Evidence for Deposition of Chloride on Mars From Small-Volume Surface Water Events Into the Late Hesperian-Early Amazonian

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Abstract We determine the environmental setting and timing of enigmatic large-scale chloride deposits on Mars, examining all available high-resolution imagery globally, building digital elevation models, surveying targeted infrared images intersecting chloride deposits for accessory minerals (e.g., clay, carbonate, and sulfate), and performing crater counting for age-dating when possible. We find that chloride deposits are commonly draped atop underlying topography, often associated with channels, sometimes perched above deep craters in local topographic lows, and span a wide range of elevations. Where measurable, chloride deposit thicknesses are typically <3 m. The deposits range in elevation over tens of meters, inconsistent with previous hypotheses of playa-like environments, which are very flat. Chloride deposit elevations within larger basins are typically asymmetric with chloride deposits much higher on the inlet channel side, indicating that (a) surface water runoff was the most likely water source and (b) the basins were likely not filled completely with water in a deep lake setting but rather chlorides formed within a series of shallow ponds. Mass balance allows local sourcing from mobilization of cations and chloride from dust/soil. Though prior global-scale studies report chloride deposits superimposed on Noachian terrains, crater-counting of local, stratigraphically-associated datable surfaces shows chlorides superimposed on 3.4–2.3 Ga volcanic terrain. This indicates that surface waters forming chloride deposits continued through the Hesperian and into the Amazonian, making them among the latest-formed, large-scale deposits of water-related minerals on Mars. Collectively, data suggest formation from meltwater from episodic ice/snow deposits continuing until 2.0–2.5 Ga.

Plain Language Summary Chloride salt deposits on Mars are intriguing because they dissolve very readily and thus record the last stage of liquid water present at Mars' surface. They are found across the ancient, clay-rich, southern highlands of Mars but also sometimes on top of younger volcanic regions, around the edges of the ancient terrain. As a result, we think that they are much younger than the underlying ancient terrains, continuing to form as recently as 2.3 billion years ago. These salt deposits are different from salt flats on Earth, because they occur over a range of elevations and sometimes on slopes, rather than in a single flat area. The chlorides are often found in small depressions, including perched above much deeper craters where no chloride is observed. They are also often found within channels. For these reasons, we think that the water source came from surface runoff, rather than deep groundwater welling up to the surface. The small amounts of water required are most likely from occasional melting of ice. Chloride could come from the top of the soil; clay-rich soils form a salt crust when evaporation pulls water and dissolved salt up from the top ~1 meter.

1. Introduction

Chloride deposits on Mars, first identified by Osterloo et al. (2008), are of particular interest because they record the last surface water present at a given location on the surface, as subsequent water events would dissolve them. These light-toned, indurated deposits (<1 km²–~1.000 km²) are found throughout the southern highlands, have been previously described as ancient (Noachian to early Hesperian in age; ~4.0–3.4 Ga), and are often found in local topographic depressions, sometimes with channel-like features (Glotch et al., 2010; Osterloo et al., 2008, 2010). In high-resolution imagery, many of these deposits appear to have polygonal fractures and/or ridges, which have been interpreted as salt polygons or desiccation features (El-Maarry et al., 2013; Osterloo et al., 2010; Ye et al., 2019).

Unlike many other minerals identified on Mars by remote sensing of characteristic absorption and emission features (clays, sulfates, olivine, pyroxene, silicates), anhydrous chloride minerals have no such features in the
Chloride formation hypotheses include ponding and evaporation of surface water and/or upwelled groundwater (favored by El-Maarry et al., 2013; Glotch et al., 2010; Glotch et al., 2016; Melwani Daswani and Kite, 2017; Osterloo et al., 2010; Ruesch et al., 2012), diagenetic or hydrothermal brines (e.g., volcanic- or impact-related), or efflorescent crust. Strictly volcanic sources have been discounted due to lack of spatial association with volcanics and lack of the accessory minerals (sulfates, silica) expected for this setting. On Earth, evaporating lakes and playas tend to leave behind zoned salts (Eugster & Hardie, 1978), corresponding to progressively more soluble minerals (generally carbonates, sulfates, then chlorides), while hydrothermal brines will often deposit silica and sulfates and oxide minerals along with chlorides. Thus far, only phyllosilicates have been found in association with chloride minerals (El-Maarry et al., 2013; Glotch et al., 2010; Huang et al., 2018; Murchie, Mustard, et al., 2009, Ruesch et al., 2012), reported at ~10% (Ruesch et al., 2012) to ~30% (El-Maarry et al., 2013) of chloride deposits investigated. Origin in deep lakes, as interpreted by Hynek et al. (2015) and Melwani Daswani and Kite (2017), would require large volumes of water present at Mars’ surface; therefore, constraining both water depth and timing of chloride formation is important for our understanding of the evolving availability of water at Mars’ surface. Hynek et al. (2015) performed detailed mapping at one site in Meridiani and found an oldest bound of 3.6 Ga; Osterloo et al. (2010) find most chlorides within terrains of middle to late Noachian or early Hesperian age on global geologic maps but suggest detailed, site-specific age estimate determinations are needed.

Since the initial detection of chloride deposits, they have been targeted for Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) and HiRISE (High Resolution Imaging Science Experiment) images, and sufficient ConTiX Camera (CTX) data is now available for a global mosaic that provides context for these deposits (Dickson et al., 2018). In previous global-scale studies, Ruesch et al. (2012) used OMEGA data with spatial resolution ~200–2.5 km/pixel. El-Maarry et al. (2013) investigated 43 chloride locations with CRISM images with >10x better spatial resolution, looking explicitly for Fe/Mg phyllosilicates. Here we use CRISM data to examine all previously reported chlorides with coverage, identify chloride deposits at smaller scale, and search for other associated minerals (e.g., sulfates, carbonates, clays) that might accompany chlorides to understand the water chemistry from which they formed. We then use high-resolution image data to study the morphology and cross-cutting relationships of the deposits as well as identify deposits to perform age-dating with crater counts. Finally, we compare results from Martian chloride deposits to proposed analogs on Earth and describe the formation conditions of the chlorides.

