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

Z. Y. Cheng¹, D. C. Fernández-Remolar², M. R. M. Izawa³, D. M. Applin⁴, M. Chong Diaz⁵, M. T. Fernandez-Sampedro⁶, M. García-Villadangos⁷, T. Huang⁸, L. Xiao¹,⁸, and V. Parro⁷

¹Planetary Science Institute, School of Earth Sciences, China University of Geosciences, Wuhan, China, ²Environmental Science Centre, British Geological Survey, Keyworth, UK, ³Department of Earth Sciences, Brock University, St. Catharines, Ontario, Canada, ⁴Hyperspectral Optical Sensing for Extraterrestrial Reconnaissance Laboratory, Department of Geography, University of Winnipeg, Winnipeg, Manitoba, Canada, ⁵Planetary Science Institute, Tucson, Arizona, USA, ⁶Department of Geological Sciences, Universidad Católica del Norte, Antofagasta, Chile, ⁷Centro de Astrobiología (INTA-CSIC), Torrejon de Ardoz, Spain, ⁸Space Science Institute, Macau University of Science and Technology, Macau, China

Abstract In this study, we report the detection and characterization of the organic minerals weddellite (CaC₂O₄·2H₂O) and whewellite (CaC₂O₄·H₂O) 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
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In this paper, we report the occurrence of the Ca-bearing oxalates weddellite (CaC₂O₄·H₂O) and whewellite (CaC₂O₄·H₂O), as well as the Mg-bearing glushinskite (MgC₂O₄·2H₂O) [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⁺⁺(C₂O₄)n/2·xH₂O) 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 oxaloacetate [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 bond 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 Diaz 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...
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 Diaz 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 Diaz 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 IO₃⁻ 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.
Interestingly enough, the occurrence of lichens is associated to the presence of highly exposed areas where they are growing in detrital materials of alluvial fans cemented by sulfates and faceted boulders (Figure S7). In addition, some ephelitic lichens have been also found in areas more exposed to UV radiation and wind, occur as epilithic communities encrusting cemented the lichen. Although lichens primarily colonize slightly cemented surfaces in more protected areas, those growing around faulted substrates cemented by sulfate minerals (Figure S6). Epilithic lichens were observed 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 Kα, λ = 1.54056 Å). All the XRD patterns were collected in the 2θ-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 mM sodium carbonate (Na2CO3) 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 Diaz 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 Diaz 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 [Ziółkowski 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 [Garreau 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). Hence, 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) 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 epilithic 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.
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 (CaC₂O₄·2H₂O) and whewellite (CaC₂O₄·H₂O). Weddellite (Figures 3, 4, and 5a and 5b) closely matches a peak near \( d = 6.2 \, \text{Å} \) (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]SO₄·6H₂O), matching the peak near \( d = 4.36 \, \text{Å} \) (20.34° 2θ); thenardite (Na₂SO₄), matching the peak near \( d = 4.7 \, \text{Å} \) (19° 2θ); glauberite (Na₂Ca(SO₄)₂), with a defining peak at \( d = 4.382 \, \text{Å} \) (2·θ = 20.267); and danseitite (Na₂Mg(SO₄)₂Cl₂), with a peak that does not overlap with those of with other phases at \( d = 2.808 \, \text{Å} \) (2·θ = 31.804); as well as detrital chlorite and biotite (a broad reflection near \( d = 7.06 \, \text{Å} \) (12.5° 2θ). In addition, a peak for nitratine (NaNO₃) may also appear in the lower unit at \( d = 3.076 \, \text{Å} \), 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·l⁻¹), whereas sulfate is the most abundant anion in leachates of the lower detrital unit (~3.3 g·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 weddelite ((Ca(C₂O₄)·2 H₂O)) 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 Kα1,2 radiation (λ = 1.5418 Å).

(c) The diffraction pattern of sample AT2-9d1 [Fernández-Remolar et al., 2013], which contains whewellite (CaC₂O₄·H₂O).
Furthermore, Cl⁻ and SO₄²⁻ 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·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 (NaCaB₅O₇(OH)₄ · 3H₂O) 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 their 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
(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$_2$C$_2$O$_4$). 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 microbiologically 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

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.
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 [Gellett et al., 2015]. Magnesium sulfates may act as a repository for Ni²⁺ 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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