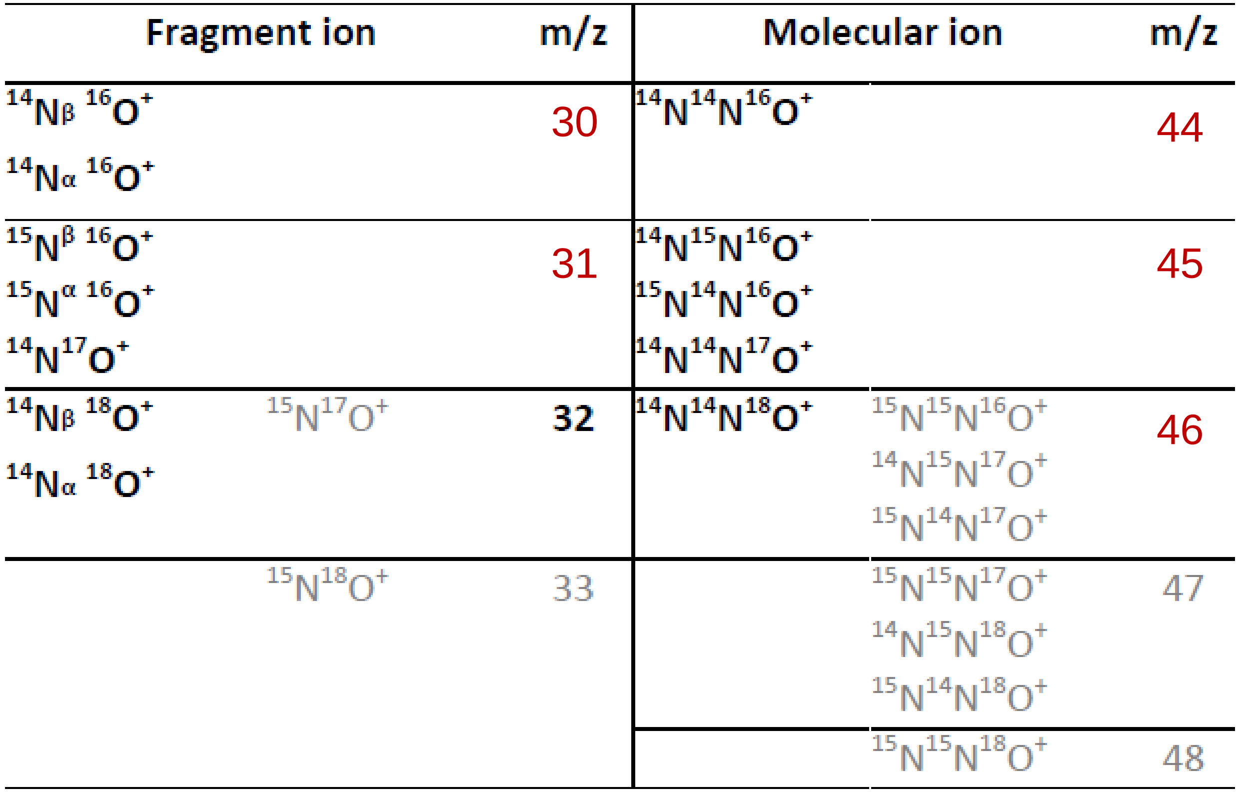
N-N-O $\xrightarrow[\text{轰击}]{\text{电子能量}}$

- N_2O^+ (75%) $\rightarrow$ $\delta^{15}N^{bulk}$
- NO^+ (fraction to N_2O^+ = 0.2~0.3) $\rightarrow$ $\delta^{15}N^{\alpha}$
- N_2^+, O^+, N^+ (fraction to N_2O^+ = 0.1, 0.03, 0.07)

$\delta^{15}N^{\beta}$, SP

碎片离子NO^+

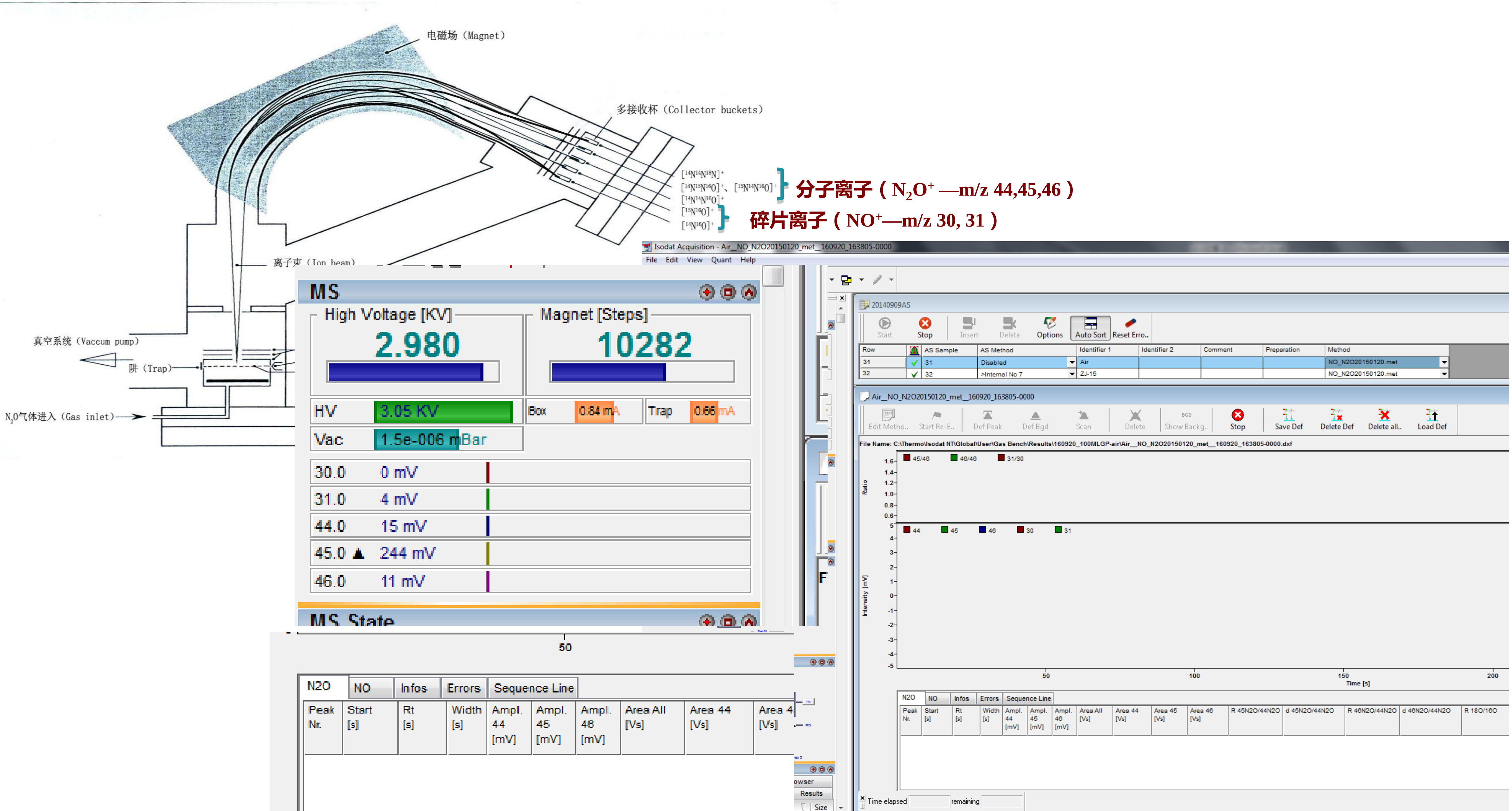
分子离子N_2O^+



Fragment ion		m/z	Molecular ion		m/z
$^{14}N_{\beta}{}^{16}O^+$ $^{14}N_{\alpha}{}^{16}O^+$		30	$^{14}N^{14}N^{16}O^+$		44
$^{15}N^{\beta}{}^{16}O^+$ $^{15}N^{\alpha}{}^{16}O^+$ $^{14}N^{17}O^+$		31	$^{14}N^{15}N^{16}O^+$ $^{15}N^{14}N^{16}O^+$ $^{14}N^{14}N^{17}O^+$		45
$^{14}N_{\beta}{}^{18}O^+$ $^{14}N_{\alpha}{}^{18}O^+$	$^{15}N^{17}O^+$	32	$^{14}N^{14}N^{18}O^+$	$^{15}N^{15}N^{16}O^+$ $^{14}N^{15}N^{17}O^+$ $^{15}N^{14}N^{17}O^+$	46
	$^{15}N^{18}O^+$	33		$^{15}N^{15}N^{17}O^+$ $^{14}N^{15}N^{18}O^+$ $^{15}N^{14}N^{18}O^+$	47
				$^{15}N^{15}N^{18}O^+$	48

