

*New Mexico Geology* recognizes the important research of students working in post-graduate M.S. and Ph.D. programs. The following abstracts are from M.S. theses and Ph.D. dissertations completed within the last 12 months that pertain to the geology of New Mexico and neighboring states.

### New Mexico Institute of Mining and Technology

**CO<sub>2</sub> SEQUESTRATION IN THE PERMIAN BASIN: EXAMINATION OF ABOVE-GROUND MINERALIZATION AND SUBSURFACE SOLUBILITY TRAPPING CAPACITIES AND EVALUATION OF DAWSONITE KINETICS IN GEOLOGIC SEQUESTRATION**, by Aaron P. Abel, 2008, M.S. thesis, Department of Earth and Environmental Science, New Mexico Institute of Mining and Technology, Socorro, New Mexico 87801, 141 pp.

Anthropogenic CO<sub>2</sub> emissions are widely proposed as a cause of global-scale temperature increases, leading to extensive research efforts on the mitigation of anthropogenic CO<sub>2</sub> emissions through a variety of carbon sequestration options.

The purpose of this study was designed to evaluate two different carbon sequestration options. Sequestration of CO<sub>2</sub> through biominerally increasing the hydration rate of CO<sub>2</sub> to accelerate the formation of solid carbonate has already been tested and proven (summarized by Bond, Abel et al.). Solid carbonate minerals effectively sequester CO<sub>2</sub> indefinitely, but formation of these minerals requires a source of cations, such as seawater or waste brines. Produced waters from the oil and gas industry have been proposed as one possible cation source in this sequestration option that we call "surface mineralization." Additionally, direct subsurface injection of bicarbonate-rich waters (by-product of surface mineralization) was considered. Carbon sequestration capacities were estimated for both the formation of solid carbonate with cations from produced waters (surface mineralization) and the storage of CO<sub>2</sub> in dissolved form within produced waters ("solubility trapping") for a study area comprising the Permian Basin of west Texas and southeastern New Mexico.

Results of the capacity study indicate that cations from produced waters in the Permian Basin could be used to sequester approximately 57% (2.97 million metric tons [Mt] of CO<sub>2</sub>) of the Permian Basin's regional CO<sub>2</sub> production (total CO<sub>2</sub> emission of 5.19 Mt), or ~20% of the total production from the Permian and San Juan Basins combined (15.5 Mt), in the form of solid carbonate minerals. Storage of CO<sub>2</sub> in dissolved form ("solubility trapping") within produced waters provides for a vast amount of CO<sub>2</sub> storage (approximately 30 Mt); however, the total inorganic carbon already present within produced waters significantly decreases the additional sequestration capacity by approximately 200 fold (0.157 Mt of CO<sub>2</sub>).

Direct injection of supercritical CO<sub>2</sub> in the Permian Basin provides for a vast storage potential; however, this method may cause significant physio-chemical effects in the reservoir, potentially affecting long-term sequestration capacities as well as short-term engineering operations.

Mineralization reactions in the "fringe" of CO<sub>2</sub> plumes may cause significant changes to porosity and permeability of rock strata, and hence to ultimate CO<sub>2</sub> migration. We hypothesize that mineralization of the plume fringe, specifically that associated with dawsonite formation, may restrict plume migration, and that flow rates, chemical kinetic relationships, and other conditions will determine whether the CO<sub>2</sub> plume will be slowed in its migration or even trapped in place by such mineralization at its fringe.

To test these hypotheses, we studied an ongoing pilot CO<sub>2</sub> injection test (West Pearl Queen reservoir pilot test). Two-dimensional numerical models of CO<sub>2</sub> flow and transport were designed to evaluate possible residence times of separate-phase CO<sub>2</sub> in the injection test. Geochemical simulations of brine-rock interactions have been used to examine mineralization and dissolution effects on the reservoir and adjacent formations.

Results of reactive transport (TRANS) and reaction path modeling (Geochemists Workbench™) of supercritical CO<sub>2</sub> injection into the West Pearl Queen reservoir indicate an overall dissolution-dominated system with a gradual increase of porosity over the model domain at the CO<sub>2</sub> injection point. A complex system of dissolution and precipitation reactions occur over the model domain with the aluminum carbonate mineral dawsonite providing an important carbon sink associated with feldspar-rich reservoir types. Increases in dawsonite volume fraction of 0.14 over the entire model domain occur over a period of approximately 40,000 yrs, whereas the pre-existing minerals anhydrite, albite, potassium feldspar, and dolomite completely dissolve over the same simulation time. In simulations of injected supercritical CO<sub>2</sub>, porosity decreases approximately 4% from the initial value (0.146 to 0.105) in the target reservoir over ~40,000 yrs. However, timing of initiation of dawsonite precipitation and associated porosity reduction can not be constrained due to inconsistencies of published mineral kinetic rate constants of the aluminum-providing feldspar minerals. Literature values of kinetic rate constants for aluminosilicate minerals such as potassium feldspar (KAlSi<sub>3</sub>O<sub>8</sub>) and albite (NaAlSi<sub>3</sub>O<sub>8</sub>) vary over 3 to 4 orders of magnitude (e.g., between 1.0 × 10<sup>-17</sup> and 1.62 × 10<sup>-13</sup> mole/cm<sup>2</sup>-seconds for KAlSi<sub>3</sub>O<sub>8</sub> and between 1.0 × 10<sup>-16</sup> and 3.63 × 10<sup>-13</sup> mole/cm<sup>2</sup>-seconds for NaAlSi<sub>3</sub>O<sub>8</sub>). The range in these kinetic rate constants leads to a range of values for dawsonite precipitation timing from less than 2 yrs up to approximately 12,000 yrs in the present study, greatly influencing the ultimate fate and transport of CO<sub>2</sub> within the system.

