SULFUR CYCLING IN GYPSUM DUNES FROM NEW MEXICO – TERRESTRIAL ANALOGS TO SULPHATE-EOLIAN DEPOSITION AND EARLY DIAGENESIS ON MARS.
A. Szynkiewicz[1], L.M. Pratt[1] and M. Glamoclija[1], [1] Indiana University (Department of Geological Sciences, 1001 East 10th Street, Bloomington, IN 47405-1405, aszynkie@indiana.edu, prattl@indiana.edu, mglamocl@indiana.edu).

Introduction: Recent data obtained by Opportunity rover and by OMEGA spectrometer on the Mars Express spacecraft reveal important occurrences of sulfate minerals at localities in the north polar region (Olympia Planitia (OP)) and at lower latitudes in Meridiani Planum (MP) and Vallis Marineris (VM)) [i.e. 1, 2]. Sulfates appear to be a constitutive and substantial part of rock and regolith exposed on the surface of Mars.

Volcanic activity and impact cratering are suggested as primary sources of sulfur (S), while subsequent weathering of S-bearing magmatic fluids and mineral phases likely caused deposition of sulfate phases at or near the surface [1]. Since Mars has a markedly variable hydrologic history and lower rate of tectonic activity compared to Earth, weathering processes of magmatic rocks in surface/subsurface environments are important potential factors influencing sulfate deposition. Eolian weathering, as the most common among geologic processes operating in modern Martian environments, appears to play a key role in distribution and formation of sedimentary deposits. Eolian sediments at MP appear to have been lithified in the presence of water allowing for development of deposits that are 7m in thickness [3]. Formation of gypsum dunes at OP likely involved short-term fluvial activity derived from ice melting events followed by eolian weathering [4]. Intermittent hydrological activity on the surface followed by infiltration would sustain diagenetic processes on the surface or in shallow subsurface environments.

Enrichment of surface sulfates suggests that Mars has a sulfur-rich mantle and core. Martian meteorites contain ~ 10× higher sulfur content than their igneous analogs on Earth. It is not clear, however, how the sulfur cycle functions on Mars. Fluxes and reservoirs remain to be determined for volcanism, acidic weathering of basaltic rock, physical erosion and transportation of S-rich sediments, and dissolution during short-term water release triggered by volcanism and/or impact cratering?

We propose a latitudinal study of Salt Basins associated with the Rio Grande Rift in order to asses the terrestrial sulfur cycle in regions influenced by volcanism and formation of sulfate-rich dunes at regional and local scales. Relatively little information is available concerning early diagenetic processes in surface and shallow subsurface environments with hydrological regimes showing marked seasonal and decadal climate variations.

Here we present preliminary data concerning sulfur and hydrogen isotope composition of gypsum deposits in two salt basins within the Rio Grande rift basin: Estancia (EB) and Tularosa (TB). Both the EB and TB salt basins are located to the east of the main structural axis of the rift. Isotopic signatures are used to reconstruct influences of evaporation, dissolution, bacterial sulfate reduction, sulfide oxidation, and magmatic/hydrothermal input. Eolian sedimentary structures recognizable from satellite images allow reconstruction of geological sequences including recent lithification and currently dune migration.

Geological settings and sampling: The Rio Grande Rift (RGR) is one of the world's principal continental rift systems, extending as a series of asymmetrical grabens and linear, sediment-filled depressions. The RGR is more than 1000 km in length with an average width of 60-70 km. Structural development of the rift occurred mainly during two time intervals with an early phase beginning at ~30 Ma and lasting 10-12 million years, and a late phase extending from ~ 10 to 3 Ma [5]. Volcanism associated with the RGR is modest compared to other continental rifts. Eruptions are dominantly basaltic and less than ~ 5 million years in age.

Evolution of the RGR resulted in formation of topographically closed basins which filled with latitudinal variable detrital and evaporitic lake sediment. During the last glacial maximum in the late Pleistocene, the climate was distinctively colder and wetter than current conditions in this area. Topographic closure favored formation of temporary, highly mineralized lakes in which thick layers of evaporitic precipitates were deposited as climate shifted to increasing aridity during the Holocene [6,7]. It was proposed that dissolution of Permian evaporates is the main source of sulfur for formation of sulfate rich-deposits.

Gypsum dunes are present in all salt basins included in this study. White Sands National Monument (WSNM) located in the TB contains the largest dunes in the RGR area. Langford [6] proposed that gypsum dunes in WSNM were formed in at least two or three episodes of intensified aridity which is consistent with two episodes of gypsum dunes formation in the EB inferred by [8].

All of the studied gypsum dunes show substantial development of gypsum cementation. This process is relatively young and probably directly associated with dunes formation. Allen [8] and Langford [6] reconstructed the main phase of dunes formation between 11,000 and 4,000 years ago. Early diagenesis of gypsum dunes in the RGR appears to be active and, notably, to be taking place in close to the dune surface. Activation of early diagenesis is related to interaction of gypsum grains with the water table and occurs in the capillary fringe and phreatic zones [9]. Seasonal downward infiltration of meteoric precipitation causes cementation in the upper parts of dune because gypsum is a readily soluble mineral. Dissolution and recrystallization lead to formation of up to 10 meter-thick, cemented, gypsum deposits. Duration of cementation, however, has not been described in details.

