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Key Points:
- Oxalate minerals were found in the hyperarid conditions of the Salar Grande basin, Atacama desert
- Biological versus abiotic pathways were recognized using mineral and geochemical techniques
- Such information can be used to reveal the origin of organic carbon on Mars

Supporting Information:
- Supporting Information S1

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Oxalate formation under the hyperarid conditions of the Atacama desert as a mineral marker to provide clues to the source of organic carbon on Mars

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Abstract In this study, we report the detection and characterization of the organic minerals weddellite ($CaC_2O_4 \cdot 2H_2O$) and whewellite ($CaC_2O_4 \cdot H_2O$) in the hyperarid, Mars-like conditions of the Salar Grande, Atacama desert, Chile. Weddellite and whewellite are commonly of biological origin on Earth and have great potential for preserving records of carbon geochemistry and possible biological activity on Mars if they are present there. Weddellite and whewellite have been found as secondary minerals occurring inside the lower detrital unit that fills the Salar Grande basin. The extremely low solubility of most oxalate minerals inhibits detection of oxalate by ion chromatography (IC). Crystalline oxalates, including weddellite and whewellite, were detected by X-ray diffraction (XRD). The association of weddellite with surface biota and its presence among subsurface detrital materials suggest the potential of a biological origin for Salar Grande weddellite and whewellite. In this regard, biological activity is uniquely capable of concentrating oxalates at levels detectable by XRD. The complementary detection of oxalate-bearing phases through IC in the upper halite-rich unit suggests the presence of a soluble oxalate phase in the basin that is not detected by XRD. The formation, transport, and concentration of oxalate in the Salar Grande may provide a geochemical analogue for oxalate-bearing minerals recently suggested to exist on Mars.

1. Introduction

Oxalate has been predicted to be a common organic component of Martian sedimentary materials due to the highly oxidizing conditions near Mars' surface [*Benner et al.*, 2000]. Wherever organic compounds near the Martian surface originate from—meteoritic, primordial, geothermal, or biological sources—they have been exposed to alteration by radiolysis and oxidative diagenesis. The long-term organic oxidation processes near the Martian surface are predicted to have led to the formation of carboxylic radicals [*Benner et al.*, 2000]. Oxalate formation from carboxyl species should then proceed by various abiotic chemical pathways mediated by OH^* hydroxyl radicals [*Benner et al.*, 2000; *Tan et al.*, 2012]. The possible occurrence of oxalates on Mars has been recently reported in different Mars regions by *Applin et al.* [2015], who reinterpreted the samples analyzed by different pyrolysis-based instruments aboard Viking, Phoenix, and Curiosity, i.e., the pyrolysis gas chromatograph–mass spectrometer, the Thermal and Evolved Gas Analyzer, and the Sample Analysis at Mars, respectively [*Biemann et al.*, 1977; *Boynton et al.*, 2009; *Mahaffy et al.*, 2012; *Ming et al.*, 2014]. Reanalyses of a Martian mudstone by X-ray diffraction (XRD) by the CheMin instrument on the Mars Science Laboratory (MSL) Curiosity rover by *Applin et al.* [2015] showed that the XRD measurements are consistent with the presence of low levels of refractory Ca, Fe, or Mg oxalates. The possible wide distribution of oxalates on the Martian surface suggests that oxalate formation is a widespread process on Mars that has the potential to affect the global cycling of carbon and the geochemistry of organic matter.

The production of oxalates from other organic compounds can proceed via both biological [e.g., *Johnston and Vestal*, 1993; *Baran*, 2014] and abiotic pathways [*Durand*, 1980; *Peltzer et al.*, 1984]. Although different organisms can produce oxalic acid, including plants, algae, free-living and mycorrhizal fungi, and bacteria

[*Nakata*, 2003; *Burford et al*., 2006; *Hess et al*., 2008], lichens are prolific producers of oxalates. Oxalate in solution rapidly forms complexes with available cations, which can then precipitate to form various oxalate salt minerals [*Jones et al*., 1980; *Wilson et al*., 1980; *Johnston and Vestal*, 1993; *Baran*, 2014]. Oxalate can act to increase the concentration of solute cations, as oxalic acid is a strong leaching agent that can promote the weathering of mineral and rock surfaces [*Johnston and Vestal*, 1993]. Many oxalate salts have very low solubility, including those that contain divalent cations such as Ca^{2+}, Mg^{2+}, and Fe^{2+}. The interaction between oxalate in solution and aqueous cations therefore rapidly leads to the formation of the very insoluble minerals weddellite ($CaC_2O_4 \cdot 2H_2O$) and whewellite ($CaC_2O_4 \cdot H_2O$), as well as the Mg-bearing glushinskite ($MgC_2O_4 \cdot 2H_2O$) [*Wilson et al*., 1980; *Chen et al*., 2000; *Frost*, 2004; *Frost and Weier*, 2003]. These minerals are extremely resistant to physical and chemical degradation. Indeed, Ca oxalate is sufficiently resistant to dissolution and chemical attack that Ca-oxalate coatings are deliberately created to preserve limestone art objects [*Cezar*, 1998]. Thus, metal oxalates ($Me^{n+}(C_2O_4)_{n/2}{\bullet}xH_2O$) are the most common ionic organic minerals on Earth [*Echigo et al*., 2005; *Hazen et al*., 2013] and are the only salts of any organic acid that are stable on geologic times scales [*Hoffman and Bernasconi*, 1998]. The biosynthesis of oxalic acid occurs through various pathways including as part of the Krebs citric acid cycle, glyoxylate oxidation [*Gadd*, 1999], hydrolysis of oxalo-acetate [*Han et al*., 2007], metabolic degradation of glucose [*Munir et al*., 2001], and ascorbic acid [*Kostman et al*., 2001].

Near the surface of the Earth, biological processes, notably fungal-mediated dissolution and bacterial oxalotrophic metabolism [*Martin et al*., 2012], are the main agents acting to decrease the concentration of oxalate on the surface. Oxalotrophic processes rapidly recycle the reduced carbon bound in oxalate in energy-yielding metabolic reactions in most Earth environments. Other biological roles for oxalate compounds include their use as chelating agents, which assist in the uptake of nutrients, and mineral dissolution reactions [*Guggiari et al*., 2011]. As a result of biological activity, oxalate is rapidly depleted in most geological materials near the surface of the Earth. In regions where oxalotrophy and other biological processes that remove oxalate are limited, inward transport or in situ generation of oxalate may cause oxalate minerals to accumulate. Among the environments that can favor oxalate accumulation are extreme desert settings, including the Atacama and the Antarctic dry valleys [e.g., *Johnston and Vestal*, 1993; *Hess et al*., 2008; *Dorn*, 2013].

In this paper, we report the occurrence of the Ca-bearing oxalates weddellite and whewellite preserved in ancient sedimentary deposits (>1 Ma–100 ka) in the Salar Grande basin in the Atacama desert, Chile. The Salar Grande is considered a good terrestrial analogue of halide-bearing deposits in Terra Sirenum, Mars [*Chong Dıaz et al*., 1999; *Sáez et al*., 2012; *Fernández-Remolar et al*., 2013]. Weddellite and whewellite are likely produced as biominerals at the margins of this basin through precipitation mediated by lichen activity. A combination of persistent hyperarid conditions and minimal biological activity has allowed the incorporation of oxalate into the sedimentary record of the Salar Grande. By analogy, the Terra Sirenum halide deposits of Mars should be expected to readily incorporate and preserve any surface oxalate. Therefore, oxalate compounds preserved in salt-rich materials can provide a record of geological and potentially biological carbon cycling in Mars-like environments.

2. Geological Setting

The Salar Grande basin lies on the hyperarid belt of the Atacama desert, which is located between 17°30′ and 27°00 S latitude, extending from southern Peru and to northern Chile (Figure 1). Since the late Paleogene to the present, the hyperarid belt of Atacama has evolved as the main base level between the Coastal Cordillera to the west and the Western Andean Cordillera to the east. Hyperarid conditions were strongly magnified by the systematic uplift of the High Andes, inducing the development of a rain shadow area with the influence of the Hadley cell and the Humboldt Current [*Allmendinger and González*, 2010; *Garreaud et al*., 2010]. The co-occurrence of these circumstances has promoted climatic stability and the emergence of a hyperarid desert zone where the average annual rainfall is less than 1 mm [*Garreaud et al*., 2010; *Hartley and Chong*, 2002] (Figure 1). Consequently, the water supply associated with Andean volcanoes changed from a surface regime to an underground and seepage configuration, resulting in the emergence of numerous dry saline lakes called *salares*, including the Salar Grande [*Bao et al*., 1999; *Pueyo et al*., 2001].

The Salar Grande is the westernmost saline basin in the hyperarid belt and is located in a tectonic depression in the Cordillera de la Costa (Coastal Range). It has been an intermontane evaporitic basin throughout the Late Tertiary and the Quaternary and lies at an elevation of 640–750 m above sea level. The Salar Grande

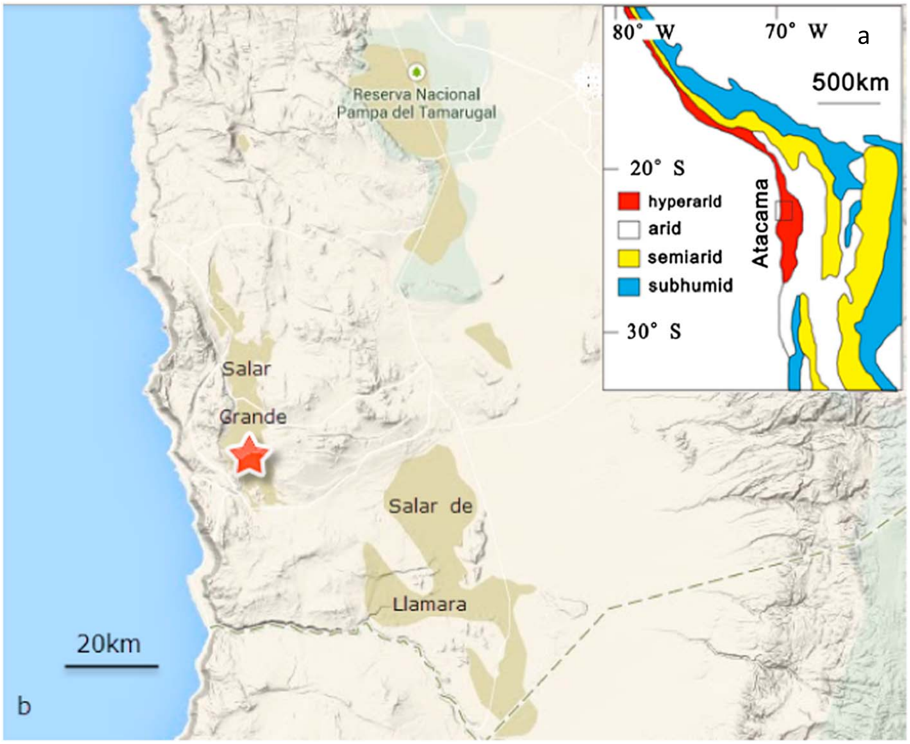

Figure 1. (a) Location map showing present-day climatic zones of western South America; the box shows area of map b. Adapted from *Sáez et al*. [2012]. (b) Location of the Salar Grande area. Maps copyright 2014 Mapcity, Google, Inav/Geosistemas SRL.

has a 45 km long by 5 km wide elongated morphology that is strongly influenced by the N-S to NNW-SSE trending Atacama Fault System [*Chong Díaz et al*., 1999; *Garcia-Veigas et al*., 1996; *Sáez et al*., 1999].

The sedimentary record of the Salar Grande basin is the result of the interaction of paleoclimate and tectonic activity in the region. It was filled over the course of three different depositional episodes [*Chong Dıaz et al*., 1999; *Sáez et al*., 1999]: (1) the initial deposition of mixed red-bed detrital and sulfate-bearing sediments in the early to middle Miocene; (2) a second episode during the late Miocene with a detrital unit composed of siliceous breccias, gravels, marls, and diatomites known as the Quillagua Formation; and (3) a cap of massive precipitated chlorides known as the La Soledad Formation. The uppermost deposits were formed under extreme hyperarid conditions, which is considered to be a good analogue for the chloride-bearing deposits of Terra Sirenum on Mars [*Fernández-Remolar et al*., 2013]. Moreover, the general progression from siliciclastic to halide-dominant sedimentation under increasingly hyperarid conditions bears some qualitative resemblances to the postulated formation history of the Terra Sirenum halide-bearing deposits [e.g., *Glotch et al*., 2010]. The saline units of the Salar Grande basin have experienced only very limited diagenesis. This is evidenced by the exceptional preservation of the sedimentary textures in primary anhydrite, which shows no signs of rehydration and would otherwise overprint and destroy the primary structures [*Pueyo et al*., 2001]. In addition, the presence of nitrate and perchlorate minerals, as well as very soluble halides (e.g., Br^-, I^-, and IO^{3-} minerals), accompanying halite and sulfates is further evidence of extreme conditions including water activity lower than 0.60 [*Fernández-Remolar et al*., 2013]. Preservation of diverse biomolecules has been reported under these stressful extreme conditions, which suggests that rapid mineralization, low water activity, and basin subsidence are key factors to increase preservation rates for very labile biomolecules, such as nucleic acids [*Fernández-Remolar et al*., 2013].

3. Methods

Sediment samples were collected every 2 m in five destructive boreholes in the Salar Grande basin (Figures 1 and S1 in the supporting information). The sampling sites were located in three distinctive geological settings

(Figure S2): (1) the active margin in the northwestern Salar Grande for the boreholes Esperanza Sondeo B and Esperanza Sondeo G (Figures S1 and S2a), (2) the eastern passive margin for the boreholes Tenardita Sondeo B (TSB) and Tenardita Sondeo D (TSD) (Figures S1 and S2b), and (3) the southern area with maximal subsidence for borehole X-Sur (Figures S1 and S2c). Stratigraphic sections were built based on different petrological features (e.g., texture and color) that were observed in the sample powder recovered from the five boreholes. Sample collection through drilling was accompanied by a field survey of the entire Salar Grande Basin (Figure S3) to characterize the main geological units and search for evidence of potential biological activity (e.g., lichens, biofilms, and/or endolithic communities) that could eventually be recorded in the sedimentary units of the basin.

The collected borehole samples were freeze-dried at −20°C and ground into powder using an agate pestle and mortar to obtain a homogeneous micrometer-sized powder for mineral and geochemical analysis. Mineralogical characterization of samples was performed using a Bruker AXS D8-Focus X-Ray diffractometer (XRD) operating at 40 kV and 40 mA with a Cu X-ray source (Cu $K\alpha_{1,2}$, $\lambda = 1.54056$ Å). All the XRD patterns were collected in the $2 \cdot \theta$-diffraction angle from 5° to 70°, with a scanning step size of 0.01°. Anions and low molecular weight organic acids were determined by ion chromatography in the soluble phase. For this analysis, 10 g of each sample was sonicated (3 × 1 min cycles) in 20 mL of water, and the mineral particles were removed by centrifugation. The supernatants were collected and loaded into a Metrohm 861 Advanced compact ion chromatographer (Metrohm AG, Herisau, Switzerland) undiluted or at dilution values of either 50% or 20%. For all the anions, the column *Metrosep A supp* 7-250 was used with 3.6 m*M* sodium carbonate ($NaCO_3$) as eluent.

4. Results

The geological survey of the Salar Grande basin revealed three distinctive units (Figures S2 and S3) that have been previously described [*Skarmeta and Marinovic*, 1981; *Chong Dıaz et al.*, 1999; *Sáez et al.*, 1999]. The lowermost layer consists of a highly weathered basement dominated by igneous material (La Negra Formation), which is covered by reddish alluvial sediments (Figure S3a) deposited during the Pliocene [*Sáez et al.*, 2012]. These materials are topped by the chloride-rich unit (Figure S3b) known as the La Soledad Formation [*Chong Dıaz et al.*, 1999, and references therein], which mainly occurs as an evaporitic deposit in the Salar Grande basin. At the basin margin, the La Soledad Formation unit occurs as overlapping beds with angular discordance on the La Negra Formation, dipping either toward the main Salar Grande basin or toward marginal and minor basins formed by neotectonic activity (Figures S3b and S3c). During the geological field survey, several different biological communities were observed, including epilithic lichens and endolithic cyanobacterial colonies, similar to previous observations from the Atacama [*Ziolkowski et al.*, 2013; *Vítek et al.*, 2014]. While the endolithic cyanobacteria were chiefly associated with the halite deposits, the lichen communities were the most widespread sign of life in the Salar Grande basin. Although the scarcity of water severely restricts biological activity in the Atacama [*Garreaud et al.*, 2010; *Hartley and Chong*, 2002], the Salar Grande basin, like many other areas in the Atacama desert, receives a limited but reliable daily supply of water in the form of a dripping fog (*camanchaca*) that originates from the Pacific Ocean (Figure S4a). However, the particular distribution of the lichen communities in the area occurring in isolated patches (Figure S4b) suggests that while the *camanchaca* fog may provide the humidity baseline, there are some other factors controlling the dispersion and growth of the lichen communities.

In this regard, signs of biological activity were detected at least in two main different settings, ranging from shadowed slopes of the western and highest mountainous terrain (Figures S4b and S4c and S5a) to the plains formed by Tertiary and Quaternary terraced deposits that are daily exposed to wind and significant UV radiation (Figures S4b–S4c and S5b). The less exposed epilithic communities of lichens were commonly found growing around faulted substrates cemented by sulfate minerals (Figure S6). Epilithic lichens were observed in states of partial mineralization associated with a whitish compound (Figure S6c) on the epicortical area of the lichen. Although lichens primarily colonize slightly cemented surfaces in more protected areas, those found in areas more exposed to UV radiation and wind occur as epilithic communities encrusting cemented detrital materials and faceted boulders (Figure S7). In addition, some ephilitic lichens have been also found in highly exposed areas where they are growing in detrital materials of alluvial fans cemented by sulfates (Figures S4c, S4e, and S8). Interestingly enough, the occurrence of lichens is associated to the presence of

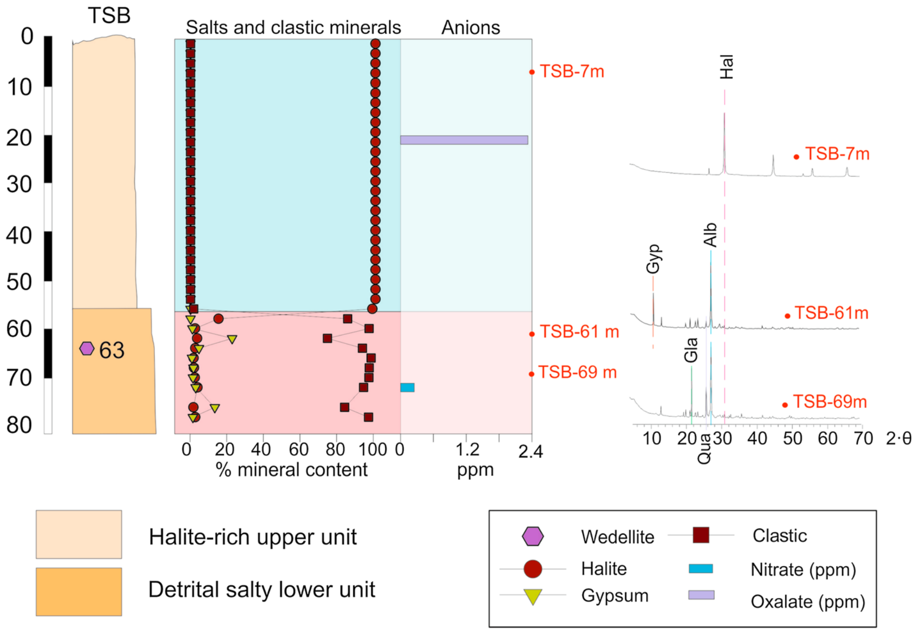

Figure 2. Stratigraphic section of the Tenardita Sondeo B (TSB) drilling site showing the mineral and anion compositions where weddellite is unequivocally detected by XRD at 63-64 m depth. Oxalate anions have been detected in the upper halite-rich sedimentary unit as well, whereas the occurrence of nitrate at around 20 m supports the presence of nitranite.

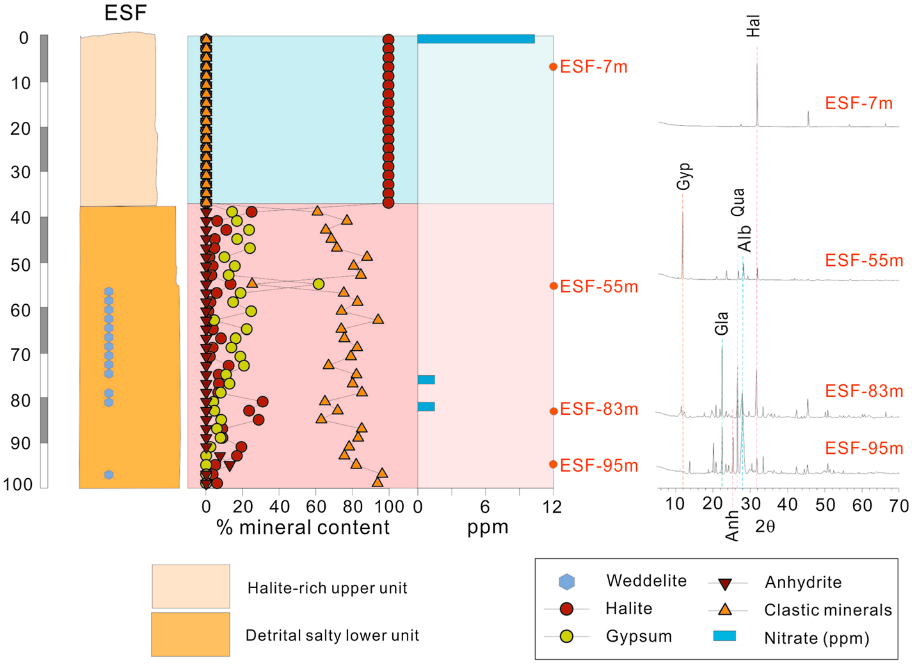

Figure 3. Stratigraphic section of the Esperanza Sondeo F (ESF) drilling site showing the mineral and anion compositions. Weddellite is a frequent and unequivocal secondary mineral below 55 m occurring in the lower detrital unit, which supports its formation in marginal areas of the basin. Detection of nitrate anion in the detrital salty lower unit strongly supports the presence of nitranite in the basin as shown by *Fernández-Remolar et al.* [2013] in the AT2 drilling site.

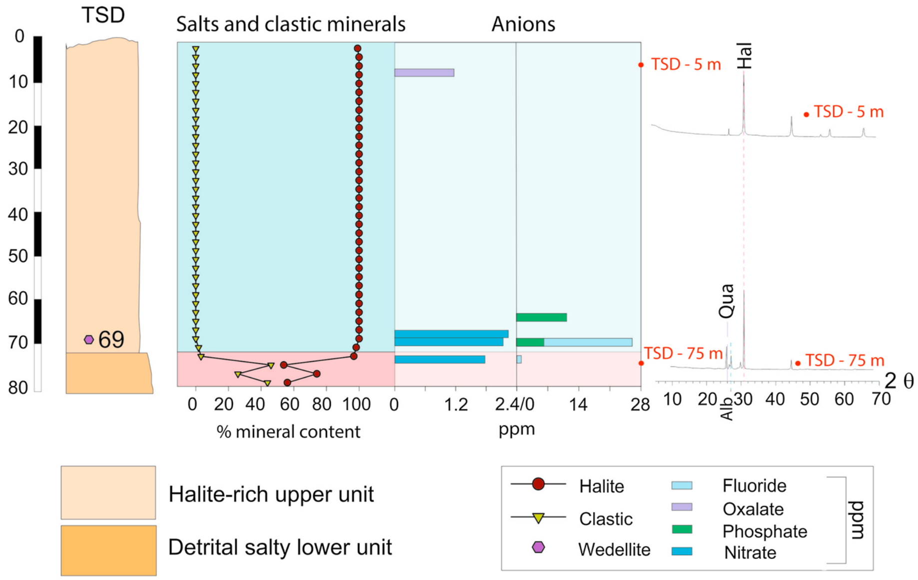

Figure 4. Stratigraphic section of the Tenardita Sondeo D (TSD) drilling site showing the mineral and ion composition where weddellite has been unequivocally found at around 69–70 m deep. Oxalate and phosphate anions have also recognized in the upper halite unit, whereas nitrate and fluoride occur in close association to the boundary of upper and lower sedimentary units. The occurrence of nitrate strongly suggests the presence of nitranite in the materials.

boulders or cemented materials by sulfates rather than chlorides, which could be one of the limiting factors constraining lichen colonization and growth.

Direct observation of the materials from the boreholes confirms that the Salar Grande consists of two different sedimentary units, a lower unit composed of reddish detrital components and an upper unit composed of saline deposits, overlying the weathered igneous basement (Figures 2–4). XRD analysis of the same set of samples was used to characterize the mineral composition. Detrital minerals (>80 wt % mineral content) dominate the lower unit, where clastic silicates (microcline, albite, riebeckite, and quartz) are associated with an ensemble of secondary saline components, including gypsum, anhydrite, and halite. In contrast to the heterogeneous lower unit, the upper unit is nearly pure halite, with very small amounts of gypsum [*Fernández-Remolar et al*., 2013]. The upper halite-rich materials correspond to the Soledad Formation, and the lower reddish detrital unit likely corresponds to proximal alluvial material interfingering with the lacustrine deposits of the Quillagua Formation [*Sáez et al*., 1999, 2012].

Furthermore, the clastic subsurface units in TSB and ESF showed XRD evidence for the presence of different minor phases (Figures 5 and S9), including the oxalate salts weddellite ($CaC_2O_4 \cdot 2H_2O$) and whewellite ($CaC_2O_4 \cdot H_2O$). Weddellite (Figures 3, 4, and 5a and 5b) closely matches a peak near $d = 6.2$ Å (14.3° 2θ) in samples from the lower detrital unit in TBS and ESF. Weddellite was also detected in the upper halite-rich unit at the TDS site (Figure 3) and in the lower detrital unit at borehole AT2 (Figure 5c), both of which show low-intensity XRD peaks corresponding to a *d*-spacing of 6.2 Å. Moreover, the results revealed the presence of some sulfates (Figure S1), such as nickel hexahydrite ($(Ni,Mg,Fe)SO_4 \cdot 6H_2O$), matching the peak near d = 4.36 Å (20.34° 2 · θ); thenardite (Na_2SO_4), matching the peak near d = 4.7 Å (19° 2 · θ); glauberite ($Na_2Ca(SO_4)_2$), with a defining peak at $d = 4.382$ Å ($2 \cdot \theta = 20.267$); and d'ansite ($Na_{21}Mg(SO_4)_{10}Cl_3$), with a peak that does not overlap with those of with other phases at $d = 2.808$ Å ($2 \cdot \theta = 31.804$); as well as detrital chlorite and biotite (a broad reflection near $d = 7.06$ Å (12.5° 2 · θ). In addition, a peak for nitratine ($NaNO_3$) may also appear in the lower unit at $d = 3.076$ Å, although this peak overlaps with reflections associated with gypsum and glauberite. The distribution of these phases is discontinuous within the clastic-dominated units, and they were not detected in halite-dominated regions (Figure S1).

Characterization of anion content in the soluble phase for the five borehole samples is consistent with the mineralogy determined by XRD analyses. Leachates of the upper halite-rich unit are dominated by chloride (~30 $g \cdot l^{-1}$), whereas sulfate is the most abundant anion in leachates of the lower detrital unit (~3.3 $g \cdot l^{-1}$)

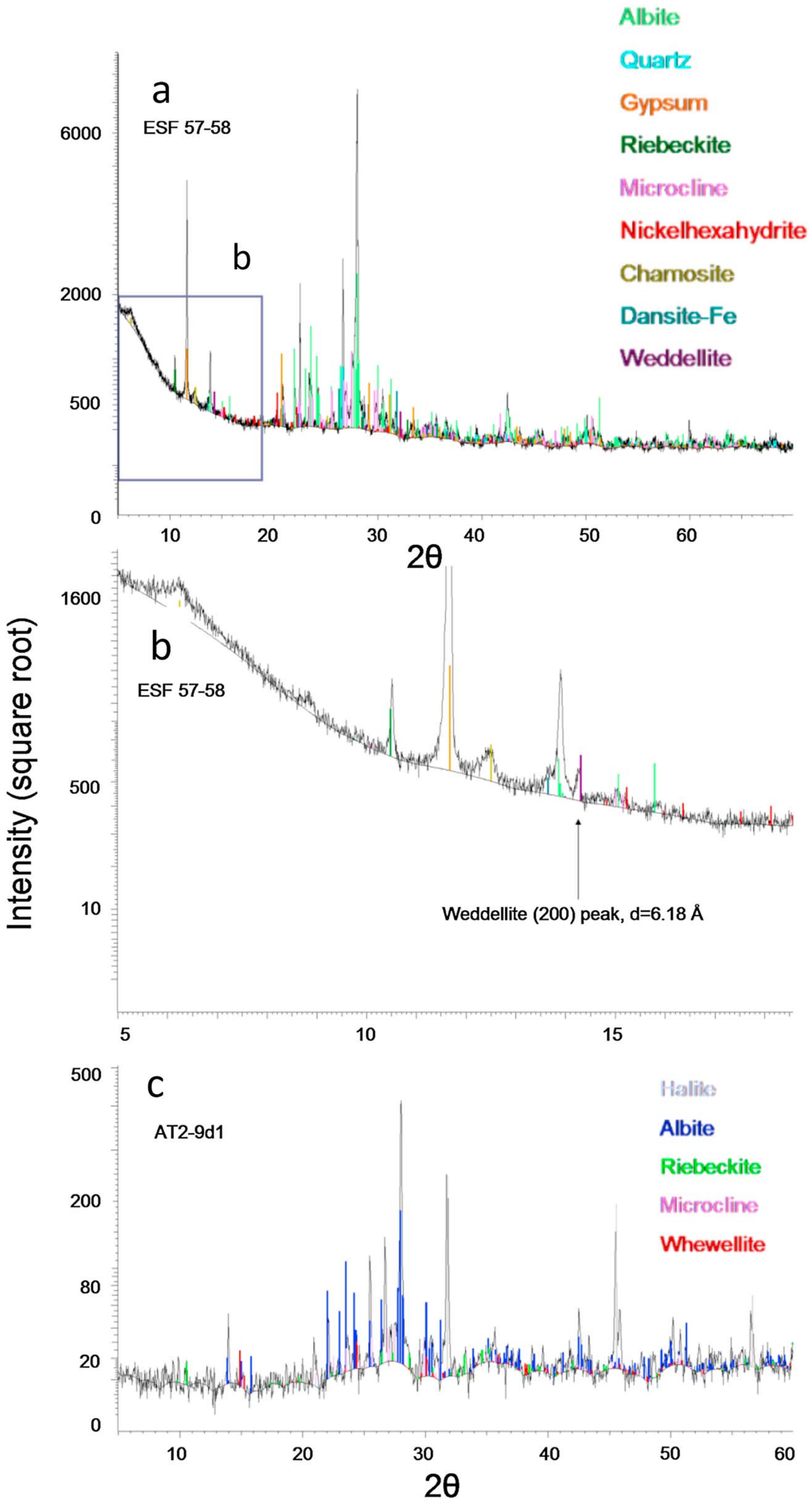

Figure 5. Identification of oxalate minerals by X-ray diffraction. (a and b) An X-ray diffraction pattern of sample ESF 57–58 with pattern matches from the Crystallography Open Database [*Grazulis et al*., 2009]. Albite, microcline, quartz, riebeckite, and chamosite are all likely detrital phases. The presence of multiple low-symmetry phases causes most diffraction peaks to be overlapped; however, a reasonable match to the (200) peak of weddellite ($(Ca(C_2O_4) \cdot 2H_2O)$) is observed near 14.3° 2θ ($d = 6.18$ Å). Diffraction patterns have been plotted as the square root of intensity to show minor peaks. Cu $K\alpha_{1,2}$ radiation ($\lambda = 1.5418$ Å). (c) The diffraction pattern of sample AT2-9d1 [*Fernández-Remolar et al*., 2013], which contains whewellite ($(Ca(C_2O_4) \cdot H_2O)$).

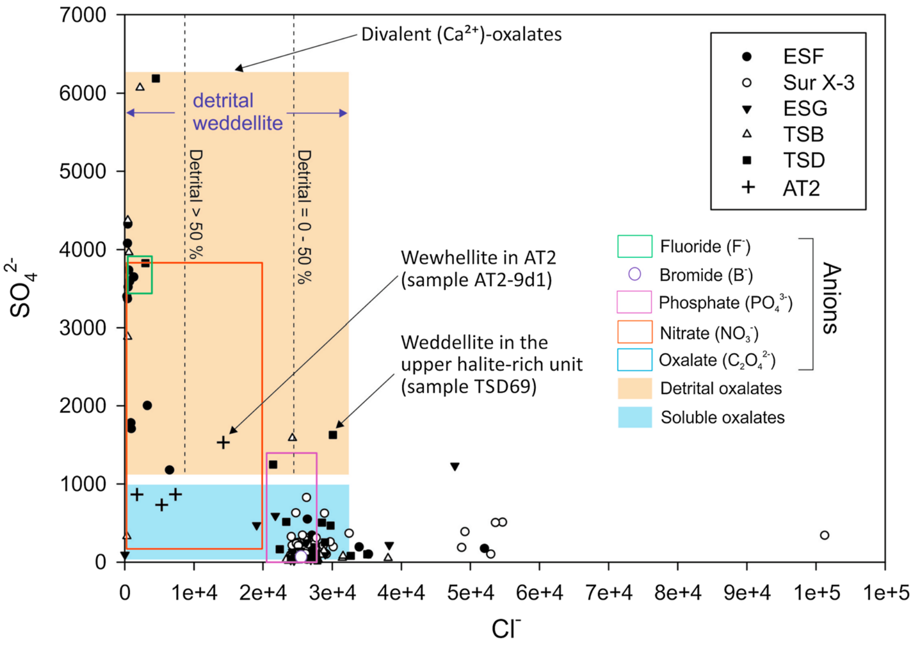

Figure 6. Scatterplot of chloride versus sulfate anions (ppm in the soluble phase) showing occurrence windows in the Salar Grande for different anions including oxalate and the crystalline phases weddellite and whewellite. It also includes data obtained in the AT2 borehole emplaced in a marginal area of the Salar Grande Basin [*Fernández-Remolar et al.*, 2013]. Weddellite distribution suggests that its primary source is detrital with some minor occurrence as precipitates upon complexing with Ca^{2+} cations in the main water body where halite is oversaturated. Detection of oxalate anions in the soluble samples from the upper halite-rich unit of the Salar Grande evidences the presence at a very low concentration (~4 ppm average) of an organic mineral much more soluble which could be a Na-bearing oxalate. Data coming from AT2 have been added.

(Figures 6 and S10). Furthermore, Cl^- and SO_4^{2-} also occur as the second most abundant anions in the units, in which they are not dominant. In the lower detrital unit, chloride has an average concentration of approximately 1.4 $g \cdot l^{-1}$, whereas in the upper halite-dominated unit, the sulfate anion concentration sharply decreases to an average of 255 ppm (Figure S10). In addition, some unusual anions (Figures 2–4 and Figures S1 and S10), such as bromide (~2 ppm), fluoride (~15 ppm), nitrate (~5 ppm), and phosphate (~10 ppm), have been recognized in the leachates of the borehole samples. While such anions have been detected in both upper and lower units (Figures 2–4 and S10), oxalate anions were only found in the upper halite-rich unit with an average concentration approximately 2.4 to 1 ppm in boreholes TSD and TSB (Figures 2 and 4 and S10), as well as in the borehole AT2 [*Fernández-Remolar et al.*, 2013] (Figure S1) with a higher concentration of 8.5 to 3 ppm. In addition, a unique and isolated occurrence of what is likely weddellite has been detected at the bottom of the upper halite-rich unit in the borehole TSD at 69 m (Figures 5 and S10). Although it is included in the upper unit, it is associated with detrital albite and probertite ($NaCaB_5O_7(OH)_4 \cdot 3H_2O$) showing a (011) reflection at 9.70° 2θ ($d = 9.137$ Å). The co-occurrence with albite and biotite strongly suggests a detrital origin for weddellite in those cases where this mineral occurs in the lower reddish detrital unit.

5. Discussion

The occurrence of oxalates in the Salar Grande basin has been confirmed by two independent techniques that can discriminate oxalate compounds based on its crystallinity and solubility [*Chen et al.*, 2000; *Baran*, 2014]. Whereas highly insoluble crystalline Ca-oxalates, such as weddellite and whewellite, are amenable to detection by XRD, monocationic oxalates and other oxalate-bearing compounds in the water-soluble phase of the samples are more readily detected by IC. Combined XRD and IC analysis reveals the presence of two different groups of oxalates, one highly soluble and the other consisting of insoluble Ca-oxalates (Figures 6 and 7). Though most weddellite and whewellite have been identified in the lower detrital unit

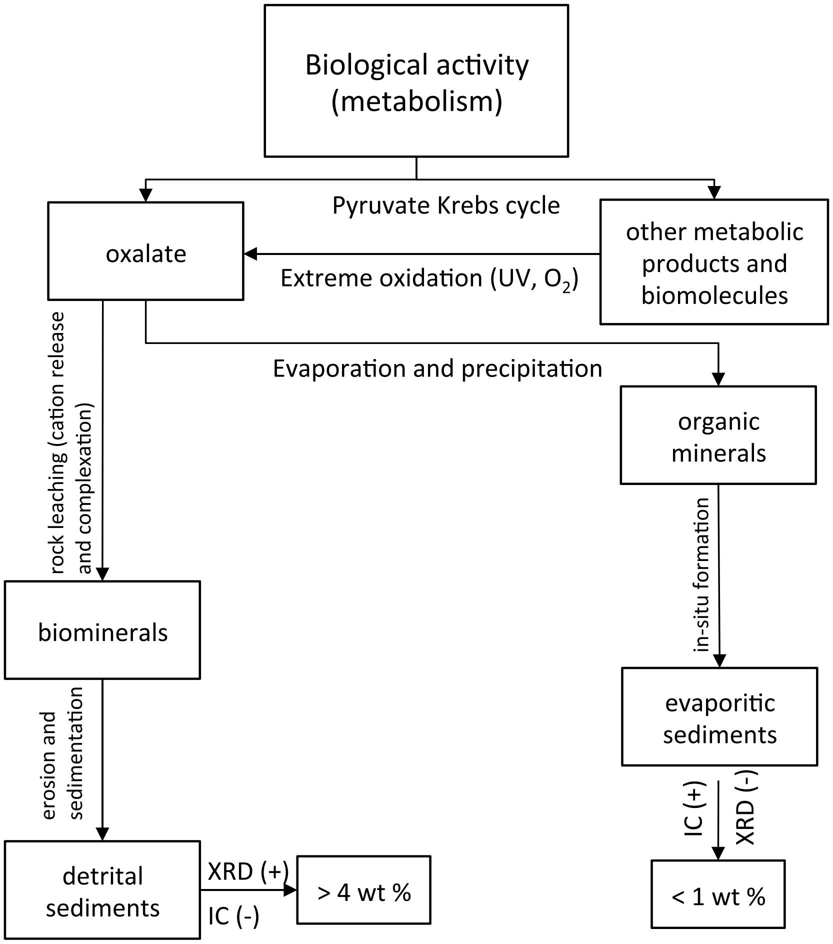

Figure 7. Two principal pathways of oxalate formation in the Salar Grande Basin, based on the complementary detection of insoluble Ca oxalate phases through XRD versus detection of soluble oxalate in IC analyses.

(Figures 2–5) using XRD to identify its crystalline structure, a second group of oxalate-bearing compounds have been found to only occur in the upper halite-rich unit using IC analysis of the soluble phase of the Salar Grande samples. The soluble host phase of oxalate in the halite-rich unit is either poorly crystalline, not abundant enough to be detectable by XRD, or both. Furthermore, the oxalate compounds detected via IC do not coexist with the crystalline oxalate phases that have been characterized via XRD (Figure 6). Estimation of the mineral concentration using the reference intensity ratio of sample ESF57-58 provided an estimate of 4% weddellite by total mass. However, no oxalate anions were detected in this sample using IC, consistent with the very low solubility of weddellite. Although the detection of the oxalate anion is clearly supported by IC, it remains uncertain which compound(s) in the sample contain this anion. Because oxalate is released into the soluble phase in samples from the upper halite-rich unit, which is enriched in Na, the potential compound could be a Na-bearing oxalate (e.g., natroxalate and $Na_2C_2O_4$). Although oxalate should have been derived from microbial metabolic activity or organic degradation [e.g., *Lapeyrie*, 1988], it does not co-occur with any other low-mass organic anions, such as formate, acetate, or propionate, that should have been detected by IC if they were present [*Fernández-Remolar et al.*, 2013]. Therefore, it is plausible that the compound containing soluble oxalate contains oxalate originating from highly degraded organic matter resulting from the long-term exposure of microbially produced compounds to the harsh conditions of the Salar Grande. In addition, the presence of persistent lichen communities in different marginal areas (Figures S5–S7) provides a plausible nearby biological source of oxalate [*Chen et al.*, 2000]. Due to its extreme resistance to degradation [e.g., *Applin et al.*, 2015], oxalate minerals should be easily transferred to the sedimentary deposits of the basin. If the link between preserved oxalates and biological activity is correct, then the oxalate preserved in the detrital and chemical sediments of the Salar Grade provides a record of biological activity during the formation and evolution of the basin spanning several million years [*Sáez et al*., 2012]. Such a process could involve an in situ record as the varnished rocks partially cemented in the sedimentary matrix with no transportation, as well as an ex situ record as erosion and sedimentation of fragmented biomineralized communities growing on the mountain slopes around the Salar Grande Basin.

Furthermore, the record of two different groups of oxalates in the Salar Grande Basin is also a response to strong environmental changes in the basin. The lower detrital unit hosting the crystalline Ca-oxalates likely formed under conditions of extremely low water availability [*Russ et al*., 1996, 2000], during which sedimentation would have been driven by very sporadic erosive episodes associated with active tectonics. Conversely, the presence of oxalate in the rich upper halite supports the presence of a transient water mass hosting microbial activity that produced organic compounds that were then exposed to photochemical oxidation to form oxalate [*Benner et al*., 2000; *Applin et al*., 2015]. This would increase the concentration of oxalate anions and the precipitation of oxalate compounds inside the halite salt body under strong evaporation.

Nickelhexahydrite in sulfate-rich Salar Grande subsurface materials may be analogous to the recently reported Ni-bearing sulfate salts detected by the MSL Curiosity rover APXS instrument [*Gellert et al*., 2015]. Magnesium sulfates may act as a repository for Ni^{2+} weathered from mafic silicates and sulfides, with some contribution from meteoritic infall. The presence of thenardite, glauberite, and d'ansite in Salar Grande deposits may also be relevant for Mars exploration, as these phases act as repositories for Na and S (and in the case of d'ansite, Cl) and might be considered to be contributors to elevated Na, S, and Cl levels in dust and weathered materials on the Martian surface.

6. Conclusions

The sedimentary deposits of the Salar Grande, a terrestrial analogue for halide-rich deposits at Terra Sirenum on Mars, were investigated using integrated geological, mineralogical, and geochemical methods. The occurrence of formate, oxalates, and molecular biomarkers in the Salar Grande halite-rich unit demonstrates the high potential for similar preservation in chloride-rich units on Mars. Oxalate is of particular relevance due to the possibility that oxalate minerals are widespread on the Martian surface [*Benner et al*., 2000; *Applin et al*., 2015]. Combining field exploration with XRD mineralogical analysis and IC geochemical analysis of borehole samples has revealed two different occurrences of oxalate minerals in the Salar Grande. Whereas the XRD mineralogical analysis recognized very refractory crystalline phases at concentrations higher than 2–4 wt % that are likely sourced from lichen activity, the IC geochemical analysis likely detected soluble oxalate phases at much lower concentrations. In this regard, the analysis of Atacama samples through other techniques such as Raman [*Frost*, 2004; *Frost and Weier*, 2003] aboard the upcoming ExoMars and Mars 2020 missions could be essential to identify the occurrence of oxalates in the red planet.