**GEOPHYSICAL INVESTIGATION TO ASSESS GEOTHERMAL ENERGY POTENTIAL, SOCORRO PEAK, NEW MEXICO**, by Richard M. Baars, 2008, M.S. thesis, Department of Earth and Environmental Science, New Mexico Institute of Mining and Technology, Socorro, New Mexico 87801, 121 pp.

The Socorro Peak uplift in central New Mexico is the center of a local zone of high heat flow indicated by shallow thermal gradient wells that encountered heat flow as high as 490 mW/m<sup>2</sup> and measured temperatures of 43°C at 60 m depth. Aqueous geochemistry and mixing relationships in warm springs (32°C) suggest that high Cl fluids at depth have temperatures of over 92°C. A variety of geochemical and geophysical studies, particularly magnetotelluric soundings and soil geochemistry

profiling, have identified a drilling location in the Rio Grande basin near Wood's Tunnel on the east flank of Socorro Peak to target a >60°C geothermal reservoir at <1,000 m depth. An exploration hole has been drilled to determine if geothermal reservoir with sufficient temperature and capacity to provide direct use heating for the New Mexico Tech campus.

High-resolution magnetotelluric traverses, conducted at a 100 m station spacing, were employed to characterize the distribution of resistivity across the range bounding fault on the east side of the Socorro Peak uplift. One- and two-dimensional inversions of the data show a steeply dipping range-bounding fault juxtaposing resistive footwall Precambrian and Paleozoic rocks and Tertiary volcanics against conductive hanging wall conglomerates. Within the hanging wall block, the MT profile data identify a 400 m thick aquitard that separates shallow aquifers from deeper target thermal waters. Other geophysical surveys were conducted to confirm the results of the magnetotellurics. Gravity data was modeled to verify Socorro Canyon fault characteristics. An interesting database of remote sensing thermal images was discovered showing initially that the Socorro Peak thermal feature can be seen from space. Further work with these images must be done to validate the thermal feature.

A choice of the drilling target was based on a synthesis of thermal gradient data, the geophysical and geochemical information (Owens 2007), geologic structure, hydrologic models, and economic factors. The slimhole well was drilled on the Woods Tunnel mine portal pad west of the Socorro Canyon fault near the area of highest measured heat flow, and near the intersection of the Socorro caldera fracture system, a transverse shear zone, and the Rio Grande rift bounding fault, and close to the New Mexico Tech campus. Fluid leakage up or across the range front fault system is a likely host for deep >65°C thermal waters. The borehole will penetrate both the faulted structural conduit as well as permeable sediments below the aquitard within the hanging wall block to evaluate multiple hypotheses for the source of the heat flow anomaly.

**OBSIDIAN HYDRATION AND ITS CONSEQUENCES FOR THE AR-AR DATING METHOD**, by Ariel K. Dickens, 2008, M.S. thesis, Department of Earth and Environmental Science, New Mexico Institute of Mining and Technology, Socorro, New Mexico 87801, 169 pp.

Volcanic glass has been a problematic material in Ar-Ar geochronological studies, in part due to hydration and the resultant element mobility of K and Ar. Ar-Ar and electron microprobe results from a systematic investigation of obsidian show that obsidian hydration can affect the precision and accuracy of apparent Ar-Ar ages, but these effects can be mitigated by specialized sample preparation techniques.

A select suite of variably hydrated obsidian samples were collected from the No Agua Peaks volcanic complex, New Mexico, to systematically investigate how four preparation and four Ar-Ar extraction techniques affect obsidian ages. Obsidian samples prepared by different preparation techniques were chemically imaged and analyzed by an electron microprobe to assess chemistry and element mobility. Microprobe results show that the hydration process does not cause significant element mobility, and most

water is concentrated within the hydration rinds. A long ultrasonic bath in water or the air abrasion preparation technique were determined the best methods to remove hydration rinds. Multi-step laser or furnace extractions were shown to be the best extraction methods. Once preparation and extraction methods were established, all other samples were dated. At the No Agua Peaks volcanic complex two temporally distinct eruptive events,  $3.86 \pm 0.06$  Ma and  $4.07 \pm 0.03$  Ma, were dated. These events are chemically distinct, and the ages match stratigraphy with a meter-thick paleosol developed between the two eruptive events.

