

## The $^{17}\text{O}$ excess of stratospheric and oceanic nitrous oxide

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Tropospheric nitrous oxide ( $\text{N}_2\text{O}$ ) displays a  $^{17}\text{O}$  excess of  $\Delta(^{17}\text{O}) = (0.9 \pm 0.1) \text{‰}$  relative to Vienna Standard Mean Ocean Water (VSMOW). The origin of this  $^{17}\text{O}$  excess is under debate: Tropospheric and stratospheric in-situ  $\text{N}_2\text{O}$  sources as well as isotope fractionation and isotope exchange during biological  $\text{N}_2\text{O}$  production are all considered to make a contribution, as might the stratospheric photolysis sink. To constrain the relative contributions of the different processes and to improve our understanding of the underlying atmospheric chemical and microbial processes, more measurements are required.

We have measured the  $^{17}\text{O}$  excess of mid-latitude stratospheric samples, from altitudes between 8 and 26 km.  $\text{N}_2\text{O}$  was extracted cryogenically at 77 K, separated from other condensable gases using a PoraPlotQ pre-column and then thermally decomposed in a gold furnace at 900 °C. The standard deviation of the  $^{17}\text{O}$  excess for repeat analysis of a 5 nmol  $\text{N}_2\text{O}$  aliquot was  $\pm 0.3 \text{‰}$ .

This new dataset significantly enhances the altitude range of oxygen triple isotope measurements in stratospheric air. Previous results were limited to the lower stratosphere between 8 and 12 km [1].

The average  $^{17}\text{O}$  excess of the stratospheric samples analysed was  $(-0.19 \pm 0.46) \text{‰}$  relative to tropospheric  $\text{N}_2\text{O}$ . Since the  $^{17}\text{O}$  excess of stratospheric  $\text{N}_2\text{O}$  is not significantly different to tropospheric  $\text{N}_2\text{O}$ , these data suggest that the  $^{17}\text{O}$  excess is not of stratospheric origin. This rules out stratospheric photolysis or reaction with electronically excited oxygen atoms as source of the  $^{17}\text{O}$  excess in  $\text{N}_2\text{O}$ . It confirms the notion that the origin of the  $^{17}\text{O}$  excess may be related to tropospheric in situ sources, e.g.  $\text{NH}_2 + \text{NO}_2$  [2], or to microbial nitrogen conversion reactions [3].

To investigate the latter hypothesis, we have measured the  $^{17}\text{O}$  excess of oceanic  $\text{N}_2\text{O}$ .  $\Delta(^{17}\text{O})$  values between 0.1 and 4.6 ‰ (relative to VSMOW) were observed during three field campaigns in the temperate, subtropical and tropical Atlantic Ocean, the Scotia Sea and the Weddell Sea. This shows that oceanic  $\text{N}_2\text{O}$  was not in equilibrium with the atmosphere, indicating a potential biological source for the  $^{17}\text{O}$  excess.

[1] Cliff *et al.* (1999) *J Geophys Res* **104**, 16171

[2] Röckmann *et al.* (2001) *Geophys Res Lett* **28** 503-506

[3] Kaiser & Röckmann (2005) *Geophys Res Lett* **32** L15808