Sulfate minerals and organic compounds on Mars

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ABSTRACT

Strong evidence for evaporitic sulfate minerals such as gypsum and jarosite has recently been found on Mars. Although organic molecules are often codeposited with terrestrial evaporitic minerals, there have been no systematic investigations of organic components in sulfate minerals. We report here the detection of organic material, including amino acids and their amine degradation products, in ancient terrestrial sulfate minerals. Amino acids and amines appear to be preserved for geologically long periods in sulfate mineral matrices. This suggests that sulfate minerals should be prime targets in the search for organic compounds, including those of biological origin, on Mars.

Keywords: Mars, sulfates, evaporites, amino acids, gypsum, jarosite, anhydrite, kerogen.

INTRODUCTION

The search for evidence of water and organic compounds, including those of possible biological origin, is one of the major goals of the Mars exploration programs of both the National Aeronautics and Space Administration (NASA) and the European Space Agency (ESA). The NASA Mars Exploration Rovers and the ESA OMEGA/Mars Express have provided the best evidence to date that liquid water was once present on Mars. Abundant sulfate minerals such as gypsum and jarosite suggest that large acidic water basins were once present and that as they evaporated sulfate minerals were precipitated (Squyres et al., 2004; Langevin et al., 2005; Gendrin et al., 2005). Although it is unknown how long these bodies of water existed, they could potentially have provided an environment capable of supporting life.

The presence of organic compounds on Mars is uncertain. The Viking missions in 1976 detected no organic compounds above a threshold level of a few parts per billion in near-surface Martian soils (Biemann et al., 1976). However, key biomolecules such as amino acids would not have been detected by the Viking Gas chromatograph and mass spectrometer (GCMS) even if several million bacterial cells per gram were present (Glavin et al., 2001). In addition, oxidation reactions involving organic compounds on the Martian surface would likely produce nonvolatile products such as mellitic acid salts that also would not have been detected by Viking (Benner et al., 2000). Thus, the Viking results did not conclusively disprove that there are organic compounds present on the surface of Mars. The only other opportunity to analyze samples from Mars has been provided by meteorites ejected from its surface and delivered to Earth. However, contamination of these meteorites by terrestrial organic material during their residence times on Earth (10^2–10^4 yr) compromises their use in assessing whether organic compounds are present on Mars (Jull et al., 1998).

Organic matter is often codeposited in terrestrial evaporites, and similar deposition processes should occur on Mars if organic molecules were present in the early oceans (Mancinelli et al., 2004). To our knowledge, there have been no systemic investigations of organic compounds in sulfate minerals on Earth. We report here the determination of the organic carbon and nitrogen contents of several sulfate minerals, as well as the abundance of amino acids and their degradation products.

METHODS

The samples investigated included gypsum from the Anza-Borrego Desert, California (4 Ma), gypsum from the Haughton impact crater, Canada (23 Ma), and gypsum, anhydrite, and jarosite samples from Panoche Valley (California) (40 Ma). A modern gypsum sample from a salt evaporation pond in Chula Vista (California) was also analyzed. Sample ages were estimated based on the geology of their respective localities.

The evaporite formations from the Anza-Borrego Desert have been studied extensively. The gypsum investigated here was collected from the Fish Creek area and has been dated as 3–5 Ma (Remeika and Lindsay, 1992). Gypsum from the Haughton impact crater is assumed to date from the time of the impact crater, 23 Ma (Parnell et al., 2004). The age of the host rock of the Panoche Valley samples is 75–65 Ma (Presser and Ohlendorf, 1987), but the age of the sulfate minerals is estimated as 40 Ma (middle Tertiary); this is when the coastal ranges were raised in this area during the Sierra Nevada uplift, which caused ocean water to withdraw and deposit evaporitic minerals in California's Central Valley. Strontium isotope analyses were conducted to verify the geologically deduced ages of the Panoche Valley samples. The Panoche Valley gypsum $^{87}Sr/^{86}Sr$ ratio was 0.707745 ($\pm$0.000005). Comparing this ratio to the strontium isotope history of seawater (Hess et al., 1986) gives an age 40 Ma, consistent with the inferred geologic age. The Panoche Valley anhydrite was estimated to be roughly the same age because anhydrite forms by dehydration of gypsum. The jarosite from Panoche Valley was likely formed by aqueous alteration of pyrite, and it is thus difficult to determine its actual age of the alteration veins, but it is probably somewhat younger than 40 Ma. The modern gypsum sample is from the South Bay salt works in Chula Vista. The area is rich in marshes and tidal flats, and there is continuous evaporite formation during tidal fluctuations. Because of the poor water quality in this region of San Diego Bay, the salts typically include significant amounts of organic material.