Six mapped lobes at Cerro del Medio were dated in this study; the age of Cerro del Medio brackets the resurgence of Redondo Peak with the eruption of the Bandelier Tuff. There are two probable scenarios for formation of Cerro del Medio, based on whether the oldest sanidine ages are influenced by xenocrystic material. In the first scenario Cerro del Medio started forming at  $1.22 \pm 0.02$  Ma in as many as three temporally resolvable pulses, periodic dome building was sustained for  $0.08 \pm 0.04$  Ma, and resurgence was completed within  $0.08 \pm 0.04$  Ma after the eruption of the Bandelier Tuff. In the second scenario, which considers the oldest lobe ages being influenced by xenocrysts, Cerro del Medio formed in as many as two temporally resolvable events starting at  $1.18 \pm 0.03$  Ma. In this scenario dome building lasted for  $0.05 \pm 0.04$  Ma, and resurgence was completed within  $0.08 \pm 0.04$  Ma.

Four samples of post 0.5 Ma units associated with the Valles caldera were dated to determine the youngest ages of activity, and to assess associated volcanic hazards. Of the four samples dated in this study, only one age appears accurate at  $0.257 \pm 0.088$  Ma. Using ages from the current and previous studies there are two preferred age scenarios: 1) the units are  $0.25 \pm 0.06$  Ma, or 2) if xenocryst contamination is affecting Ar-Ar ages, then an age of  $0.054 \pm 0.005$  Ma, based on results from four non-K-based methods, may be more accurate.

**SENSIBLE AND LATENT HEAT FLUX ESTIMATION USING OPTICAL SCINTILLOMETRY**, by *Jesus D. Gomez*, 2008, M.S. thesis, Department of Earth and Environmental Science, New Mexico Institute of Mining and Technology, Socorro, New Mexico 87801, 90 pp.

The estimation of spatial and temporal distributions of sensible (H) and latent ( $\lambda ET$ ) heat fluxes is a long standing challenge for hydrologic science. In this study, we present our experiences with the emerging method of scintillometry. Large Aperture Scintillometers (LAS) operating at optical wavelengths are employed to measure the sensible heat flux over irrigated fields, riparian areas, deserts, lava flows, and mountain highlands in New Mexico. The LAS transects were used to explore this measurement technique as a potentially useful tool in hydrological applications.

The main theoretical and technical aspects of the setup, operation, and analysis of LAS data are discussed. The advantages of a larger footprint, compared with other standard techniques used for the measurement of H, are explained, particularly in the context of the calibration and validation of remote sensing algorithms used for the estimation of turbulent fluxes, and hydrologic

and meteorological models. Although, the measured data were not compared with remote sensing data, some of the main issues of this comparison are addressed and will be the objective of future research. Finally, scintillometer data were used for the estimation of sensible (averages over 10-min and daily time intervals) and latent (averages over daily time intervals) heat fluxes.  $\lambda ET$  was estimated as the residual of the surface energy balance (SEB), assuming closure, as an example of the estimation of evapotranspiration rates for hydrologic applications at scales of the pixel-size of satellite images or grid cells of hydrologic and meteorological models ( $\sim 0.1$ – $10$  km<sup>2</sup>).

**MINERALOGICAL AND GEOCHEMICAL CHANGES ASSOCIATED WITH SULFIDE AND SILICATE WEATHERING IN NATURAL ALTERATION SCARS, TAOS COUNTY, NEW MEXICO**, by *Gabriel J. Graf*, 2008, M.S. thesis, Department of Earth and Environmental Science, New Mexico Institute of Mining and Technology, Socorro, New Mexico 87801, 180 pp.

Natural alteration scars occur along the Red River valley, New Mexico, and were studied as mineralogical analogs to future weathering in rock piles created by Chevron Mining, Inc., (formerly Molycorp, Inc.) during open-pit mining from the Questa mine. These natural alteration scars provide a glimpse into weathering that may affect these rock piles in the long term (up to 4.5 m.y.; Lueth et al. 2006). The alteration scars provided excellent analogs to the rock piles because they are located within proximity ( $\sim 2$  mi) of the Questa mining operation and contain similar lithologies and hydrothermal alteration mineral suites. The weathering processes (sulfide and silicates) and overall architecture of these systems (open) appear very similar.

Three distinct weathering profiles were collected in the Hansen and Southwest Hansen alteration scars to document chemical and mineralogical changes that occur related to sulfide and silicate weathering. These weathering profiles are different from classic weathering profiles because they were profoundly influenced by hydrothermal alteration and commonly contain multiple lithologies.