2. Methods

We exported 642 polygons that approximate chloride deposit locations from JMARS (Osterloo et al., 2010) into ArcGIS and used CRISM footprints (downloaded from NASA’s Planetary Data System (PDS) to find all acquired CRISM targeted long wavelength (158 + 8 nearby, covering 119/642 chloride deposits), HiRISE (273 images over 177 deposits), and HiRISE stereo images (29 pairs over 21 deposits) that intersected the chloride polygons (Figure S1 in Supporting Information S1). Because there are often many small chloride deposit polygons clustered together, we used ArcGIS tools to draw a 10-km buffer around the polygons and aggregated those whose buffers intersected, assuming that they likely shared a genetic relationship due to spatial proximity (e.g.,
Figure 1. Chloride cluster in the chaos terrain in Margaritifer Terra (20.74°W, 3.12°S). (a) Chloride deposits are perched above a crater and deep fractures that lie within a 10-km buffer. (b) Chloride deposit (blue tones) in THEMIS-875 decorrelation stretch image; channels are not visible at this resolution (100 m/pixel). (c) Same chloride deposit at CTX resolution (6 m/pixel), where fine channels are visible (white arrow). (d) The chloride deposit appears light purple in HiRISE color, which, when coverage is available, makes it possible to distinguish its boundaries with adjacent light-toned fractured units (note greyscale (left) versus color (right) in (d)). A small chloride-filled channel is present in the lower right (white arrow). Chloride has a sharp contact with surrounding units and appears to drape SW–NE trending aeolian bedforms.

2.1. CRISM Analysis

In its targeted mode, the CRISM instrument takes hyperspectral images of Mars' surface at ∼18–40 m/pix, covering a wavelength range of 0.36–3.9 μm (Murchie et al., 2007, Murchie, Seelos, et al., 2009). We used a standard approach for secondary mineral detection. Targeted CRISM I/F images from the long wavelength sensor, which covers key absorptions for hydrated minerals, were downloaded from PDS, and processed using the CRISM Analysis Toolkit (Morgan, 2009) in ENVI (photometrically corrected (division by cos(i)), atmospheric correction using the default 61C4 volcano scan, after McGuire et al. (2009)). Images were then ratioed using a simple column median denominator to remove residual atmospheric and detector artifacts. If ratioing artifacts due to absorptions in adjacent materials were suspected during analysis, a small spectrally bland area was instead manually chosen as a denominator to ensure that the features persisted using a different denominator. Because many of the CRISM image cubes covering chlorides were taken later in the mission after cooler set point temperatures were raised, these images are significantly noisier than those earlier in the mission, and so band depth calculations on unsmoothed data tend to show only noise. To mitigate this issue, we used an 11 × 11 × 11 spatial/spectral median filter to smooth the image before calculating band parameters. For each CRISM image, we used these band parameter maps calculated on smoothed data in tandem with ratioed, unsmoothed data to verify mineral detections. We focused on the band depths at 1.9, 2.1, 2.2, 2.3, and 2.5 μm, in addition to the slope at 2.4 μm. These wavelength ranges allow detection of hydrated minerals such as Fe/Mg clays (e.g., nontronite, saponite, chlorite), Al-clays (e.g., kaolinite, montmorillonite), serpentine, carbonate, and mono- and poly-hydrated sulfates, as well as water ice (e.g., Murchie, Mustard, et al., 2009). For images where we found Fe/Mg clays, whose absorptions at 1.9 and 2.3 μm can overlap with carbonates, we also looked at the 3–4 μm part of the spectrum to look for features at 3.4 and 3.9 μm associated with carbonates. A known limitation is that the smoothing necessary to work with noisy images can also obscure deposits that are <100 pixels in size.

2.2. Morphology and Elevation

High resolution imagery (CTX and HiRISE) and digital elevation models (DEM’s) were used to understand the context and morphology of deposits and the stratigraphic relationships between geologic units. We use a global CTX mosaic (6m/pix) (Dickson et al., 2018) together with the gridded Mars Orbiting Laser Altimeter (MOLA) elevation product (463 m/pixel, e.g., Smith et al., 2001), available for almost all clusters. Within the 10 km buffer...
connecting all parts of each chloride cluster, we searched for: sinuous channels (e.g., Figure 1c), whether they are filled with light-toned deposits, the range of elevation among chloride deposits in the cluster, and the difference between the lowest chloride elevation and the lowest point in the 10 km buffer zone to determine whether the chloride is perched relative to surrounding topography.

HiRISE color images (25 cm/pixel, with band centers at 536 nm (blue-green), 694 nm (red), and 874 nm (near-infrared); Delamere et al., 2010; McEwen et al., 2007) are particularly useful because in greyscale HiRISE images, fractured clay-bearing units can look morphologically indistinguishable from the chlorides (also noted in El-Maarry et al., 2013). HiRISE color in conjunction with CRISM show a consistent pattern with mineralogy; chloride deposits appear as bright light purple (low VNIR slope) and contrast with yellow-beige tones of the clay-bearing units (Figure 1d). We utilize HiRISE color imagery where available to ensure that we do not misidentify clays as chlorides. In surveying the morphology of chloride deposits, we looked for color variation, fracture patterns, thickness, concentric patterns, whether edges of the deposit appeared sharp or diffuse, whether they appear to be draped or in stratigraphy, and whether they were associated with other landforms, for example, channels.