The surface of each sample was thoroughly rinsed with doubly distilled water (ddH_2O) followed by 1M ddHCl, then again with ddH_2O. The identity of each mineral was verified by X-ray diffraction (XRD) analyses using a Scintag XDS-2000 powder diffractometer. Samples were analyzed for total organic carbon and nitrogen using a Costech elemental combustion C-N analyzer. Carbon and nitrogen isotopic ratios were determined with a Thermofinnigan Delta-XP Plus stable isotope ratio mass spectrometer. In order to remove carbonate from the samples, they were pretreated with an excess of 3N ddHCl and dried down on a vacuum centrifuge at 45 °C for 1

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TABLE 1. TOTAL ORGANIC CARBON (TOC), TOTAL ORGANIC NITROGEN (TON), AND ISOTOPIC ANALYSES

Location (Ma)	TOC (mg/g)	TON (mg/g)	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	AA+Amines TOC (%)	AA+Amines TON (%)
South Bay Gypsum (0)	6.91	1.01	−17.3	+11.0	0.041	0.117
Anza-Borrego Gypsum (4)*	0.29	0.02	−34.9	+1.7	0.042	0.265
Haughton Crater Gypsum (23)†	0.77	0.03	−31.3	+0.1	0.007	0.105
Panoche Gypsum (40)§	0.12	0.01	−30.0	+13.1	0.110	0.399
Panoche Anhydrite (40)§	0.09	0.02	−29.0	+4.2	0.359	0.718
Panoche Jarosite (~40)#	1.28	0.15	−26.2	+3.9	0.012	0.038

Note: The last two columns represent the mass percent of the TOC and TON accounted for by amino acids and amines. The uncertainties are roughly ±5% for TOC, ±10% for TON and ± 0.5–1.0‰ for the isotopic values.
*33°00′N, 116°10′W; (Remeika and Lindsay, 1992)
†75°22′N, 89°41′W; (Cockell and Lee, 2002).
§36°35′N, 120°42′W; (Presser and Ohlendorf, 1987).
#36°27′N, 120°39′W.

h before analyses for total organic carbon and total organic nitrogen.

Amino acids were isolated by vapor-phase acid hydrolysis (6 N HCl, 24 h, 100 °C) of ground samples followed by desalting (Amelung and Zhang, 2001). Amines were isolated by microdiffusion from the powdered mineral treated with 1N NaOH, into a 0.01N HCl solution at 40 °C for 6 days (Conway, 1963). Extracts were analyzed for amino acids and amines by reverse-phase high performance liquid chromatography (RP-HPLC) using pre-column derivatization with *o*-phthalaldehyde/N-acetyl L-cysteine using a Shimadzu RF-530 fluorescence detector (Zhao and Bada, 1995) and a Phenomenex Synergi Hydro-RP column (250 × 4.6 mm). Quantification of amino acids and amines included background level correction using a serpentine procedural blank and a comparison of the peak areas with those of an amino acid standard. A D/L-norleucine internal standard was added to normalize amino acid recoveries from desalting and derivatization. The recovery of the amines carried through the extraction procedure was found to be near 100% using spiked procedural samples.

To investigate the possible presence of modern bacterial contamination in the various minerals, we determined total adenine concentrations. Both a liquid extraction involving treatment of 1 g of sample with 2 mL of 95% formic acid solution for 24 h at 100 °C and a sublimation extraction method at 500 °C for 5 min were performed. Adenine concentrations were quantified by HPLC with ultraviolet (UV) absorption detection (260 nm) and converted to bacterial cell densities (*E. coli* equivalents/g) as described in Glavin et al. (2004).

