Atmos. Chem. Phys. Discuss., 11, C10640–C10645, 2011
www.atmos-chem-phys-discuss.net/11/C10640/2011/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Sulfur isotope fractionation during oxidation of sulfur dioxide: gas-phase oxidation by OH radicals and aqueous oxidation by H_2O_2, O_3 and iron catalysis" *by* E. Harris et al.

E. Harris

eliza.harris@mpic.de

Received and published: 20 October 2011

We thank the anonymous reviewer for agreeing to review our manuscript. We will address the reviewer's comments pointwise below.

- Page C10432 L3 - Page C10433 L3: "There are many factors influencing anthropogenic sulfur isotope composition, like isotope composition of sulfur in coal which later on is used as a fuel and result in SO_2 emission in flue gases (A.G.Chmielewski et al, Sulfur isotope composition of selected Polish coals, Nuk-

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

leonika, 4(Supplement 1) S67 - S68 (2002). Moreover widely introduced FGD systems change sulfur isotope composition further (M.Derda et al, Isotopes in Environmental and Health Studies, 43(1), 57-53 (2007). The Authors should consider and comment these facts. Since they state in the conclusions: "This will allow stable sulfur isotopes to be used to understand the partitioning between these pathways in atmospheric samples"."

The isotopic composition of many anthropogenic sources of SO_2, including the isotopic composition of many coals, are covered in the reference Krouse et al. (1991) which has been added in response to Reviewer 2 (see 'Reply to Reviewer 2', Page C10444 L7-8). The fractionation factor for flue gas desulphurization is small compared to the fractionation factors for atmospheric oxidation (α_{34} 1.0026 when Rayleigh fractionation calculations are used and α_{34} is expressed the same way as the fractionation factors in the discussion paper for the data in Derda et al. (2007)). However, as the efficiency is high the resultant isotopic effect on the residual SO_2 can be significant and should still be accounted for: the combined effect of combustion, fly ash collection and flue gas desulfurization results in a δ^{34}S for the released SO_2 of -4‰ while the coal itself had a δ^{34}S of 7-11‰. We have thus added to P23963 L24-P23964 L1:

'The isotopic composition of many major sources of atmospheric sulfur have been measured (e.g., Rees et al., 1978; Krouse et al., 1991; Nielsen et al., 1991; Sanusi et al., 2006). The isotopic composition of anthropogenic sources is highly variable on a global scale, though individual sources are often well constrained. The isotopic composition of industrial emissions is also affected by process technology such as the flue gas desulfurization unit of an industrial plant (Derda et al., 2007). However, for field studies measuring the isotopic composition of both ambient SO_2 and sulfate, the major limitation to interpreting atmospheric isotope measurements is the lack of laboratory studies of the isotopic fractionation factors involved in the most common atmospheric reactions of sulfur (Tanaka et al.,

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

1994; Novak et al., 2001; Tichomirowa et al., 2007).'

The isotopic effect of flue gas desulfurization can also be used as another estimate for the value of α_{34} for aqueous oxidation at high pH, so we have added the following in P23979 L18:

'...the terminating oxidation to O_3 may have little effect on isotopic fractionation. Results investigating the isotopic effect of flue gas desulfurization provide another value for comparison: Derda et al. (2007) measured α_{34} of 1.0026 for aqueous oxidation in a wet lime solution producing gypsum (the fractionation factor has been adjusted to have the same definition as the present study). This would provide a first estimate for the isotope fractionation during oxidation in an alkaline solution, but meaningful comparison with the results obtained in the present study is difficult, since an industrial scale process is not comparable to the carefully controlled environment of a laboratory reactor, and the process temperature has not been reported by Derda et al. (2007). The difference between measured fractionation during oxidation...'

As the expression of α in Derda et al. (2007) was different (~inverse) to in our paper, we have realised the importance of clarifying exactly what α means. Our definition of α is consistent with previous publications such as Leung et al. (2001) and Eriksen et al. (1972). The following was added to P23963 L16:

'When the reactant is present as an infinite reservoir and not affected by the reaction, α_{34} can be calculated from the isotopic compositions of products and reactions:

$$\alpha_{34} = \frac{R_{products}}{R_{reactants}} \tag{1}$$

where R = $\frac{^{34}S}{^{32}S}$. Thus, $\alpha>1$ indicates...'