- 浅灰色的离子因含两个或以上的稀有同位素原子，所占比例不显著
- m/z 32因受O_2干扰，不计入
- m/z < 33 或m/z > 46的离子因含量极少，不计入

五杯模式下稳定同位素比值质谱示意图



分子离子（N_2O^+ —m/z 44,45,46）

碎片离子（NO^+—m/z 30, 31）

High Voltage [KV] 2.980

Magnet [Steps] 10282

HV 3.05 KV

Box 0.84 mA

Trap 0.66 mA

Vac 1.5e-006 mBar

30.0	0 mV
31.0	4 mV
44.0	15 mV
45.0 ▲	244 mV
46.0	11 mV

Peak Nr.	Start [s]	Rt [s]	Width [s]	Ampl. 44 [mV]	Ampl. 45 [mV]	Ampl. 46 [mV]	Area All [Vs]	Area 44 [Vs]	Area 4 [Vs]

20140909AS

Row		AS Sample	AS Method	Identifier 1	Identifier 2	Comment	Preparation	Method
31	✓	31	Disabled	Air				NO_N2O20150120.met
32	✓	32	>Internal No 7	ZJ-15				NO_N2O20150120.met

Air_NO_N2O20150120_met_160920_163805-0000

File Name: C:\Thermo\Isodat NT\Global\User\Gas Bench\Results\160920_100MLGP-air\Air__NO_N2O20150120_met__160920_163805-0000.dxf

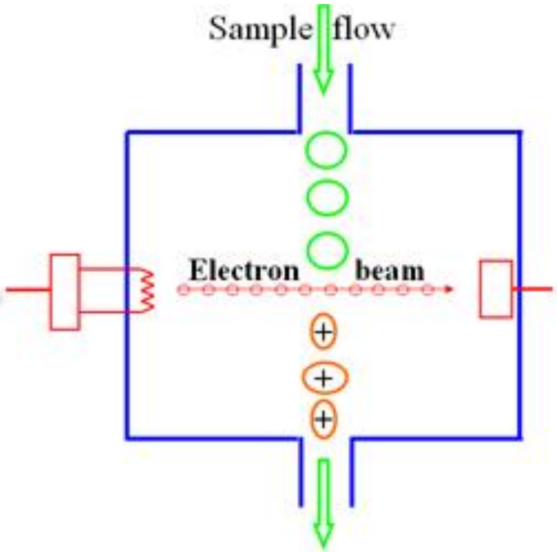
Peak Nr.	Start [s]	Rt [s]	Width [s]	Ampl. 44 [mV]	Ampl. 45 [mV]	Ampl. 46 [mV]	Area All [Vs]	Area 44 [Vs]	Area 45 [Vs]	Area 46 [Vs]	R 45N2O/44N2O	d 45N2O/44N2O	R 46N2O/44N2O	d 46N2O/44N2O	R 18O/16O

- **NO-N_2O模式下离子源条件的优化**
- **重排因子(rearrangement/scrambling factor)的测定**
- **N_2O工作标准气体的校准**
- **其他测定问题**

NO-N_2O五杯模式下离子源条件的优化

- N_2O气体电离碎化形成多种离子（N_2O^+, NO^+, N_2^+, N^+, O^+），需保证碎片离子分布的稳定性
- NO^+的产率仅为N_2O^+的1/3，适当提高NO^+产率可提高精确度
- N_2O^+和NO^+的最适离子源条件可能不同

改变电子能量（Electron Energy）



● 不同电子能量下N_2O的离子分布比例（Delta V Plus）

电子能量 (Electron Energy)	离子流强度（mV）					碎化率		
	m/z 30 ($1\times10^{10}\Omega$)	m/z 31 ($3\times10^{11}\Omega$)	m/z 44 ($3\times10^{8}\Omega$)	m/z 45 ($3\times10^{10}\Omega$)	m/z 46 ($1\times10^{11}\Omega$)	m/z 30/44	m/z 31/30	no. of measurements
124 eV	29470	3560	3124	2394	2191	**0.2830**	0.004	n=3
100 eV	25940	3137	2889	2213	2038	**0.2694**	0.004	n=3
70 eV	17036	2044	1874	1432	1309	**0.2727**	0.004	n=3

● Toyoda et al.(1999)的测定结果（MAT 252）

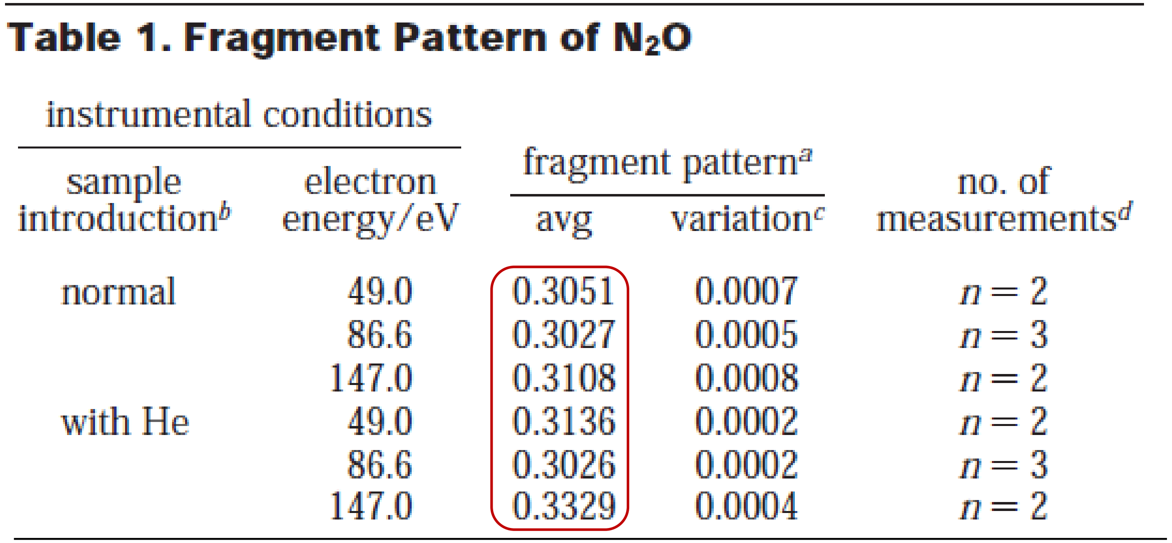


Table 1. Fragment Pattern of N_2O

instrumental conditions		fragment pattern[a]		
sample introduction[b]	electron energy/eV	avg	variation[c]	no. of measurements[d]
normal	49.0	0.3051	0.0007	$n = 2$
	86.6	0.3027	0.0005	$n = 3$
	147.0	0.3108	0.0008	$n = 2$
with He	49.0	0.3136	0.0002	$n = 2$
	86.6	0.3026	0.0002	$n = 3$
	147.0	0.3329	0.0004	$n = 2$

● 电子能量变化对离子流强度的影响

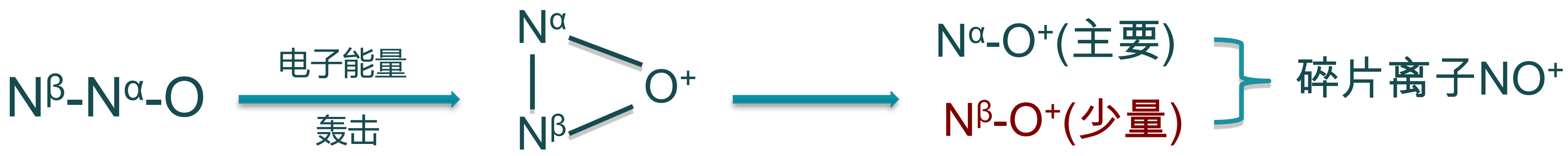
电子能量 (Electron Energy)	m/z44 信号衰减率 (%)				m/z30 信号衰减率 (%)			
	1	2	3	Mean	1	2	3	Mean
100 eV	17.52	16.08	14.83	**16.14**	11.98	11.28	10.79	**11.35**
70 eV	40.01	42.14	41.15	**41.10**	42.19	44.49	43.99	**43.56**

