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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Seasonal variations of triple oxygen isotopic compositions of atmospheric sulfate, nitrate and ozone at Dumont d'Urville, coastal Antarctica" *by* Sakiko Ishino et al.

Anonymous Referee #2

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General Comments: My main concern after reading this manuscript is that it does not do more to quantify to what extent the triple oxygen isotopic compositions of sulfate and nitrate can be used as a measure of atmospheric oxidation capacity. Dumont d'Urville (DDU) should represent a well known case where the many contributing factors could be examined by applying statistics and modeling. I am convinced that the analytical method is sound, the samples come from a unique and potentially very important location, and a nice time series is delivered. It is not clear whether the goal is to establish the technique of using a combined oxygen triple isotope analysis in O3, NO3- and SO4– as an important proxy, or to use these measurements to tell us something new

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and interesting about the earth system (in which case what?).

Specific Comments: The abstract starts with a big promise: 'Reconstruction of the oxidative capacity of the atmosphere is of great importance...Triple oxygen isotopic compositions..in the Antarctic ice cores have shown potential as stable proxies because they reflect the oxidation chemistry involved in their formation processes.'

A useful proxy must have a good correlation with the thing we can't measure directly. In this case the authors propose that the triple oxygen isotope anomalies in nitrate and sulfate are a useful proxy for the oxidative capacity of the atmosphere. This is a great goal because potentially, sulfate and nitrate in ice cores (or from other places, sediments, fern..) could be used to deduce past oxidative capacity. My concern is that the authors have not defined what it is exactly they are trying to determine based on their oxygen isotope measurements, and, they have not demonstrated that there is a correlation between the measurements and whatever that is, and therefore, they cannot claim that the triple oxygen istope anomalies in NO3- and SO4– are useful proxies. First, the authors should define what they mean by oxidative capacity. The oxidative capacity is not an exactly defined property as it could mean oxidation by O2, O3, OH, HO2, RO2, H2O2, O(1D), O(3P), NO3, Cl, BrO and so on. Oxidative capacity is sometimes taken to mean OH, but oxidation is a general process, not a specific one. The use of D17O would seem to be a better measure of relative exposure to ozone than [OH], since OH in the troposphere does not carry the D17O signal. The authors note (R2), oxidation by OH, will not transfer any of the anomaly from ozone to sulfate, and reactions R3, R4 and R5 transfer variable amounts of the ozone anomaly to sulfate. Because of the many pathways of SO2 oxidation it is difficult or impossible to find the relative contributions of the four proposed formation mechanisms based on one observable. In any case, since R2-R4 are all oxidation reactions converting S(IV) to S(VI), they all qualify as components of the atmosphere's oxidation capacity. The authors should be more exact about what it is that they propose to do with the measurements. Second, the discussion contains a lot of speculation about what may

or may not cause the patterns shown in Figure 2. No firm conclusions are ever made from this discussion, and clearly, if you cannot show what causes the signal that is measured, there is no hope to use that same signal, measured at a different location, to make conclusions about its origin. There is a bit of a 'chicken vs egg' element to the discussion in which the data are assumed to be important and then used to justify assertions in the abstract about the O3/ROx and hypohalous acid mechanisms, and I would like the authors to be more clear in the logical progression: first show that this is a useful proxy (i.e. correlated to some observable e.g. [O3] or [OH]), and then as a second step, if possible, use the proxy to make a prediction or conclusion about the atmosphere.

Equation (2) is used to determine non sea salt sulfate. The amount of sea salt sulfate is approximated by multiplying the sodium concentration by a factor 'k' which is the mass ratio of sulfate to sodium in sea water (0.25), and this is subtracted from total sulfate, leaving non sea salt sulfate. The ratio of the concentration of sulfate to sodium in sea water is well known, 0.25, but a value of '0.13 plus or minus 0.04' is used for samples collected from May to October to account for 'sea salt fractionation processes that affect the Antarctic region in winter when temperatures drop below -8oC'. First, please rewrite to clarify that this is a chemical and not an isotopic fractionation. Second, how was the error of plus or minus 0.04 propagated in the calculation? I do not see error bars in the corrected valued in Figure 2. Third, the paper by Jourdain and Legrand (2002) states that the summer sulfate to sodium ratio exceeds the seawater value due to biogenic sulfate, ornithogenic sulfate DDU is famous for having many penguins) and heterogeneous uptake of SO2. Why wasn't a similar correction applied to summer sulfate? Fourth, the winter chemical fractionation is believed to be due to the precipitation of mirabilite when seawater freezes, and is thus dependent on the location of sea ice relative to DDU. Have there been any changes in sea ice and sea surface temperatures around DDU over the last 15 years that would have influenced the fractionation? Finally, if the correction is an empirical value taking into account sea ice, biogenic sulfate, penguin activity, heterogeneous chemistry and sea surface temperature, is the

resulting value truly representative of just sea salt aerosol?

