

Isotopic Composition of Natural Chlorate

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Natural ClO_3^- and ClO_4^- commonly co-occur at a molar ratio ≥ 1 . Terrestrial natural ClO_4^- has at least a partial atmospheric source based on its elevated ratios of $^{36}\text{Cl}/\text{Cl}$ and non-zero $\Delta^{17}\text{O}$ values. The isotopic composition of ClO_3^- could be useful in understanding the origins of per(chlorate) on Earth and Mars. We developed a method to isolate and purify ClO_3^- for isotopic analysis and measured the isotopic composition of ClO_3^- isolated from NO_3^- rich caliche from the Atacama Desert and southern Death Valley (DV) region of the Mojave Desert. Caliche type materials were extracted in water and ClO_3^- was purified using multiple processes including: solvent extraction, selective precipitation, ion exchange, dialysis, microbial reduction of NO_3^- , and solid phase adsorbents. ClO_3^- stable isotopic composition ($\delta^{37}\text{Cl}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$) was determined by dual-inlet isotope-ratio mass spectrometry. ClO_3^- in DV and Atacama samples had distinct ranges of $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values, but similar $\delta^{37}\text{Cl}$ values (Table 1). Compared to Atacama ClO_4^- , Atacama ClO_3^- had higher $\delta^{18}\text{O}$, similar $\Delta^{17}\text{O}$, and much higher $\delta^{37}\text{Cl}$ values. Compared to DV ClO_4^- , DV ClO_3^- had lower $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values but higher $\delta^{37}\text{Cl}$ values. Our results indicate natural ClO_3^- is produced in part by processes involving O_3 , as is natural ClO_4^- ; however, the formation mechanisms and(or) subsequent isotopic exchanges or fractionations may affect these compounds differently.

Table 1. Ranges of Isotopic Compositions of ClO_3^- and ClO_4^- .

Location	Compound	$\delta^{18}\text{O}$, ‰	$\Delta^{17}\text{O}$, ‰	$\delta^{37}\text{Cl}$, ‰
Atacama	ClO_3^-	+7 to +11	+6	-2 to +1
Atacama	ClO_4^-	-12 to -2	+7 to +11	-20 to -9
DV	ClO_3^-	-7 to +1	0 to +3	+1
DV	ClO_4^-	+3 to +26	+8 to +13	-4 to -1