GEOCHEMICAL AND MINERALOGICAL ANALYSIS OF A "SIMPLE" EVAPORITE WITH ORGANIC CARBON ASSOCIATIONS: A ROVER'S-EYE VIEW OF THE TODILTO FORMATION. D. T. Vaniman[1], S. J. Chipera[1], and D. L. Bish[2], [1]Group EES-6, MS D462, Los Alamos National Laboratory, Los Alamos, NM 87545 (vaniman@lanl.gov), [2]Department of Geological Sciences, Indiana University, 1001 E 10th St., Bloomington, IN 47405.

Introduction: Analogies between martian and terrestrial evaporites are limited by differences in brine origins (via groundwater interaction with basaltic crust on Mars, unlike terrestrial granodioritic average crust [1]) and in different environments of subsequent brine evolution. Nevertheless, terrestrial experience in analysis and interpretation of evaporites can aid in the interpretation of martian evaporites, particularly when viewed with an eye to the capabilities of a well-equipped rover, such as the 2009 Mars Science Laboratory (MSL). MSL will combine APXS chemical analyses, standoff chemical analyses by laser-induced breakdown spectroscopy (ChemCam), mineralogy by X-ray diffraction/fluorescence (XRD/XRF - CheMin), and gas chromatography/mass spectrometry (SAM).

The Todilto Formation: The Todilto Formation (Figure 1) is a major mid-Jurassic evaporite sequence that extends over 150,000 km^2 of NW New Mexico and SW Colorado, USA [2,3]. Despite great areal extent, the deposits are thin (<30 m) and in broad scale mineralogically simple, with a basal limestone unit and an upper Ca-sulfate unit (gypsum where burial is shallow, anhydrite where deeply buried beneath later strata of the Colorado Plateau). The deposits are also simply zoned, vertically and concentrically, with the limestone unit more widespread and the Ca-sulfates more restricted, centrally located, and overlying the limestone.

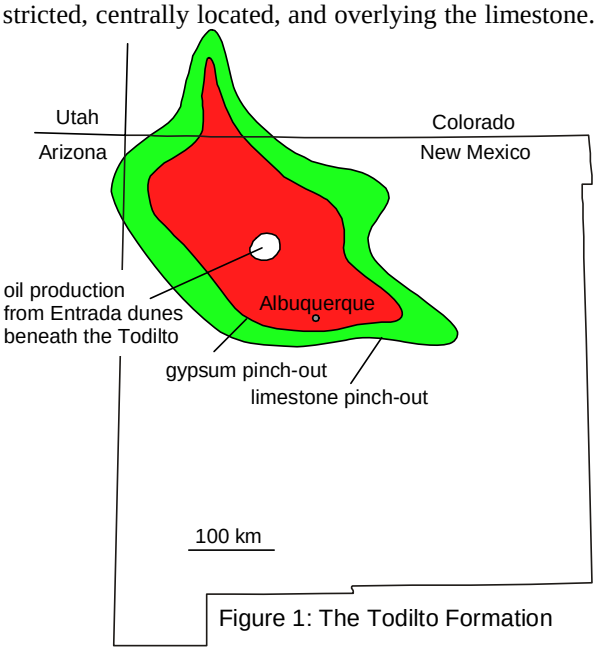

Figure 1: The Todilto Formation

Despite apparent simplicity, the origin of the Todilto is controversial, with conflicting marine and lacustrine interpretations. Current interpretation favors origin as a salina that flooded the eolian dune field of the underlying Entrada Formation, very rapidly yet gently enough to preserve underlying dune forms [3,4]. Viewed from orbit, the visible outcrops could be pieced together to present a large, simple target with many spots where a rover might be deployed. The fact that the lower limestone section of the Todilto hosts high total organic carbon is a critical feature that would be important to target but would likely not be seen from orbit.

New Data: We sampled a Todilto section north of Echo Amphitheater, NM. Samples were analyzed by optical petrography, electron microprobe, XRD, and solution ICP-MS of mineral separates. The basal limestone, ~1 m thick, is finely laminated and fissile with 98% calcite, 1% gypsum (both ~5 μm), and traces of kaolinite and detrital quartz (~20 μm) with thin bituminous laminae. This limestone is overlain by a zone of ~2 m with 75% calcite (clusters of ~5 μm grains rimmed by 20 μm grains), 24% gypsum (~0.5 mm, subhedral), and traces of smectite plus detrital quartz; this zone is poorly stratified and the gypsum occurs in nodules up to ~3 cm. The upper unit is massive, ~10 m thick, with 6% calcite, 1% dolomite (both 5-40 μm), 92% gypsum (~1 mm, anhedral), and traces of bassanite, smectite, and detrital quartz. This unit has a "chicken wire" fabric of 1-5 cm gypsum nodules separated by carbonate-mineral septae a few mm thick.