All HiRISE stereo pairs overlapping chloride deposits and a select subset of CTX stereo pairs were made into DEMs using the Ames Stereo Pipeline (Beyer et al., 2018). These were used to measure the thickness of chloride deposit (where possible), infer maximum and minimum water depths, and measure the slope/asymmetry of deposits. We measured mostly in the middle of chloride deposits (rather than the edges), as these are more likely to represent that typical thickness and avoid the edges of potentially draping deposits. High resolution LiDAR DEM of Death Valley for comparison with Earth playa topography at similar resolution was obtained through OpenTopography (data set: Snyder, 2005).

2.3. Age Dating

We first used the Tanaka et al. (2014) global geologic map to update the approximate age distribution of the terrains containing the chloride deposits, as the original Osterloo et al. (2010) survey used Tanaka (1986) and Greeley and Guest (1987). For all of the sites, we also searched for cross-cutting relationships that establish whether the chloride pre-dated, post-dated, or was contemporaneous with nearby units, sometimes smaller than those identified in global maps, to improve understanding relative to simple reporting of occurrence within global-scale map units. We used crater counting to bound the age of the chlorides at all locales where stratigraphic relationships between sufficiently large units permitted it. We follow Warner et al. (2015) who propose areas should exceed 1,000 km² with preference for counts in >10,000 km² areas; all our count areas are >7,000 km². Unit boundaries were determined based on breaks in slope and morphological similarities, and crater counting was performed using the CTX mosaic. Most bounds were oldest-possible age bounds, established by crater counting units that underly chloride deposits at select sites. In one instance, a youngest-possible age bound could be established from an overlying unit (see Section 3.3.1). Craters that were entirely subdued (no topographic rim expression whatsoever) were excluded; those where the relationship with a unit was not clear were included, so as not to skew the count to young ages. The diameters were calculated in ArcMap and exported to Craterstats2 (developed by G.G. Michael, available: https://www.geo.fu-berlin.de/en/geol/fachrichtungen/planet/software/), using the Mars production function of Hartmann and Daubar (2017) and chronology function of Hartmann (2005) updated by Michael (2013) to determine ages.

3. Results

3.1. Relationship With Other Minerals and Ice

3.1.1. Chlorides and Clays: Occurrence and Contact Relationships

Even using machine learning techniques (Dundar et al., 2019; Plebani et al., 2021) and searching every targeted longwave CRISM image that intersects chloride, no sulfates or silica were found in association with the chloride deposits, in agreement with Ruesch et al. (2012)’s coarser spatial scale survey. We also do not detect oxycarbonate or hydrated chloride species, which are spectrally active and are predicted products from cold Martian brine evaporation (e.g., Toner et al., 2014). We detect Fe/Mg clay deposits in 73/158 CRISM images of 39/97 aggregated chloride clusters (~40%) (Figure 2a; Figure S2 in Supporting Information S1). Despite explicitly searching for
other accessory minerals, we only found 4 locations with any other minerals in the same CRISM image as chlorides. Three of the four are small Al-clay deposits (Fig. 2a; Figure S2 in Supporting Information S1), identified by absorptions at 1.4, 1.9, and a narrow absorption at 2.2 μm. In one of these locations (Figure S2f in Supporting Information S1), there is a shoulder at 2.4 μm that could be consistent with sulfate; however, the data are too noisy.

Figure 2. (a) Fe/Mg clays (green squares) are found with chlorides across Mars in ~40% of the images with targeted CRISM coverage. They can occur directly in contact with chlorides (dark green squares) or nearby within the same CRISM image (light green squares). Aluminum clays are only found with chlorides in the Terra Sirenum region, west of Tharsis. (b) Global distribution of water ice detected near chloride deposits (all on pole-facing slopes, poleward of 27.8°S). Where repeat CRISM images exist, these water ice deposits are only seen in southern hemisphere winter (Ls 91–151). (c) Global distribution of chloride deposits within channels at CTX (blue circles) and HiRISE (blue triangles) resolution. The distribution of chloride deposits is similar to the valley network density (after Hynek et al. (2010)); this could be due to a related water source for the features, or later chloride-bearing waters exploiting existing channel networks. (d) Perched chloride deposits—where there is a feature at lower elevation than the chloride (magnitude indicated by symbol shading) within a 10 km buffer—are found across the globe, with no obvious spatial trends. This pattern is consistent with surface runoff (rather than groundwater upwelling) as a primary source of water for the chloride deposits.
for certainty. In all three Al-clay instances, the dominant mineral identified is Fe/Mg clay (thousands of pixels), and far smaller Al-clay deposits are not in direct contact with the chlorides nor do they appear to be genetically related. Additionally, we find one location with a carbonate spectral signature in the same image as a chloride deposit (Figure S3 in Supporting Information S1). This spectrum has paired strong 2.3 and 2.5 μm absorptions with positions consistent with MgCO$_3$ (Figure S3c in Supporting Information S1). The carbonate appears to be part of the large Fe/Mg clay-bearing unit underlying chlorides; it is indistinguishable morphologically from the clay-bearing unit in HiRISE (Figure S3b in Supporting Information S1), and the spectral mean for the clay-bearing unit throughout the image has a minor 2.5-μm absorption, consistent with intermixed carbonate.