* 均以124 eV的离子流强度为基准计算

● 不同电子能量对N_2O同位素异位体^{15}N丰度的测定影响

电子能量 (eV)	**$\delta^{15}N^{bulk}$ (‰)**	**$\delta^{15}N^{\alpha}$ (‰)**	**Mean (‰)**	**$\delta^{15}N^{\beta}$ (‰)**	**Mean (‰)**	**SP (‰)**	**Mean (‰)**
70 eV	-1.686	-6.831	**-6.721**	3.459	**3.348**	-10.290	**-10.068**
		-6.673		3.301		-9.974	
		-6.656		3.284		-9.940	
100 eV	-1.686	-4.266	**-4.475**	0.894	**0.940**	-5.160	**-5.252**
		-4.106		0.734		-4.840	
		-4.564		1.192		-5.756	
124 eV	-1.686	-4.436	**-4.444**		**1.072**		**-5.516**
		-4.257					
		-4.639					

重排因子(rearrangement/scrambling factor)的测定



N^{β}-N^{α}-O $\xrightarrow[\text{轰击}]{\text{电子能量}}$ N^{α}, N^{β}, O^{+} ⟶ N^{α}-O^{+}(主要)、N^{β}-O^{+}(少量) } 碎片离子NO^{+}

$$^{15}R^{\alpha}_{obs} = (1-y)^{15}R^{\alpha} + y\,^{15}R^{\beta}$$

- 确定重排因子 (y) 后，可通过公式校正测定结果：

$$\delta^{15}N^{\alpha} = \delta^{15}N^{\beta}_{obs} + 2y(\delta^{15}N^{\alpha}_{obs} - \delta^{15}N^{bulk}) / \{A(1 - 2y)\}$$

$$\delta^{15}N^{\beta} = \delta^{15}N^{bulk} + A(\delta^{15}N^{bulk} - \delta^{15}N^{\alpha}) / (2 - A)$$

A是常数，$A=(^{15}R^{\alpha}/^{15}R^{bulk})_{std}$

- 不同IRMS仪器的重排因子(y)不同: y=0.07-0.09 (MAT 252 253); y=0.19-0.27 (Isoprime)；
- 重排因子不随^{15}N丰度变化，但受离子源条件影响；

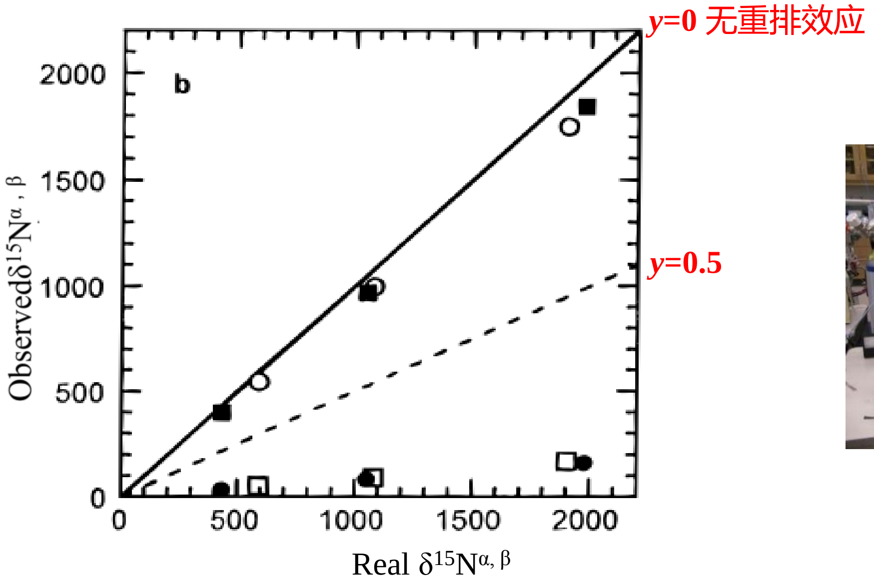
(Toyoda et al. 1999; Westley et al. 2003; Sutka et al. 2006)

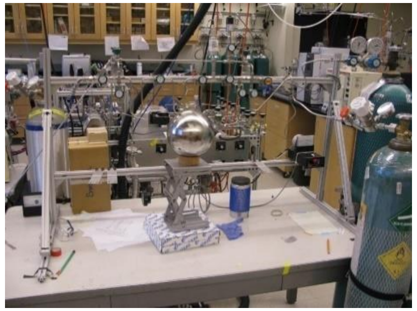
已知丰度（$\delta^{15}N$、$\delta^{18}O$、SP）的N_2O气体，比较测定值和理论值

- **方法一：NH_4NO_3热解法**

$$NH_4{}^{15}NO_3 \longrightarrow N^{15}NO+2H_2O$$

$$^{15}NH_4NO_3 \longrightarrow {}^{15}NNO+2H_2O$$



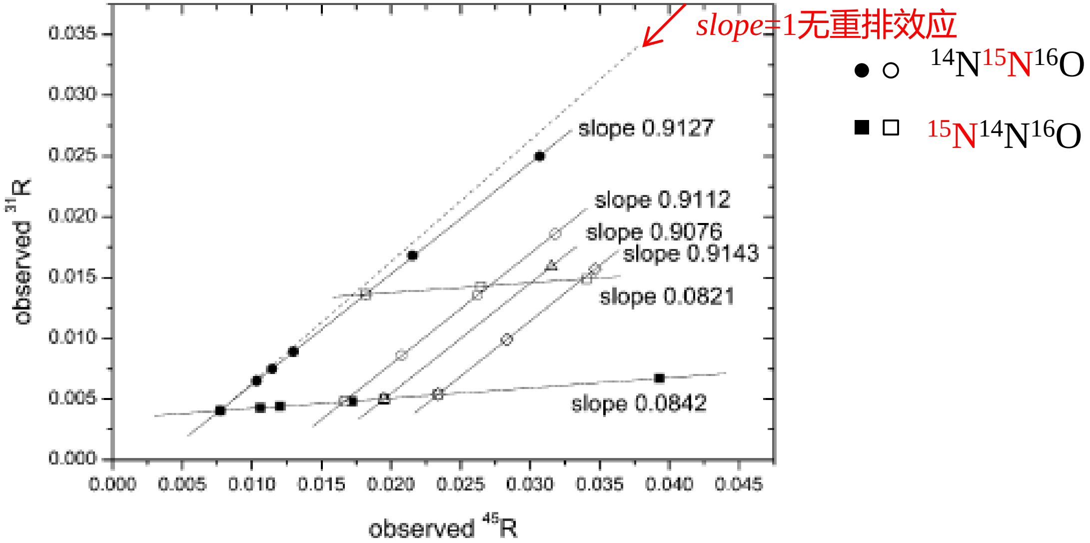


- **方法二：标记气体混合法**

高纯高丰度^{15}NNO或$N^{15}NO$气体

+

高纯自然丰度N_2O气体稀释



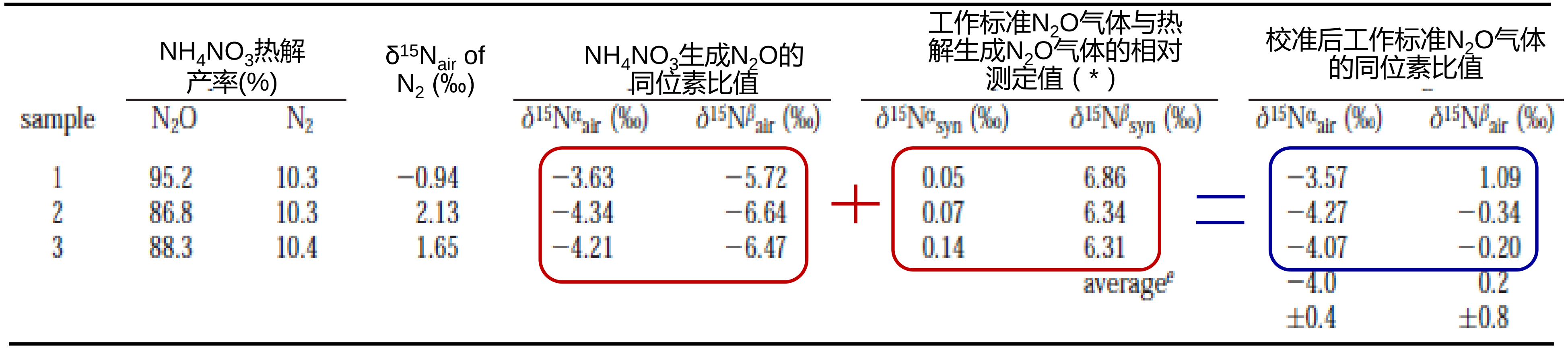
（Toyoda et al. 1999; Westley et al. 2007; Kaiser et al, 2004; Rockman et al, 2003）