Within each profile particle size decreases upward, which suggests physical weathering processes are active. The mineralogical changes associated with grain size reduction include pyrite oxidation with the precipitation of gypsum, jarosite, and Feoxides. Acid base accounting has documented limited acid consuming minerals (i.e., calcite) to buffer the acid created during pyrite oxidation. Stable isotope analysis of pyrite and gypsum indicate  $\delta^{34}S$  pyrite range from  $-1.0$  to  $-6.6\%$ .  $\delta^{34}S$  of gypsum range from  $-2.1$  to  $-5.1\%$  and gypsum  $\delta^{18}O_{SO_4}$  range from  $-7.0$  to  $5.2\%$ . These data provide convincing evidence that sulfates within the alteration scars are formed only in the weathering environment.

Silicate mineralogical changes through the weathering profiles include decreasing feldspar and increasing clay upward. The working hypothesis was silicate mineral changes result from feldspar weathering to form secondary clay minerals. Clay mineral analysis, however, indicates the clay minerals are similar to hydrothermal alteration minerals. Much of the fining upward character may be due to hydrothermal alteration. Clay mineral stable isotope analysis,

$\delta^{18}O$  ( $-0.3$  to  $4.6\%$ ) and  $\delta D$  ( $-65$  to  $-95\%$ ), documents the clays analyzed are hydrothermal in origin and provide no evidence for weathering clays. Review of USGS (Nordstrom et al. 2005) ground and surface water geochemistry, along with silicate mineral observations, indicate congruent dissolution of silicate minerals is active in the alteration scars.

The major active chemical weathering system in the alteration scars is the oxidation of pyrite. The soil pH of 2 to 3 is compatible with silicate minerals dissolution, and the chemical conditions do not favor precipitation of new clay minerals. Physical weathering in the alteration scars continues by freeze-thaw and precipitation of gypsum that causes a volume increase, providing pathways for fluid and oxygen for the further oxidation of pyrite. This acidic environment is responsible for the precipitation of jarosite and gypsum and dissolution of silicate minerals. Sulfide weathering will continue to occur in the alteration scars until the remaining pyrite has oxidized.

**EVALUATION OF CO<sub>2</sub> TRAPPING MECHANISMS AT THE SACROC NORTHERN PLATFORM: SITE OF 35 YEARS OF CO<sub>2</sub> INJECTION**, by *Weon Shik Han*, 2008, Ph.D. dissertation, Department of Earth and Environmental Science, New Mexico Institute of Mining and Technology, Socorro, New Mexico 87801, 426 pp.

The main purpose of this study is to assess the potential fate of CO<sub>2</sub> when it is injected in the deep subsurface for storage. In the coming year (2008), more than 20 field geologic sequestration tests are being designed and scheduled for deployment in the United States. An additional 23 are ongoing or slated for deployment soon in other countries. For large-scale geologic sequestration to be deployed and sustainable over the long-term, a meaningful assessment of CO<sub>2</sub> trapping mechanisms is essential. Therefore, the chapters in this dissertation are each part of a detailed study of the physical and chemical processes associated with CO<sub>2</sub> trapping mechanisms.

First, two integrated equations of state (EOS) algorithms were assembled to evaluate multi-phase transport of carbon dioxide (CO<sub>2</sub>). One integrated EOS is based on Redlich and Kwong's original algorithm developed in 1949, and the other is based on a more recent algorithm developed by Span and Wagner in 1996. Both algorithms calculate solubility, compressibility factor, density, viscosity, fugacity, and enthalpy of CO<sub>2</sub> in gaseous and supercritical phases, and mixtures or solutions of CO<sub>2</sub> in water, as functions of pressure and temperature. In general, the predictions of thermophysical properties for both algorithms are close, except for a contrast in the predicted fugacity coefficient of CO<sub>2</sub>, which subsequently propagates to a contrast in predicted solubility in water/brine.

To facilitate a general comparison of these EOS algorithms, one-dimensional flow models were developed. Simulation results suggest that dissolution rates of separate-phase CO<sub>2</sub> predicted from the two EOS algorithms are significantly different, resulting in markedly different CO<sub>2</sub> migration patterns.

Finally, a specific case study of CO<sub>2</sub> trapping mechanisms and related processes was carried out using numerical simulation. The site of the case study was the SACROC (Scurry Area Canyon Reef Operators Committee) Unit in the

Permian Basin of Texas, the oldest continuous CO<sub>2</sub> enhanced oil recovery (EOR) site in the United States. SACROC has been subjected to CO<sub>2</sub> injection for 35 yrs, and thus it provides an excellent field laboratory for this analysis. Not all CO<sub>2</sub> injected for EOR has been recovered, and thus some is trapped in the subsurface. A comprehensive numerical model was developed for analyzing the range of possible trapping mechanisms and other related physical and chemical effects of the injected CO<sub>2</sub>. Data used to parameterize the three-dimensional model include spatial distributions of seismic- and core-derived porosity and permeability that were estimated by the Texas Bureau of Economic Geology.