El-Maarry et al. (2013) proposed that a clay substrate might underlie all fractured chloride deposits, positing that clay desiccation might be responsible for the fracturing observed. In some instances, chloride deposits drape on top of clay-bearing units (notably in Terra Sirenum; e.g., Glotch et al., 2010). However, in other locations, a definitive genetic relationship is either inconclusive or the chlorides occur in underlying units (e.g., Knobel crater, Ehlmann & Buz, 2015; Huang et al., 2018). We find clays are in direct contact with or surround the chloride deposit in ~50% of instances (45/73 CRISM images with clays; 20/39 chloride clusters). In other cases, the clays are nearby, but appear unrelated to the chlorides. It appears that while chlorides occur around Fe/Mg clay-bearing terrains, they do not require direct contact with clays in order to form.

3.1.2. Water Ice

In our search for hydrated minerals, we unexpectedly found spectral signatures for water ice in 8 CRISM images associated with chlorides (8 deposits, 7 clusters; Figure 2b; Figure S4 in Supporting Information S1). These ice deposits are found on pole-facing slopes between 42.8°S and 27.8°S. All of these images were taken during local winter (Ls 91–151); other CRISM images taken during other seasons, available for three clusters, did not show water ice. The ice is most likely a seasonal frost, consistent with the findings of Vincendon et al. (2010), who found seasonal water ice up to 13°S. While the current climate of Mars is too cold/low pressure for liquid water to occur seasonally today, seasonal deposits in the past may have been able to melt, providing a possible source of localized, small volumes of water across the southern hemisphere of Mars.

3.2. Morphology and Elevation

Chloride deposits are typically found either associated with sinuous features, draped in thin layers on top of underlying topography, or in local lows in intercrater plains that are often perched above nearby impact crater depressions (Figures 2c and 2d). Investigation of individual deposits shows chlorides are often found over a range of elevations in the same deposit and tend to be at higher elevation on the side of a basin, where channels lead into the deposits.

3.2.1. Thin, Draped Chloride Deposits

Estimating the thickness of chloride deposits on Mars is useful for mass balance calculations (e.g., Melwani Daswani and Kite, 2017; Milliken et al., 2009) and to constrain plausible depositional environments. Previous thickness estimates were typically 1–15 m on the basis of unit topography (Glotch et al., 2010; Hynek et al., 2015; Melwani Daswani and Kite, 2017). We made careful thickness measurements where chloride deposits have a “chipped” appearance, are cross-cut by impact craters, or exposed in fractures (e.g., Figure S5 in Supporting Information S1). The chloride thickness is often below the vertical resolution of HiRISE DEMs, where available, <~3 m thick (Table S1 in Supporting Information S1). Multiple locales have similar traits. Fractures cross-cutting chloride deposits reveal that they do not extend into the subsurface (Figures 3a–3d), and small impact craters (≤10 m diameter, excavating <3 m) expose dark material from beneath the chloride (Figure S5e in Supporting Information S1). At Terra Meridiani, erosional windows show thicknesses of <1.5 m (Figure 3d), and a small impact crater excavating dark materials from the subsurface similarly constrains thicknesses of chloride-bearing materials to <2–3 m (Figure 3e). In the southwest part of the Tharsis region, chloride drapes lineations that are ~3 m high, while taller features (black arrows) are left uncovered; where eroded, the chloride is a <~1 m thick (Figures 4c–4e), rather than the full volume of the landform. This is consistent with later, shallow water bodies depositing thin chloride precipitates on top of extant topography.
3.2.2. Sinuous Features and Chlorides in Channels

Chloride appears in channels across the globe (Figure 2c) and is mostly associated with locations of valley networks and, indeed, is often within the valley networks (e.g., Figure 1c; Figures S6-S7 in Supporting Information S1). Chloride deposits follow small channels within a wider valley draining into Knobel crater, with larger deposits in localized depressions (Figure S6 in Supporting Information S1), and in several volcanically resurfaced planum around the Tharsis region (Figures 5 and 6). At the CTX scale, about 70% of chloride clusters (269/387) have sinuous channels that extend topographically lower toward the main deposit within the 10 km buffer, and ~20–25% of chloride deposit clusters (82/387 in CTX; 31/124 in HiRISE) have a light-toned unit consistent with chloride directly within channels (Figure 2c). This occurrence rate is a significant increase from the lower resolution data available at the time of the Osterloo et al. (2010) survey, which found ~8% of the deposits to have sinuous or linear features.

Figure 3. Chloride deposit near Meridiani Planum (8.5 W, 3.1S; CTX stereo pair P17 007770 1794 & P20 008917 1763). (a) Light-toned chloride unit (outlined in yellow) is present over ~50 m of elevation, including in channels leading into the main deposit. (b) HiRISE DEM (PSP 008917 1770 & PSP 007770 1770) shows a small stream leading into a higher elevation pond (top right), and a spill point into the deeper basin 15–30 m below. Chloride-covered basin floor elevation ranges by ~15 m. A mound at an intermediate elevation between the pond and the basin floor is chloride-free. (c) Concentric rings in a small crater suggest multiple stages of evaporation. (d) Chloride deposit thickness, measured near the center of the deepest part of the basin is ~1.5 m. Fractures in chloride continue across minor topographic changes, indicating that it is a single layer draped on top of underlying topography. (e) A small impact crater punches through the chloride deposit, spreading dark ejecta (depth of crater <~3 m). (f) Chloride deposits exist at a wide range of elevations (>50 m) and over slopes in contiguous parts of the deposit.
3.2.3. Perched Chloride Deposits

While almost all chlorides are present in local lows (as noted in Osterloo et al., 2008, 2010), MOLA gridded data shows that the majority (228/392%; 58%) are not actually at the lowest elevation within the 10 km buffer (e.g., Figure 1). Of these perched deposits, about half (103/228) are >100 m above the lowest elevation; ∼7% (17/228) are >500 m above (Figure 2d). They are typically in intercrater plains between and topographically above ancient impact craters. There do not appear to be region-specific trends, that is, perched chloride deposits occur throughout the southern highlands.

Osterloo et al. (2010) noted that while chlorides were widespread in the southern highlands, they were missing in major basins. Our findings are consistent with this, but also demonstrate that the trend holds at smaller scales: chlorides will often be found in intercrater plains but not in adjacent crater bottoms, even when (a) craters are so degraded that there is not a significant crater rim to prevent spilling over, and (b) CRISM data show other minerals in crater floors, indicating dust obscuration is not precluding detection (e.g., Cross crater, Columbus crater).
3.2.4. Multi-Elevation and Asymmetric Chloride Deposits

Most deposits are at multiple elevations in highly localized topographic lows but taller ridges/knobs do not have chloride; examples are provided from four sites (Figures 3 and 4; Figures S6-S7 in Supporting Information S1), two of which are detailed below. In gridded MOLA elevation data, 171/392 (44%) of chloride deposit clusters range over >10 m elevation between different parts of same deposit or cluster (median: 40 m, maximum: 300 m) (Figure S8 in Supporting Information S1). This is very different from playa salt deposits on Earth (Figure S9 in Supporting Information S1). On Mars, contiguous chloride deposits typically have slopes around 1% (~0.5–5%; Table S1 in Supporting Information S1), while terrestrial salt flats have slopes around 0.05% (one to two orders of magnitude flatter).

Figure 5. Age of three chloride deposits near Thaumasia Planum and Bosporous Planum, East Tharsis. (a) Three regions with chloride are defined by topographic boundaries. (b) In the small purple region, light toned chloride deposit is found within a channel that cross-cuts a dateable surface (see also Figure S7 in Supporting Information S1) (c) In the green region, the chloride deposit partially infills a channel at the surface on the wrinkle ridged dateable surface. (d) The magenta region in Bosporus Planum contains many chloride deposits, many of which are also in channels crossing the surface. (e) Purple region has a resurfacing age of ~3.3 Ga (resurfaced terrain ~3.7 Ga). (f) Green region has a resurfacing age of ~3.4 Ga, resetting craters smaller than ~10 km diameter, and an older age at 3.7 Ga. (g) Magenta region yields a uniform age of ~3.3 Ga.
3.2.4.1. Chloride Adjacent to Meridiani Planum

This deposit exists within a larger basin (Figures 3a and 3b) and has chloride-filled channels leading into it from the east. Fractured chlorides on the basin floor have crust-like morphologies, similar to chlorides at Death Valley (Figure S9 in Supporting Information S1). Around the edge of the deposit, a crater with a set of concentric rings likely records stages of evaporation (Figure 3c). While chloride is present at a range of elevations (Figure 3f), there is an asymmetry typical of Martian chloride deposits. Chloride occurs on the side of the basin where the channels are leading in; there is not matching chloride on the opposite side of the basin, as we would expect if the basin had been filled to the level of the highest chloride deposit. We see no trace of chloride on many mound/islands, despite being surrounded by chloride on all sides. This limits the maximum water depth to \( \sim 5–10 \) m at most; markedly different from the interpretation of Hynek et al. (2015) and Melwani Daswani and Kite (2017),
who argue for lakes >100m deep, based on the overall basin shape. Instead, the basin was likely carved during an earlier, wetter era; later, small briny water volumes then slowed into these existing depressions, not filling them completely.

3.2.4.2. Southwest Tharsis Chloride

Channels lead into this deposit (white arrow, Figures 4a and 4b), and a mostly contiguous layer of chloride fills the majority of a basin, atop a volcanic unit (Figure 4b). Chloride is found atop topographic elements ≤∼3 m high, while taller features are left uncovered (Figures 5d and 5e). In cross section (Figure 4f), chloride exists at a ~55 m range of elevations. Again, the elevation distribution is asymmetric, with the chlorides existing at higher elevations on the southern side of the deposit, where channels feed in. A flat-topped volcanic unit is present to the north, with no chloride detections on top of it (Figures 4a and 4f), but chloride occurs at elevations up to 10 m higher than the flat top of the volcanic unit, indicating that this deposit was likely fed by surface water runoff from the south, and the basin never filled to capacity. The maximum water level was lower than the top of the volcanic unit, that is, <∼20 m.

3.3. Age Dating

Osterloo et al. (2010), using published maps from 1986 (Tanaka) and 1987 (Greeley and Guest), found that most deposits were within Noachian terrains and ~24% within Hesperian terrains. Using the updated Tanaka et al. (2014) global map of Mars with unit ages, we find that only 7 deposits (/642) are in terrains mapped as Hesperian, near the edges of the Tharsis and Hesperia volcanic terrains and 1 is within an Amazonian/Hesperian impact unit. The rest are within Noachian terrains, consistent with work by Hill and Christensen (2019). However, this type of analysis only provides an oldest-bound on the age. We found a number of sites where chloride was clearly on top of volcanic terrain, for example, chloride in superimposed channels or on top of a surface with wrinkle ridges. When possible, we performed crater-counting to obtain more constrained oldest-bound ages, using the best local constraints. In one location, we obtained a youngest-bound age, using cross cutting fracture relationships (Figure 7).

3.3.1. Icaria Fossae, South Tharsis

The Icaria Fossae region south of Tharsis hosts chloride deposits that are cut by fractures (Figures 7a–7c), indicating that the chloride was deposited prior to fracturing but after the underlying terrain was formed. Nearby, a similar flat basin exists where the same suite of fractures that cut the chlorides are erased by deposition of a younger unit (Figure 7d). This surface unit must thus be younger than the chloride deposits, providing both an upper and lower age bound to constrain chloride age in this location. The terrain underlying chloride (red) is dated at 3.3 Ga, while the nearby (blue) basin was resurfaced 2.0 Ga (Figures 7e and 7f), meaning the chlorides were deposited between 3.3–2.0 Ga, Late Hesperian to Early Amazonian. By contrast, in the global scale Tanaka et al. (2014) map, these terrains are respectively classified as Late Noachian highlands and Early Hesperian volcanics.

3.3.2. East Tharsis (Bosporos & Thaumasia Planum)

On volcanic units east of Tharsis, chlorides are present at three distinct elevations (Figure 5a). In a small basin in Thaumasia Planum, chloride is deposited within a channel (Figure 5b), immediately downhill from remnants of Noachian highlands with Fe/Mg clays (Figure S10 in Supporting Information S1), and in an adjacent depression, a local depression has chloride-infilled channels cut into a volcanic unit (Figure 5c). To the south, Bosporus Planum hosts a unit with many chlorides occurring within dissecting channels (Figure 5d). At these three locales, terrains immediately under the chlorides were resurfaced at 3.3–3.4 Ga (Figures 5e and 5f), prior to chloride deposition. The two high elevation localities also record an older 3.7 Ga age. In the global scale Tanaka et al. (2014) map, these terrains are respectively classified as Late Noachian highlands and Early Hesperian volcanics.

3.3.3. East Hesperia Planum

At the eastern edge of Hesperia Planum, chlorides are detected atop volcanic terrain and in Noachian highlands nearby (Figure 6a). The chloride in Hesperia Planum is located within a channel (Figure 6b), indicating that it was emplaced after the volcanic unit. This unit has a resurfacing age of 3.4 Ga (older age is 3.6 Ga); chlorides
must be younger than 3.4 Ga (Late Hesperian). In the global scale Tanaka et al. (2014) map, this unit is classified as Early Hesperian volcanic.

3.3.4. SW Tharsis

Chlorides are present on top of a smooth volcanic unit southwest of Tharsis, (Figure 6d), where they are sometimes found in channels (Figure 6e). This large, flat volcanic unit is dated at 2.3 Ga. Because the chlorides are on top of it, they must be younger than ∼2.3 Ga, Early Amazonian. In the global scale Tanaka et al. (2014) map, this unit is classified as Early Hesperian volcanic.

3.3.5. Noachis Terra

Here, chlorides are on top of an older volcanic unit (flat area with wrinkle ridges; Figure 6g), present in channels (white arrow in Figure 6h) and draping over a wrinkle ridge (black arrow, Figure 6h). This unit has a resurfacing age of 3.6 Ga (underlying terrain dated to 3.8 Ga). In the global scale Tanaka et al. (2014) map, this unit is classified as Late Noachian highland.

4. Discussion

4.1. Earth Analogs for Surface Water-Deposited Martian Chlorides

In our analysis of Martian chlorides, all lines of evidence point to surface water runoff. We observe even more channels feeding into the deposits than reported previously. Evidence for small volumes of water includes ponding at multiple elevations, asymmetry in deposits (high on one side, where channels lead in, and much lower on the other side), and draping textures where slightly higher topographic highs (>3 m) are generally not covered by chlorides. For a larger volume of water, deposits would have been more likely to form a flat layer rather than
being influenced by underlying topography. Thickness estimates, $\sim 3$ m and typically $\sim 1$ m thick, are also consistent with small volumes of water.

On Earth, large-scale chloride deposits are most commonly associated with arid playa environments, such as the halite salt flats in Badwater Basin (Death Valley, California; Figure S9 in Supporting Information S1). These environments have meter-scale polygonal ridges and/or fractures (Figures S9d and S9e in Supporting Information S1), similar to the characteristics of martian chlorides. However, these environments are extremely flat ($\sim 1$ m elevation change over $\sim 2.5$ km; Figure S9c in Supporting Information S1; LiDAR data from Snyder, 2005), groundwater fills the basin and cycles of flooding and evaporation level the topography. As the last salt to crystalize in a sequence, playa chlorides are typically in the lowest topographic depressions and their chloride deposits many tens of meters-thick as they are zones of groundwater upwelling for local watersheds. This is very dissimilar to the martian chloride examples.

More analogous terrestrial environments are paternoster lakes, glacial-fed lakes that are connected by streams, occurring at different elevation steps. A saline example is found in the Antarctic Dry Valleys (Figure 8) (e.g., Meyer et al., 1962). Don Juan pond is in a local topographic low in the valley bottom with a bright white ring of salt around a shallow muddy pond (Figure 8c). Salt crusts show a sharp contact at the edge (Figure 8d) with salt encrusting short boulders ($\sim 10$ cm). Both groundwater (e.g., Toner and Sletten, 2013) and deliquescence plus snowmelt (Dickson et al., 2013) have been proposed as water sources for Don Juan Pond. Dickson et al. (2013) observed seasonal flow of chloride-rich brines on top of a permafrost layer a few meters below the surface. Downstream in the valley is Lake Vanda, which has chloride-rich bottom waters (Angino & Armitage, 1963). The $\sim 15$ m elevation difference over 10–15 km is similar to martian chloride deposits; they do not exhibit the polygonal fracturing/ridges that we see in playa environments and on Mars, probably because they are still active/wet.

