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Nitrate, perchlorate, and iodate co-occur in coastal and inland deserts on Earth

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ABSTRACT

Deserts accumulate soluble salts from atmospheric deposition that impact human health, are a source of nutrients for organisms, and provide insight into how landscapes evolved on Earth and Mars. We quantified perchlorate, nitrate, and iodate abundances and co-occurrence in terrestrial deserts to identify fundamental controls on soluble salt deposition and post-depositional cycling. Soils and nitrate deposits were examined in Death Valley, USA; Atacama Desert, Chile; Kumtag Desert, China; and along an environmental gradient in the Transantarctic Mountains, Antarctica. Concentrations of soluble salts were highest in the Transantarctic Mountains and Atacama Desert, where stable, hyper-arid landscapes accumulate atmospheric salts over million-year time scales. Average nitrate concentrations of 61.3 g kg^{-1} in the Transantarctic Mountains and 53.0 g kg^{-1} in the Atacama Desert were significantly greater than respective averages of 8.60 g kg^{-1} and 5.14 g kg^{-1} in Kumtag Desert and Death Valley. Perchlorate and iodate concentrations in the Atacama Desert averaged 206 mg kg^{-1} and 344 mg kg^{-1}, respectively, which were two to three orders of magnitude greater than in Antarctica and other sites. Our findings suggest that local processes in the Atacama Desert result either in higher rates of perchlorate and iodate deposition, or a greater preservation of these salts relative to nitrate when compared to Antarctic landscapes. Lower salt concentrations in the Death Valley and Kumtag Desert deposits likely result from relatively wet present-day and paleoclimatic conditions, a more active geologic history, and a greater likelihood that biocycling disrupted long-term salt accumulation. Associations of perchlorate and nitrate were significantly higher than iodate-nitrate and iodate-perchlorate correlations in the four deserts. Perchlorate-nitrate relationships ranged from insignificant to highly significant with stronger correlations in the Atacama Desert and Kumtag Desert compared to the Transantarctic Mountains and Death Valley. Weaker geochemical associations with iodate were attributed to differences in local deposition rates or post-depositional cycling. Interestingly, relationships among perchlorate, nitrate, and iodate were generally stronger when examined by site within each desert compared to analyzing the soils for each desert as a whole, suggesting more localized controls on soluble salt preservation. We conclude that soluble salts vary in concentration and type across Earth's deserts as a result of present-day environment, paleoclimate conditions, biocycling, and geologic age.

1. Introduction

Soluble salts, including perchlorate, iodate, and nitrate, are compounds of human health concern (Townsend et al., 2003; Fields, 2004; Parker, 2009; Leung et al., 2010) that accumulate in arid environments on Earth (Ericksen, 1983; Kounaves et al., 2010) and Mars (Hecht et al., 2009; Ming et al., 2014; Stern et al., 2015a). Soluble salts form, redistribute, and co-accumulate in deserts where high evapotranspiration rates prevent the leaching of mobile anions (Ewing et al., 2006; ITRC (Interstate Technology Regulatory Council), 2007). Regional mechanisms of soluble salt production and deposition are still poorly understood despite connections to health (Srinivasan and Viraraghavan, 2009), organism growth (Townsend et al., 2003), and the biogeochemical evolution of landscapes (Catling et al., 2010). Here, we examine how perchlorate, iodate, and nitrate co-occur in four deserts spanning different latitudes, degrees of geomorphic stability, and paleoclimatic histories to understand the distribution of soluble salts that have health and geochemical significance.

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The discovery of perchlorate on Mars prompted a renewed interest in how soluble salts are produced on Earth (Rao et al., 2010) and subsequently preserved in desert soils that may serve as viable analogs for Martian landscapes (Ewing et al., 2006; Catling et al., 2010). Perchlorate, a highly soluble anion, interferes with iodide uptake in the human thyroid if ingested at high concentrations (Srinivasan and Viraraghavan, 2009), making the perchlorate levels (~0.3–0.6%) on Mars a potential challenge for future exploration (Hecht et al., 2009; Leshin et al., 2013). On Earth, perchlorate forms through photochemical reactions with chloride and ozone in the atmosphere (Dasgupta et al., 2005; Rao et al., 2010), yet regional production mechanisms are still under investigation (Jackson et al., 2015). Iodine deficiency is compounded by perchlorate exposure in humans (Leung et al., 2010), rendering iodate, a soluble salt converted to iodide for use in the thyroid, a health-relevant subject of study (Snyder et al., 2009). Iodate originates from atmospheric production, marine sedimentary rocks, and geothermal fluids (Chatfield and Crutzen, 1990; Baker et al., 2001; Alvarez et al., 2015). Nitrate is a bioessential compound with similar solubility to perchlorate that is assimilated by organisms and integrated into amino acids that comprise proteins (Townsend et al., 2003; Fields, 2004). Nitrate forms through both photochemistry and biotic nitrogen fixation (Galloway et al., 2004; Schumann and Huntrieser, 2007) and its heterogeneous distribution in desert soils requires additional research (Noble and Mansfield, 1922; Ericksen, 1983, 1988; Andraski et al., 2014).

Nitrate, perchlorate, and/or iodate co-occur on Earth (Bohlke et al., 1997; Jackson et al., 2004; Dasgupta et al., 2005; Rajagopolan et al., 2006, 2009a, 2009b; Jackson et al., 2010; Kounaves et al., 2010; Lybrand et al., 2013; Jackson et al., 2015) and Mars (Hecht et al., 2009; Smith et al., 2014; Stern et al., 2015a, 2015b). Perchlorate and nitrate exhibit strong relationships in arid soils (Rao et al., 2007; Kounaves et al., 2010; Lybrand et al., 2013; Jackson et al., 2015), wet deposition (Rajagopolan et al., 2009a, 2009b), and groundwater (Jackson et al., 2015), whereas perchlorate-iodate strongly associate in Texas high plains groundwater (Dasgupta et al., 2005; Rajagopalan et al., 2006). Perchlorate also correlates with nitrate on Mars (Stern et al., 2015b) where perchlorate concentrations are ~1–2 orders of magnitude greater than nitrate in Martian sedimentary and eolian deposits (Hecht et al., 2009; Leshin et al., 2013; Kounaves et al., 2014; Stern et al., 2015a, 2015b). On Earth, nitrate concentrations are ~1–2 orders of magnitude higher than perchlorate in desert soils (Kounaves et al., 2010; Lybrand et al., 2013; Jackson et al., 2015). Martian perchlorate and nitrate may differ in abundance due to the continued present-day production of perchlorate (Catling et al., 2010; Smith et al., 2014; Carrier and Kounaves, 2015). Conversely, nitrate is presumably a relic of ancient Mars that underwent little to no decomposition (Stern et al., 2015a); however, more research on Martian perchlorate and nitrate production is necessary.

Our objective was to quantify how nitrate, perchlorate, and iodate salts co-accumulate in desert soils to understand environmental controls on soluble salt preservation and to examine the role of terrestrial deserts as analogs for Martian landscapes. New iodate data sets are reported for Death Valley, USA; the Atacama Desert, Chile; the Kumtag Desert, China, and soils exposed along an environmental gradient in Antarctica. We also present unpublished perchlorate and nitrate concentrations for the Atacama Desert and three groups of sites encompassed by the Transantarctic Mountains, Antarctica. Our findings are compared with published geochemical data to explore how soluble salts co-occur on Earth and Mars. We predicted that the Atacama Desert and Transantarctic Mountains would contain the highest salt concentrations and exhibit the strongest correlations among perchlorate, nitrate, and iodate given similarities in atmospheric production and post-depositional preservation. Lower salt concentrations and weaker correlations were expected in Death Valley and Kumtag Desert where younger nitrate deposits formed in more geologically active and wetter paleoclimate environments. We hypothesize that nitrate, perchlorate, and iodate accumulate and co-occur to the greatest degree in stable, arid landscapes, such as the Atacama Desert and Transantarctic Mountains, suggesting that post-depositional preservation of soluble salts is controlled, in part, by geologic age, degree of landscape stability, present-day climate, salt origin, and paleoclimate.

