

Towards understanding the N₂O production in dust-rich Antarctic iceLison Soussaintjean¹, Jochen Schmitt¹, Joël Savarino², Andy Menking³, Edward Brook⁴, Barbara Seth¹, Thomas Röckmann⁵, Hubertus Fischer¹¹Climate and Environmental Physics, Physics Institute & Oeschger Centre for Climate Change Research, University of Bern, Switzerland²Institut des Géosciences de l'Environnement, CNRS, Univ. Grenoble Alpes, France, ³Australian Antarctic Program Partnership, Institute for Marine and Antarctic Studies, University of Tasmania, Hobart & Environmental Research Unit, Commonwealth Scientific and Industrial Research Organisation, Aspendale, Victoria, Australia⁴College of Earth, Ocean, and Atmospheric Sciences, Oregon State University, USA, ⁵Institute for Marine and Atmospheric research Utrecht, Utrecht University, the Netherlands

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Nitrous oxide (N₂O) is a potent greenhouse gas involved in ozone destructionN₂O (ppb)

200 250 300

INTRODUCTION – What happened to the N₂O record?

Air bubbles trapped in ice cores are unique archives of the past atmosphere. They have allowed the reconstruction of greenhouse gas concentrations over the past 800,000 years. But we still lack a continuous record for N₂O...

Why? Non-atmospheric N₂O is formed in dust-rich ice core sections [1]. This in situ produced N₂O gets added to the atmospheric N₂O and can lead to misinterpretation in terms of past atmospheric concentrations. To eventually correct the N₂O record, let's investigate the production process:

- What is the chemical precursor of in situ N₂O?
- What is the chemical reaction?

METHODS – The detective geochemist's tools

Isotopes give us information on the history of the molecule. In dusty samples from different Antarctic ice cores – Vostok, NGRIP, EDC, EDML, Taylor Glacier, TALDICE – we carried out:

- Bulk isotope analysis ($\delta^{15}\text{N}_{\text{bulk}}$) of N₂O in air bubbles
- Position-specific isotope analysis ($\delta^{15}\text{N}_{\alpha}$, $\delta^{15}\text{N}_{\beta}$) of N₂O
- Isotope analysis ($\delta^{15}\text{N}$) of NO₃⁻ in meltwater