Two separate models were developed for the analysis of CO<sub>2</sub> trapping mechanism. The first model was designed for simulating CO<sub>2</sub> trapping mechanisms in a reservoir saturated with brine. The other model was designed for simulating CO<sub>2</sub> trapping mechanisms in a reservoir saturated with both brine and oil.

CO<sub>2</sub> trapping mechanisms in the brine-only model show a distinctive set of stages. In stage I (1972~2002), the same as the original injection period, hydrostratigraphic trapping is dominant. In stage II (2002~2017), residual trapping dramatically increases. In stage III (2017 to several hundreds years), solubility trapping becomes important because over time both the residual and mobile CO<sub>2</sub> dissolve in the brine. Finally, at stage IV (~after several thousand years), mineral trapping is predicted to be greater than any other mechanisms. In sum, the major CO<sub>2</sub> trapping mechanisms were hydrostratigraphic (mobile), residual, and solubility trapping during 200 yrs.

However, in the brine (28%) plus oil (72%) model, the CO<sub>2</sub> trapping mechanisms do not vary much over time. Separate-phase CO<sub>2</sub> is stored as a free (mobile) form due to its high saturation, but it behaves like residual (immobile) CO<sub>2</sub> because of the smaller contrast between fluid densities of oil and CO<sub>2</sub>. Further, CO<sub>2</sub> mobility is hindered by other fluids such as brine and oil in the model due to the reduction of relative permeability. In sum, both oil trapping and hydrostratigraphic (mobile) trapping were dominant mechanisms during 200 yrs.

The combined results of these two model analyses suggest that injecting CO<sub>2</sub> into brine formations below oil reservoirs will provide several advantages in terms of CO<sub>2</sub> storage capacity and protection from potential leakage.

Results of this dissertation are intended to provide insight regarding effective approaches for geologic CO<sub>2</sub> sequestration. Specifically, understanding the potential range of CO<sub>2</sub> trapping mechanisms in typical reservoirs may help scientists and engineers evaluate sequestration operations to maximize trapping and minimize risks.

**MAPPING REGIONAL DISTRIBUTIONS OF ENERGY BALANCE COMPONENTS USING OPTICAL REMOTELY SENSED IMAGERY**, by *Sung Ho Hong*, 2008, Ph.D. dissertation, Department of Earth and Environmental Science, New Mexico Institute of Mining and Technology, Socorro, New Mexico 87801, 355 pp.

Precise spatio-temporal distributions of surface energy balance components in arid/semiarid riparian areas are critical information for sustainable management of water resources as well as for a better understanding of water and heat

exchange processes between the land and surface atmosphere. However, the distributions of surface fluxes over large areas are difficult to obtain from ground measurements alone. Therefore their prediction from remote-sensing data is very attractive because it enables large area coverage with a high repetition frequency.

In this study, a remote-sensing image processing algorithm, the Surface Energy Balance Algorithms for Land (SEBAL), was selected to estimate the energy balance components in the arid/semiarid riparian areas in the southwestern United States. The main objective of this study is to investigate the potential and limitations of remote sensing for the assessment of spatio-temporal distributions of surface energy balance components using optical imagery from Landsat and MODIS satellites. This study first compares instantaneous and daily SEBAL fluxes derived from Landsat 7 imagery to surface-based measurements with eddy covariance flux towers; then it investigates how up- and down-scaling affect the SEBAL-derived maps of evapotranspiration.

For the up-scaling study, "output" and "input" up-scaling procedures were conducted in which aggregation was accomplished by both simple averaging and nearest neighboring resampling techniques. For the down-scaling study also, input and output down-scaling procedures were evaluated in which disaggregated maps were obtained by two different processes: subtraction and regression.

SEBAL yields accurate estimates of energy balance components in riparian areas in the southwestern United States using both Landsat 7 and MODIS images. The up- and down-scaling schemes proposed in this study generate evapotranspiration maps having a good agreement with maps directly derived from Landsat (30 m) and MODIS (250 m) satellites.

**THE EFFECTS OF GEOLOGIC STRUCTURE AND DIAGENESIS ON OIL PRODUCTION IN UPPER PENNSYLVANIAN AND LOWER PERMIAN PHYLLOID ALGAL MOUNDS, SOUTHEASTERN NEW MEXICO**, by *Jake D. Sharp*, 2008, M.S. thesis, Department of Earth and Environmental Science, New Mexico Institute of Mining and Technology, Socorro, New Mexico 87801, 114 pp.

The Bough zones of southeastern New Mexico are made up of phylloid algal mound complexes. Deposition of these mound deposits occurred preferentially on bathymetric highs and on shelfal areas within the study area. This resulted in a heterogeneous distribution of thicker sections within the study area.

Three dominant rock types are found in the studied strata: 1) biomicrites, 2) altered biomicrites, and 3) dolomites. These rock types were able to be identified in thin section but could not be differentiated based on gamma-ray log analysis. This was due to the similar gamma-ray log curves associated with the different rock types.