● N_2O工作标准气体的校准

➢ NH_4NO_3热解法

NH_4NO_3热解产生系列已知丰度的N_2O气体，与工作标准N_2O气体相对测定校准其$\delta^{15}N^{\alpha}_{air}$和$^{15}N^{\beta}_{air}$值

- Toyoda等人(1999)运用NH_4NO_3热解法校准工作标准N_2O气体

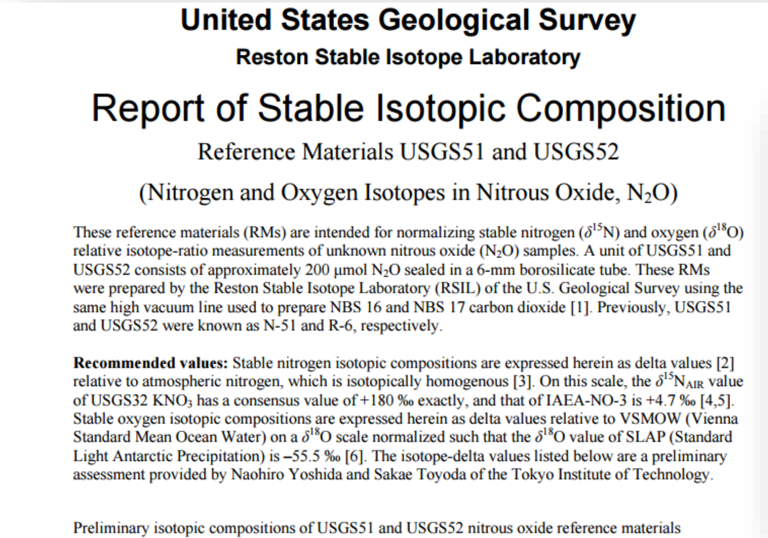


	NH_4NO_3热解产率(%)		$\delta^{15}N_{air}$ of N_2 (‰)	NH_4NO_3生成N_2O的同位素比值		工作标准N_2O气体与热解生成N_2O气体的相对测定值（*）		校准后工作标准N_2O气体的同位素比值	
sample	N_2O	N_2		$\delta^{15}N^{\alpha}_{air}$ (‰)	$\delta^{15}N^{\beta}_{air}$ (‰)	$\delta^{15}N^{\alpha}_{syn}$ (‰)	$\delta^{15}N^{\beta}_{syn}$ (‰)	$\delta^{15}N^{\alpha}_{air}$ (‰)	$\delta^{15}N^{\beta}_{air}$ (‰)
1	95.2	10.3	−0.94	−3.63	−5.72	0.05	6.86	−3.57	1.09
2	86.8	10.3	2.13	−4.34	−6.64	0.07	6.34	−4.27	−0.34
3	88.3	10.4	1.65	−4.21	−6.47	0.14	6.31	−4.07	−0.20
							average[e]	−4.0 ±0.4	0.2 ±0.8

* 已校正重排效应

➢ 购买标准气体相对测定法

使用已准确校准$\delta^{15}N^{bulk}$，$\delta^{18}O$，$\delta^{15}N^{\alpha}$，$\delta^{15}N^{\beta}$和SP值的N_2O气体作为测试样品，反标参考气。



United States Geological Survey

Reston Stable Isotope Laboratory

Report of Stable Isotopic Composition

Reference Materials USGS51 and USGS52

(Nitrogen and Oxygen Isotopes in Nitrous Oxide, N_2O)

These reference materials (RMs) are intended for normalizing stable nitrogen ($\delta^{15}N$) and oxygen ($\delta^{18}O$) relative isotope-ratio measurements of unknown nitrous oxide (N_2O) samples. A unit of USGS51 and USGS52 consists of approximately 200 µmol N_2O sealed in a 6-mm borosilicate tube. These RMs were prepared by the Reston Stable Isotope Laboratory (RSIL) of the U.S. Geological Survey using the same high vacuum line used to prepare NBS 16 and NBS 17 carbon dioxide [1]. Previously, USGS51 and USGS52 were known as N-51 and R-6, respectively.

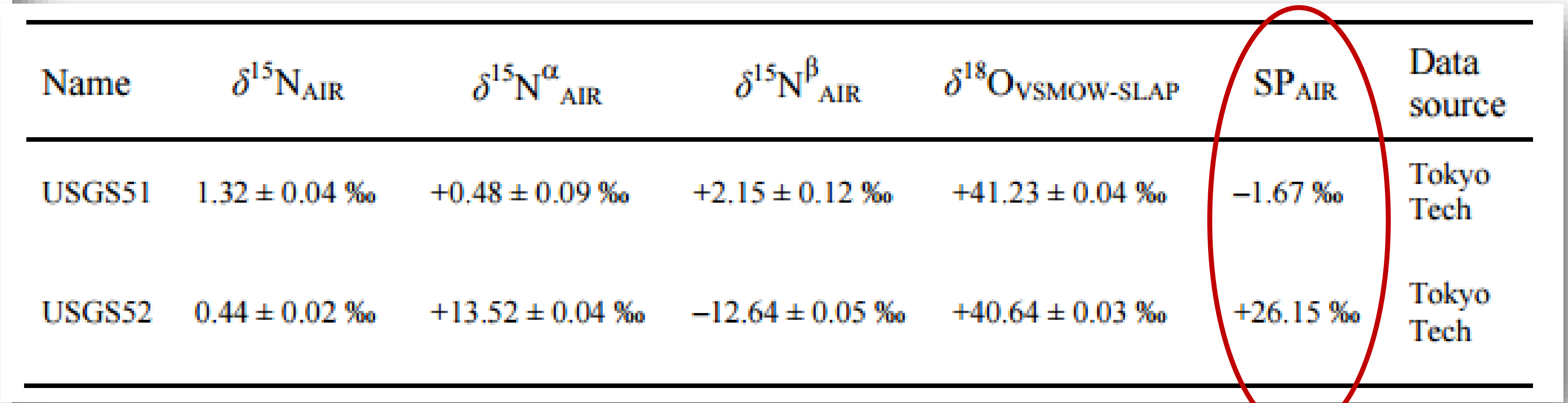
Recommended values: Stable nitrogen isotopic compositions are expressed herein as delta values [2] relative to atmospheric nitrogen, which is isotopically homogenous [3]. On this scale, the $\delta^{15}N_{AIR}$ value of USGS32 KNO_3 has a consensus value of +180 ‰ exactly, and that of IAEA-NO-3 is +4.7 ‰ [4,5]. Stable oxygen isotopic compositions are expressed herein as delta values relative to VSMOW (Vienna Standard Mean Ocean Water) on a $\delta^{18}O$ scale normalized such that the $\delta^{18}O$ value of SLAP (Standard Light Antarctic Precipitation) is –55.5 ‰ [6]. The isotope-delta values listed below are a preliminary assessment provided by Naohiro Yoshida and Sakae Toyoda of the Tokyo Institute of Technology.