Figure 8. Chloride deposit in McMurdo Dry Valleys, Antarctica (Earth). (a) Google Earth image shows a glacier in the upper parts of the valley and the locations of Don Juan Pond and Lake Vanda. (b) These salty water features are at different elevations (range, $\sim 25$ m) and connected by channels. (c) Don Juan Pond (photo J. Dickson), showing the white salt crust and very shallow water level (muddy patch) within the larger valley, downstream from the glacier. (d) Close-up of sharp salt contact (bottom edge) and salt crust that has covered shorter boulders, climbing up $\sim 10$ cm.
4.2. Water Source for the Chloride Deposits

Meltwater runoff from snow/ice, either seasonal or episodic, likely supplied the overland water flow necessary for the chloride deposits. Today, we only see thin seasonal water frosts in the southern highlands of Mars (e.g., Figure S4 in Supporting Information S1; Vincendon et al., 2010), which would likely not provide enough brine for the km²-scale chloride deposits, even if temperatures and pressures were high enough to allow for melting rather than sublimation. However, in the Hesperian and late Amazonian, such southern highlands surface ice deposits and subsurface ice or permafrost may have been more widespread, thicker, and able to melt and provide a water source, during certain obliquity regimes (e.g., Wordsworth et al., 2015). A few locations show concentric rings in chloride deposits (Figure 3c and S7d in Supporting Information S1), which might reflect multistage evaporation or repeated wet/dry cycles.

An alternative source for small volumes of water is deliquescence, where salt minerals present in the soil can adsorb water vapor from the air and form a concentrated brine when the relative humidity is high enough (as observed in Antarctica; Dickson et al., 2013). This may contribute to the observed deposits but does not seem likely to generate the overland flow seemingly required for 1–3 m thickness of chloride enrichment in some locales.

4.3. Ion Sources for Chloride Deposits

Our results concur with previous studies that have noted chloride deposits' relationship with Fe/Mg clays as well as a lack of association with other salts (sulfate, carbonate) that are typically associated with large-scale chloride deposits on Earth (El Maary et al., 2013; Ruesch et al., 2012) nor perchlorate, found elsewhere on Mars by landers (e.g., Toner et al., 2014 and refs therein). We do not observe phases other than Fe/Mg clay minerals when impact craters have broken through a chloride-enriched layer to kilometers depth. Thus, it appears carbonate and sulfates may be effectively absent, or if present, be buried deeper than is typical for playa mineralization sequences with CO₃²⁻, SO₄²⁻, and Cl⁻ ions.

Chloride ion sources include magmatic gases from volcanism as globally distributed atmospheric gases, leaching and alteration from igneous crust, or remobilization of older chloride deposits. Chloride contents of soils, dust, and sedimentary rocks on Mars range from ~0.3–3 wt. % with unaltered igneous rocks sometimes lower (Berger et al., 2016; Haskin et al., 2005; Thomas et al., 2019). We assume halite and estimate how much material would (a) have to be fully leached to generate all chloride deposits observed and (b) how much material contains enough chloride to account for a median chloride deposit (~10 km², ~1 m thick). Across the southern highlands, the total area of the chloride deposits is ~14,000 km² (Osterloo et al., 2010). Assuming a layer ~1 m thick of 25% halite (Glotch et al., 2016), this translates to ~1 × 10¹⁴ mols Cl. For a density of typical rocky materials (3,000 kg/m³), this amount of chloride would be present in a layer 0.7–7 mm thick across the southern highlands (area ~6.5 × 10⁸ km²). But the chloride deposit-forming processes appear to be more locally controlled, involving small amounts of water moving through local topographic lows, so as a more appropriate metric, we find that chloride derived from the top 3–30 cm of typical martian materials would need to be leached over a 1,000 km² area to create a median chloride cluster. Indeed, ~1,000 km² is about the same size as the typical area within the 10 km buffer zone around a deposit (e.g., Figure 1a) and is the size of several of the larger basins in which small chloride deposits are found. Since we know capillary action can access the top meters of porous media, these calculations mean leaching from the top soil layer is a plausible chlorine source, if the fluid and rock chemistry and duration enables leaching.

We propose a conceptual model that explains the observed characteristics of chloride deposits (Figure 9). Either large-scale volcanic processes or chemical weathering enrich Cl in Martian dust, soils, weathered igneous rocks and sedimentary rocks (e.g., Clark & van Hart, 1981; Nekvasil et al., 2019; Settle, 1979). Widespread Fe/Mg clays across the Noachian highlands are an indication that chloride ions may already have been released into more mobile phases by significant earlier alteration of igneous rock (Milliken et al., 2009). To generate large-scale areas of concentrated chlorides, capillary action with small water volumes derived from melt dissolves Cl-bearing phases in the top ~1 meter of soil and generates surfaces/near-surfaces enriched in chloride precipitated during water evaporation/sublimation. Small volumes of low temperature water preferentially dissolve just the most soluble salts (chlorides), providing a mechanism for separating chlorides and retention of less-soluble sulfates like Ca sulfates in the subsurface, where they are hidden from remote sensing. Such mobility has been observed in soils at Gusev crater where both Cl and S are enriched in soils but Cl is more enriched at the surface relative to S
Similarly, modeling of Martian brine chemistries shows chlorides (and perchlorates) are the last phases to precipitate, that is, most soluble (e.g., Toner et al., 2014; Tosca and McLennan, 2006). Small volumes of meltwater—likely repeatedly—then mobilize small salt deposits and aggregate them in local topographic lows. Clay-bearing soils (e.g., Warrence et al., 2002) or permafrost (Dickson et al., 2013) may serve to inhibit infiltration of meltwaters into the subsurface. Additionally, the freezing point depression from halides may inhibit freezing of the briny water (e.g., Clark & van Hart, 1981), facilitating its downstream transport.

