Distribution and stable isotopic composition of ClO_4^- in the Atacama Desert.

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High concentrations of atmospheric ClO_4^-, ClO_3^-, and NO_3^- occur in the Atacama Desert where dry and oxic conditions allow oxyanions to accumulate near the surface over long periods. We collected sediment samples from vertical profiles (~1-3 m depth) over a 1000 km longitudinal transect along the central depression in the Atacama. ClO_4^-/NO_3^- molar ratios (350-3,500) and NO_3^- stable isotopes were relatively consistent both with depth and along the longitudinal transect except for locations receiving >2 cm of annual precipitation. ClO_4^-/ClO_3^- molar ratios were similar for most sites (~1). In contrast, ClO_4^- exhibited substantial variation in its stable isotopic composition ($\delta^{18}O$ and $\Delta^{17}O$) with respect to location along the longitudinal transect. In addition, the $\delta^{18}O$ and $\Delta^{17}O$ of O in ClO_4^- were strongly correlated (r^2=0.89). Elevated $\Delta^{17}O$ values indicate ClO_4^- formed largely by O_3 mediated oxidation of Cl, possibly in the stratosphere. However, substantial variation in $\delta^{18}O$ (-25 to -3 per mil) and $\Delta^{17}O$ (+4 to +10 per mil) of ClO_4^- is intriguing given the long salt accumulation times (~10^6 years). This isotopic variation may indicate some unknown process is controlling deposition over a large area for long time periods, atmospheric ClO_4^- isotopic composition has varied in geologic time, or some surface process (generation or alteration) that varies spatially is affecting the ClO_4^- isotope composition by transformation, exchange, or dilution. Insights from our work are relevant to models of oxyanion production and accumulation in areas with little biologic activity.

Enstatite Chondrites and the Composition of the Earth

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The nearly identical O isotopic compositions of the enstatite chondrites (EC), Earth's mantle, and Moon were used [1] to argue that the EC provide the best Solar System material for estimating the chemical composition of the Earth. A possible link between the EC and Earth is further supported by recent observations that EC and Earth have the same isotopic compositions for both major and minor elements (O, Ca, Ti, Cr) which exhibit substantial variations among different chondrite groups [e.g., 2-4], with Si being the only exception.

However, there is a huge mismatch in chemical compositions between the EC and Earth. For example, the EC have much too high Rb/Sr and K/U ratios and are depleted in FeO and refractory lithophile elements compared to the composition of Earth’s mantle deduced from terrestrial rocks. This discrepancy could be resolved by assuming that the Earth and EC had a common nebular precursor but they have experienced different chemical evolution. Such an assumption is supported by the mineralogy and O isotopic data for the most primitive EH3 chondrites.

The abundant FeO-bearing silicates, compositionally similar to those in other classes of chondrites, are well documented in ECs [5-8], with most silicates having O isotopic compositions of the bulk EC values [7-8]. Recent studies [9-11] showed that the chalcophile behaviour of Ca, Mg, Na, and other elements in EC is due to secondary processing of FeO-bearing silicates in an H-poor environment with high f_{S2} (Fe-FeS buffer) and f_{O2} close to the CO-CO_2 buffer.

We propose that the nebular reservoir that produced the precursor material for EC has also produced the building blocks for the Earth, chemically similar to the widely accepted Earth’s composition of [12]. Interestingly, the Nd isotope variations in the Earth and EC are consistent with a bulk mantle-crust system that followed the CHUR evolution curve [13].

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