Diagenesis of these rocks occurred due to exposure to meteoric waters, rising local sea level, and burial. Diagenetic alteration resulted, most notably, in the creation of moldic and vugular porosity. The presence of secondary porosity coupled with the deposition of the mounds in proximity to source rocks made them good reservoirs.

The most important factors controlling oil production were thickness of the stacked phylloid

algal mound deposits and diagenetic history. Oil production within the Bough A and B is higher on the margins of thicker algal mound deposits. This is likely due to dissolution occurring preferentially on the margins of phylloid algal mound complexes. Production from the Bough C does not follow this pattern and must be controlled by some other factor, most likely a different depositional and diagenetic history.

**NONEQUILIBRIUM SORPTION OF VOLATILE PETROLEUM HYDROCARBONS BY SURFACTANT-MODIFIED ZEOLITE**, by *Joshua A. Simpson*, 2008, M.S. thesis, Department of Earth and Environmental Science, New Mexico Institute of Mining and Technology, Socorro, New Mexico 87801, 226 pp.

The sorption process significantly affects the transport of reactive solutes through geologic media. Nonequilibrium sorption complicates breakthrough curve (BTC) predictions because early-time breakthrough and extended tailing occur. These conditions have adversely affected the accuracy of BTC predictions of volatile petroleum hydrocarbons—specifically benzene, toluene, ethylbenzene, and xylenes (BTEX)—through surfactant-modified zeolite (SMZ) columns.

According to our conceptual model, BTEX molecules are kinetically sorbed on bilayer surfactant sites where the solutes must penetrate external surfactant hydrophilic head groups before partitioning into the hydrophobic tail region of the SMZ. Monolayer SMZ sites allow instantaneous sorption because BTEX molecules immediately partition into the hydrophobic surfactant tail groups. Concentration effects on the kinetics of nonequilibrium sorption of BTEX by SMZ were studied by applying a first-order bicontinuum sorption model to batch experiment data. The modeling results indicate that a constituent's distribution coefficient ( $K_d$ ) is not affected by concentration variations. However, the first-order sorption rate coefficient ( $k_2$ ) and the fraction of instantaneous sorption sites ( $F$ ) are both inversely related to the initial BTEX concentration. A 30–45% reduction in  $k_2$  and a 35–45% reduction in  $F$  occurred as the total BTEX concentration increased from 0.25 to 1.5 mmol L<sup>-1</sup>. According on the batch results, these nonequilibrium parameters are controlled by the total initial BTEX concentration rather than the concentrations of individual compounds. The variation in  $F$  was unexpected based upon a conceptual model of BTEX partitioning into surfactant monolayers and bilayers. The batch-determined kinetic measurements were used to parameterize a nonequilibrium transport model to predict BTEX breakthrough curves for varying input concentrations.

Monolayer SMZ batch tests were run to test our conceptual model, and the results were in agreement with the conceptual model. As hypothesized, only minor variations between the monolayer and bilayer  $k_2$  results were observed. The significant increase (3 to 10 times) in the monolayer  $F$  results was anticipated because of the increase in the fraction of surface covered by a surfactant monolayer. The monolayer  $K_d$  results, adjusted for partial coverage, agreed with the bilayer  $K_d$  results.

The nonequilibrium transport model fully parameterized with values from the batch experiments was not successful in predicting BTEX transport through SMZ laboratory

columns. Predicted breakthrough was earlier than the observed breakthrough for each solute, with the degree of overestimation increasing with increasing hydrophobicity. Sensitivity analysis revealed that the retardation factor,  $R$ , (calculated from the distribution coefficient) limited the prediction capabilities. When  $R$  was inversely fit to the BTC data while retaining values of  $k_2$  and  $F$  from the batch studies, the nonequilibrium model provided reasonable agreement for each constituent's transport behavior. On average,  $R$  values fitted to the transport results were three times those calculated from the batch-derived  $K_d$ s. Aqueous phase surfactant monomers are present in SMZ batch systems due to surfactant wash-off, but are constantly flushed from transport systems. Consequently, the BTEX solubility might increase in the batch systems, producing lower  $K_d$  values in SMZ/BTEX batch systems than transport systems.

**HYPOGENE KARST AND SULFATE DIAGENESIS OF THE DELAWARE BASIN: SOUTHEASTERN NEW MEXICO AND FAR WEST TEXAS**, by *Kevin W. Stafford*, 2008, Ph.D. dissertation, Department of Earth and Environmental Science, New Mexico Institute of Mining and Technology, Socorro, New Mexico 87801, 311 pp.

Hypogene speleogenesis is widespread throughout the Delaware Basin region as evidenced by intrastratal dissolution, hypogenic caves, and suites of diagenetic minerals. The world famous carbonate caves of the Capitan reef facies of the Guadalupe Mountains have long been associated with sulfuric acid processes and recently have been associated with semi-confined, hypogene dissolution. However, evaporite karst within Permian backreef and basin-filling facies has been traditionally associated with surficial, epigene processes. On the eastern edge of the Delaware Basin cavernous porosity associated with oil reservoirs in Permian carbonates have been attributed to eogenetic karst processes.

