

# Identifying sources of sulfate preserved in high elevation lava tubes from Mauna Loa, Hawaii

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Volcanic sulfates record a history of their formation pathways in their triple oxygen isotope compositions, making them a powerful target for understanding atmospheric chemistry. To understand how these isotopic signals may be preserved in sulfate minerals, we investigate multiple O and S isotopes of thenardite, mirabilite, and gypsum from in a Mars analog environment: a pair of lava tubes near the summit of Mauna Loa, Hawaii. Based on <sup>16</sup>O-<sup>17</sup>O-<sup>18</sup>O compositions, the primary oxygen sources for sulfates in the lava tube are atmospheric oxygen (O<sub>2</sub>), peroxide (H<sub>2</sub>O<sub>2</sub>), and ozone (O<sub>3</sub>). We suggest the isotopic signature of O<sub>2</sub> originates from combustion of reduced sulfur gases and/or elemental sulfur at the eruptive source or within the lava tube soon after skylight collapse. Sulfate with isotopic signatures of peroxide and ozone are typically expected from aqueous reactions in cloud droplets. Chemical modeling indicates the observed proportion of ozone sourced sulfate requires pH greater than ~5.4, higher than measured cloud water pH, instead suggesting the observed O<sub>3</sub> signature could not have formed in cloud water droplets. We interpret that sulfate possessing an ozone signature in the lava tube sulfates formed on wetted surfaces of the lava tubes with alkalinity from alteration of basaltic glass. Furthermore, the oxygen and sulfur isotopes of the sulfate are uncorrelated. Multiple sulfur isotopes (<sup>32</sup>S-<sup>33</sup>S-<sup>34</sup>S-<sup>36</sup>S) from the Mauna Loa sulfates are consistent with ocean island basalt from Pitcairn, suggesting the sulfate-sulfur has not been modified compared to its volcanic source. The findings of this study indicate that oxidation by ozone plays a key role in the formation of sulfate within lava tubes. We also find that combustion is a significant pathway toward sulfuric acid formation in volcanic environments. Similar signatures should be expected on other planets if volcanism is a significant sulfate source, as has been suggested for Mars. If true, sulfates in returned samples from Mars may hold key information on pO<sub>2</sub>, pCO<sub>2</sub> and planetary scale oxygen fluxes at the time of sulfate formation.