4.4. Timing

Although chloride deposits are found overwhelmingly in Noachian and early Hesperian terrain (3.9–3.6 Ga) when considered at Tanaka et al. (2014) global map scale (see also Osterloo et al., 2010), because the chlorides drape on these surfaces, this only provides a no-older-than bound. Where crater counts on local units with clear stratigraphic relationships are possible, these typically indicate much younger oldest bounds. Hynek et al. (2015) date the Meridiani chlorides to be < 3.6 Ga, while Ehlmann and Buz (2015) and Huang et al. (2018) date the underlying Knobel terrain to ~3.7 Ga and the overlying capping rock to 1.1 Ga. Here we have shown several chloride deposits must be younger than ~3.3–3.4 Ga (Hesperian), one must have formed between 3.3 Ga and 2.0 Ga, and there is even one that is on top of Amazonian terrain (younger than 2.3 Ga).
Taking into account our estimated ages and those of previous studies, we conclude that chloride deposits might have started to form in the Noachian, but the processes creating these deposits continued until at least the Early Amazonian \( \sim 2.3 \) Ga. Given the crisp, fresh appearance of these deposits in spite of being within erodible deposits in dusty regions, we hypothesize that a significant proportion of them may even be on the younger side of the age range, simply exploiting earlier-formed fluvial structures, though dateable units are not available to prove. The persistence of episodes of small volumes of water into the Amazonian is consistent with other recent observations in Gale crater of young small valleys and Amazonian age dates of diagenetic minerals (e.g., Ehlmann & Buz, 2015; Grant & Wilson, 2019; Martin et al., 2017).

### 4.5. Explaining the Global Spatial Distribution of Chloride Deposits

A puzzling fact about the chloride deposits is that they are almost all in highlands south of the equator and not in highlands regions north of the equator (e.g., Mawrth Vallis, NE Syrtis). This is a clue about Martian palaeoenvironmental conditions rather than merely a detectability issue because many other alteration minerals are found in these terrains (Ehlmann & Edwards, 2014). Prior work has suggested chloride deposits follow the same approximate distribution as the valley networks (Hynek et al., 2010; see Figure 2a). We agree but also conclude that the fact that valley networks north of the equator lack the chloride deposits detectable at THEMIS resolution (Figure 2a) is important to understanding chloride deposit origin and timing. Bouley et al. (2016) propose that the valley networks formed prior to true polar wander, induced by reorientation of the volcanic Tharsis bulge to the equator. They demonstrate that the densest valley networks line up with a \( \sim 0^\circ-30^\circ S \) zone of maximum modeled precipitation in Mars' expected pre-Tharsis orientation. We note that the chloride deposits instead align with a \( \sim 0^\circ-30^\circ S \) zone of maximum expected precipitation in the present orientation of Mars (Bouley et al., 2016), thus indicating that the chloride deposits likely formed after this true polar wander was complete (Hesperian or later). That is, the chlorides do indeed occur in locations with prior valley networks—and highlands clays deposits that indicate paleoweathering—but, importantly, only where climate models favor precipitation. Future work with climate models should focus on modeling conditions that enable late Amazonian surface waters to form chloride deposits with the minimum water quantities needed to reproduce the thin, perched, draped deposits.

### 5. Conclusions

Chloride deposits found across the southern highlands of Mars likely represent small volumes of surface water, deposited in existing topographic lows such as old channels and resurfaced lake basins. Chloride deposits tend to be draped on top of underlying topography, and at a range of elevations, unlike playa environments or evaporites from deep lakes on Earth. The deposits are thin (<3 m) and asymmetric with greater thicknesses near inlet channels. Despite being found in local topographic lows, many chloride deposits are within 10 km of even deeper lows with no signs that groundwater upwelling is responsible for these deposits. Instead, surface runoff is the most likely water source, from sources like seasonal or episodic melting of ice or permafrost. Their distribution south of the equator is coarsely consistent with predictions for ice deposition as snow on Amazonian Mars over obliquity cycles. Saline paternoster lakes in the Dry Valleys, Antarctica are an analogous terrestrial analog environment. Weathering of basaltic materials to clay minerals releases cations. Mass balance calculations show sufficient chloride anions to generate the observed deposits could be leached from the top layer (<1 m) of soil/dust in the highlands surrounding the topographic lows. Supply of Cl in volcanic aerosols may also contribute. The deposits are self-consistently explained by chloride sourced in nearby clay-bearing Noachian highlands—by leaching of rocks and sediments or remobilizing earlier-formed salt deposits—and transport of small volumes of meltwater downhill, leading to deposition atop younger terrains.

While our update of statistics relative to the latest global-scale geologic maps shows the vast majority (>97%) of chlorides are superimposed on Noachian terrains, these are simply oldest-bounds on the age of the chlorides. Those sites that allow detailed age-dating by crater counting of local units with superposition relationships show, in multiple cases, chloride deposit formation between 3.4–2.3 Ga. Thus, we conclude that Mars' chloride deposits record the last large-scale waters on Mars and continued to form into the Amazonian by surface liquid water flow.
Conflict of Interest
The authors declare no conflicts of interest relevant to this study.

Data Availability Statement
All Mars data used in this paper are publicly available through the NASA PDS node (http://ode.rsl.wustl.edu/mars/), and we thank Mikki Osterloo for making the Osterloo et al. (2010) polygons of chloride detections from THEMIS readily available on the Arizona State JMARS site. Derived statistical data compiled to construct figures are available in tabular form at the CaltechDATA site https://doi.org/10.22002/D1.2176 (Leask & Ehlmann, 2021).

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