Preliminary isotopic compositions of USGS51 and USGS52 nitrous oxide reference materials

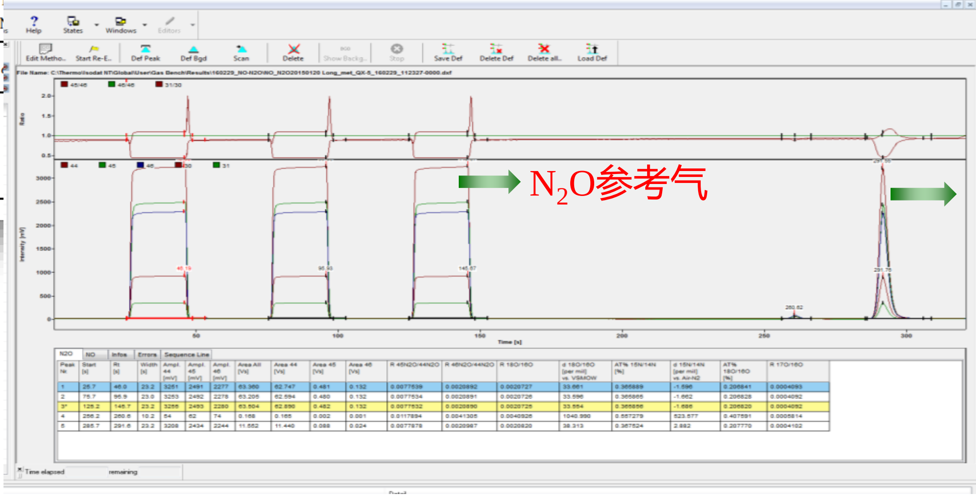
[The superscripts α and β refer to the central and outer

preference (SP) is the difference between $\delta^{15}N^{\alpha}$ and δ^{15}

Name	$\delta^{15}N_{AIR}$	$\delta^{15}N^{\alpha}{}_{AIR}$	$\delta^{15}N^{\beta}{}_{AIR}$
USGS51	1.32 ± 0.04 ‰	+0.48 ± 0.09 ‰	+2.15 ± 0.12 ‰
USGS52	0.44 ± 0.02 ‰	+13.52 ± 0.04 ‰	–12.64 ± 0.05 ‰



Name	$\delta^{15}N_{AIR}$	$\delta^{15}N^{\alpha}{}_{AIR}$	$\delta^{15}N^{\beta}{}_{AIR}$	$\delta^{18}O_{VSMOW\text{-}SLAP}$	SP_{AIR}	Data source
USGS51	1.32 ± 0.04 ‰	+0.48 ± 0.09 ‰	+2.15 ± 0.12 ‰	+41.23 ± 0.04 ‰	–1.67 ‰	Tokyo Tech
USGS52	0.44 ± 0.02 ‰	+13.52 ± 0.04 ‰	–12.64 ± 0.05 ‰	+40.64 ± 0.03 ‰	+26.15 ‰	Tokyo Tech



N_2O参考气

N_2O标准气体

$$\delta^{15}N^{\alpha} = ({}^{15}R^{\alpha}/{}^{15}R^{\alpha}_{st} - 1) \times 1000$$

$$\delta^{18}O = ({}^{18}R/{}^{18}R_{st} - 1) \times 1000$$

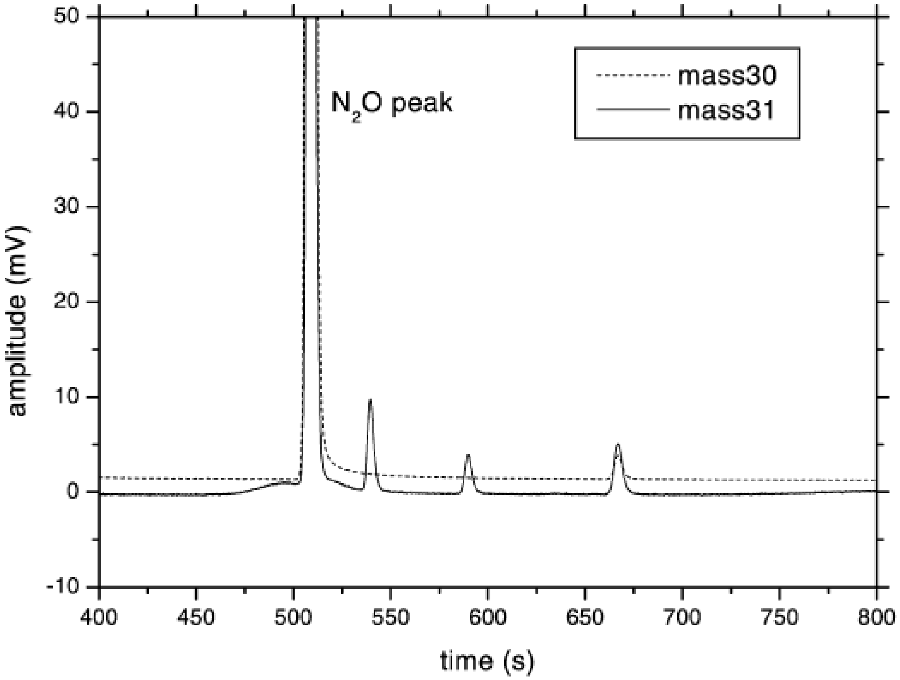
$${}^{31}R = {}^{17}R + {}^{15}R^{\alpha}$$

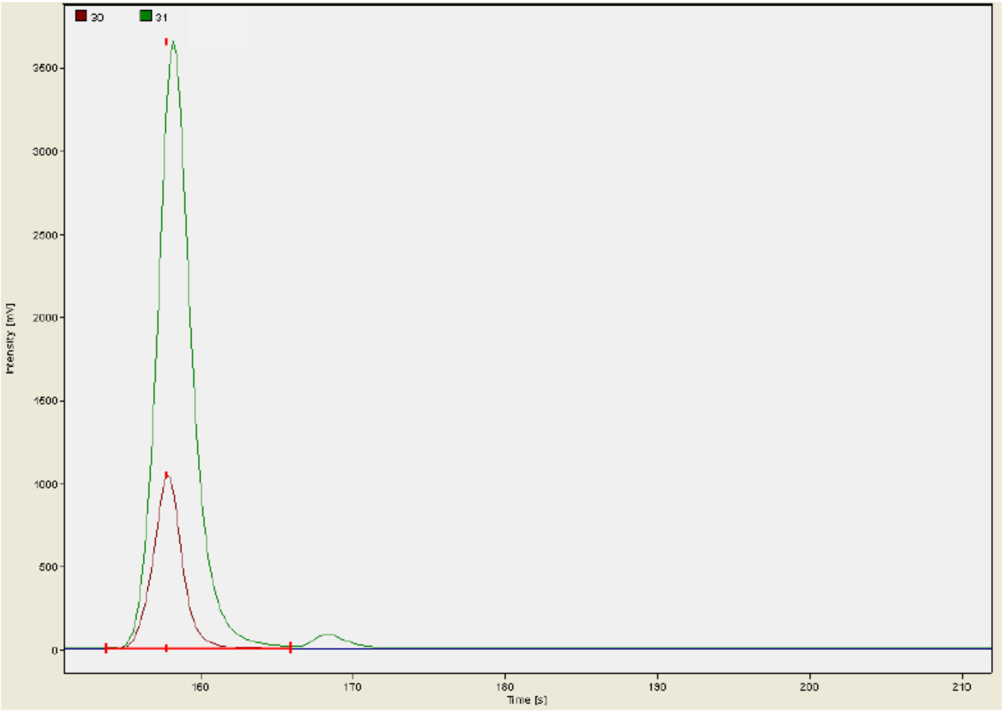
$${}^{31}R_{ref}/{}^{31}rR_{ref} = {}^{31}R_{N2Ostd}/{}^{31}rR_{N2Ostd}$$

其他测定问题

碳氟化合物等杂质对m/z 31的干扰

CHF_3→ $^{12}C^{17}F^+$对m/z 31信号有明显干扰，可通过调节流速和柱温、延长色谱柱来分离杂质，或加阀反吹去除杂质





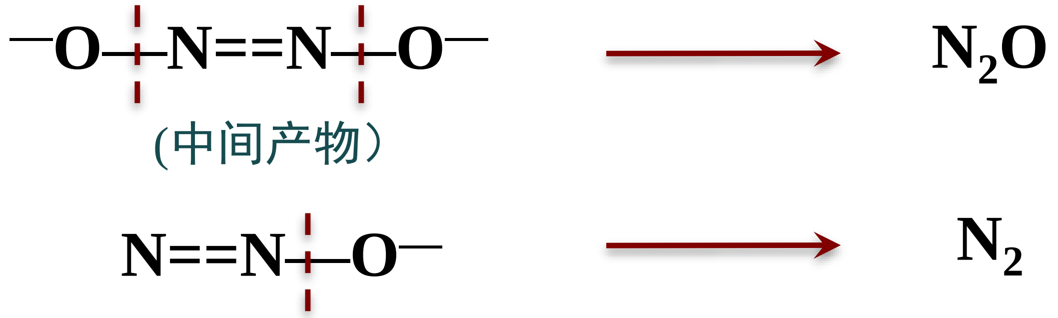
(Rockman et al. 2003)