Interbedded (evaporite/carbonate), backreef facies within the mid-Permian Seven Rivers Formation exhibit characteristics of hypogene karst associated with semi-confined dissolution controlled by the eastward migration and entrenchment of the Pecos River. Coffee Cave is a good example of hypogene dissolution, forming a multi-storey, rectilinear maze with abundant distinctive morphologic feature suites (i.e., risers, channels, and cupolas) indicative of hypogene speleogenesis. Other caves within the Seven Rivers and Rustler Formations show similar patterns, although often less well developed.

Within the Delaware Basin, Castile Formation evaporites have been extensively modified by hypogene processes. Field mapping coupled with GIS analyses clearly shows that karst development and evaporite calcitization are highly clustered throughout the outcrop area. Individual caves commonly exhibit complex morphologies, including complete suites of morphologic features indicative of intrastratal dissolution. Clusters of hypogene caves are commonly associated with clusters of evaporite calcitization and often occurrences of secondary selenite bodies, suggesting all three are genetically related. Precipitated cores and associated native sulfur deposits indicate that calcitized evaporites are the result of semi-confined sulfate reduction in the presence

of ascending hydrocarbons. Hypogene caves are currently being overprinted by epigene processes as surface denudation results in breaching of previously confined solutional conduits. However, calcitized evaporites stand as resistant masses attesting to the widespread importance of hypogene processes within the Castile Formation.

On the southern end of the Central Basin platform, the spatial distribution of cavernous porosity, secondary mineralization, and abundant karst fabrics within the Yates field carbonate strata provide convincing evidence that karst porosity, at least locally, within the San Andres and overlying Permian strata is the result of hypogene speleogenesis. Porosity development appears to have been enhanced by high geothermal gradients and the addition of sulfuric acid-rich fluids, reminiscent of the same processes that have been proposed for the extensive carbonate caves of the Guadalupe Mountains.

Recognition of the widespread occurrence of hypogene speleogenesis throughout the Delaware Basin region indicates that the regional diagenetic evolution has been significantly affected by confined fluid migration, including not only the development of porosity but also the emplacement of many secondary mineral deposits. Therefore, future natural resource management plans must consider the nature of hypogene karst in site evaluations throughout the region in order to better predict geohazards, potential ground water contamination, and characterize mineral resources.

**SENSITIVITY TO ARROYO DEVELOPMENT SCENARIOS: INSIGHTS FROM A DISTRIBUTED HYDROLOGIC MODEL**, by *Robert L. Wyckoff*, 2008, M.S. thesis, Department of Earth and Environmental Science, New Mexico Institute of Mining and Technology, Socorro, New Mexico 87801, 193 pp.

Rainfall-runoff relationships in semiarid environments are highly nonlinear due to the spatial and temporal variability of precipitation and watershed antecedent soil moisture conditions. Specifically within dryland regions, precipitation is often short in duration, limited in spatial extent, and characterized by high intensities. When combined with seasonal periods of elevated basin wetness, rainfall in semiarid watersheds can lead to large flood and flash flood events within ephemeral channels. Because channel network geomorphology strongly influences flood wave generation and propagation in semiarid watersheds, it is important to understand geomorphologic controls on streamflow behavior for both flood forecasting and water resources management. Specifically, semiarid channel networks have experienced rapid geomorphological change that can significantly impact the timing, peak magnitude, and duration of flood events.

As an example, during the initial incision stage of arroyo development, streams cut downward through the valley alluvium forming deep, narrow channel networks. Downcutting through valley fill increases arroyo cross sectional area, thus allowing flood transmission through the channel network without incurring discharge losses to overbank flow. In addition, upslope extension of the channel network head results in the dissection of watershed terrain. The increase in arroyo drainage density reduces overland runoff path lengths and concentrates hillslope

runoff in the channel network, which can lead to progressively larger flood events.

Furthermore, during the latter stages of arroyo development, establishment of riparian vegetation on the inner floodplain promotes arroyo stability. Vegetative root systems anchor streambank sediments and also increase the resistance to streamflow along channel margins. As flood waves interact with vegetation, sediment deposition occurs and the arroyo network narrows and aggrades thereby increasing the propensity for overbank flow. Consequently, observed flood events may decrease in magnitude once arroyos shift from a generally downcutting and widening phase to a period of channel aggradation.

In this study, the TIN-based Real-time Integrated Basin Simulator (tRIBS) is used to simulate rainfall-runoff transformations and flood production within a large (> 1,000 km<sup>2</sup>) semiarid watershed under different scenarios of arroyo development. In the initial phase of the study, model parameters are calibrated using observed stream gage data from the upper Río Puerco in northwestern New Mexico. Model calibration is focused on simulating flood events that developed in early September 2003 in response to widespread convective activity associated with the North American monsoon.