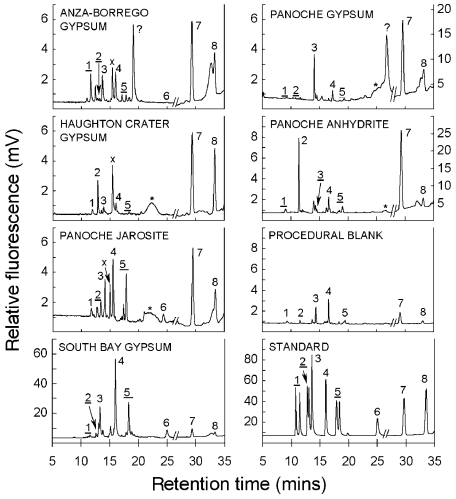

Figure 1. Combined reverse-phase high performance liquid chromatography chromatograms of recovery-corrected amino acids (hydrolyzed/desalted, 5–25 min) and amines (microdiffusion, 27–35 min) in sulfate minerals. Chromatograms represent elutions with identical gradients. Chromatograms on left and the standard have later retention times because they were separated with a different buffer than samples on right. Detection limits were ~1 ppb for amino acids and ~0.5 ppb for amines. 1 = (D + L)-aspartic acid, 2 = (D + L)-serine, 3 = glutamic acid, 4 = glycine, 5 = (D + L)-alanine, 6 = L-valine, 7 = methylamine, 8 = ethylamine, asterisk = residual ammonia from extraction process, x = resin impurity. Underlined numbers indicate resolution of L- and D-enantiomers for that respective amino acid. Peaks labeled with question mark are currently unidentified. Y-axis scales are listed on left for each separation. Right axis has been labeled accordingly if amine data are at different attenuation.

RESULTS

The XRD results verified each mineral identity. The gypsum samples that were obtained from Anza-Borrego, Panoche Valley, and Haughton crater were selenite, pure gypsum in discrete layers. The Chula Vista gypsum sample was the least pure.

The organic carbon and nitrogen data are tabulated in Table 1. The organic carbon content range was 0.12–0.77 mg·C/g in the 3 gypsum samples; the contemporary gypsum from South Bay showed significantly higher percent organic carbon (6.9 mg·C/g) due to the sample's origin in a highly contaminated region. The Panoche anhydrite was consistent with the gypsum samples with an organic carbon content of 0.09 mg·C/g and the Panoche jarosite was showed a much higher value of 1.28 mg·C/g. The nitrogen trends were similar in that the gypsum and anhydrite samples ranged from 0.01 to 0.03 mg·N/g. The jarosite was significantly more nitrogen rich with a content of 0.15 mg·N/g.

The organic C/N ratios in old gypsum and jarosite range from 9 to 30, indicating that the major organic component present in the sulfate minerals is likely a humic acid- and/or kerogen-like material (Ertel and Hedges, 1983), a conclusion that is consistent with the measured carbon and nitrogen isotopic values. The exceptions are the Chula Vista gypsum with a C/N ratio of ~7 and the Panoche anhydrite with a ratio of ~5. These numbers are more indicative of recent biological material. Even though amino acids and amines constitute only a fraction of the total organic carbon and nitrogen present in the sulfate minerals (Table 1), they are readily detected and characterized (Fig. 1; Table 2).

The detected levels of amino acids and their enantiomers, as well as methylamine (MA) and ethylamine (EA), the decarboxylation products of glycine and alanine, on average account for ~0.1% of the total organic carbon and ~0.27% of the total organic nitrogen for the 6 samples (the Panoche gypsum showed an unknown peak that eluted near valine and was not included in the average).

Adenine was detected in every sample except the Anza-Borrego gypsum. The adenine levels detected (2–6 ppb) indicate that the *E. coli* equivalents per gram of sample (ECE/g) are in the range of 10^6–10^7 cells/g. With the exception of the Anza-Borrego gypsum, which is the most pristine, the various samples all have low cell counts, indicating that some of the organic matter is likely associated with bacterial remains.

DISCUSSION

The organic matter detected in each mineral is likely ancient organic matter trapped within the matrix, along with material derived from the remnants of more recent sulfate-reducing microbial communities. The presence of the D-enantiomers (produced by racemization) of several amino acids in the gypsum samples suggests that these compounds are mostly original components of the depositional environment and not recent contaminants; however, their presence could partially be due to bacterial cell wall material. The correlation between the ratios of the amino acids glycine and alanine and their degradation products, MA and EA, respectively, also suggests that the organic material is a component of the original evaporite. The ratio of degradation amines to the amino acids increases with the age of the sample. Amines are not typically detected in ancient terrestrial carbonate minerals (Glavin and Bada, 1998), presumably because they are volatile and lost from the basic

