

Bekki et al. report calculations of the oxygen isotopic composition of sulfate formed in volcanic plumes with the goal of understanding why observations show very little O-17 enrichment. They use a box model including gas phase oxidation by OH and aqueous-phase oxidation by H₂O₂, O₃ and TMI-catalysis. They conclude that oxidation by OH and TMI are the dominant pathways for secondary sulfate formation in volcanic plumes, and that the TMI pathway is necessary to explain the observations because OH has an O-17 enrichment in volcanic plumes. H₂O₂ is not important because it is quickly depleted by high concentrations of SO₂, and O₃ is not important because of the acidic environment.

The only significant comment I have is that I think the paper should put more into a discussion of the implications of the lack of reactive halogen chemistry. Even in a volcanic eruption with zero halogens (is this possible?), entrainment of background air would supply some halogens. Could this be important? Perhaps it wouldn't take much from background to have halogen recycling in this acidic environment. What are the implications for sulfate O-MIF formed in volcanic plumes?

Other than that, this manuscript is well written and I have only relatively minor comments that are detailed below.

One general comment: I think it would be good to help to highlight the observations of sulfate O-MIF, including the types of volcanoes measured, in the paper. I suggest adding a Table describing the observations with appropriate references. As currently written it's hard for readers to compare model results with observations.

Abstract: I think a comment about reactive halogens belongs in the abstract. Perhaps say you are only considering volcanoes that are thought to have little halogen production.

Page 2 line 22: How much is "most"? The current thinking is that globally, DMS oxidation is the largest natural source of SO₂ to the troposphere.

Page 3 line 3: The year for the Harris et al. reference is missing.

Page 5 line 1: How common are these types of volcanoes that are halogen-poor? Are the observations of sulfate O-17 excess from these types of volcanoes?

Page 6 equation 6: I think it would be helpful to explicitly show the equation for J_i. At least provide the page number where this can be found in the textbook that is cited.

Page 7 line 2: There is a missing end parentheses.

Page 7 R1: There is no other ion that can influence acidity? Ion balance equations are not the best way to calculate pH. In the future, perhaps it would be better to explicitly calculate the droplet pH in the model. This would certainly be necessary if these calculations were for ambient air, and not an SO₂ rich volcanic plume.

Page 7: Why consider sulfate loss via deposition but not SO₂? Globally, dry deposition of SO₂ represents about half of tropospheric SO₂ loss.

Page 12 line 28 and elsewhere: I think "gr" should be written as "g"

Page 13 line 6 and elsewhere: There are lots of citations for this textbook. It's better to cite original references when possible. This seems like an example of where you should be able to do this.

Page 16 line 27: I don't understand this sentence: "The sharp drop in H₂O₂..." I thought H₂O₂ concentrations decrease because of the high amounts of SO₂.

Page 17 line 6: Does the O-17 excess of OH decrease as SO₂ decreases? I think you should state why this is happening.

Page 17 lines 8-9: This sentence does not make sense. If you want to produce an O-MIF in sulfate, you need an oxidant with an O-MIF, not "null O-MIF".

Page 17 line 11: Perhaps remind the reader here that your calculations do not include halogens.

Page 20 line 8: "budget", not "buded"

In the figures, I don't understand why SO₂ concentrations do not decrease over time. Sulfate increases, so mass balance suggests that SO₂ should decrease, unless there is a continuous supply of SO₂.

Figure 7: What is the y-axis unit?

Table 2: Needs a unit (%) for the 4th column.