Results and discussion: Stable sulfur isotope compositions have determined for: 1) lake sediments deposited along the margin of Late Pleistocene Lake Otero in the TB and 2) lake sediments in the older part (>25,000 years) of the exposed lacustrine sequence in the EB. Both basins show significant variation in $\delta^{34}S$ of gypsum deposits and show distinct differences from $\delta^{34}S$ of Permian evaporates (average 12.33 ‰) considered as a main source of sulfate in that area. In TB, $\delta^{34}S$ for gypsum in lake sediment varies from -1.08 to 12.71 ‰ and in EB, from -2.09 to 19.71 ‰.

In TB, there are two events in which $\delta^{34}S$ of sulfate show excursions to negative values, Event 1 occurred around 30,000 years ago and Event 2 around 20,000 years ago. Negative excursions in $\delta^{34}S$ of gypsum are most easily explained by oxidation of previously anoxic sediment containing sulfide (pyrite, monosulfide minerals or sulfidic pore water) produced during decomposition of organic matter by sulfate reducing bacteria.

The sulfate derived from oxidation of hydrogen sulfide with biological and magmatic origins have overlapping but generally distinct sulfur isotope compositions. Common values of $\delta^{34}S$ for biogenic sulfide in saline lakes range from -40 to 0 ‰ while magmatic sulfides from basaltic sources are general in the range of -2 to +2 ‰. A calculation based on isotope mass balance suggests that negative excursions in TB sediments can be explained by mixing of sulfate from Permian evaporates with: 1) 15 to 55 % of bacterial sulfide reoxidized to sulfate or 2) 30 to 90 % of magmatic sulfide reoxidized to sulfate. More detailed study of sulfur and oxygen isotopic signatures for sulfate combined with hydrogen and oxygen isotopic signatures in associated hydration water will help to constrain these types of calculations.

Eolian deposits: Landsat images of TB barchan dunes revealed partially buried, underlying cemented paleodunes. Orientation of cross bedding indicates a consistent direction of dune migrations. Internal structure and shape, however, suggest different hydrological regimes and depth to top of groundwater. Current eolian erosion and deposition is driven by winds from the southwest. Active dune migration exposes underlying cemented portions of older dunes. This process is probably important in erosion of gypsum sand and formation of new eolian deposits. More detailed chemical and isotope analyses will be required to estimate rates of cementation and changes in precipitation patterns.

Eolian dunes in EB are smaller than the dunes in TB and do not show easily recognized sedimentary structures on Landsat images due to coverage by grass. The values of $\delta^{34}S$ for two dune deposits in the south part of EB showed very narrow range from 19.1 to 20.5 ‰ suggesting relatively homogenous sources of gypsum for eolian deposition. Values of $\delta^{2}H$ for hydration water in gypsum vary from -57 to -51 ‰ and correlates well with $\delta^{2}H$ for modern precipitation.

Geochemical (major and trace elements) and stable isotopic (S, O, and H) compositions of field samples will be combined with geomorphological analysis of satellite images in order to study: 1) local and regional influences of volcanism on sulfur cycles in the salt basins associated with the Rio Grande Rift; 2) formation and transformation of sulfate-rich deposits in saline lakes and playas from closed-drainage basins; 3) erosion of evaporitic crusts and eolian grain transportation at sites of gypsum dune formation; 4) conditions required for early diagenesis in gypsum dunes under arid and semi-arid climate condition. A latitudinal study extending 700 km along the Rio Grande Rift will improve predictions about sulfur cycling due to eolian processes and intermittent surface water on Mars.

Acknowledgments: This study was supported by the NASA Astrobiology Institute team award directed by L.M. Pratt. Sincerest thanks are due to Bruce Allen for recommending field sites and providing gypsum sediments from Tularosa Basin.

References: [1] Fishbaugh K.E. et al. (2006) *LPSC XXXVII,* Abstract#1642. [2] Hynek B.M. (2004) *Nature,* 43, 156-159. [3] Knoll G.H. et al. (2005) E*PSL, 240, 179-189*. [4] Fishbaugh K.E. and Head J.W. (2005) *Icarus,* 174, 444-474. [5] Olsen et al. (1987) *Tectonophys, 143, 119-139*. [6] Langford R.P. (2003) *Quatern Internat, 104, 31-39*. [7] Allen B.D. (2005) *New Mexico Museum of Natural History and Science, Bulletin 28, p. 107-114*. [8] Allen B.D. (1991) *New Mexico Bureau of Mines and Mineral Resources 137, 166-171*. [9] Schenk C.J. and Fryberger S.G. (1988) *Sedimen Geol 55, 109-120*.