TABLE 2. AMINO ACID CONCENTRATIONS OF VARIOUS SULFATE MINERALS

Location (Ma)	Asp	Ser	Glu	Gly	Ala	Val	MA	EA	Z*
South Bay Gypsum (0)	77.7†	1495†	176	1591	3172†	731	37.2	173	0.04
Anza-Borrego Gypsum (4)	137†	8.3†	116	10.3	30.0†	Trace	10.2	8.8	0.5
Haughton Crater Gypsum (23)	21.7	65.9	13.5	N.D.	6.7†	Trace	17.7	18.7	5.4
Panoche Valley Gypsum (40)	5.6†	3.3†	234	N.D.	2.9†	??	40.3	21.2	21.2
Panoche Valley Anhydrite (40)	55.5†	587	93.4†	N.D.	58.9†	46.2	72.4	7.9	1.4
Panoche Valley Jarosite (~40)	62.8	50.3†	39.0	28.1	120†	55.8	11.9	10.5	0.15

Note: All values are blank-corrected and reported in mass ppb. Uncertainties in the measurements are ±10%.

*$z = \frac{MA + EA}{gly + ala}$

†D-enantiomer detected.

N.D.—Not detected above blank level.

??—Valine is not possible to evaluate because of interference from an unknown component.

mineral matrices. However, they are apparently retained in these minerals, perhaps as their nonvolatile sulfate salts.

The amino acids should be racemic (D/L = 1) in the ancient samples because they have ages in excess of several million years (Bada et al., 1999), but this was not the case in all of the samples. The Anza-Borrego gypsum is the only sample in which the D/L alanine ratio is close to unity, and this sample therefore appears to be the most pristine. Anza-Borrego also has no detectable adenine, so we are confident that the amino acids are not from recent contamination and are an ancient biosignature. The other samples may contain some levels of organic matter of more recent origin, especially the anhydrite and the jarosite samples.

The ratio *Z*, the concentrations of MA + EA divided by the concentrations of glycine + alanine, increases with age in the gypsum samples (Table 2). In both the Panoche Valley jarosite and anhydrite samples, *Z* is less than expected for gypsum minerals from the same deposit, suggesting that the rate of decomposition of amino acids is slower in iron-rich or dehydrated sulfates, that volatile amines are more easily lost from such minerals, or that the organic material is much more recent in origin in comparison to that in the gypsum samples.

Assuming that the change in the relative amounts of MA + EA and glycine + alanine in the various gypsum samples is entirely due to decarboxylation, then the data in Table 2 would be expected to obey the following irreversible first-order kinetic relationship:

$$\ln\left(\frac{AA_t}{AA_0}\right) = -k_{DC}\cdot t, \quad (1)$$

where AA_t = glycine + alanine concentration at time *t*, AA_0 is the original glycine + alanine concentration in the sample, and k_{DC} is the rate of decarboxylation of glycine and alanine. Assuming amines are retained in gypsum and that the major sources of MA and EA are glycine and alanine decarboxylation, respectively, then:

$$AA_0 = AA_t + \mathrm{AMINES}_t, \quad (2)$$

where AMINES_t is the MA + EA concentration at time *t*. This also assumes that only trace levels of amines were present in the original gypsum, which is what we found for the modern gypsum from Chula Vista ($Z = 0.04$). Substituting equation 2 into equation 1 yields:

$$\ln(1 + Z) = k_{DC}\cdot t. \quad (3)$$

Equation 3 was used to estimate the rate of decarboxylation (k_{DC}) in gypsum from the various sample localities and these values were used to calculate the half-lives ($t_{1/2}$) for decarboxylation (Table 3).

The calculated $t_{1/2}$ values are in general consistent with the estimated average exposure temperature history of the gypsum samples since deposition. Although the present temperatures at Haughton crater are very cold (average annual temperature of −16 °C), when the crater and sulfate minerals were formed there was an extended period of high-temperature hydrothermal activity (Parnell et al., 2005). Even at 2–3 Ma, temperatures in this region were likely significantly warmer than today (Brigham-Grette and Crater, 1992). At the Anza-Borrego site, present average temperatures are ~23 °C (Remeika and Lindsay, 1992) although average temperatures over the past 5 m.y. have likely been somewhat cooler, especially during Pleistocene ice ages. The modern Panoche Valley average temperature is ~17 °C, but over the past 40 m.y. depositional history of the region, the average exposure temperature was likely higher (Park and Downing, 2001).