- Page C10433 L3-L6: "I do not understand well why r is taken as a path of diffusion (D is the diffusion coefficient and r is the radius of the reactor, since the sulfuric acid molecules(or aggregates, if the water vapor is present?), can be present in the gas stream closer to the wall."

We do not take r as the path of diffusion; these wall loss equations were developed to estimate wall loss in a fast flow reactor with radius r by Zasypkin et al. (1997) and were used in an almost identical system by Young et al. (2008).

- "I agree with many points mentioned by Anonymous Referee #2, whose review is so well elaborated."

  We have responded in detail to all the points raised by Referee #2 and would like to draw the attention of Referee #3 to that response.

Derda, M., Chmielewski, A. G., and Licki, J.: Sulphur isotope compositions of components of coal and S-isotope fractionation during its combustion and flue gas desulphurization, Isotopes in Environmental and Health Studies, 43, 57-63, 2007.

Eriksen, T. E.: Sulfur Isotope Effects 1. Isotopic Exchange Coefficient for Sulfur Isotopes 34S-32S in System SO2(g)-HSO3(aq) at 25, 35, and 45 Degrees C, Acta Chemica Scandinavica, 26, 573, 1972.

Krouse, H., Grinenko, L., Grinenko, V., Newman, L., Forrest, J., Nakai, N., Tsuji, Y., Yatsumimi, T., Takeuchi, V., Robinson, B., Stewart, M., Gunatilaka, A., Plumb, L., Smith, J., Buzek, F., Cerny, J., Sramek, J., Menon, A., Iyer, G., Venkatasubramanian, V., Egboka, B., Irogbenachi, M. and Eligwe, C.: Krouse, H. and Grinenko, V. (Eds.) Stable Isotopes: Natural and Anthropogenic Sulphur in the Environment, Chapter 8. Case Studies and Potential Applications. John Wiley and Sons, 307-416, 1991.

Leung, F. Y., Colussi, A. J., and Hoffmann, M. R.: Sulfur isotopic fractionation in the gas-phase oxidation of sulfur dioxide initiated by hydroxyl radicals, Journal of Physical Chemistry A, 105, 8073-8076, 2001.

Nielsen, H., Pilot, J., Grinenko, L., Grinenko, V., Lein, A., Smith, J. and Pankina, R.: Krouse, H. and Grinenko, V. (Eds.) Stable Isotopes: Natural and Anthropogenic Sulphur in the Environment, Chapter 4. Lithospheric Sources of Sulfur. John Wiley and Sons, 65-132, 1991.

Novak, M., Jackova, I., and Prechova, E.: Temporal Trends in the Isotope Signature of Air-Borne Sulfur in Central Europe, Environ. Sci. Technol., 35, 255–260, 2001.

Rees, C. E., Jenkins, W. J. and Monster, J.: Sulfur Isotopic Composition of Ocean Water Sulfate. Geochimica et Cosmochimica Acta, 42, 377-381, 1978.

Sanusi, A. A., Norman, A.-L., Burridge, C., Wadleigh, M. and Tang, W.W.: Determination of the S isotope composition of methanesulfonic acid. Analytical Chemistry, 78, 4964-4968, 2006.

Tanaka, N., Rye, D. M., Xiao, Y., and Lasaga, A. C.: Use of Stable Sulfur Isotope Systematics for Evaluating Oxidation Reaction Pathways and in-Cloud Scavenging of Sulfur-Dioxide in the Atmosphere, Geophys. Res. Lett., 21, 1519–1522, 1994.

Tichomirowa, M., Haubrich, F., Klein, M., and Matschullat, J. Regional and temporal (1992-2004) evolution of air-borne sulphur isotope composition in Saxony, southeastern Germany, central Europe. Isotopes in Environmental and Health Studies, 43, 295-305, 2007.

Young, L. H., Benson, D. R., Kameel, F. R., Pierce, J. R., Junninen, H., Kulmala, M., and Lee, S.-H.: Laboratory studies of H_2SO_4/H_2O binary homogeneous nucleation from the SO_2+OH reaction: evaluation of the experimental setup and preliminary results, Atmospheric Chemistry and Physics, 8, 4997-5016, doi:10.5194/acp-8-4997-2008, 2008.

Zasypkin, A., Grigor'eva, V., Korchak, V., and Gerschenson, Y.: A formula for summing of kinetic resistances for mobile and stationary media: I. Cylindrical reactor, Kinetics and Catalysis, 38, 842–851, 1997.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 23959, 2011.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper