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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 Atacama Desert and Transantarctic Mountains, where stable, hyper-arid landscapes accumulate atmospheric salts over million-year time scales. Average nitrate concentrations of 53.0 g kg<sup>-1</sup> in the Atacama Desert and 61.3 g kg<sup>-1</sup> in the Transantarctic Mountains were significantly greater than respective averages of 8.60 g kg<sup>-1</sup> and 5.14 g kg<sup>-1</sup> in Kumtag Desert and Death Valley. Perchlorate and iodate concentrations in the Atacama Desert averaged 206 mg kg<sup>-1</sup> and 344 mg kg<sup>-1</sup>, 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.

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### 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

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different latitudes, degrees of geomorphic stability, and paleoclimatic histories to understand the distribution of soluble salts that have health and geochemical significance.

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; Rajagopalan 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 (Rajagopalan 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  $1100 \mu\text{g kg}^{-1}$  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  $73^\circ\text{S}$  to  $85^\circ\text{S}$  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 ( $73^\circ\text{S}$  to  $77^\circ\text{S}$ ;  $n = 10$ ). 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 ( $79^\circ\text{S}$  to  $80^\circ\text{S}$ ;  $n = 10$ ) and Group 3 soils were collected from upper Beardmore Glacier ( $84$  to  $85^\circ\text{S}$ ;  $n = 30$ ). 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

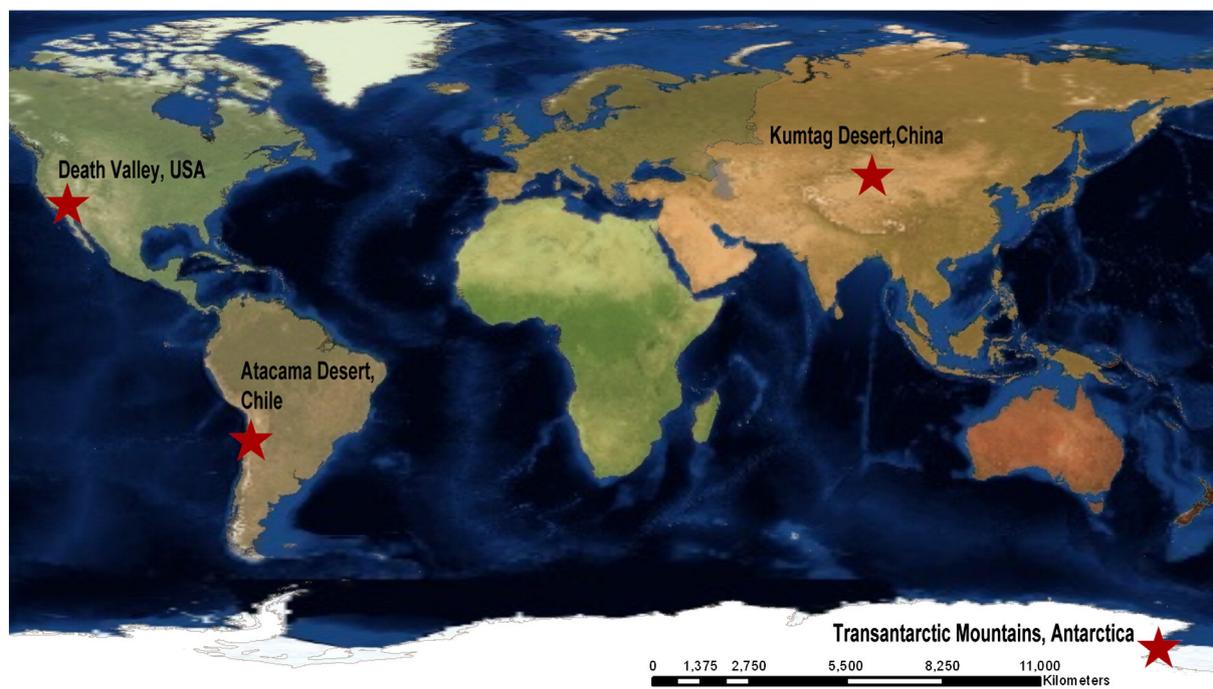


Fig. 1. A map documenting the four deserts in our study, which include Death Valley, USA; Atacama Desert, Chile; Kumtag Desert, China; and Transantarctic Mountains, Antarctica.

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  $< 100 \text{ mm yr}^{-1}$  with a Mean Annual Air Temperature of  $-30 \text{ }^{\circ}\text{C}$  or colder (Bockheim and Hall, 2002; Bockheim, 2013). Beardmore Glacier features landscapes composed of soils from diorite-sandstone drift deposits spanning 14 ka to 2 Ma (Bockheim, 1990) and the Darwin Glacier sites are Pliocene to Miocene (Bockheim, 2013).

## 2.2. Death Valley, Mojave Desert, USA

The Death Valley nitrate deposits formed in ancient lake sediments when saline, gypsiferous clays and sands were deposited in evaporating lakes and buried by nearby alluvial fans (Noble and Mansfield, 1922). The deposits were deformed by faulting and folding with subsequent exposure by alluvial incision. The deposits display loose, blistered soils that are not covered by protective desert pavement or vesicular horizons as observed elsewhere (Wells et al., 1985; McFadden et al., 1987; Turk and Graham, 2011). The nitrate salts likely originate from a “bottom-up” mechanism (Lybrand et al., 2013) where sporadic rains redistribute the underlying deposits into overlying soils through capillary rise and evapo-concentration.

The Death Valley nitrate deposits range from Miocene to Pleistocene in age (Noble and Mansfield, 1922). Death Valley is a hot and dry desert, with 30-year rainfall averages from 63 to 107  $\text{mm yr}^{-1}$  (1981–2010; PRISM Climate Group). Perchlorate, nitrate, and other anions co-occur to varying degrees in specific deposits including Bully Hill, Confidence Hills, Owl Hole Springs, Saratoga Springs, Sperry, and Tecopa (Fig. S1b; Jackson et al., 2010; Lybrand et al., 2013; Jackson et al., 2015). We selected 34 Death Valley soils from Lybrand et al. (2013) for iodate analysis and referenced Lybrand et al.'s perchlorate and nitrate data sets to compare concentrations in Death Valley to salt abundances in other deserts. Our subsamples for iodate analysis span geologic age (0.01 to 11.3 Ma), depth, and encompass the aforementioned sites except Saratoga Springs.

## 2.3. Kumtag Desert, Turpan-Hami Basin, China

We sampled two soil profiles in Kumtag Desert where nitrate deposits are common in surface soils ( $< 50 \text{ cm}$  depth) of Pleistocene-

aged conglomerates and form in low-lying basins that are located  $\sim 2500 \text{ km}$  from the nearest coastline (Fig. S1c; Qin et al., 2012). Precipitation averages 30–50  $\text{mm yr}^{-1}$  in the form of rain (Li et al., 2011) with evaporation rates that are 200 times that of precipitation inputs (Sun and Deng, 1987). We analyzed 20 samples from two soil profiles that reached  $> 175 \text{ cm}$  in depth. Nitrate deposits from Kumtag Desert are similar in age to Bully Hill and Sperry in Death Valley (1.8–0.01 Ma), and much younger than deposits in the Atacama Desert and Transantarctic Mountains (Rech et al., 2006).

## 2.4. Atacama Desert, Chile

Nitrate deposits in the Atacama Desert are well-characterized (Bohlke et al., 1997; Michalski et al., 2004; Catling et al., 2010; Perez-Fodich et al., 2014; Alvarez et al., 2015) and exhibit strong nitrate-perchlorate relationships (Ericksen, 1981, 1983; Jackson et al., 2015). Iodate was detected in Atacama samples (Ericksen, 1981; Bohlke et al., 1997) with soluble ore estimates of 0.060% (Grossling and Ericksen, 1971).

The Atacama Desert nitrate deposits formed across old (Pliocene and early Pleistocene), stable, hyper-arid landscapes receiving  $< 5 \text{ mm yr}^{-1}$  of rain (McKay et al., 2003), with little surface runoff or erosion. Our study focused on sulfate-rich horizons in the upper 40 cm and underlying salt-cemented nitrate deposits that reached depths of several meters (Prellwitz, 2007). We analyzed perchlorate and nitrate concentrations in 68 samples from four field localities (Site SP5, Oficina Ercilla, Valenzuela, and Rencoret NW) situated along a  $\sim 40 \text{ km}$  north-south transect in a valley between Sierra Valenzuela and Sierra Rencoret (Fig. S1d). We selected 52 samples for iodate analysis that spanned the four field sites and depth ranges from 0 to  $> 300 \text{ cm}$ . Soils from Site SP5 are situated atop the distal end of an alluvial fan, and are buried by Pleistocene stream alluvium from Quebrada Saco. Upstream ( $\sim 10 \text{ km}$ ) alluvium contains a volcanic ash that was Ar/Ar dated to 760,000 years (Placzek et al., 2009), leading to buried soil age estimates of Pliocene to early Pleistocene at Site SP5. Soils from Oficina Ercilla, Valenzuela, and Rencoret NW are estimated to be Pliocene to early Pleistocene, and formed on top of alluvial fans, or in the case of Valenzuela, a fluvial terrace (Prellwitz, 2007).

### 3. Methods

#### 3.1. Chemical analysis

Soil and sediment were sampled by morphologic horizon or incremental depths, air-dried, sieved (<2-mm), and homogenized, with the exception of cemented samples which were crushed prior to processing (Prellwitz, 2007). The concentrations of soluble salts in the soil samples were determined using a dilute extraction method (1000:1) (Lybrand et al., 2013). Briefly, soluble salts were extracted from 100 mg of a bulk soil sample that was diluted with 15–30 mL of Type I deionized water, shaken, and centrifuged, with the process repeated three times or until the supernatant was <100  $\mu\text{S cm}^{-1}$ .

An aliquot of the supernatant was combined with a  $\text{Cl}^{18}\text{O}_4^-$  internal standard and processed for chemical analysis. Perchlorate was measured using electrospray-ionization-mass-spectrometry on a Dionex ion chromatograph equipped with an IonPac AS16 analytical column and an IonPac AG16 guard column (Dionex Corp, 2003a; Environmental Protection Agency, 2005). A second aliquot of the decanted solution was analyzed for iodate following a modified method from Henday et al. (2008). The conditions modified for the chromatographic separation of iodate in our study included an injection volume of 50  $\mu\text{L}$ , a mobile phase gradient from 5 to 35 mmol KOH/L in 16 min, and a source temperature of 475 °C. Nitrate and iodate were measured by ion chromatography through two separate analyses, both of which used a Dionex IonPac AS18 analytical column (2 × 250 mm) and an IonPac AG18 guard column (2 × 50 mm) (Dionex Corp, 2003b). Potassium hydroxide was used as the eluent for the methods as IonPac AS16 and IonPac AS18 are hydroxide- and anion-selective columns.

##### 3.1.1. Method detection limit (MDL)

The perchlorate method detection limit of 0.055  $\text{mg kg}^{-1}$  was determined by Lybrand et al. (2013) using the EPA Method 314.0 (Environmental Protection Agency, 1999):

$$\text{MDL} = ts$$

where  $t = 2.82$  for nine degrees of freedom (df) and  $s$  is the standard deviation of perchlorate determined for ten replicate samples. When perchlorate concentrations were less than the MDL, the sample was categorized as non-detectable and set to 0.0275  $\text{mg kg}^{-1}$ , or half of the MDL (Environmental Protection Agency, 1999). The minimum reporting limit (MRL) for perchlorate in this study was 0.165  $\text{mg kg}^{-1}$ , which was three times that of the MDL. The MDL determined for iodate was 0.0004  $\text{mg kg}^{-1}$  with a corresponding MRL of 0.0012  $\text{mg kg}^{-1}$ . The MDL and MRL for nitrate were 0.015  $\text{g kg}^{-1}$  and 0.045  $\text{g kg}^{-1}$ , respectively.

#### 3.2. Statistical analysis

Linear regressions, summary statistics, and one-way ANOVAs were performed in JMP (v. 11.0, SAS Institute Inc.) on log-transformed concentrations of perchlorate, nitrate, and iodate. Salt concentrations and molar ratios were averaged for each desert and field site. We tested for significant differences in average and maximum salt concentrations among the four deserts using one-way ANOVAs paired with Tukey-Kramer HSD posthoc tests. Linear regressions were employed to compare soluble salt concentrations among the four deserts and within each field area where soils differed in geologic age, climate, and stability. Coefficients of determination,  $r^2$ , were interpreted according to Evans (1996) with  $r^2$  values categorized as very weak (0 to 4%), weak (4 to 16%), moderate (16 to 36%), strong (36% to 64%), and very strong (64% to 100%). Variables,  $r^2$  values, and P-values are reported in Table 1 and Table S4. Superscripts represent significance level where \*\*\* $P < 0.001$ , \*\* $P < 0.01$ , and \* $P < 0.05$ .

### 4. Results

#### 4.1. Soluble salt concentrations and ratios by desert

##### 4.1.1. Transantarctic Mountains, Antarctica

Samples from salt-cemented B horizons in the Transantarctic Mountains presented notable variation in perchlorate, nitrate, and iodate, averaging 1.85  $\text{mg kg}^{-1}$ , 61.3  $\text{g kg}^{-1}$ , and 27.7  $\text{mg kg}^{-1}$ , respectively (Table 1). Average perchlorate content was within the upper limit of 1.1  $\text{mg kg}^{-1}$  previously reported for Taylor Valley and orders of magnitude greater than published values of <0.025  $\text{mg kg}^{-1}$  in Wright Valley and 0.062  $\text{mg kg}^{-1}$  in Victoria Valley (Kounaves et al., 2010). We observed the highest average nitrate concentrations in the Transantarctic Mountains including 73.9  $\text{g kg}^{-1}$  in Group 1 and 65.8  $\text{g kg}^{-1}$  in Group 2. Iodate concentrations ranged from 16.1  $\text{mg kg}^{-1}$  in Group 2 to 34.8  $\text{mg kg}^{-1}$  in Group 3 and presented the second lowest overall average in our study next to Kumtag Desert. Maximum perchlorate concentrations of 2.46  $\text{mg kg}^{-1}$  in Group 1, 15.3  $\text{mg kg}^{-1}$  in Group 2, and 8.91  $\text{mg kg}^{-1}$  in Group 3 occurred in weakly to strongly salt-cemented horizons. A maximum nitrate concentration of 327  $\text{g kg}^{-1}$  was measured for Groups 1 and Group 3, which was most similar to soils in the Atacama Desert. Maximum iodate concentrations ranged from 76.5 to 36.1  $\text{mg kg}^{-1}$  in Groups 1 and 2 compared to 116  $\text{mg kg}^{-1}$  in Group 3. Molar ratios reflected variable salt content among the soils, with an average  $\text{NO}_3^-/\text{ClO}_4^-$  ratio of ~123,000, and ranges from ~62,000 in Group 2 to ~144,000 at Group 3. We report  $\text{NO}_3^-/\text{ClO}_4^-$  ratios that are 1–2 orders of magnitude greater than reported values of  $10^3$ – $10^4$  for Antarctic soils (Jackson et al., 2015). The average  $\text{NO}_3^-/\text{IO}_3^-$  ratio of ~112,000 was the highest of our study compared to an  $\text{IO}_3^-/\text{ClO}_4^-$  ratio of ~41 which was the second lowest of the sites.

##### 4.1.2. Death Valley, Mojave Desert, USA

Death Valley soils exhibited the lowest average perchlorate and nitrate concentrations of the deserts, with respective means of 0.383  $\text{mg kg}^{-1}$  and 5.14  $\text{g kg}^{-1}$  (Lybrand et al., 2013) whereas iodate presented the second highest average in our study (Table 1). Average perchlorate concentrations range from 0.06  $\text{mg kg}^{-1}$  to 1.24  $\text{mg kg}^{-1}$  and nitrate from 0.778  $\text{g kg}^{-1}$  to 17.5  $\text{g kg}^{-1}$ . Comparatively, perchlorate in Mojave salt bulges, desert pavement landscapes, and clay hill deposits span 0.0001  $\text{mg kg}^{-1}$  to 5.5  $\text{mg kg}^{-1}$  (Jackson et al., 2015). Most notably, a maximum perchlorate concentration of 23.4  $\text{mg kg}^{-1}$  (Lybrand et al., 2013) was reported for the Sperry deposits (Lybrand et al., 2013), representing the highest perchlorate concentration for Death Valley, Kumtag Desert, and the Transantarctic Mountains. An average iodate concentration of 69.7  $\text{mg kg}^{-1}$  was two-fold greater than averages for Kumtag Desert and Transantarctic Mountains. The Tecopa deposits in Death Valley exhibited the second highest iodate concentration next to the Atacama Desert, with an average of 223  $\text{mg kg}^{-1}$ . The Death Valley  $\text{NO}_3^-/\text{ClO}_4^-$  ratio averaged ~98,000, coinciding with the  $10^4$ – $10^5$  range reported for the Mojave deposits (Jackson et al., 2015). The Death Valley  $\text{NO}_3^-/\text{IO}_3^-$  ratio was the lowest of the deserts at 835 whereas the  $\text{IO}_3^-/\text{ClO}_4^-$  ratio of 178 was the highest.

##### 4.1.3. Kumtag Desert, Turpan-Hami Basin, China

The Kumtag Desert soils contained average perchlorate, nitrate, and iodate concentrations of 1.84  $\text{mg kg}^{-1}$ , 8.60  $\text{g kg}^{-1}$ , and 21.1  $\text{mg kg}^{-1}$  respectively (Table 1). We measured a maximum perchlorate concentration of 5.35  $\text{mg kg}^{-1}$ , which was three times lower than a previously reported maximum of 16  $\text{mg kg}^{-1}$  for the Turpan-Hami Basin (Jackson et al., 2015). Average nitrate contents spanned 2.92  $\text{g kg}^{-1}$  to 11.0  $\text{g kg}^{-1}$  in the SR and RP profiles where concentrations were most similar to Death Valley. Iodate concentrations were the lowest of the deserts, with averages ranging from 14.4  $\text{mg kg}^{-1}$  to 24.0  $\text{mg kg}^{-1}$  in the two profiles. We observed an average  $\text{NO}_3^-/\text{ClO}_4^-$  ratio of 12,474 in the Kumtag Desert, which overlapped with a published ratio of 12,000 (Jackson et al., 2015), and was lower than ratios for Death Valley and

**Table 1**

Perchlorate, nitrate, and iodate concentrations and molar ratios for the Transantarctic Mountains, Antarctica; Atacama Desert, Chile; Kumtag Desert, China; and Death Valley, USA. The Antarctica sites include Group 1 (Wright Valley, Arena Valley, and Mt. Fleming), Group 2 (Darwin Glacier), and Group 3 (Beardmore Glacier). Average concentrations followed by the same letter for a chemical concentration within a desert are not significantly different ( $p < 0.05$ ).

Location	Site	Average concentration			Maximum concentration			Molar ratio		
		[ClO <sub>4</sub> <sup>-</sup> ] (mg kg <sup>-1</sup> )	[NO <sub>3</sub> <sup>-</sup> ] (g kg <sup>-1</sup> )	[IO <sub>3</sub> <sup>-</sup> ] (mg kg <sup>-1</sup> )	[ClO <sub>4</sub> <sup>-</sup> ] (mg kg <sup>-1</sup> )	[NO <sub>3</sub> <sup>-</sup> ] (g kg <sup>-1</sup> )	[IO <sub>3</sub> <sup>-</sup> ] (mg kg <sup>-1</sup> )	[NO <sub>3</sub> <sup>-</sup> ]/[ClO <sub>4</sub> <sup>-</sup> ]	[NO <sub>3</sub> <sup>-</sup> ]/[IO <sub>3</sub> <sup>-</sup> ]	[IO <sub>3</sub> <sup>-</sup> ]/[ClO <sub>4</sub> <sup>-</sup> ]
Atacama Desert, Chile	All	206	53	344	801	324	2128	1675	34,505	18
	Oficina Ercilla	283 A	69.1 A	303 A	637	172	2128	935	80,138	9
	Rencoret NW	65.1 B	19.4 B	512 A	225	45.4	1849	970	187	30.4
	Site SP5	322 A	64.7 A, B	297 A	801	324	1107	801	26,121	0.752
	Valenzuela	11.9 B	27.3 A, B	293 A	76.9	111	1354	5220	699	36.93
Death Valley, USA	All	0.383	5.14	69.7	23.4	61.5	223	98,499	835	178
	Bully Hill	0.371 A	17.5 A	51.1 B	3.42	61.5	62.3	297,292	1704	83
	Confidence Hills	0.0616 A	1.38C	63.3 B	0.419	13.6	92.8	45,111	874	226
	Owl Hole Springs	0.249 A	2.68C	85.8 B	3.15	14.9	179	60,510	190	313
	Saratoga	0.123 A	0.778C	–	3.03	6.5	–	45,232	–	–
	Sperry	1.24 A	9.59 B	47.6 B	23.4	51.9	99.2	168,173	1042	34
	Tecopa	0.137 A	2.33C	198 A	2.24	39	223	30,442	47	654
Kumtag Desert, China	All	1.84	8.6	21.1	5.35	25.7	122	12,474	2351	57
	RP Profile	1.94 A	11.0 A	24.0 A	5.16	25.7	122	13,008	2954	55
	SR Profile	1.59 A	2.92 A	14.4 A	5.35	9.73	23.1	11,229	946	63.9
Transantarctic Mountains, Antarctica	All	1.85	61.3	27.7	15.3	327	116	123,012	112,330	42.51
	Group 1	0.797 A	73.9 A	18.1 A	2.46	327	76.5	121,586	524,454	40.8
	Group 2	2.80 A	35.1 A	16.1 A	15.3	179	36.1	62,796	13,647	35.6
	Group 3	1.89 A	65.8 A	34.8 A	8.91	327	116	143,558	7850	45.4

the Transantarctic Mountains. Kumtag Desert soils exhibited an average NO<sub>3</sub><sup>-</sup>/IO<sub>3</sub><sup>-</sup> ratio of 2351, which was greater than Death Valley soils yet 2–3 orders of magnitude less than soils from the Atacama Desert and Transantarctic Mountains. The average IO<sub>3</sub><sup>-</sup>/ClO<sub>4</sub><sup>-</sup> ratio of 57 was an order of magnitude less than Death Valley yet similar to the Atacama Desert and the Transantarctic Mountains.

#### 4.1.4. Atacama Desert, Chile

The Atacama Desert samples exhibited the highest soluble salt contents in our study, where perchlorate, nitrate, and iodate concentrations averaged 206 mg kg<sup>-1</sup>, 53.0 g kg<sup>-1</sup>, and 344 mg kg<sup>-1</sup>, respectively (Table 1). Average perchlorate values ranged from 11.9 mg kg<sup>-1</sup> in Valenzuela to 322 mg kg<sup>-1</sup> in Site SP5. Perchlorate concentrations were up to several orders of magnitude greater in the Atacama Desert than other deserts and occurred within the reported range of 0.0005 mg kg<sup>-1</sup> to 1000 mg kg<sup>-1</sup> (Jackson et al., 2015). Nitrate averages spanned 19.4 g kg<sup>-1</sup> in Rencoret NW to 69.1 g kg<sup>-1</sup> in Oficina Ercilla compared to average iodate contents from 293 mg kg<sup>-1</sup> in Valenzuela to 512 mg kg<sup>-1</sup> in Rencoret NW. We observed a maximum perchlorate concentration of 801 mg kg<sup>-1</sup> compared to maximums of 23.4 mg kg<sup>-1</sup> in Death Valley (Lybrand et al., 2013), 15.3 mg kg<sup>-1</sup> in the Transantarctic Mountains, and 5.35 mg kg<sup>-1</sup> in Kumtag Desert. A maximum nitrate concentration of 324 g kg<sup>-1</sup> in the Atacama Desert was nearly identical to 327 g kg<sup>-1</sup> in the Transantarctic Mountains, and was up to one order of magnitude greater than the other two deserts. Similar to perchlorate, iodate concentrations in the Atacama Desert exceeded observations at other sites with a maximum concentration of 2128 mg kg<sup>-1</sup> compared to 223 mg kg<sup>-1</sup> in Death Valley, 122 mg kg<sup>-1</sup> in Kumtag Desert, and 116 mg kg<sup>-1</sup> in the Transantarctic Mountains. The associated NO<sub>3</sub><sup>-</sup>/ClO<sub>4</sub><sup>-</sup> ratio of 1675 was similar in magnitude to reported Atacama soil ratios of ~1400 (Jackson et al., 2015) and lower than other deserts. The Atacama Desert NO<sub>3</sub><sup>-</sup>/IO<sub>3</sub><sup>-</sup> ratio was the second highest in our work next to the Transantarctic Mountains, with Atacama sites ranging from 187 at Rencoret NW to 80,000 at Oficina Ercilla. Conversely, an average IO<sub>3</sub><sup>-</sup>/ClO<sub>4</sub><sup>-</sup> ratio of 18 was the lowest of the deserts where ratios spanned 0.75 at Site SP5 to 36.9 at Valenzuela.

The Atacama Desert was the closest Earth analog to sites on Mars with respect to soluble salt concentrations and ratios (Jackson et al.,

2015; Hecht et al., 2009; Stern et al., 2015b). Maximum perchlorate concentrations of ~800 to 1000 mg kg<sup>-1</sup> in the Atacama Desert approach the lowest perchlorate end members on Mars, where concentrations range from ~1000 to ~10,000 mg kg<sup>-1</sup> (Hecht et al., 2009; Stern et al., 2015b). Nitrate concentrations on Mars are lower (<1 g kg<sup>-1</sup>) than an average of 53 g kg<sup>-1</sup> in the Atacama Desert, leading to a NO<sub>3</sub><sup>-</sup>/ClO<sub>4</sub><sup>-</sup> ratio of ~0.1 on Mars compared to 10<sup>3</sup> for the Atacama soils (Stern et al., 2015b).

#### 4.2. Soluble salt relationships varied among deserts

Perchlorate–nitrate relationships varied from insignificant to highly significant, with weaker correlations in Death Valley and the Transantarctic Mountains compared to the Kumtag Desert and Atacama Desert (Fig. 2a–d). Perchlorate and nitrate exhibited the greatest association in soils from Kumtag Desert ( $r^2 = 0.792^{***}$ ; Fig. 2a) and the Atacama Desert, where moderate ( $r^2 = 0.585^{***}$ ) to strong ( $r^2 = 0.834^*$ ; Jackson et al., 2010) correlations were observed (Fig. 2b). Perchlorate and nitrate co-occurred in Death Valley, exhibiting weak to strong relationships as identified by Jackson et al., 2010 ( $r^2 = 0.186$ ,  $p = 0.468$ ), Lybrand et al., 2013 ( $r^2 = 0.321^{***}$ ), and Jackson et al., 2015 ( $r^2 = 0.66^{***}$ ). Perchlorate–nitrate associations in the Transantarctic Mountains were weak yet significant ( $r^2 = 0.11^*$ ; Fig. 2d) with strong site-specific correlations in Beacon Valley ( $r^2 = 0.82$ ) and University Valley ( $r^2 = 0.96$ ) (Kounaves et al., 2010).

Iodate did not strongly co-occur with perchlorate (Fig. S2a–d) or nitrate (Fig. S3a–d) in Death Valley, the Atacama Desert, or the Transantarctic Mountains. The iodate–perchlorate relationship was moderate and significant ( $r^2 = 0.247^*$ ) in Kumtag Desert soils (Fig. S2a) whereas the associated iodate–nitrate correlation was positive ( $r^2 = 0.152$ ) albeit insignificant (Fig. S3a).

#### 4.3. Site-specific correlations of soluble salts within deserts

Site-specific soluble salt concentrations, specifically perchlorate–nitrate and to a lesser degree, iodate–nitrate, exhibited significant relationships that were often stronger than those for the overall desert (Table S4). For example, moderate to strong associations were recognized for sites in Antarctica, including perchlorate–nitrate ( $r^2 =$

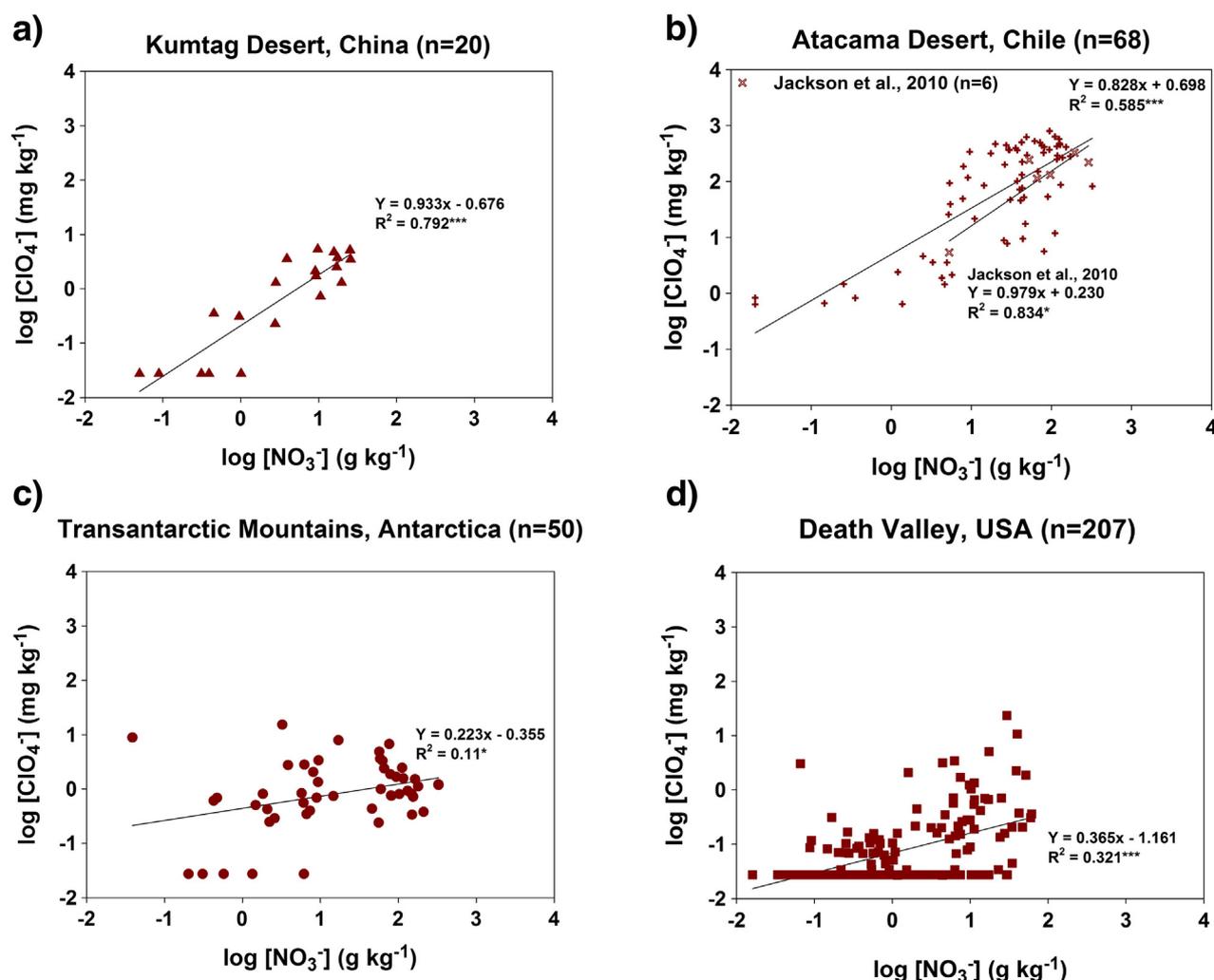


Fig. 2. Perchlorate and nitrate concentrations for a) Kumtag Desert, China, b) Atacama Desert, Chile, c) Transantarctic Mountains, Antarctica, and d) Death Valley, USA. Note: Fig. 2d is referenced from Lybrand et al. (2013) for comparison to the new geochemical data sets presented in Fig. 2a–c.

0.587\*\*) in Group 1 and iodate-nitrate in Group 2 ( $r^2 = 0.478^{***}$ ). Similarly, the Atacama Desert sites exhibited moderate to moderately strong significant perchlorate-nitrate relationships at Oficina Ercilla ( $r^2 = 0.535^{***}$ ), Rencoret NW ( $r^2 = 0.714^{**}$ ), and Valenzuela ( $r^2 = 0.535^{**}$ ). Conversely, weak, significant iodate-nitrate associations were identified in soils from Oficina Ercilla ( $r^2 = 0.218^*$ ) and site SP5 ( $r^2 = 0.473^*$ ). Perchlorate-nitrate correlations were also strong in the Kumtag Desert, specifically the RP ( $r^2 = 0.843^{***}$ ) and SR soils ( $r^2 = 0.769^*$ ) whereas iodate-nitrate and iodate-perchlorate associations were weak and insignificant (Table S4).

Soluble salt relationships varied in Death Valley soils where weak to moderately strong perchlorate-nitrate relationships were identified in the Confidence Hills ( $r^2 = 0.188^{**}$ ), Owl Hole Springs ( $r^2 = 0.464^{***}$ ), Sperry ( $r^2 = 0.325^{***}$ ), and Tecopa ( $r^2 = 0.385^{***}$ ). We observed no significant differences in perchlorate-nitrate at Bully Hill or Saratoga. Sperry exhibited moderately strong, significant relationships between iodate-nitrate ( $r^2 = 0.446^*$ ) and iodate-perchlorate ( $r^2 = 0.396^*$ ). Iodate-nitrate and iodate-perchlorate correlations were moderately strong, albeit insignificant, for Bully Hill and Confidence Hills (Table S4).

## 5. Discussion

Soluble salts accumulate in desert soils that reflect present day and paleoclimatic environments, geologic age, biocycling by plants and

microorganisms, and contrasting deposition pathways. Perchlorate, nitrate, and iodate salts exhibited variability in concentration and relative abundance within and by desert, likely resulting from regional climate conditions, variable sources of iodate, and in situ pedogenic processes.

### 5.1. Climate, landscape stability, and solubility influence salt distribution in desert soils

#### 5.1.1. Climate and landscape stability

We attribute high salt contents in the Atacama Desert and Transantarctic Mountains to dry, evaporative conditions and stable depositional landscapes where nitrate concentrations were significantly greater than Kumtag Desert and Death Valley. Perchlorate and iodate concentrations were 1–2 orders of magnitude higher in the Atacama Desert than other deserts (Table 1). Hyper-arid regions in the Atacama Desert receive  $<5 \text{ mm yr}^{-1}$  of rain (McKay et al., 2003), with an established record of soluble salt accumulation (Grossling and Erickson, 1971; Erickson, 1983; Bohlke et al., 1997; Prellwitz, 2007; Jackson et al., 2010). The Transantarctic Mountains are also moisture-limited ( $3\text{--}50 \text{ mm yr}^{-1}$ ; Fountain et al., 2009) and contain high concentrations of atmospherically deposited salts that accumulated beneath desert pavements over the last 3 ka to 15 Ma (Nichols, 1963; Bockheim, 2007; Bockheim, 2010; Kounaves et al., 2010; Jackson et al., 2015).

Lower nitrate and perchlorate concentrations in Kumtag Desert and Death Valley suggest a contrast in landscape stability, climate, and/or salt preservation mechanisms when compared to the Atacama Desert and Transantarctic Mountains (Qin et al., 2012; Lybrand et al., 2013; Jackson et al., 2015). Lower salt concentrations in Kumtag Desert may reflect a shorter length in stability of the Pleistocene-aged deposits despite the dry ( $\sim 30\text{--}50\text{ mm yr}^{-1}$ ) conditions of the present-day landscape (Li et al., 2011; Sun and Deng, 1987; Qin et al., 2012). Soluble salts in the Kumtag Desert concentrate in surface soils from depth through capillary rise and high evaporation rates (Qin et al., 2012), in contrast to the primarily top-down accumulation mechanism presented for the Atacama Desert and Transantarctic Mountains.

Death Valley, which contained soils with the lowest concentrations of nitrate and perchlorate (Table 1), receives more rainfall ( $\sim 40\text{ mm yr}^{-1}$ ) and has experienced greater tectonic deformation than other deserts (Noble and Mansfield, 1922). The Death Valley deposits are associated with impervious clay-rich soils that swell during episodic rain events and prevent the leaching of underlying salts (Noble and Mansfield, 1922; Ericksen, 1988). Nitrate and perchlorate are preserved in near-surface deposits that migrate into surface soils through a bottom-up mechanism (Lybrand et al., 2013) similar to processes described for Kumtag Desert (Qin et al., 2012). Death Valley contained the second highest iodate concentrations with values of 40–140 ppm (Ericksen, 1988). Our findings confirm that arid, stable landscapes accumulate salts over geologic timescales (ka to Ma), yet suggest that mineral solubility, salt origin, and geomorphic history should also be examined.

### 5.1.2. Solubility

Perchlorate and nitrate salts show a higher degree of solubility in water than iodate (CRC Handbook of Chemistry and Physics, 2015), suggesting that solubility may explain the stronger perchlorate–nitrate relationships compared to iodate–perchlorate (Fig. S2a–d) and iodate–nitrate (Fig. S3a–d). Aqueous solubility, reported here as mass percent of solute, ranged from  $\sim 50\text{--}65$  for perchlorate compounds (i.e.,  $\text{Mg}(\text{ClO}_4)_2$ ,  $\text{Ca}(\text{ClO}_4)_2$ ,  $\text{NaClO}_4$ ),  $\sim 42\text{--}59$  for nitrate (i.e.,  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{NaNO}_3$ ) and  $\sim 0.3\text{--}8.7$  for iodate ( $\text{Mg}(\text{IO}_3)_2$ ,  $\text{Ca}(\text{IO}_3)_2$ ,  $\text{INO}_3$ ). Based on solubility, perchlorate and nitrate would leach to greater depths than iodate, leading to a vertical zonation of salts as observed in the Atacama Desert where nitrate deposits underlie sulfate-rich surface soils (Ericksen, 1983; Prellwitz, 2007) and to a lesser degree in Death Valley (Noble and Mansfield, 1922; Ericksen, 1988). Surprisingly, iodate salts concentrate at depth with maximums of  $2128\text{ mg kg}^{-1}$  at  $\sim 330\text{ cm}$  in the Atacama Desert,  $223\text{ mg kg}^{-1}$  at  $\sim 60\text{ cm}$  in Death Valley,  $122\text{ mg kg}^{-1}$  at  $\sim 155\text{ cm}$  in Kumtag Desert, and  $116\text{ mg kg}^{-1}$  from  $\sim 4\text{--}14\text{ cm}$  at Beardmore Glacier in the Transantarctic Mountains. Our findings support the potential for alternative sources of iodate preservation in the nitrate deposits given its low solubility and accumulation at depth.

## 5.2. The impact of soluble salt origin on geochemical relationships

### 5.2.1. Nitrate

Nitrate concentrations were highest in the Transantarctic Mountains and the Atacama Desert deposits that comprise atmospherically derived nitrate (Table 1; Michalski et al., 2004, 2005; Jackson et al., 2015) compared to Death Valley and Kumtag Desert where nitrate originates from a mixture of biologic and atmospheric sources (Lybrand et al., 2013; Jackson et al., 2015). Biologic and atmospheric nitrate are differentiated using an  $\Delta^{17}\text{O}$  isotope technique where  $\Delta^{17}\text{O} \approx 0\%$  signifies biologically fixed nitrate and  $\Delta^{17}\text{O} \approx 20$  to  $50\%$  indicates an atmospheric origin (Michalski et al., 2002; Thiemens and Heidenreich, 1983). Nitrate is exclusively atmospheric in the Transantarctic Mountains, with  $\Delta^{17}\text{O}$  signatures of 28.9 to 32.7% (Michalski et al., 2005), which coincide with the highest average nitrate concentration (Table 1). Similarly, nitrate in the Atacama Desert is predominately atmospheric, ranging from

$\Delta^{17}\text{O} \approx 13.7$  to 21.6% (Michalski et al., 2004; Jackson et al., 2010), with the second highest nitrate concentrations measured. Lower isotopic end members in the Atacama Desert demonstrate that salts are dominantly atmospheric with biological nitrate inputs in sites with slightly higher moisture (Ewing et al., 2006).

We predict that relatively wetter climates in Death Valley and Kumtag Desert led to more biologically active paleoenvironments that were conducive to N cycling and plant uptake. Perchlorate and nitrate exhibit different fates when cycled by desert plants in the present-day Mojave Desert. Perchlorate is largely conserved, assimilated by plant leaves and returned to the soil by leaf drop, whereas nitrate is integrated into plant tissue (Andraski et al., 2014). If considered in a paleoclimate context, nitrate was likely biocycled to a greater extent under the wetter, more ecologically productive Pleistocene conditions in Death Valley compared to drier paleoenvironments in the Atacama Desert or Transantarctic Mountains. Our hypothesis is supported by a precipitation proxy based on the oxygen–17 anomaly that provides evidence for a dry-to-wet transition in Death Valley where the climate changed from moisture-limited at 2.15 Ma (MAP  $\sim 50\text{ mm}$ ) to wetter conditions at 1.8 Ma (Wang et al., 2016). Interestingly, the mechanisms that drove the long-term preservation of bioavailable nitrate in the presumably wetter paleoenvironment of Death Valley are poorly understood (Lybrand et al., 2013), and need additional interpretation.

### 5.2.2. Perchlorate

Perchlorate concentrations are 2–3 orders of magnitude greater in the Atacama Desert (Table 1), suggesting localized production and/or accumulation mechanisms that differ from other deserts (Jackson et al., 2015). The  $\Delta^{17}\text{O}$  signatures of perchlorate are less documented than nitrate, but suggest a unique isotopic enrichment in the Atacama Desert (Jackson et al., 2010). On Earth, natural perchlorate forms through atmospheric photochemistry (Catling et al., 2010; Rao et al., 2010) although specific pathways are still under investigation (Kang et al., 2009; Roberts, 2009; Rao et al., 2012). Conversely, the photochemical production of perchlorate and chlorate on chloride-bearing mineral surfaces may account for a substantial portion of perchlorate accumulation on Mars (Carrier and Kounaves, 2015). The production of perchlorate or its redistribution across landscapes may vary with site-specific mechanisms that merit further research.