大气N_2O样品的SP值测定

测定次数	m/z 44 (mV)	m/z 31 (mV)	$\delta^{15}N_{Air}$ (‰)	$\delta^{18}O$(‰)	SP (‰)
1	574	204	6.176	44.367	20.726
2	583	207	6.138	44.718	18.702
3	555	197	6.189	44.952	19.916
4	549	195	6.183	44.824	20.142
5	544	193	6.198	44.328	20.691
6	557	197	6.189	44.276	18.172
7	565	208	6.179	44.588	19.484
8	560	205	6.165	44.763	20.989
Mean (‰)			**6.177**	**44.602**	**19.853**
S.D. (‰)			**0.019**	**0.253**	**1.009**

- 对流层空气中N_2O的SP = 18.7±2.2‰ (Toyoda et al. 1999)

$N^{\beta}N^{\alpha}O \xrightarrow{?}$ N_2O source partition



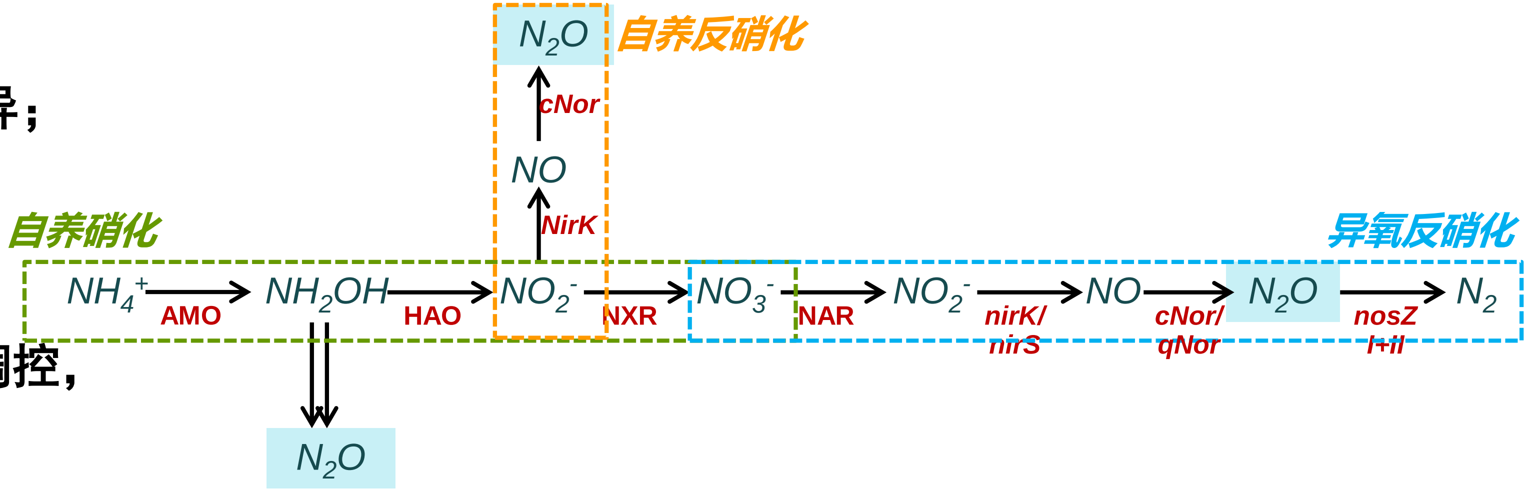
N_2O production： —O—N==N—O— → N_2O

(中间产物)

N_2O reduction to N_2： N==N—O— → N_2

- 不同位置**N-O键的断裂**决定了SP值的差异；
- 键的断裂受**微生物及相关的酶**调控
- 不同的N_2O产生途径受不同微生物和酶调控，

  键断裂的位点有所差异，SP值亦不同。

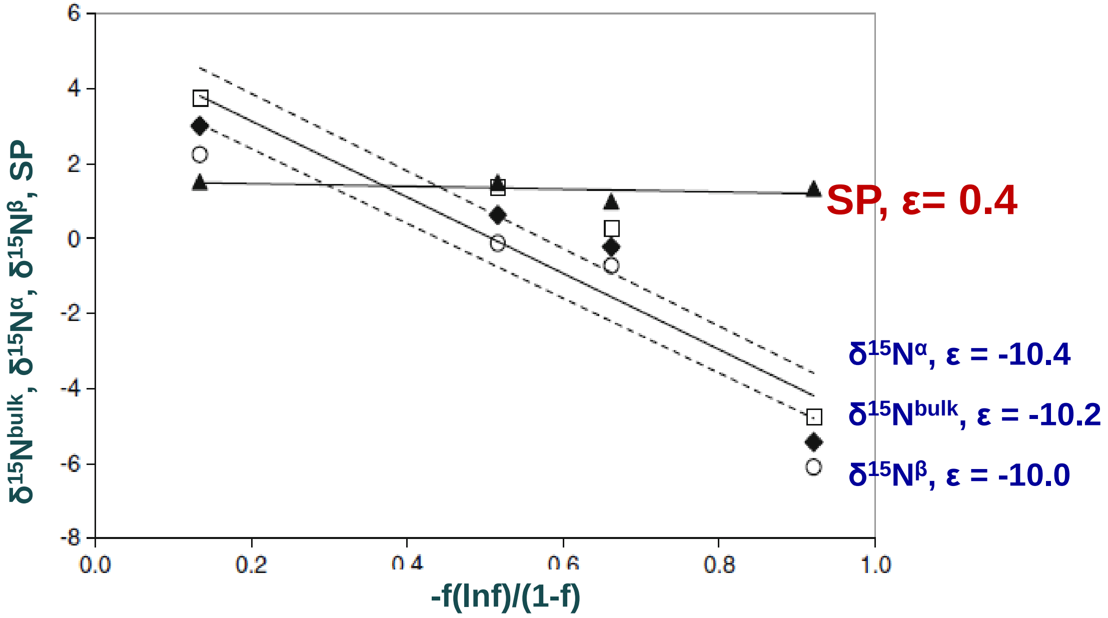


- **SP值基本不受底物(NH_4^+, NO_3^-, NO_2^-)δ^{15}N值的影响**

  ——N_2O production　(不受影响)

  ——N_2O consumption (有一定影响)

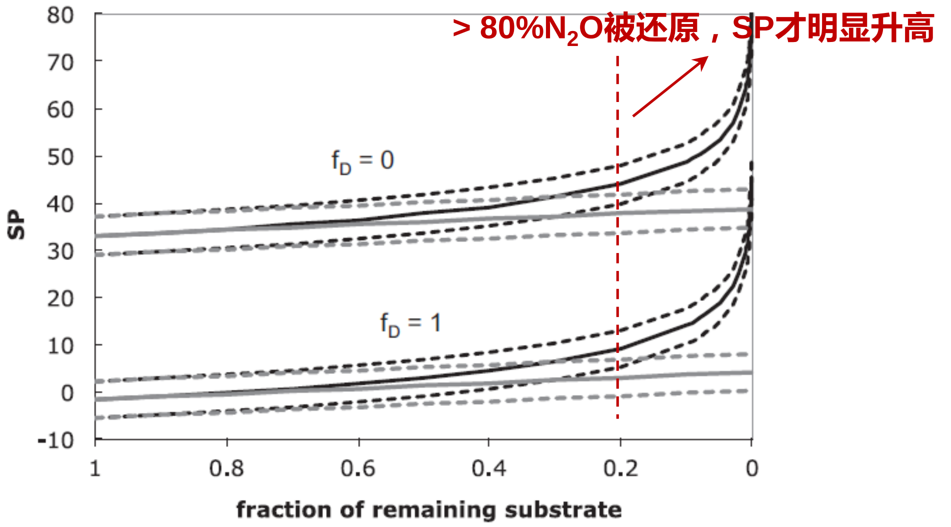
  N_2O还原为N_2会引起SP值升高



- **定性、半定量分析N_2O产生和消耗途径**

  ——不同途径N2O的SP特征值(纯培养或土壤培养)