As discussed, the D17O(SO4–) anomaly results from a combination of four mechanisms. The D17O(NO3-) anomaly depends on D17O of NO2, and of the oxidation mechanism. The authors discuss that NO2 formed from NO + O3 will contain a terminal oxygen atom from ozone, and these carry the D17O anomaly, resulting in preferential transfer to the NO2. First, what is known about photolysis? It plays a role in the equilibrium between NO, NO2 and O3, but does it produce an isotope anomaly? Second, in Section 4.1.2 I would have appreciated an estimate of the D17O value in nitrate for each of the mechanisms discussed. Third, would the authors estimate how much of NO3- is produced via NO2 + OH + M –> HNO3 + M, and how much by the dark reaction NO2 + O3 –> NO3, NO3 + RH –> HNO3.

Consider adding reaction schemes or figures to describe the S(IV) –> S(VI) and N(IV) –> N(V) conversions and the propagation of ozone in these mechanisms.

Many mechanisms are discussed, but it would be useful to have a statistical link between the data shown in Figure 2 and other data, for example, the output of a chemical model or a transport model (back trajectories, sea surface/ice conditions, etc), or measurements of [O3] and so on. This would clearly show whether these measurements are a good proxy for the oxidation capacity. Many atmospheric measurements have been made at the DDU station, and it seems that it ought to be possible to look for statistical correlations between the data in Figure 2 and station measurements (ozone, sunlight, humidity, NOx, modeled radical concentrations, temperature, wind speed and direction) – this data would be the key to establishing what the D17O proxies means.

The authors conclude that the seasonal changes in D17O in sulfate and nitrate are not due to seasonal trends in D17O in ozone; presumably the trend is due rather to different relative contributions by ozone oxidation to the oxygen in the sulfate and nitrate.

It seems difficult to figure out where sulfate and nitrate come from (sea salt, many atmospheric chemistry mechanisms, transported by katabatic wind from the stratosphere

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or entrained upper troposphere or wind from the sea), and without the knowledge of how the material formed, how is it possible to determine the amount of ozone or OH that was present along the trajectory? And, if all that additional knowledge was necessary to determine the oxidation capacity along the path, this would seem to severely limit the power of this proxy. Ideally the DDU measurements would be an easy ideal test case to establish the proxy, a well studied site where all of the contributing factors can be qualtified. But, if the oxygen isotope anomaly cannot even be understood here, what hope is there for these measurements at less well studied sites, and at times in the past when there is uncertainty about basic things like extent of sea ice, air flow patterns, atmospheric chemistry, etc.

Technical Comments: 2,3 it is not clear from the grammar if 'its' refers to 'The reconstruction of changes in the past oxidative capacity' or 'climate change' 2,4 assuming that past oxidatidative capacity is what is meant, then I don't understand the inclusion of HCFCs in the list as these are a modern anthropogenic trace gas whose lifetime is only determined by the modern oxidative capacity, no comparison to preindustrial atmospheric chemistry can be made. 2,18 please double check definition or ROx, which would seem to indicate organic odd oxygen species (organic oxy and peroxy radicals). Is it standard to include OH and H2O2? 8,2 check 'summer,.as *has often been reported previously' 14, 2-3 'complex photochemistry' 'strong oxidizing canopy' 'highly oxidative' in each case I am wondering what these modifiers mean. Complex, strong and highly relative to what? I think many locations could be found with a much higher oxidizing capacity than DDU, and also, with photochemistries more complex than at DDU. 19, 33 Seinfeld and Pandis published the second edition of their book Atmospheric Chemistry and Physics in 2006 and the third edition in 2016. They did not publish any book with this title in 2012? Please specify edition and year.

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