

### Clumped isotope analysis in nitrous oxide by mid-IR laser spectroscopy: analytical developments and validation

<u>Kristýna Kantnerová</u>, Longfei Yu, Daniel Zindel, Mark S. Zahniser, David D. Nelson, Béla Tuzson, Lukas Emmenegger, Mayuko Nakagawa, Sakae Toyoda, Naohiro Yoshida, Stefano M. Bernasconi, Joachim Mohn





🏓 Empa

Materials Science and Technology



#### N<sub>2</sub>O absorption bands in mid-IR



446 and singly substituted – HITRAN2012 clumped – simulations in PGOPHER based on spectroscopic constants from Amiot 1976, Toth 1991, Wang et al. 2009 and Jun-he Du et al. 2011

Kantnerová et al. Rapid Commun. Mass Spectrom. 2020, submitted.



Kantnerová et al. Rapid Commun. Mass Spectrom. 2020, submitted.

## New reference scale for clumped N<sub>2</sub>O

 $y_{458}$  $y_{446}$ 

- using a working standard gas
  - thermal equilibration of the working standard 1.
    - $\rightarrow$  real mole fraction of clumped species in the gas (from statistical thermodynamics)

wstd

absolute calibration based on mole 2. fractions of all measured isotopocules in the working standard

 $\rightarrow$  gravimetric mixtures of the working standard in  $N_2$ 

mole fraction of singly substituted species derived from known  $\delta$  values





Wang et al., Geochim. Cosmochim. Acta 68 (23), 2004, 4779 - 4797.

4 5 8

5 4 8

# Validation of the new reference scale



- for singly substituted isotopocules only
- > validation gas different isotopic composition, concentration in the calibration range
- compared to another QCLAS and IRMS that use the conventional δ-calibration scale



method	δ456 / ‰	δ546 / ‰	δ448 / ‰
dual-laser QCLAS (this work)	15.53 ± 0.16	16.27 ± 0.17	55.13 ± 0.24
QCLAS	15.82 ± 0.06	16.80 ± 0.08	$53.93 \pm 0.06^{*}$
IRMS	-	-	55.96 ± 0.07

 $^{\ast}$  deviation due to limited span of available standards for  $\delta^{18}O$ 

Kantnerová et al. Rapid Commun. Mass Spectrom. 2020, submitted.

### Comparison of QCLAS and HR-IRMS





Thermo Scientific<sup>™</sup> 253 Ultra<sup>™</sup>

method	measurement time (incl. calibration)	precision / ‰	amount of N <sub>2</sub> O / µmol
dual-laser QCLAS (this work)	45 min	0.10 - 0.50	4
HR-IRMS	8 – 10 hrs	0.10 - 1.30	10

Magyar et al., Rapid Commun. Mass Spectrom. 30, 2016, 1923–1940.

# Comparison of QCLAS and HR-IRMS



- for all isotopocules (except 556, HR-IRMS is not able to measure it)
- three gases differing in bulk isotopic composition ( $\delta^{15}N_{bulk}$ ,  $\delta^{18}O$ ) VG2, VG3, VG4
- gases thermally equilibrated at 100 and 200 °C
- comparison with theoretical predictions based on statistical thermodynamics

Wang et al., Geochim. Cosmochim. Acta 68 (23), 2004, 4779 – 4797.

- HR-IRMS no correction for true content of 458 and 548 in their working standard gas, it was not characterized
- see the next slide comparison plots:
- HR-IRMS has clear problems with distinguishing the two isotopomers 458 and 548 (panel d)
- QCLAS has a very good agreement with theoretical predictions





# Comparison of QCLAS and HR-IRMS



......



## Conclusion

- new absolute calibration scheme for clumped  $N_2O$  isotopes
- validated using gas with different isotopic composition
- comparison with currently prevailing HR-IRMS

advantages of QCLAS – less time-consuming, better precision,
accuracy, and repeatability, possibility of on-line sampling

- no need for complex correction schemes

#### Application

- N<sub>2</sub>O produced by denitrifier *Pseudomonas aureofaciens* collaboration with Tokyo Institute of Technology under JSPS fellowship
- UV photolysis of  $N_2O$  ongoing experiments
  - collaboration with University of Copenhagen

(Malte F. Jespersen and Matthew S. Johnson)



Acknowledgement for funding:

#### FNSNF

Fonds national suisse Schweizerischer Nationalfonds Fondo nazionale svizzero Swiss National Science Foundation