The Salar Grande halite-rich unit was formed via extreme solute concentration in transient water masses inside the endorheic basin, leading to the precipitation of massive halite units. It is plausible that the oxidative and photochemical degradation of organic matter (including microbial biomass present in transient water bodies) led to the formation of oxalate, as postulated to occur on the surface of Mars by *Benner et al*. [2000]. Insoluble Ca-oxalate minerals may also have been physically transported and incorporated into siliciclastic and chemical sediments in the Salar Grande. Persistently, low levels of oxalotrophic microbial activity and hyperarid conditions, combined with the stability of oxalate salts, have enabled the long-term preservation of oxalate compounds within detrital and chemical sediments in the Salar Grande. The formation and accumulation of oxalate minerals in the Salar Grande present a plausible geochemical analogue for the sequestration of oxalate in chloride- and sulfate-rich Martian rocks. On Mars, it is expected that conditions have been even more arid and that near-surface biological activity, including oxalotrophy, has not been active for billions of years (if ever). Therefore, oxalate preservation should be even more favored in analogous Martian rocks, such as the halide-rich units thought to exist at Terra Sirenum.

While lichens are living forms that produce oxalates, there are other communities consisting of fungi and bacteria that have an essential role in the formation of these biominerals [*Hess et al*., 2008; *Rusakov et al*., 2016]. Although the lichen communities are the main producer of oxalates in Atacama, the detection of oxalate minerals in the sedimentary infill of the Salar Grande demonstrates the potential of oxalates within chloride-rich sedimentary rocks as biosignatures to detect microbial activity on Mars. Particularly, some bacteria can form the same Ca-bearing oxalate species that are formed by lichens [*Rusakov et al*., 2016]. As a consequence, they can become in persistent biosignatures due to its resistance to degradation and considerable facility of detection by current crystallographic and geochemical techniques.

Applin et al. [2015] proposed that oxalate minerals at the ~0.5–1% level in the Martian near-surface might account for some of the observed CO_2-release behavior of Martian soils observed by Viking, Phoenix, and Curiosity. Confirmation of the presence, distribution, and type of oxalate salts present on Mars can provide new insights into the Martian carbon cycle. In this regard, the Terra Syrenum chloride-rich deposits [*Osterloo et al*., 2008] must be regarded as a high-value target to constrain the local- and planetary-scale geochemistry of Martian carbon. Identifying the sources, sinks, and reservoirs of carbon on Mars is an important goal, and understanding the past and present Martian carbon cycle will be necessary to identify any biological perturbations recorded in Martian rocks. Oxalate phases, such as those preserved in the Mars analogue conditions of the Salar Grande, may be an important reservoir of near-surface carbon on Mars, especially in light of the lack of widespread biological oxalate-consuming reactions. Whether Martian oxalates and organics include carbon formed through Martian biological processes or are of purely abiotic origin is an important question for current and future Mars exploration missions.

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References

Allmendinger, R. W., and G. González (2010), Invited review paper: Neogene to Quaternary tectonics of the coastal Cordillera, northern Chile, *Tectonophysics*, *495*(1), 93–110.

Applin, D. M., M. R. M. Izawa, E. A. Cloutis, D. Goltz, and J. R. Johnson (2015), Oxalate minerals on Mars?, *Earth Planet. Sci. Lett.*, *420*, 127–139.

Bao, R., A. Sáez, S. Servant-Vildary, and L. S. Cabrera (1999), Lake-level and salinity reconstruction from diatom analyses in Quillagua formation (late Neogene, Central Andean forearc, northern Chile), *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *153*(1), 309–335.

Baran, E. J. (2014), Review: Natural oxalates and their analogous synthetic complexes, *J. Coord. Chem.*, *67*(23–24), 3734–3768, doi:10.1080/00958972.2014.937340.

Benner, S. A., K. G. Devine, L. N. Matveeva, and D. H. Powell (2000), The missing organic molecules on Mars, *Proc. Natl. Acad. Sci. U.S.A.*, *97*, 2425–2430.

Biemann, K., et al. (1977), The search for organic substances and inorganic volatile compounds in the surface of Mars, *J. Geophys. Res.*, *82*(28), 4641–4658, doi:10.1029/JS082i028p04641.

Boynton, W. V., et al. (2009), Evidence for calcium carbonate at the Mars Phoenix landing site, *Science*, *325*(5936), 61–64.

Burford, E., S. Hillier, and G. M. Gadd (2006), Biomineralization of fungal hyphae with calcite (CaCO 3) and calcium oxalate mono- and dihydrate in carboniferous limestone microcosms, *Geomicrobiology*, *23*, 599–611.

Cezar, T. (1998), Calcium oxalate: A surface treatment for limestone, *J. Conserv. Mus. Stud.*, *4*, 15–31.

Chen, J., H.-P. Blume, and L. Beyer (2000), Weathering of rocks induced by lichen colonization—A review, *Catena*, *39*(2), 121–146.

Chong Díaz, G., M. Mendoza, J. García-Veigas, J. J. Pueyo, and P. Turner (1999), Evolution and geochemical signatures in a Neogene forearc evaporitic basin: The Salar Grande (Central Andes of Chile), *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *151*(1–3), 39–54.

Dorn, R. (2013), Rock coating, in *Weathering and Soils Geomorphology*, edited by G. A. Pope, pp. 70–97, Elsevier, Amsterdam.

Durand, B. (1980), *Kerogene: Insoluble Organic Matter from Sedimentary Rocks*, Éditions Technip, Paris.

Echigo, T., M. Kimata, A. Kyono, M. Shimizu, and T. Hatta (2005), Re-investigation of the crystal structure of whewellite [$Ca(C_2O_4)H_2O$] and the dehydration mechanism of caoxite [$Ca(C_2O_4)3H_2O$], *Mineral. Mag.*, *69*, 77–88.

Fernández-Remolar, D. C., et al. (2013), Molecular preservation in halite- and perchlorate-rich hypersaline subsurface deposits in the Salar Grande basin (Atacama desert, Chile): Implications for the search for molecular biomarkers on Mars, *J. Geophys. Res. Biogeosci.*, *118*, 922–939, doi:10.1002/jgrg.20059.

Frost, R. L. (2004), Raman spectroscopy of natural oxalates, *Anal. Chim. Acta*, *517*(1–2), 207–217.

Frost, R. L., and M. L. Weier (2003), Raman spectroscopy of natural oxalates at 298 and 77 K, *J. Raman Spectrosc.*, *34*(10), 776–785, doi:10.1002/jrs.1052.

Gadd, G. M. (1999), Fungal production of citric and oxalic acid: Importance in metal speciation, physiology and biogeochemical processes, *Adv. Microb. Physiol.*, *41*, 47–92.

Garcia-Veigas, J., G. Chong, and J. Pueyo (1996), Mineralogy and geochemistry of the Salar Grande salt rock (I Región de Tarapacá, Chile): Genetic implications, in *Géodynamique Andine: Résumé Étendus = Andean Geodynamics: Extended Abstracts*, pp. 679–682, ORSTOM, Paris.

Garreaud, R. D., A. Molina, and M. Farias (2010), Andean uplift, ocean cooling and Atacama hyperaridity: A climate modeling perspective, *Earth Planet. Sci. Lett.*, *292*(1), 39–50.

Gellert, R., et al. (2015), Chemical evidence for an aqueous history at pahrump, Gale Crater, Mars, as seen by the APXS, Lunar Planet. Sci. Conf. 46th, Houston, Pap. 1855.

Glotch, T. D., J. L. Bandfield, L. L. Tornabene, H. B. Jensen, and F. P. Seelos (2010), Distribution and formation of chlorides and phyllosilicates in Terra Sirenum, Mars, *Geophys. Res. Lett.*, *37*, L16202, doi:10.1029/2010GL044557.

Grazulis, S., D. Chateigner, R. T. Downs, A. F. T. Yokochi, M. Quirós, L. Lutterotti, E. Manakova, J. Butkus, P. Moeck, and A. Le Bail (2009), Crystallography Open Database - An open-access collection of crystal structures, *J. Appl. Crystallogr.*, *42*, 726–729.

