

Origins of volcanic SO₂ on Earth

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SO₂ is a principal volcanic gas today. The two important questions to be addressed are: (i). the origin of S atoms in volcanic SO₂; and (ii) whether or not SO₂ was an important volcanic gas of early Earth. I have approached these questions from: (a) thermodynamic- and kinetic analyses of various reactions involving S-bearing species in silicate melts, fluids, rocks, minerals, and aqueous solutions at T = 0-1500 °C and P = 1-10 kb, and (b) examinations of the chemical and S-isotopic characteristics of volcanic gases and rocks in various tectonic settings on modern Earth. Here are some of the important suggestions from these investigations:

1. All of the S-bearing species from submarine volcanic eruptions have been nearly completely trapped in oceans through reactions such as: $\text{H}_2\text{S}_{(\text{g})} = \text{H}_2\text{S}_{(\text{aq})}$; $4\text{SO}_{2(\text{g})} + 4\text{H}_2\text{O} = 3\text{HSO}_4^- + \text{H}_2\text{S}_{(\text{aq})} + 3\text{H}^+$; $\text{S}_{8(\text{g})} = 8\text{S}_{(\text{s})}$; and $7\text{H}_2\text{S}_{(\text{aq})} + \text{HSO}_4^- + 4\text{Fe}^{2+} = 4\text{FeS}_{2(\text{py})} + 7\text{H}^+ + 4\text{H}_2\text{O}$. S-bearing volcanic gases have only been emitted into the atmospheres by subaerial eruptions. Therefore, on the ocean-covered planets, possibly including the pre-3.0 Ga Earth, S-bearing gases have not been emitted into the atmospheres.

2. The fluids that originated from normal-mantle-derived-magmas (i.e., $\log f\text{O}_2 = \text{FMQ}-2$ to $\text{FMQ}+0.5$) were initially H₂S-rich and SO₂-poor, whereas those from subduction-related arc magmas (i.e., $\log f\text{O}_2 = \text{FMQ}+0.5$ to $\text{FMQ}+3$) were initially SO₂- and/or H₂S-rich.

3. H₂S-rich magmatic fluids may become SO₂-rich gas, if: (i) the fluids were derived from high fO₂ magmas (i.e., $\log f\text{O}_2 > \text{FMQ}$) and ascended slowly through conduits (i.e., diffusive eruptions) and re-equilibrated with wall-rocks at $P_{\text{H}_2\text{O}} < 10$ bars, or (ii) the fluids are oxidized by reactions with an O₂-rich atmosphere, -groundwater and/or high-fO₂ wall-rocks during and/or after the ascent through conduits. In the absence of (i) and (ii), such as the Earth prior to the oxygenation of the atmosphere, H₂S-rich magmatic fluids were not transformed to SO₂ during eruptions.

4. SO₂-rich fluids from arc magmas would remain SO₂-rich during explosive or diffusive eruptions. However, if the fluids cool down to $< \sim 700^\circ\text{C}$, SO₂ transforms to H₂S.

5. Volcanic SO₂ from arc magmas was transformed from seawater sulfate through the following processes: (i) formation of pyrite, hematite and anhydrite by reactions between SO₄²⁻-rich seawater and hot basalts on MORs; (ii) devolatilization of H₂O- and SO₂-rich fluids from the subducting oceanic crust; (iii) formation of oxidized- and SO₄²⁻-rich magmas by partial melting of peridotite in the mantle wedges, and (iv) degassing of SO₂-rich fluids from these magmas. If the oceans were SO₄²⁻-poor, volcanic gases from arc magmas would be SO₂-poor.

6. Oceanic SO₄²⁻ has been produced mostly by the oxidative weathering of pyrite on land. Therefore, subaerial volcanic gases on planets with O₂-poor atmospheres would be SO₂-poor and H₂S-rich. Then, the current paradigm concerning the origin of mass-independent-fractionations of sulfur isotopes (MIF-S) in Archean-aged sedimentary rocks (i.e., the UV photolysis of volcanic SO₂ in an O₂-poor atmosphere) becomes invalid. Consequently, the MIF-S record in sedimentary rocks is not supportive evidence for the "Great Oxidation Event" at ~ 2.5 Ga ago. Furthermore, the current atmospheric O₂-evolution models,

which are based on the premise of SO₂-rich volcanic gases throughout geologic time, become invalid.

(7). The MIF-S in the Archean- and younger sedimentary rocks may have been created by the chemisorption isotope effects during thermochemical reductions of seawater sulfates by hydrothermally-generated, very reactive organic matter.

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