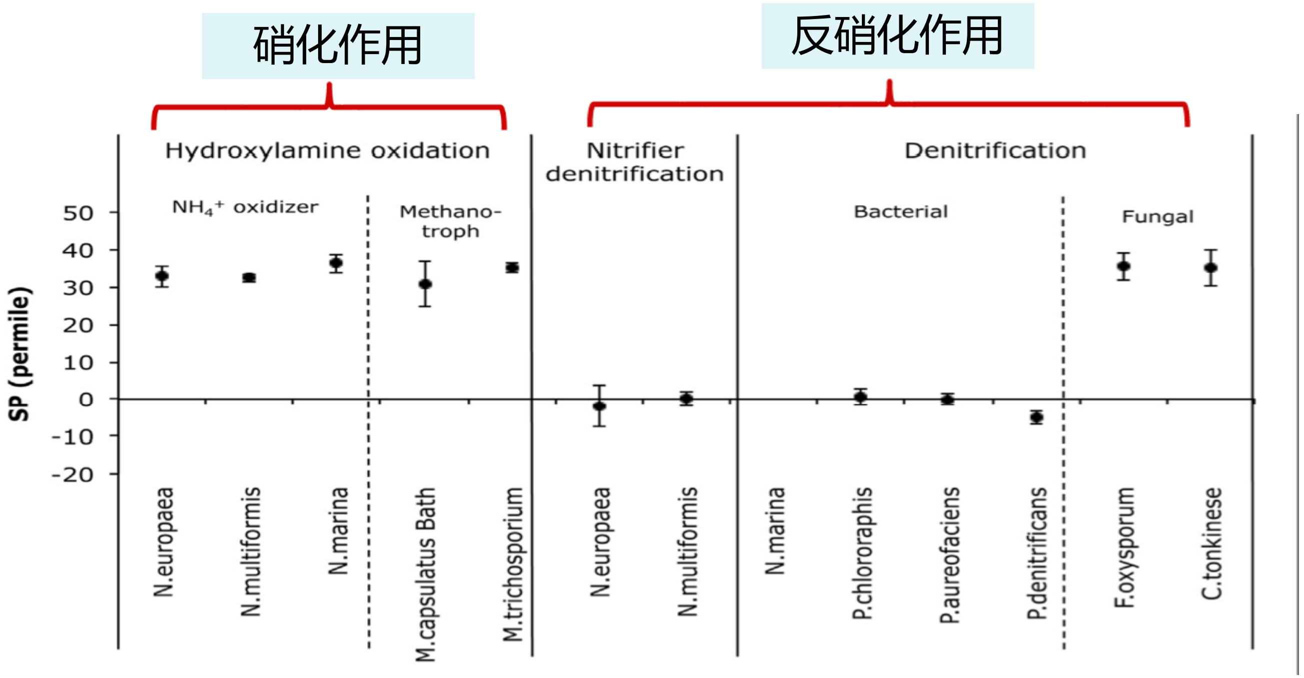
  ——结合δ^{15}N, δ^{18}O, SP评估不同途径的贡献率

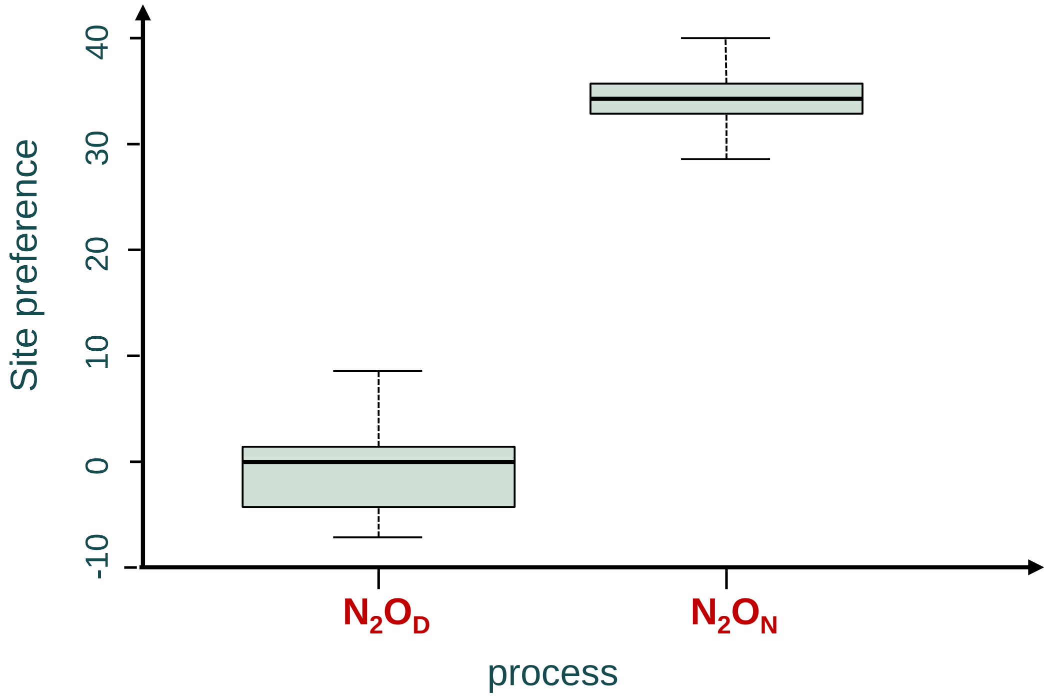


> 80%N_2O被还原，SP才明显升高

(Koba et al. 2009; Toyoda et al. 2011; Well et al. 2012; Decock et al., 2013)

N_2O 产生途径	SP特征值（‰）
自养硝化 (n=18)	33.0±1.6
细菌异养反硝化 (n=26)	-2.2±3.2
硝化细菌反硝化 (n=26)	-1.0±4.3
真菌反硝化 (n=8)	37.0±4.3
化学反硝化 (n=8)	29.9±1.5
AOA产N_2O (n=6)	30.3±1.2
异养硝化（真菌/细菌）	待研究
DNRA	39-57





- N_2O_D: 细菌异养反硝化、硝化细菌反硝化

  N_2O_N: 自养硝化、真菌反硝化、AOA产N_2O等

- 可作为定性或半定量区分 N_2O 来源的基点

(Decock et al. 2013)

同位素异位体法分析N_2O排放贡献

- **样品测定：**底物（NH_4^+,NO_3^-）的浓度和$\delta^{15}N_{substrate}$、$\delta^{18}O_{substrate}$值，

  N_2O的浓度和$\delta^{15}N_{N2O}$、$\delta^{18}O_{N2O}$、SP值

- **已有文献：**不同N_2O产生途径的分馏系数（$^{15}\varepsilon$、$^{18}\varepsilon$）

  N_2O还原为N_2的分馏系数（$^{15}\varepsilon_{reduction}$、$^{18}\varepsilon_{reduction}$ 和$^{sp}\varepsilon_{reduction}$）

- 不同产生途径N_2O的$\delta^{15}N$、$\delta^{18}O$和SP特征值范围

定性分析

N_2O 产生过程

$$\delta^{15}N_{N2O} = \delta^{15}N_{substrate} + {}^{15}\varepsilon$$

$$\delta^{18}O_{N2O} = \delta^{18}O_{substrate} + {}^{18}\varepsilon$$

N_2O 消耗过程

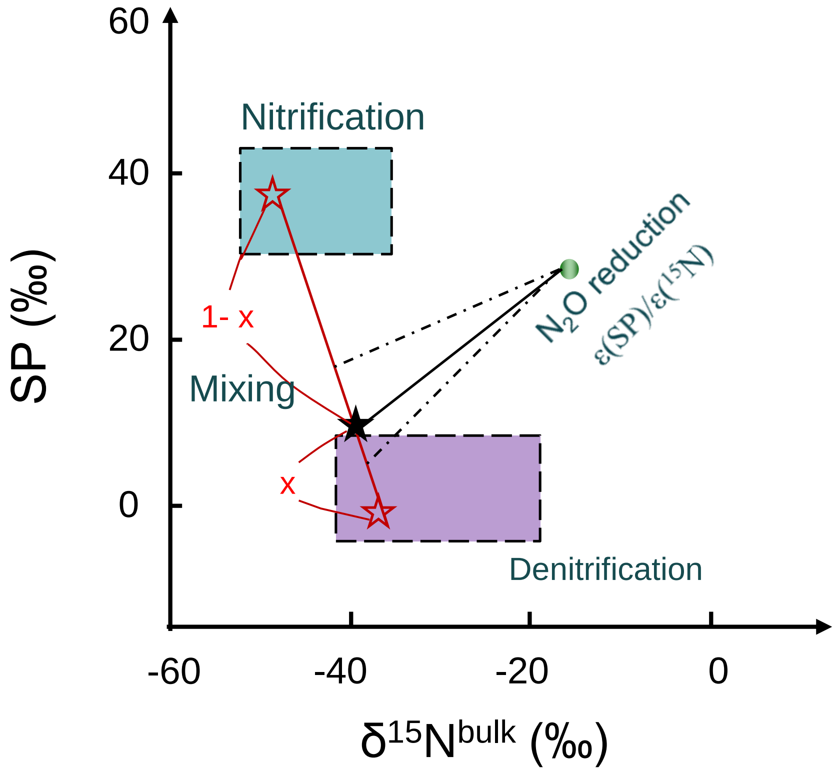
$$\delta^{15}N_{N2O} = \delta^{15}N_{source} + {}^{15}\varepsilon_{reduction}\ln(f)$$