Guggiari, M., R. Bloque, M. Aragno, E. Verrecchia, D. Job, and P. Junier (2011), Experimental calcium-oxalate crystal production and dissolution by selected wood-rot fungi, *Int. Biodeterior. Biodegrad.*, *65*, 803–809.

Han, Y., H. J. Joosten, W. Niu, Z. Zhao, P. S. Mariano, M. McCalman, J. van Kan, P. J. Schaap, and D. Dunaway-Mariano (2007), Oxaloacetate hydrolase, the C-C bond lyase of oxalate secreting fungi, *J. Biol. Chem.*, *282*, 9581–9590.

Hartley, A. J., and G. Chong (2002), Late Pliocene age for the Atacama desert: Implications for the desertification of western South America, *Geology*, *30*(1), 43–46.

Hazen, R. M., R. T. Downs, A. P. Jones, and L. Kah (2013), Carbon mineralogy and crystal chemistry, *Rev. Mineral. Geochem.*, *75*, 7–46.

Hess, D., D. J. Coker, J. M. Loutsch, and J. Russ (2008), Production of oxalates in vitro by microbes isolated from rock surfaces with prehistoric paints in the Lower Pecos Region, Texas, *Geoarchaeology*, *23*, 3–11.

Hoffman, B. A., and S. M. Bernasconi (1998), Review of occurrences and carbon isotope geochemistry of oxalate minerals: Implications for the origin and fate of oxalate in diagenetic and hydrothermal fluids, *Chem. Geol.*, *149*, 127–146.

Johnston, C. G., and J. R. Vestal (1993), Biogeochemistry of oxalate in the antarctic cryptoendolithic lichen-dominated community, *Microb. Ecol.*, *25*(3), 305–319, doi:10.1007/BF00171895.

Jones, D., M. J. Wilson, and J. M. Tait (1980), Weathering of a basalt by *Pertusaria corallina*, *Lichenologist*, *2*, 277–289.

Kostman, T. A., N. M. Tarlyn, F. A. Loewus, and V. R. Franceschi (2001), Biosynthesis of L-ascorbic acid and conversion of carbons 1 and 2 of L-ascorbic acid to oxalic acid occurs within individual calcium oxalate crystal idioblasts, *Plant Physiol.*, *125*, 634–640.

Lapeyrie, F. (1988), Oxalate synthesis from soil bicarbonate by the mycorrhizal fungusPaxillus involutus, *Plant Soil*, *110*(1), 3–8, doi:10.1007/BF02143532.

Mahaffy, P. R., C. R. Webster, M. Cabane, P. G. Conrad, P. Coll, S. K. Atreya, and D. W. Ming (2012), The sample analysis at Mars investigation and instrument suite, *Space Sci. Rev.*, *170*, 401–478.

Martin, G., M. Guggiari, D. Bravo, J. Zopfi, G. Cailleau, M. Aragno, D. Job, E. Verrecchia, and P. Junier (2012), Fungi, bacteria and soil pH: The oxalate-carbonate pathway as a model for metabolic interaction, *Environ. Microbiol.*, *14*, 2960–2970.

Ming, D. W., et al. (2014), Volatile and organic compositions of sedimentary rocks in Yellowknife Bay, Gale Crater, Mars, *Science*, *343*(6169), doi:10.1126/science.1245267.

Munir, E., J. J. Yoon, T. Tokimatsu, T. Hattori, and M. Shimada (2001), A physiological role for oxalic acid biosynthesis in the wood-rotting basidomycete *Fomitopsis palustris*, *Proc. Natl. Acad. Sci. U.S.A.*, *98*, 11,126–11,130.

Nakata, P. A. (2003), Advances in our understanding of calcium oxalate crystal formation and function in plants, *Plant Sci.*, *164*, 901–909.

Osterloo, M. M., V. E. Hamilton, J. L. Bandfield, T. D. Glotch, A. M. Baldridge, P. R. Christensen, L. L. Tornabene, and F. S. Anderson (2008), Chloride-bearing materials in the Southern Highlands of Mars, *Science*, *319*(5870), 1651–1654.

Peltzer, E. T., J. L. Bada, G. Schlesinger, and S. L. Miller (1984), The chemical conditions on the parent body of the murchison meteorite: Some conclusions based on amino, hydroxy and dicarboxylic acids, *Adv. Space Res.*, *4*(12), 69–74.

Pueyo, J. J., G. Chong, and A. Jensen (2001), Neogene evaporites in desert volcanic environments: Atacama desert, northern Chile, *Sedimentology*, *48*(6), 1411–1431.

Rusakov, A. V., A. D. Vlasov, M. S. Zelenskaya, O. V. Frank-Kamenetskaya, and D. Y. Vlasov (2016), The crystalization of calcium oxalate hydrates formed by interation between microorganisms and minerals, in *Biogenic-Abiogenic Interactions in Natural and Anthropogenic Systems*, edited by O. V. Frank-Kamenetskaya, E. Panova, and D. Y. Vlasov, pp. 357–377, Springer, Basel.

Russ, J., R. L. Palma, D. H. Loyd, T. W. Boutton, and M. A. Coy (1996), Origin of the whewellite-rich rock crust in the Lower Pecos Region of Southwest Texas and its significance to paleoclimate reconstructions, *Quat. Res.*, *46*(1), 27–36, doi:10.1006/qres.1996.0041.

Russ, J., D. H. Loyd, and T. W. Boutton (2000), A paleoclimate reconstruction for southwestern Texas using oxalate residue from lichen as a paleoclimate proxy, *Quat. Int.*, *67*(1), 29–36, doi:10.1016/S1040-6182(00)00006-9.

Sáez, A., L. Cabrera, A. Jensen, and G. Chong (1999), Late Neogene lacustrine record and palaeogeography in the Quillagua-Llamara basin, Central Andean fore-arc (northern Chile), *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *151*(1–3), 5–37, doi:10.1016/S0031-0182(99)00013-9.

Sáez, A., L. Cabrera, M. Garcés, D. Bogaard, A. Jensen, and D. Gimeno (2012), The stratigraphic record of changing hyperaridity in the Atacama desert over the last 10 Ma, *Earth Planet. Sci. Lett.*, *355–356*, 32–38, doi:10.1016/j.epsl.2012.08.029.

Skarmeta, J., and N. Marinovic (1981), Hola Quillagua, Región de Antofagasta, hoja num 51.

Tan, Y., Y. B. Lim, K. E. Altieri, S. P. Seitzinger, and B. J. Turpin (2012), Mechanisms leading to oligomers and SOA through aqueous photooxidation: Insights from OH radical oxidation of acetic acid and methylglyoxal, *Atmos. Chem. Phys.*, *12*, 801–813.

Vítek, P., J. Jehlička, C. Ascaso, V. Mašek, B. Gómez-Silva, H. Olivares, and J. Wierzchos (2014), Distribution of scytonemin in endolithic microbial communities from halite crusts in the hyperarid zone of the Atacama desert, Chile, *FEMS Microbiol. Ecol.*, *90*(2), 351–366.

Wilson, M. J., D. Jones, and W. J. McHardy (1980), The weathering of serpentinite by Lecanora Atra, *Lichenologist*, *13*, 167–176.

Ziolkowski, L. A., J. Wierzchos, A. F. Davila, and G. F. Slater (2013), Radiocarbon evidence of active endolithic microbial communities in the hyperarid core of the Atacama desert, *Astrobiology*, *13*(7), 607–616, doi:10.1089/ast.2012.0854.