

Interactive comment on “Simulation of the diurnal variations of the oxygen isotope anomaly ($\Delta^{17}\text{O}$) of reactive atmospheric species” by S. Morin et al.

Anonymous Referee #1

Received and published: 20 January 2011

General comments

This paper provides an overview of the assumptions used in interpretation of the oxygen isotope anomaly ($\Delta^{17}\text{O}$) in reactive nitrogen species and hydrogen peroxide. These isotope anomalies have been used extensively to understand the atmospheric chemical mechanisms that lead to formation of these species from ozone. The paper is somewhat lengthy but quite well organized. It gives a general framework for understanding the transfer of the isotope anomaly from ozone to other species, as well as its potential transfer between different species and its scrambling through gas phase atmospheric reactions. It then presents several test cases and a model analysis to show how these assumptions affect the interpretation of observations. Tests include time of day, season and pollutant level (i.e., initial NO_x).

C12627

The paper relies heavily on model analysis for its conclusions – reviewing this as an experimentalist, I am able to comment on the results but less on the methods of the model itself. Also, it is clear that some of the material and formalisms here has been presented in other model analyses (for example, the Alexander 2009 paper cited here). To my understanding, the authors have done well in citing the recent modeling literature and in differentiating the contribution of this paper. Someone more familiar with the details of past model efforts may be better able to comment on this aspect, however.

I have only a relatively small number of specific comments as outlined below. Two general comments are as follows. First, the paper presents many of its results in table format. While this is certainly clear, it would be more useful to the reader and perhaps easier for the casual reader to understand if some of these tables were converted to graphics (e.g., bar graph format). I leave this as a suggestion for the authors. Second, the paper has a section on open questions or unknowns. It appears to me that the recent discovery that N_2O_5 leads to large production of ClNO_2 , which is photolabile and recycles NO_x , has changed the conventional picture of the atmospheric chemistry of nighttime formation of NO_3 . This chemistry has not been considered here in terms of its isotope anomaly, but perhaps should be.

Specific comments:

Reactions R1-R4: This set of reactions pertains to inorganic nitrate only. The authors may wish to distinguish inorganic from organic nitrate in the sentence that precedes it.

Section 3.2.1: $\text{NO}_2 + \text{O}_3$ is assumed to have the same mechanistic characteristics as $\text{NO} + \text{O}_3$. Is this justified? Are there any experimental data at all? Also, it is not clear why photolysis of N_2O_5 or HNO_4 should differ from thermal dissociation in terms of isotopic scrambling. Either process, it seems, would simply break the weakest bond in the molecule. Why would one expect a difference?

Section 4.1.1 The diurnal variation of HONO seems inconsistent with most field data that show it to be larger at night than during the day. Why the difference? Is the only

C12628

source of HONO here due to OH + NO rather than heterogeneous reactions of NO₂?

Section 4.2.3 Is the NO_x mixing ratio changed by a factor of 10⁻⁵, or by 100, as stated in the conclusion? An initial NO_x of 2 ppbv (i.e., 2 nmol mol⁻¹) would seem more reasonable than 20 ppmv (20 μmol mol⁻¹) and would be consistent with the conclusion.

Typographical:

“Reactions” should be pluralized in several places. P. 30407, line 11, P. 30410, line 1.

Page 30412, line 10: “channel” rather than “channels”

Page 30413, line 12: “metric” rather than “metrics.”

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 30405, 2010.