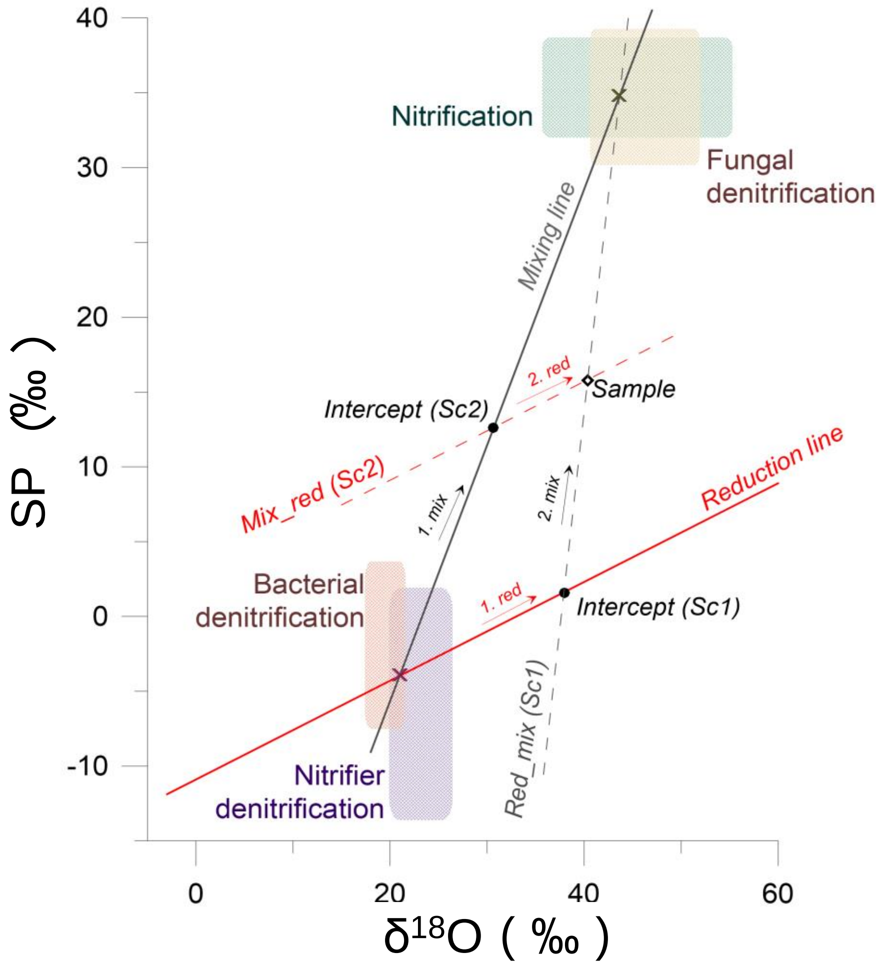
$$\delta^{18}O_{N2O} = \delta^{18}O_{source} + {}^{18}\varepsilon_{reduction}\ln(f)$$

$$SP_{N2O} = SP_{source} + {}^{sp}\varepsilon_{reduction}\ln(f)$$

- **定量分析——基于二源同位素混合模型**
- **关键问题——如何区分N_2O还原为N_2过程对SP值的影响**

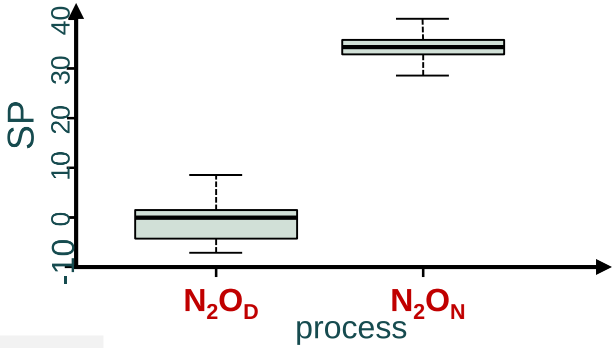
$$\delta_{soil} = x\delta_{nit} + (1-x)\delta_{denit} - k\varepsilon_{redution}$$

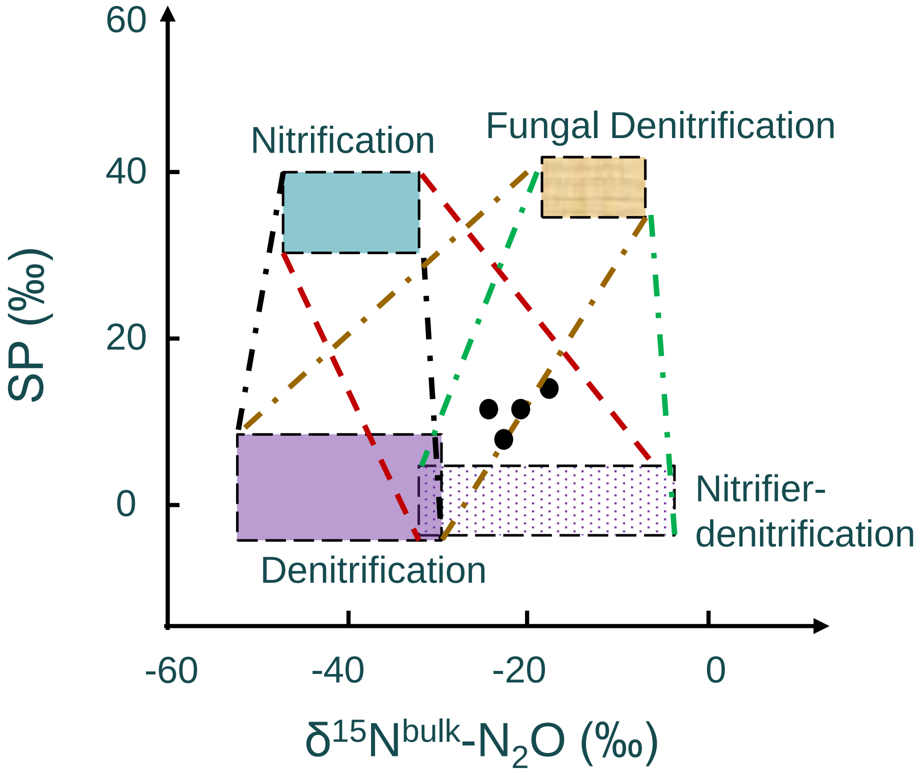




(Koba et al. 2009; Toyoda et al. 2011; Well et al. 2012; Opdyke et al. 2009; Ostrom et al. 2012; Lewicka-Szczebak et al. 2017)

- **场景假设（Case study）**
- **二源同位素混合模型分别计算每个场景(Case)下的各N_2O产生途径的贡献率**





Case 1	**NN v.s. DD**
Case 2	**NN v.s. ND**
Case 3	**FD v.s. ND**
Case 4	**FD v.s. DD**

Case 1		**Case 2**		**Case 3**		**Case 4**	
贡献率（%）		贡献率（%）		贡献率（%）		贡献率（%）	
DD	**NN**	**NN**	**ND**	**FD**	**DD**	**FD**	**ND**
64-72	28-36	10-25	75-90	8-26	74-92	11-43	57-89

谢谢，敬请指正！