2. Study areas

We examined nitrate, perchlorate, and iodate distribution in four deserts that vary in depositional environment, age, nitrate origin, and climate (Fig. 1). Geographic coordinates for our sites and general maps of each desert are provided (Table S1; Fig. S1). Supplemental cation data are available for the Atacama Desert (Table S2), Antarctica (Bockheim, 1997; Bockheim, 2013), and Death Valley (Table A3 in Lybrand et al., 2013). Additional sample information for the Transantarctic Mountains is also given (Table S3).

2.1. Transantarctic Mountains, Antarctica

Soluble salts, including nitrate, accumulate in Antarctica's cold deserts as a result of atmospheric deposition (Claridge and Campbell, 1977; Keys and Williams, 1981; Bockheim, 1997), where desert pavements and vesicular horizons preserve salts in soil by reducing eolian deflation (Nichols, 1963; Bockheim, 2007; Bockheim, 2010). Over time, soluble salts form indurated soil horizons, referred to here as salt pans, in xerous and ultraxerous sites with mean annual water-equivalent precipitation ranges from 3 to 50 mm (Fountain et al., 2009). In ultraxerous soils, indurated salt pan horizons are thin and the depth to the salt pan is less than the depth to salt pans in xerous soils (Bockheim, 1997), indicating that salt pan depth and thickness corresponds to depth of snowmelt. Salt concentrations positively correlate with soil age, suggesting an atmospheric deposition-preservation mechanism (Bockheim and Wilson, 1992).

Strong ($r^2 > 0.6$) perchlorate-nitrate and perchlorate-chloride relationships were identified in Antarctic ultraxerous soils from Beacon Valley (Kounaves et al., 2010) and University Valley (Kounaves et al., 2010; Jackson et al., 2015), which were attributed to similar atmospheric deposition and preservation patterns in hyperarid systems. Perchlorate varied from non-detectable to 1100 μg kg^{-1} in xerous and subxerous soils of Wright Valley and Taylor Valley (Kounaves et al., 2010), where more frequent wetting events led to a heterogeneous distribution of soluble salts.

The dry valleys of the Transantarctic Mountains are ice-free areas where soluble salts accumulated to varying degrees over the last 15 Ma (Bockheim, 1990; Bockheim and McLeod, 2006; Bockheim, 2007). We subsampled soils from salt-rich horizons (i.e., Bwz, Bwzm) in exposed terrain that were collected during Bockheim's 1977–1980, 1982, and 1985 field seasons. Our study quantified nitrate, perchlorate, and iodate concentrations in 50 soils from three groups of sites spanning 73°S to 85°S in latitude. The sites were grouped by latitude to represent changes in climate along the environmental gradient (Fig. S1a).

Group 1 sites included soils from Wright Valley, Arena Valley, and Mt. Fleming (73°S to 77°S; n = 10). Soils in Wright Valley formed on inland granitic-gneiss drift deposits ranging from 3.7 ka to 2 Ma in age (Bockheim and McLeod, 2006; Bockheim, 2013) compared to Arena Valley soils that formed on dolerite and sandstone bedrock in a stable upland environment spanning 120 ka to 15 Ma (Bockheim, 2007). The Mt. Fleming soils developed on till of the Upper Wright Glacier that was derived from sandstone and dolerite.

Group 2 sites encompassed soils from the Britannia Range of the Darwin Glacier area (79°S to 80°S; n = 10) and Group 3 soils were collected from upper Beardmore Glacier (84 to 85°S; n = 30). The Darwin and Beardmore Glacier regions formed on sandstone from the Beacon Supergroup sediments with intrusions by dolerite sills of the Ferrar Group (Bockheim, 2013). Darwin Glacier and Beardmore Glacier are outlet glaciers that drain the East Antarctic ice sheet, extending from the Polar Plateau to the Ross Sea Coast. Both sites occur in stable upland landscapes that receive <100 mm yr^{-1} with a Mean Annual Air Temperature of −30 °C or colder (Bockheim and Hall, 2002; Bockheim, 2013). Beardmore Glacier features landscapes composed of soils from diorite-