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Isotope compositions of diverse natural perchlorate measured by ESI-Orbitrap-MS

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Multiple mechanisms have been proposed to account for the curiously rich ClO_4^- in Martian soils. The stable isotopes ($\delta^{37}Cl$, $\delta^{18}O$, and $\Delta^{17}O$) of ClO_4^- provide fingerprints for its formation pathways as well as post-depositional processes. Yet similar isotopic tools applied to terrestrial perchlorate reveal a striking discrepancy: existing reaction-transport models [1] consistently overestimate $\Delta^{17}O$ values compared to the few observed ones, suggesting either an overestimation of ozone-mediated oxidation in models or significant contributions from non-ozone pathways in natural samples. Contribution from non-ozone oxidation pathways should have a $\Delta^{17}O$ value at ~0‰, whereas contribution from ozone-mediated pathways should yield $\Delta^{17}O$ >20‰ in natural samples (e.g., snow, rain, aerosols).

To test the prediction, we collected ClO_4^- from anthropogenic sources, Yangtze River water, and East China snow, as well as previously collected Atacama Desert caliche. Isotopic measurements of natural ClO_4^- usually require the processing of a large quantity of host water or rock samples with complex matrices, which has been analytically prohibitive until now. We have developed an ESI-Orbitrap-MS method capable of high-precision isotopic analysis of <10 nmol ClO_4^- with an accuracy better than 1‰ for all $\delta^{18}O$, $\delta^{37}Cl$, and $\Delta^{17}O$ parameters [2]. Natural samples went through a resin-based enrichment and Ion Chromatography (IC) fraction collection and purification protocol. Preliminary results show that Yangtze River water and East China snow have a large fraction of ClO_4^- that has no ^{17}O anomaly. The accompanied $\delta^{18}O$ and $\delta^{37}Cl$ data range from −19‰ to −9‰ and 0‰ to 5‰, respectively. Our expanding natural ClO_4^- $\delta^{18}O$, $\delta^{37}Cl$, and $\Delta^{17}O$ database of high spatial/temporal resolution promises the eventual resolution of the discrepancies between models and observation.

[1] Chan, Jaeglé, Campuzano-Jost, Catling, Cole-Dai, Furdui, Jackson, Jimenez, Kim, Wedum & Alexander (2023), *Geophys. Res. Lett.* 50, e2023GL102745.

[2] Zhu, Hong, Hattori, Wang, Wei, Peng, Kuhlbusch & Bao (2026), *Anal. Chem.*