Origins of volcanic SO$_2$ on Earth

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SO$_2$ is a principal volcanic gas today. The two important questions to be addressed are: (i). the origin of S atoms in volcanic SO$_2$; and (ii) whether or not SO$_2$ 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: $\text{H}_2\text{S}(g) = \text{H}_2\text{S}(aq)$; $4\text{SO}_2(g) + 4\text{H}_2\text{O} = 3\text{HSO}_4^- + \text{H}_2\text{S}(aq) + 3\text{H}^+$; $\text{S}_8(g) = 8\text{S}(s)$; and $7\text{H}_2\text{S}(aq) + \text{HSO}_4^- + 4\text{Fe}^{2+} = 4\text{FeS}_2(py) + 7\text{H}^+ + 4\text{H}_2\text{O}$. 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., $\log$fO$_2$ = FMQ-2 to FMQ+0.5) were initially H$_2$S-rich and SO$_2$-poor, whereas those from subduction-related arc magmas (i.e., $\log$fO$_2$ = FMQ+0.5 to FMQ+3) were initially SO$_2$- and/or H$_2$S-rich.

3. H$_2$S-rich magmatic fluids may become SO$_2$-rich gas, if: (i) the fluids were derived from high fO$_2$ magmas (i.e., $\log$fO$_2$ > 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 O$_2$-rich atmosphere, groundwater and/or high-fO$_2$ 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, H$_2$S-rich magmatic fluids were not transformed to SO$_2$ during eruptions.

4. SO$_2$-rich fluids from arc magmas would remain SO$_2$-rich during explosive or diffusive eruptions. However, if the fluids cool down to <$\sim$700°C, SO$_2$ transforms to H$_2$S.

5. Volcanic SO$_2$ from arc magmas was transformed from seawater sulfate through the following processes: (i) formation of pyrite, hematite and anhydrite by reactions between SO$_4^{2-}$-rich seawater and hot basalts on MORs; (ii) devolatilization of H$_2$O- and SO$_2$-rich fluids from the subducting oceanic crust; (iii) formation of oxidized- and SO$_4^{2-}$-rich magmas by partial melting of peridotite in the mantle wedges, and (iv) degassing of SO$_2$-rich fluids from these magmas. If the oceans were SO$_4^{2-}$-poor, volcanic gases from arc magmas would be SO$_2$-poor.

6. Oceanic SO$_4^{2-}$ has been produced mostly by the oxidative weathering of pyrite on land. Therefore, subaerial volcanic gases on planets with O$_2$-poor atmospheres would be SO$_2$-poor and H$_2$S-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 SO$_2$ in an O$_2$-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 O$_2$-evolution models,
which are based on the premise of \(\text{SO}_2\)-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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