Chlorate and Perchlorate Occurrence and Transformation: Implications to Terrestrial and Extra-Terrestrial Chlorine Cycling

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Perchlorate (ClO_4^-) and chlorate (ClO_3^-) are ubiquitous throughout the terrestrial surface environment, can accumulate to near percent levels in terrestrial hyper-arid areas, and are present in meteorites and lunar regolith [e.g. 1, 2]. ClO_4^- isotopic composition supports a stratospheric source including variable involvement of O_3 mediated oxidation reactions and perhaps other non-O_3 photochemical pathways [3,4]. Heterogeneous photochemical reactions may also occur at the Earth's surface, although their overall significance is unclear [5,6]. ClO_3^-/ClO_4^- molar ratios in terrestrial and extra-terrestrial samples are typically >1:1, except in cases where ClO_3^- has been lost due to biotic or abiotic post depositional transformation [1,7]. The occurrence of both ClO_4^- and ClO_3^- is significantly correlated to the occurrence of NO_3^- in arid terrestrial areas [2]. This strong correlation is likely related to a common atmospheric production mechanism as well as similar biogeochemical stability. (Per)chlorate isotopic composition can be further used to constrain the potential for post depositional transformation and may in some cases constrain the time of accumulation based on either mass accumulation or radioactive decay of ^{36}Cl in accumulated ClO_4^- [4,5]. (Per)chlorate occurrence and variation in post depositional stability can be used to evaluate biogeochemical cycling of Cl and other oxy-anions (e.g. NO_3^-) on Earth and may aid in interpreting (per)chlorate and NO_3^- occurrence and activity on Mars [8]. Of particular relevance are data from terrestrial martian analogs. Data obtained on (per)chlorate from the McMurdo Dry Valley (Antarctica) soils suggest that ClO_3^- but not ClO_4^- may be abiotically transformed in reactions that could be relevant to ancient Mars, whereas biotic reductive transformation in MDV lakes may be a useful analog for predicting the potential for life in other extreme aquatic environments [8].

[1] Jackson et al., (2015), EPSL 430,470. [2]Jackson et al. (2015), GCA 164, 502. [3]Jackson et al. (2010), ES&T 44, 4689. [4]Sturchio et al., (2009), ES&T 43, 6934. [5] Dasgupta et al., (2005), ES&T 39, 1569. [6] Carrier and Kounaves (2015), EPSL 42, 3739. [7] Rao et al., (2010), ES&T 44, 6934. [8] Jackson et al., (2012), GCA 98, 19.