The Todilto provides an opportunity for examining minor-element partitioning between calcite/dolomite and coexisting gypsum in an evaporite sequence. Table 1 compares compositions determined by solution ICP-MS for gypsum and Ca,Mg-carbonates early in the Todilto sequence (transition zone) and late (upper unit). Barium, transition metals, lanthanides, and actinides are ~4x to 100x concentrated in early carbonate (calcite) relative to early gypsum. In the later deposit, minor element enrichment in carbonate versus sulfate minerals is similar except for strontium, which may be concentrated in bassanite [5]. Magnesium concentration in the later deposits is minimal in gypsum but a 6x increase in carbonate magnesium (Table 2) produces dolomite along with calcite.

Table 1: Early→Late Minor and Trace Elements in Todilto Carbonates (carb) and Gypsum (gyp) (μg/g)

carb[1]	Mn	Zn	Sr	Ba	La	U
early	360	4.1	4450	200	0.25	1.1
late	480	2.2	230	30	0.44	1.4
gyp	Mn	Zn	Sr	Ba	La	U
early	3.4	1.2	3300	40	0.02	n.d.[2]
late	2.5	1.3	800	4	0.01	<0.1

[1]early carbonate is calcite; late carbonate is 86% calcite, 14% dolomite; [2]n.d. = nondetect

Table 2: Late Appearance of Dolomite: Mg in μg/g

	early	late
cc → cc + dol	4500	27,000
gypsum	38	70

Relevance to Mars? We state in the introduction that analogies between terrestrial and martian evaporites are limited. However, many features of the Todilto suggest useful comparisons.

Catastrophic flooding of eolian deposits. Preservation of the underlying Entrada dune field has been interpreted as evidence for rapid flooding that "froze" it in place [4]. Flooding was deep enough (~90 m [2]) that tidal and wave action did not perturb the initial Todilto limestone precipitation, which laminated and preserved the underlying dunes. Evidence of catastrophic flood events is widespread on Mars; such floods may account for Ca-sulfate deposits seen from orbit [6]. If eolian deposits were as widespread on Mars at the time of flooding as now, sedimentologic settings similar to the Todilto/Entrada could occur.

Carbonate to sulfate evolution. It is unlikely that any Mars brine was "just like" the brines that produced the Todilto. Carbonate-sulfate assemblages in martian meteorites point to Fe-rich systems in which initial carbonate precipitation is siderite, not calcite [7]. The smaller octahedral site in siderite (13.1 $Å^3$, vs. 17.5 $Å^3$ in calcite) may limit accumulation of alkaline earth, lanthanide, and actinide elements. Will gypsum that coexists with siderite incorporate more of these elements, or will other salts acquire them (e.g., celestine?). If bassanite is more common, it could incorporate much of the strontium in the brine [5]. The chemical and mineralogical capabilities of MSL can answer questions such as these.

Shielding - and obscuring - carbonate minerals. Surface and orbital missions point to a Mars-wide lack of visible carbonate minerals. However, if the Todilto were on Mars, would the lower limestone unit be seen? Acid weathering would likely have leached most of the carbonate minerals in the upper gypsum unit (the basal limestone may be preserved but it is hidden from view). The concentric zoning characteristic of evaporite basins – for the Todilto, gypsum ringed by calcite (Figure 1) – would be destroyed if weathering has altered most of the outer carbonate zone. If small amounts of carbonate remain, MSL can identify carbonate minerals in abundances as low as ~1%.

Gypsum, bassanite, anhydrite, or all three? Although gypsum is the principal sulfate mineral in Todilto outcrops, small amounts of bassanite also occur, apparently formed late in the evaporation sequence when activity of water was very low. Would bassanite be more common in evaporites of a water-starved planet? More certain is the formation of anhydrite where units with primary gypsum are buried under later sediments or heated by igneous or impact processes. Beneath the Colorado Plateau the Todilto is buried under ~1800 m of younger sediments; at these depths anhydrite occurs rather than gypsum. Along Valles Marineris, Ca-sulfates are exposed in the canyon walls at depths of several km [6]; such depths of burial may provide P,T conditions sufficient to convert gypsum to anhydrite (with 21 wt.% water evolution). The phases in which Ca-sulfates occur carry significant petrogenetic information, and these phases will be determined by the XRD/XRF capability on MSL.

Exobiology? Brines are not a favored habitat for most higher life forms, as evidenced by paucity of fossils within the Todilto, yet the Todilto is a hydrocarbon source. Oil has migrated beneath the Todilto and accumulated in preserved dune crests of the Entrada. The oil is unique, with a low pristine/phytane (acyclic C_{19}/acyclic C_{20}) ratio and a lack of lighter species ($<C_{10}$) in gas chromatography [8]. This organic carbon is likely derived from algae and bacteria [2]. Remnant bitumens left after oil migration are concentrated in the basal Todilto limestone. The link to Mars is speculative, but consider that MSL will carry a gas chromatograph/mass spectrometer with a sample pyrolysis oven capable of releasing and characterizing bituminous or kerogen forms of organic carbon.

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