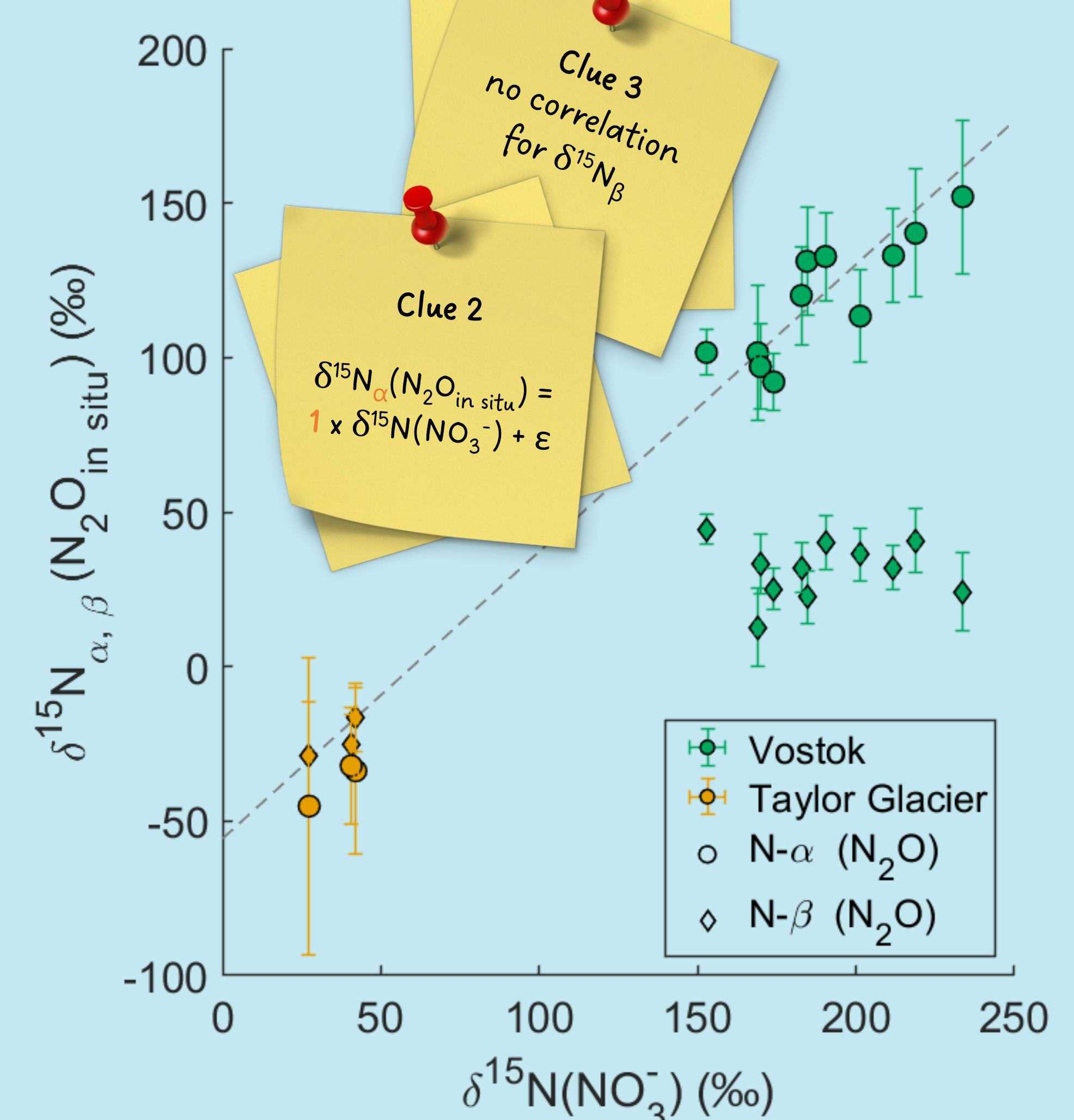
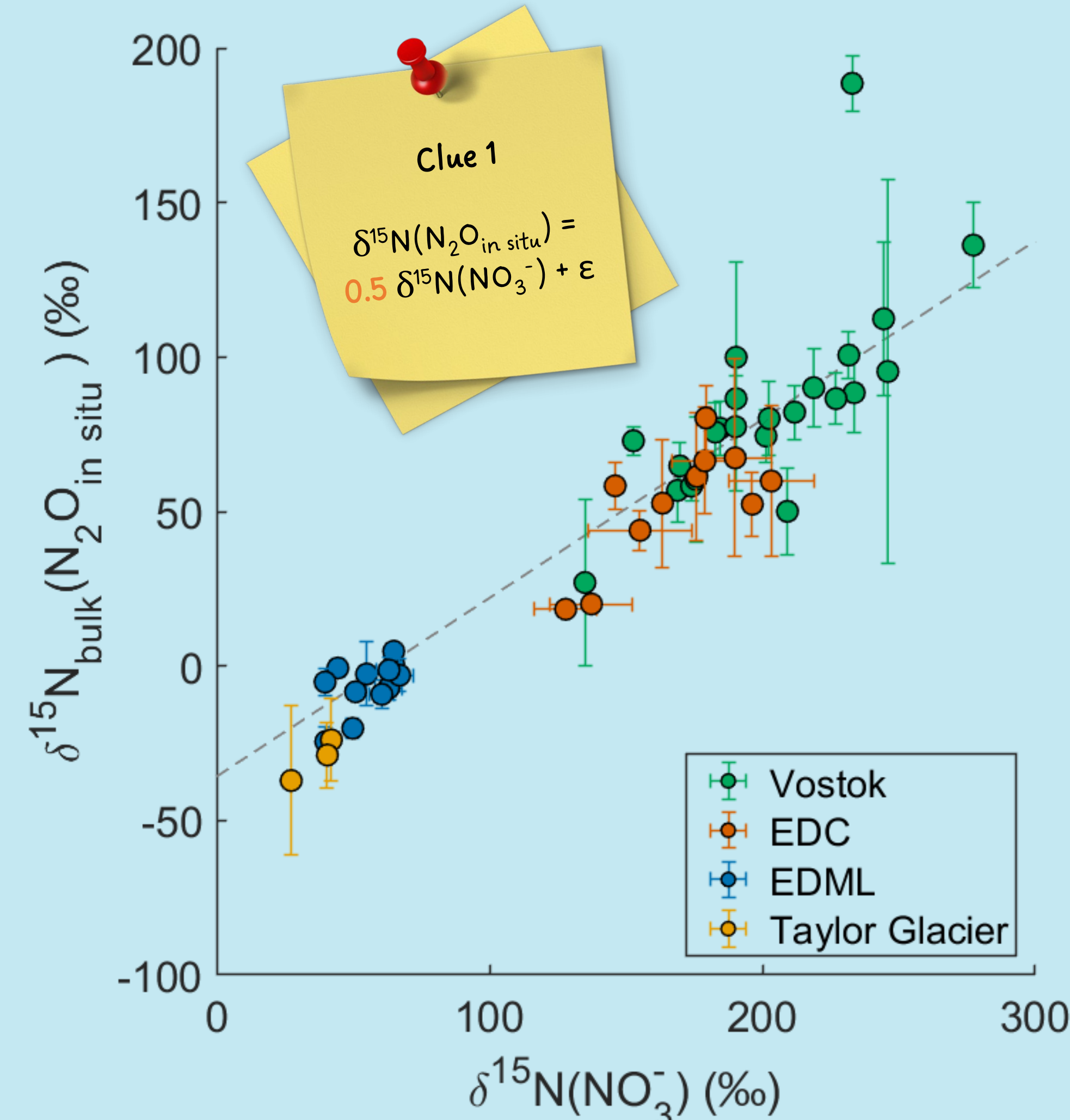
The isotopic composition of the **in situ N₂O fraction** was calculated using the N₂O record from the TALDICE ice core as atmospheric values:

$$\delta_{\text{in situ}} = \frac{\delta_{\text{measured}} \times [\text{N}_2\text{O}]_{\text{measured}} - \delta_{\text{TALDICE}} \times [\text{N}_2\text{O}]_{\text{TALDICE}}}{[\text{N}_2\text{O}]_{\text{measured}} - [\text{N}_2\text{O}]_{\text{TALDICE}}}$$

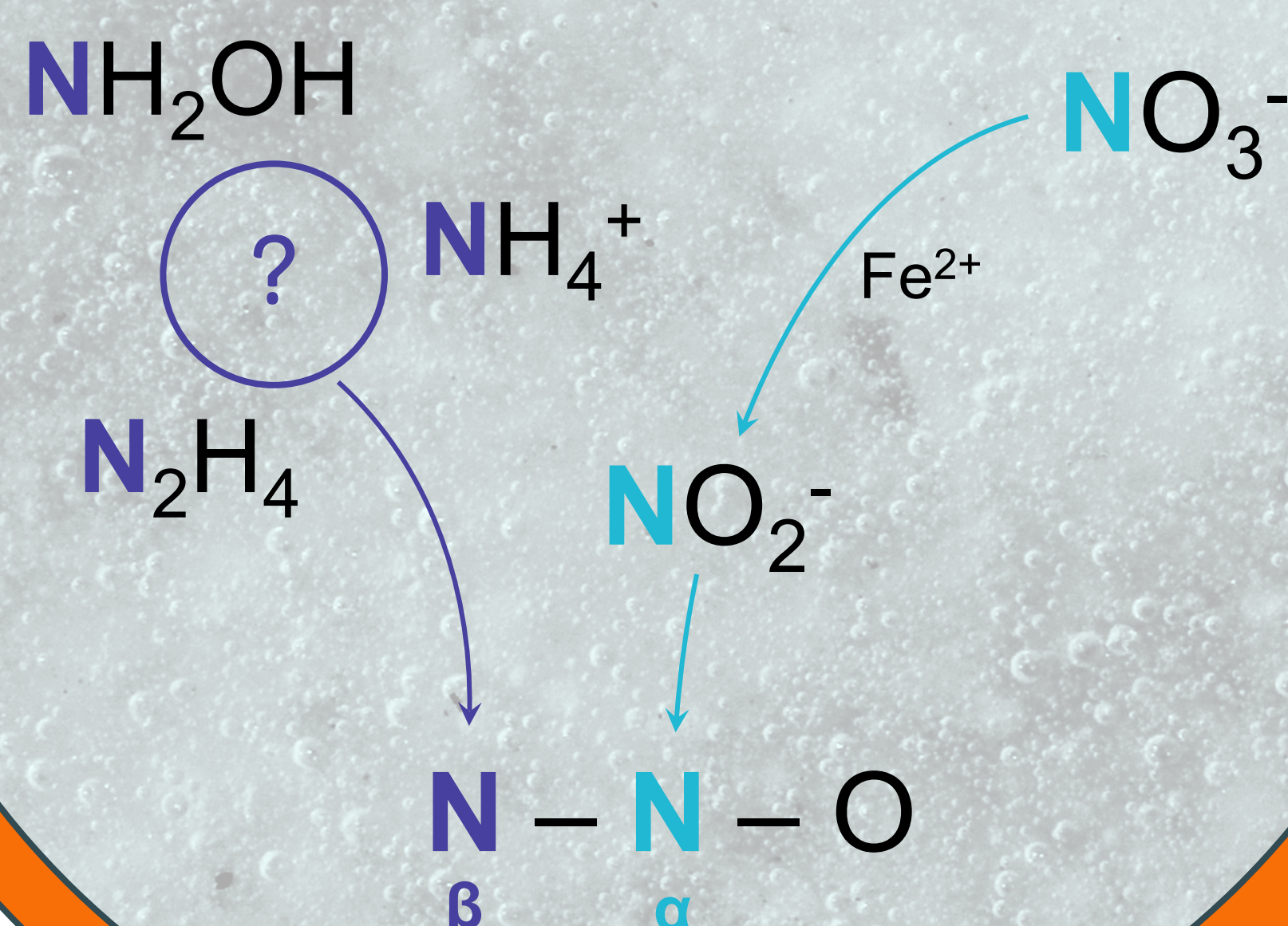
BACKGROUND – Nitrate, our chemical precursor suspect