High perchlorate concentrations and unique  $\Delta^{17}\text{O}$  signatures in the Atacama Desert led to hypotheses on its depositional history including a regionally high atmospheric production rate, an unknown localized formation mechanism, or greater perchlorate production under paleoatmospheric conditions (Jackson et al., 2015). The Atacama Desert is conducive to long-term perchlorate accumulation with minimum perchlorate age estimates of 750,000 years (Sturchio et al., 2009). The Transantarctic Mountains also present a history of landscape stability with substantial nitrate accumulation (Bockheim, 2010), yet perchlorate concentrations are substantially lower and most similar to Death Valley and Kumtag Desert (Table 1).

### 5.2.3. Iodate

Iodate is most enriched in the Atacama Desert (Table 1; Grossling and Ericksen, 1971; Bohlke et al., 1997) where a proposed groundwater source model supports the prevalence of iodate in the Atacama nitrate deposits (Perez-Fodich et al., 2014; Alvarez et al., 2015). Maximum Atacama iodate concentrations of  $\sim 1000\text{--}2000\text{ mg kg}^{-1}$  at  $>200\text{ cm}$  suggest an alternative iodate source given its low solubility and unexpected accumulation at depth. Our observations align with mixing models for iodine cycling in the Atacama Desert where sources include “old” organic iodine in weathered marine sedimentary rocks and “young” iodine from geothermal fluids, pore water, and meteoric water (Perez-Fodich et al., 2014). Atacama iodine underwent significant mixing and remobilization over a  $\sim 30\text{ Ma}$  time period (Alvarez et al., 2015). Tectonic uplift, and an associated climate transition from  $>200\text{ mm yr}^{-1}$  to  $<20\text{ mm yr}^{-1}$  of precipitation (Rech et al., 2006),

promoted groundwater flow from the Andes into the Central Depression, leading to subsequent precipitation of iodate salts (Perez-Fodich et al., 2014). The groundwater transport and precipitation mechanism for iodine in the Atacama Desert coincides with the deposition of atmosphere-derived nitrate and perchlorate. We hypothesize that weak iodate-nitrate and iodate-perchlorate relationships result from the potential for variable sources of iodate compared to the top-down accumulation of nitrate and perchlorate.

We observed iodate concentrations of ~100–200 mg kg<sup>-1</sup> at depths of >30 cm in Death Valley (Table 1), with maximum iodate in soils from Tecopa (223 mg kg<sup>-1</sup>) and Owl Hole Springs (179 mg kg<sup>-1</sup>). We hypothesize that iodate in the Death Valley deposits originates from multiple sources; however, iodine cycling in Death Valley is not well-documented. Tecopa and Owl Hole Springs soils exhibit similar perchlorate-nitrate relationships yet differ in age and geologic history (Lybrand et al., 2013). Tecopa contains younger Pleistocene-Pliocene sediments with a low distribution of nitrate deposits (Noble and Mansfield, 1922). The Owl Hole Springs deposits are late Miocene to Pliocene in age, demonstrate a complex geologic history with evidence for cutting by numerous faults, and contain widespread lakebed deposits cemented by sodium chloride with low (<1.5%) to non-detectable nitrate. Future work should examine iodate content with depth and in groundwater sources to understand iodate distribution in desert landscapes.

The biocycling of iodine species, specifically plant uptake and reduction mechanisms, requires consideration when examining the weak relationships between iodate-perchlorate (Fig. S2a–d) and iodate-nitrate (Fig. S3a–d). Iodate is a relatively stable form of iodine in natural systems, particularly alkaline environments (Fuge and Johnson, 2015), where its strong sorption to soil leads to little uptake by plant roots (Kodama et al., 2006; Dai et al., 2009; Hu et al., 2012). However, the potential for iodate uptake by plants is possible as shown in a hydroponic study on biofortifying lettuce with different forms of iodine (Voogt et al., 2010) and another that analyzed the interactive effects of perchlorate, nitrate, and iodate on uptake in lettuce (Voogt and Jackson, 2010). The authors demonstrate that iodate supplied in nutrient solutions accumulates in plant roots and outer leaves, albeit in lower concentrations than iodide, and acknowledge the difficulty in extrapolating results to field-grown lettuce given the complexity of the soil matrix. Interestingly, the reduction of iodate in natural systems is well-established (Spokes and Liss, 1996; Farrenkopf et al., 1997) and the conversion of iodate to organoiodine has been documented in incubated soils under moist conditions that contain sufficient amounts of organic matter (Hu et al., 2009; Yamaguchi et al., 2010). The cycling and speciation of iodine in natural soil environments is outside the scope of this study yet is of strong interest for additional research, particularly in the context of the intricate paleoenvironment systems presented in our work where potential organic matter reservoirs are not fully understood.

### 5.3. Intra-site anion relationships suggest regional controls on soluble salt distribution

#### 5.3.1. Death Valley, USA

Relationships among soluble salts are stronger when examined by site (Table S4). In Death Valley, Sperry soils exhibited positive significant correlations between perchlorate-nitrate ( $r^2 = 0.325^{***}$ ), iodate-nitrate ( $r^2 = 0.446^*$ ), and iodate-perchlorate ( $r^2 = 0.396^*$ ) that were higher than Death Valley soils as a whole. Perchlorate and nitrate were positively correlated in soils from Confidence Hills ( $r^2 = 0.188^{**}$ ), Owl Hole Springs ( $r^2 = 0.464^{***}$ ), and Tecopa ( $r^2 = 0.385^{***}$ ). Iodate-nitrate and iodate-perchlorate relationships were positive, albeit insignificant, at Bully Hill and Confidence Hills. We confirm the need to examine soluble salts at localized scales, particularly to capture interactions among salt accumulation, topography, plants (if present), and hydrologic processes (Andraski et al., 2014). Deposit age, geologic history, biological activity, and paleoclimate conditions require consideration when examining the heterogeneous distribution of salts

preserved in geologic strata (Noble and Mansfield, 1922; Ericksen, 1988; Lybrand et al., 2013).

#### 5.3.2. Transantarctic Mountains, Antarctica

We observed site-specific trends in the Transantarctic Mountains where perchlorate-nitrate-iodate relationships were most apparent in soils from Group 1 (Arena Valley, Wright Valley, Mt. Fleming) and Group 3 (Beardmore Glacier) compared to Group 2 (Darwin Glacier). Group 1 exhibited the strongest, significant perchlorate-nitrate relationship compared to Groups 2 and 3. The iodate-nitrate relationship was highly significant in the ultraxerous Beardmore Glacier region where drier microclimate conditions likely improve geochemical relationships. Darwin and Beardmore Glacier soils formed in stable upland environments that are drier (3–10 mm yr<sup>-1</sup>) and more conducive to salt accumulation than inland Wright Valley sites (10–50 mm yr<sup>-1</sup>) (Bockheim, 2013). Likewise, strong perchlorate-nitrate correlations occurred in ultraxerous soils from Beacon Valley and University Valley whereas perchlorate was infrequently detected in Wright Valley and Taylor Valley (Kounaves et al., 2010).

