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Geochimica et Cosmochimica Acta 164 (2015) 502–522

Geochimica et Cosmochimica Acta

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# Global patterns and environmental controls of perchlorate and nitrate co-occurrence in arid and semi-arid environments

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Received 2 June 2014; accepted in revised form 7 May 2015; available online 14 May 2015

## Abstract

Natural perchlorate ($ClO_4^-$) is of increasing interest due to its wide-spread occurrence on Earth and Mars, yet little information exists on the relative abundance of $ClO_4^-$ compared to other major anions, its stability, or long-term variations in production that may impact the observed distributions. Our objectives were to evaluate the occurrence and fate of $ClO_4^-$ in groundwater and soils/caliche in arid and semi-arid environments (southwestern United States, southern Africa, United Arab Emirates, China, Antarctica, and Chile) and the relationship of $ClO_4^-$ to the more well-studied atmospherically deposited anions $NO_3^-$ and $Cl^-$ as a means to understand the prevalent processes that affect the accumulation of these species over various time scales. $ClO_4^-$ is globally distributed in soil and groundwater in arid and semi-arid regions on Earth at concentrations ranging from $10^{-1}$ to $10^6$ μg/kg. Generally, the $ClO_4^-$ concentration in these regions increases with aridity index,

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http://dx.doi.org/10.1016/j.gca.2015.05.016

but also depends on the duration of arid conditions. In many arid and semi-arid areas, $NO_3^-$ and $ClO_4^-$ co-occur at molar ratios ($NO_3^-/ClO_4^-$) that vary between ~$10^4$ and $10^5$. We hypothesize that atmospheric deposition ratios are largely preserved in hyper-arid areas that support little or no biological activity (e.g. plants or bacteria), but can be altered in areas with more active biological processes including $N_2$ fixation, N mineralization, nitrification, denitrification, and microbial $ClO_4^-$ reduction, as indicated in part by $NO_3^-$ isotope data. In contrast, much larger ranges of $Cl^-/ClO_4^-$ and $Cl^-/NO_3^-$ ratios indicate $Cl^-$ varies independently from both $ClO_4^-$ and $NO_3^-$. The general lack of correlation between $Cl^-$ and $ClO_4^-$ or $NO_3^-$ implies that $Cl^-$ is not a good indicator of co-deposition and should be used with care when interpreting oxyanion cycling in arid systems. The Atacama Desert appears to be unique compared to all other terrestrial locations having a $NO_3^-/ClO_4^-$ molar ratio ~$10^3$. The relative enrichment in $ClO_4^-$ compared to $Cl^-$ or $NO_3^-$ and unique isotopic composition of Atacama $ClO_4^-$ may reflect either additional *in-situ* production mechanism(s) or higher relative atmospheric production rates in that specific region or in the geological past. Elevated concentrations of $ClO_4^-$ reported on the surface of Mars, and its enrichment with respect to $Cl^-$ and $NO_3^-$, could reveal important clues regarding the climatic, hydrologic, and potentially biologic evolution of that planet. Given the highly conserved ratio of $NO_3^-/ClO_4^-$ in non-biologically active areas on Earth, it may be possible to use alterations of this ratio as a biomarker on Mars and for interpreting major anion cycles and processes on both Mars and Earth, particularly with respect to the less-conserved $NO_3^-$ pool terrestrially.