The $\delta^{15}\text{N}$ values of in situ N₂O vary significantly with the location of ice cores and the snow accumulation rate. Because the snow accumulation rate also controls the $\delta^{15}\text{N}$ values of nitrate (NO₃⁻) archived in the ice [2], NO₃⁻ (attached to dust) is suspected to be the precursor of in situ N₂O. We therefore compare the isotopic compositions of NO₃⁻ and in situ N₂O to investigate a potential source-product relationship.

RESULTS – Collecting clues



Possible reaction:
Formation of hybrid N₂O
by N-nitrosation reaction [3]



INTERPRETATION & CONCLUSION

The $\delta^{15}\text{N}_{\text{bulk}}(\text{N}_2\text{O}_{\text{in situ}})$ and $\delta^{15}\text{N}(\text{NO}_3^-)$ values are correlated, which supports the hypothesis of NO₃⁻ as a precursor of in situ N₂O. However, the slope is 0.5. If all the nitrogen in N₂O came from NO₃⁻, a slope of 1 would be expected. The $\delta^{15}\text{N}_{\text{bulk}}$ signature of in situ N₂O reflects a mixing between the isotopic composition of NO₃⁻ and that of another nitrogen source.

The $\delta^{15}\text{N}_{\alpha}(\text{N}_2\text{O}_{\text{in situ}})$ and $\delta^{15}\text{N}(\text{NO}_3^-)$ values are correlated with a slope of 1. The $\delta^{15}\text{N}_{\beta}(\text{N}_2\text{O}_{\text{in situ}})$ and $\delta^{15}\text{N}(\text{NO}_3^-)$ values are not correlated. This result indicates that the central-position N atom (α) of in situ N₂O comes from NO₃⁻ and the terminal-position N atom (β) comes from a different nitrogen source.

The N₂O produced in situ is **hybrid N₂O**, i.e. the two N atoms come from different sources. Using our understanding of the production process and isotopic analyses of N₂O and NO₃⁻, we aim to correct the N₂O record for the in situ fraction and determine the past atmospheric concentrations of N₂O.

[1] Schilt A et al. (2010) Earth and Planetary Science Letters 300: 33–43 <https://doi.org/10.1016/j.epsl.2010.09.027>[2] Frey MM et al. (2009) Atmos Chem Phys 9: 8681–8696 <https://doi.org/10.5194/acp-9-8681-2009>[3] Spott O et al. (2011) Soil Biology and Biochemistry 43: 1995–2011 <https://doi.org/10.1016/j.soilbio.2011.06.014>