We detected the highest perchlorate concentrations in samples from Darwin Glacier (15.32 mg kg<sup>-1</sup>) and Beardmore Glacier (8.91 mg kg<sup>-1</sup>) (Table 1), both of which corresponded to relatively low nitrate values of 3.24 g kg<sup>-1</sup> and 0.04 g kg<sup>-1</sup>, respectively. The perchlorate-nitrate discrepancy led to unexpectedly low ClO<sub>4</sub><sup>-</sup>/NO<sub>3</sub><sup>-</sup> ratios of 10<sup>0</sup> and 10<sup>2</sup> in these soils compared to ratios of 10<sup>3</sup> to 10<sup>4</sup> that are characteristic of Antarctic desert soils (Table 1; Kounaves et al., 2010; Jackson et al., 2015). Both samples were collected from cemented salt pans at 2–14 cm in the Beardmore profile and 0.5–13 cm at Darwin Glacier. More research is required to understand the contrasting perchlorate and nitrate concentrations in the salt-cemented horizons, and the generally weak perchlorate-nitrate-iodate relationships in the Transantarctic Mountains overall (Figs. 2c, S2c, S3c). The related broad ranges in ClO<sub>4</sub><sup>-</sup>/NO<sub>3</sub><sup>-</sup> ratios for cemented salt pans in the Transantarctic Mountains are not understood. Variable perchlorate concentrations in Group 1, specifically Wright Valley, are attributed to more frequent wetting events that irregularly distribute salts in soil (Kounaves et al., 2010). We subsampled Antarctic salt-rich soils in cemented salt pan horizons; therefore, soil depth profiles were outside the scope of study. Analyses of depth profiles for our sites may reveal nitrate accumulation in adjacent underlying and overlying horizons with respect to perchlorate-rich salt pans. Future work should also consider the possibility that perchlorate, nitrate, and iodate salts were produced, deposited, and/or cycled at different rates given the age and long-term stability of the Antarctic landscapes that have been accumulating salts for up to 15 Ma (Bockheim, 1990; Bockheim and McLeod, 2006; Bockheim, 2007).

#### 5.3.3. Atacama Desert, Chile

Site-specific patterns of soluble salt accumulation in the Atacama Desert included significant perchlorate-nitrate correlations in Oficina Ercilla, Valenzuela, and Rencoret NW (Table S1). Iodate-nitrate relationships were significant in Oficina Ercilla and Site SP5. Strong yet insignificant correlations between iodate-nitrate and iodate-perchlorate were observed in Valenzuela and Rencoret NW. We hypothesize that site-specific relationships in the Atacama Desert result from substantial variation in soil age and associated paleoclimate histories that span millions of years. Soils from Oficina Ercilla and SP5 are predicted to be older than Rencoret NW and Valenzuela and have experienced unique climatic histories that impact salt cycling. For example, multi-source geochemical mixing models developed for iodine cycling in the Atacama Desert (Perez-Fodich et al., 2014; Alvarez et al., 2015) include “young” and “old” iodine sources. Iodine originates from different periods in geologic time and likely accumulates to varying degrees given the climate, topography, and other post-depositional processes at a site.

### 5.3.4. Kumtag Desert, China

Perchlorate, nitrate, and iodate correlations were similar between the two sites in Kumtag Desert (Table S1). Perchlorate-nitrate relationships were strongly associated and significant at the RP site and the SR site whereas iodate-nitrate and iodate-perchlorate were also correlated, albeit insignificant, at the SR site. Our findings suggest that the two soils were subject to similar paleoclimate conditions and geologic histories. As in other deserts, high spatial variability in nitrate distribution and composition was identified in the Turpan-Hami Basin (Qin et al., 2012). Isotopic differences in nitrate salts from Kumtag Desert reflect different mineral phases of nitrate (i.e., sodium nitrate, niter), contrasting post-depositional processes, and an aridity gradient that controls microbial activity and associated N cycling (Qin et al., 2012).

### 5.4. A comparison to Martian soils

Soluble salts, including perchlorate and nitrate, were detected in Mars surface materials (Hecht et al., 2009; Stern et al., 2015a) and in Mars meteorite EETA79001 (Kounaves et al., 2014). Concentrations of Martian perchlorate range from ~1000 to ~10,000 mg kg<sup>-1</sup> compared to a maximum perchlorate concentration of ~800 mg kg<sup>-1</sup> in the Atacama Desert. Martian nitrate is <1 g kg<sup>-1</sup> compared to averages from 5.14 g kg<sup>-1</sup> in Death Valley to 61.3 g kg<sup>-1</sup> in Transantarctic Mountains (Table 1). Associated NO<sub>3</sub><sup>-</sup>/ClO<sub>4</sub><sup>-</sup> ratios for Martian materials are ~0.1 compared to terrestrial desert averages of 10<sup>3</sup> to 10<sup>5</sup>. Differences in salt accumulation on Mars and Earth are likely due to the present-day production of perchlorate in the Martian atmosphere (Catling et al., 2010) or through photochemical reactions on Martian minerals (Carrier and Kounaves, 2015) compared to the long-term preservation of relic nitrate putatively produced by nitrogen fixation on ancient Mars (Stern et al., 2015a). Perchlorate and nitrate salts correlate on Mars despite contrasting depositional histories (Stern et al., 2015b). Site-specific variability in Martian nitrate may be comparable to the heterogeneous distribution of salts in desert soils on Earth. For example, nitrate concentrations spanned 0.01 to 0.03% in John Klein Martian mudstone compared to ~0.1% in Cumberland mudstone located ~1.5 m apart (Stern et al., 2015a). The order of magnitude difference in nitrate was attributed to more leaching due to greater alteration of the John Klein mudstone or to an ancient in-situ source for nitrate fixation in the Cumberland mudstone. The spatial variability observed in the distribution of soluble salts requires consideration in the study of terrestrial desert and Martian landscapes.

## 6. Summary

Our research was the first to compare iodate concentrations across multiple deserts and to examine the environmental controls on the preservation of iodate, perchlorate, and nitrate in arid environments. We observed the highest perchlorate, nitrate, and iodate concentrations in the Atacama Desert and Transantarctic Mountains, where soluble salts accumulated on stable landscapes over million-year time scales. Lower salt concentrations occurred in the Kumtag Desert and Death Valley which contain younger nitrate deposits that formed in wetter and likely more productive paleoenvironments. Perchlorate and iodate concentrations were orders of magnitude greater in the Atacama Desert than in other deserts whereas nitrate was comparable between the Atacama Desert and Transantarctic Mountains. Kumtag Desert exhibited the strongest perchlorate-nitrate, iodate-perchlorate, and iodate-nitrate associations of our study, contrary to our predictions for the strongest correlations in the Atacama Desert. Iodate did not strongly co-occur with perchlorate or nitrate as hypothesized. Our results provide support for a localized, unknown source of perchlorate in the Atacama Desert and a multi-source iodine model, explaining Atacama iodate enrichment and weak correlations with atmospherically deposited salts. We attribute high iodate concentrations in the Atacama Desert and a lack of covariation among deserts to paleoclimate conditions and

alternative iodate sources, particularly in Atacama landscapes that have been exposed to contrasting paleoclimate regimes for upwards of millions of years. When compared to Mars, perchlorate concentrations in the Atacama Desert approach the lower end members for Martian perchlorate, whereas nitrate concentrations are considerably higher in all four terrestrial deserts compared to Martian nitrate. Our findings confirm the critical role of hyper-aridity and landscape stability in the preservation of soluble salts. We conclude that soluble salt concentrations vary with geologic age, paleoclimate conditions, present-day climate, and require more local scale assessments in desert soils to interpret geochemical relationships on Earth and Mars.

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