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## 1. INTRODUCTION

The oxyanion perchlorate ($ClO_4^-$) has received increasing attention due to its widespread occurrence on Earth and Mars, and yet its distribution and relation to other more understood atmospheric species are poorly defined. Terrestrial $ClO_4^-$ is largely produced in the atmosphere and deposited in dry and wet deposition (Rajagopalan et al., 2009; Andraski et al., 2014). It is abiotically stable in most near-surface environments but can be irreversibly reduced biologically under anoxic conditions. In these respects $ClO_4^-$ is similar to $NO_3^-$, although $NO_3^-$ may be biologically reduced preferentially to $ClO_4^-$ in mixed redox conditions. Major differences between the two species include a biological production mechanism for $NO_3^-$ (nitrification) and the assimilation of $NO_3^-$ by plants, from which N may be removed from the $NO_3^-$ reservoir into stored organic matter or returned through subsequent nitrification. The terrestrial $NO_3^-$ mass balance is complicated further by varying amounts of $N_2$ fixation, which may result in net changes to the free $NO_3^-$ reservoirs in soils and groundwaters. Given these attributes, $NO_3^-$ and $ClO_4^-$ should co-occur in arid environments. In the driest and coldest locations, where biological activity is minimal, the ratio of $NO_3^-/ClO_4^-$ should be similar to that of total atmospheric deposition; whereas in less arid environments, $NO_3^-/ClO_4^-$ ratios could be higher or lower than the deposition ratio, depending on the relative importance of net biologic $NO_3^-$ (or N) addition or removal. Further, the isotopic composition of $NO_3^-$ in relation to the $NO_3^-/ClO_4^-$ ratio should be consistent with the net effects of mixing of atmospheric and biogenic $NO_3^-$, commensurate with the degree of assimilation and reprocessing of the $NO_3^-$ atmospheric fraction. Such a conceptual model can be used to evaluate environmental conditions under which atmospherically deposited species accumulate and the net effects of soil processes on these species.

Until recently, $ClO_4^-$ was considered to be present in the environment largely from military and commercial sources, but its occurrence in pre-industrial soils and groundwater in the Atacama Desert (Ericksen, 1981), Antarctic Dry Valleys (Kounaves et al., 2010; Jackson et al., 2012), Mojave Desert and Southern High Plains (Jackson et al., 2010), Middle Rio Grande Basin (Plummer et al., 2006), as well as on the surface of Mars (Hecht et al., 2009; Glavin et al., 2013), all demonstrate that $ClO_4^-$ forms naturally. Isotope data including $\Delta^{17}O$ and $^{36}Cl/Cl$ values of natural $ClO_4^-$ indicate that it is produced largely in the stratosphere from oxidative reactions of chloro-oxyanions by $O_3$ oxidation and/or perhaps UV-mediated photo-oxidation (Bao and Gu, 2004; Sturchio et al., 2009; Jackson et al., 2010). $ClO_4^-$ is deposited at the Earth's surface by wet and dry atmospheric deposition. Modern $ClO_4^-$ wet deposition rates measured in North America averaged 64 mg/ha-year (Rajagopalan et al., 2009) and total deposition rates measured in the Amargosa Desert (southwestern Nevada) over a 6-year period averaged 343 mg/ha-year (Andraski et al., 2014). Accumulations of $ClO_4^-$ (93–1050 g/ha) have been observed in deep unsaturated-zone salt bulges throughout the southwestern United States (U.S.) that accumulated during the late Quaternary, roughly over the last 100,000–10,000 years based on $Cl^-$ deposition rates and inventories (Rao et al., 2007).

$ClO_4^-$ is abiotically unreactive under typical terrestrial conditions but can be microbially (Archea and Bacteria) reduced under anoxic conditions as an electron acceptor (Coates and Achenbach, 2004; Liebensteiner et al., 2013). Reduction of $ClO_4^-$ can be coupled to oxidation of various electron donors including organic matter, sulfide, and $H_2$. In electron donor-limited environments, the presence of $NO_3^-$ at greater concentrations has been shown to inhibit $ClO_4^-$ reduction (Tan et al., 2004a; Farhan and Hatzinger, 2009). The capacity for $ClO_4^-$ reduction appears to be common and has been demonstrated in a number of environments including Antarctic Dry Valley lakes (Jackson et al., 2012). Plants accumulate $ClO_4^-$ primarily in transpiring tissue (e.g. leaves) (Jackson et al., 2005; Voogt and Jackson, 2010), and do not generally appear to transform it substantially (Tan et al., 2006; Seyfferth et al., 2008), although this may occur in some cases (Van Aken and