The values in Table 3 can be used to estimate the half-life to decarboxylation in gypsum at the temperatures characteristic of Mars using the Arrhenius equation:

$$\ln\left[\frac{t_{1/2}(T_1)}{t_{1/2}(T_2)}\right] = \frac{E_A\cdot\Delta T}{\mathrm{R}\cdot T_1\cdot T_2}, \quad (4)$$

where $t_{1/2}(T_1)$ and $t_{1/2}(T_2)$ are the half-lives of decarboxylation at temperatures T_1 and T_2, respectively, E_A is the activation energy, and R is the universal gas constant (8.314 $\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$). Assuming a mean exposure temperature of ~0 °C for Haughton crater and ~20 °C for Anza Borrego and Panoche Valley, and using the average of the aqueous Arrhenius activation energies for glycine and alanine (~160 kJ/mol) determined in Li and Brill (2003), the half-lives of glycine and alanine decarboxylation in sulfate minerals at Martian temperatures can be estimated (Table 3).

Temperatures on Mars over the past 4 b.y. are considered to be similar to those (<0 °C) that prevail today (Shuster and Weiss, 2005). If the surface paleotemperature on Mars has averaged 0 °C, then $t_{1/2}$ for decarboxylation of glycine and alanine in gypsum is estimated to be $\sim 8 \times 10^8$ yr based on the Anza-Borrego results, $\sim 1 \times 10^9$ using the Panoche sample, and $\sim 2 \times 10^6$ for the Haughton crater sample. If the surface temperature on Mars has averaged −20 °C, then $t_{1/2}$ for decarboxylation of glycine and alanine is much longer, ranging from $\sim 2 \times 10^{11}$ yr based on the Anza-Borrego gypsum, to $\sim 3 \times 10^{11}$ for Panoche Valley, and $\sim 2 \times 10^9$ from the Haughton crater gypsum. The apparently shorter half-lives predicted using the Haughton crater gypsum may be explained by its exposure to either a warmer climate or hydrothermal conditions after deposition, or this may be the result of more recent amino acid contamination diluting the *Z* value. Because of the pristine nature

TABLE 3. ESTIMATED RATES OF DECARBOXYLATION IN GYPSUM

Location	Average Exposure T (°C)	K_{DC} $(\mathrm{years})^{-1}$	$t_{1/2}$ (years)*	$t_{1/2}$ on Mars −20°C (years)	$t_{1/2}$ on Mars 0°C (years)
Anza-Borrego Gypsum	20	1.0×10^{-7}	6.8×10^6	2.2×10^{11}	8.5×10^8
Haughton Crater Gypsum	0	8.1×10^{-8}	8.6×10^6	2.3×10^9	8.6×10^6
Panoche Gypsum	20	7.8×10^{-8}	8.9×10^6	2.9×10^{11}	1.1×10^9

*$t_{1/2} = \frac{0.693}{k_{DC}}$

of the Anza-Borrego gypsum, we consider the $t_{1/2}$ values based on this sample to be the most reliable. These results imply that at modern Martian surface temperatures, amino acids in gypsum should be preserved for periods in excess of several billion years.

The estimated decarboxylation rates in sulfate minerals on Mars are so slow that the limiting factor in the survival of amino acids is likely to be radiolysis in the upper 1–2 m of the regolith by galactic cosmic radiation (Kminek, 2003) and UV-induced (Benner et al., 2000) or metal-catalyzed oxidation (Sumner, 2004). The Martian iron-oxide rich soils may provide a barrier against cosmic radiation, and organic material preservation may be increased at greater depths in the regolith. If jarosite is present at these locations, then its high iron content might assist preservation by offering further shielding against radiolysis. While pure crystalline gypsum is transparent to visible and UV light (Parnell et al., 2004), impure Antarctic gypsum crusts are essentially opaque to radiation below 400 nm (Hughes and Lawley, 2003), and a few millimeters of a similar mineral on Mars should be able to shield gypsum from UV penetration. In the absence of UV light, the contribution of metal-catalyzed oxidation should be minimal. Therefore, amino acids and other organic compounds should be extremely persistent in sulfate minerals at the low temperatures on Mars.

CONCLUSIONS

These results demonstrate that amino acids and other organic compounds are well preserved in terrestrial sulfate minerals. Based on these results, it is predicted that organic matter should be preserved over billions of years on Mars. Amino acids are excellent indicators for the presence of other organic material because they can be detected at very low levels using modern analytical techniques, including ones that potentially can be used to carry out spacecraft-based in situ analyses (Skelley et al., 2005). Their structural diversity and chirality may also provide a unique biological signature, making amino acids excellent targets in the search for evidence of life on Mars (Bada, 2001). Investigations of sulfate-rich evaporite deposits, such as those seen at Meridiani Planum, should be potential targets for organic compounds on Mars.

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