Results for the calibration phase of the study demonstrate that the tRIBS model reproduces the major sequence of flood events observed in the upper Río Puerco during September 2003 despite large uncertainties in calibrated soil parameter values and NEXRAD rainfall estimates (e.g., spatial and temporal resolution, absolute magnitude). However, tRIBS does not consistently replicate time to peak discharge, peak discharge magnitudes, or rapid recession limb characteristics observed in the stream gage discharge time series.

Following model calibration, parameters for the upper Río Puerco tRIBS simulation are used in a series of modeling exercises designed to investigate streamflow response under different scenarios of arroyo development. Model simulations attempt to quantify changes in watershed flood production according to a conceptual hypothesis of arroyo development formulated from observations within Río Puerco watershed by Elliott et al. (1999). Within a small test basin watershed (< 20 km<sup>2</sup>), combinations of channel length, width, and roughness are used to simulate stream flow response to different phases of the arroyo geomorphological cycle. Following simulations in the test basin, model runs are performed in the upper Río Puerco for similar variations in tRIBS channel network representation.

Results for model simulations that investigate different stages of arroyo incision reveal the greatest model sensitivity to changes in channel network length. Channel network extension associated with arroyo incision increases flood event magnitude and decreases time to peak. As arroyo headcuts migrate upslope, the distance to the channel decreases, which results in quick runoff arrival at the stream network. Once runoff is in the channel, longer stream networks efficiently route water to the basin outlet.

tRIBS model simulations that considered different parameterizations of channel roughness demonstrated a slight increase in peak discharge and a decrease in time to peak for lower roughness values. However, for the basin

scales and flood events explored in this study, model sensitivity to changes in channel roughness is limited. Likewise, the different channel width representations utilized in this study had minimal influence on simulated stream flow response. As a result, for this work, the effect of arroyo development is to magnify flood events primarily through the dissection of the watershed terrain with minor contributions from changes in channel roughness or width.

#### New Mexico State University

**EVALUATION OF THE ALLOCHTHONOUS MODEL AND PROPOSAL OF AN ALTERNATIVE GAS SEEP MODEL FOR THE FORMATION OF MISSISSIPPIAN WAULSORTIAN MUD MOUNDS IN THE SACRAMENTO MOUNTAINS, SOUTH-CENTRAL NEW MEXICO**, by *Jairo Geovanni Romero Rodero*, 2008, M.S. thesis, Department of Geological Sciences, New Mexico State University, Las Cruces, New Mexico 88003, 211 pp.

Syn-depositional deformation and facies distribution, controlled by differential compaction and methanogenic seepage and mud volcanism, are suggested here to be integral components in the buildup of Mississippian "Waulsortian mud mounds" in the Sacramento Mountains, New Mexico. Recent detailed mapping of structural and stratigraphic characteristics of the entire Mississippian section has shown that such deformation is restricted to mound systems, where it is pervasive. Detailed mapping of mound facies show cores as chaotically bedded accumulations of brecciated udstone to grainstone, with early-cemented, little-compacted coarsegrained facies being most abundant. Angular unconformities and soft-sediment deformation such as slump folds and scars are commonly present. Microbial carbonate mud-filled injection dikes cut across

these core facies. Stratal geometries of mound flank facies indicate syn-depositional topographic growth, displaying both thinning and onlapping of highly-compacted, late-cemented and coarse-grained beds as they approach the mound core, as well as stratal truncation and rotation patterns.

The documented style of deformation and facies architecture are inconsistent with the two end-member models (biohermal and allochthonous) previously proposed for the formation of these mounds. In the biohermal model, mound relief is generated by in situ biotic buildup and there is no associated syn-depositional deformation. In the allochthonous model mound relief is generated by sedimentologic and structural buildup by mass wasting processes and predicts the presence of a particular suite of deformational features. Such implied features have not been documented in the study area. It is concluded from the analysis that the mounds were built by a combination of biotic buildup and in situ deformation possibly related to over-pressured mud/fluids and/or gases moving upward from beneath the mounds as seeps.

**CHARACTERIZATION OF <sup>239,240</sup> PLUTONIUM RADIONUCLIDE SORPTION TO SOIL PARTICLES AND MINERAL DUST AEROSOLS**, by *Danielle Pinkerton Tatro*, 2008, M.S. thesis, Department of Geological Sciences, New Mexico State University, Las Cruces, New Mexico 88003, 133 pp.

Eolian resuspension of fallout-contaminated surface soils facilitates the widespread distribution of plutonium, a radioactive element introduced into nature primarily by atmospheric testing of nuclear weapons from 1945–1980. It is unknown how Pu binds to dust; hypotheses include Pu sorption to iron oxides and oxyhydroxides, organic acids, or silicate minerals. The hypoth-

esis of <sup>239,240</sup>Pu sorption to Fe oxides and oxyhydroxides is evaluated using soil and dust samples collected from the Project Gnome Site near Carlsbad, New Mexico, the Jemez Mountains near Los Alamos, New Mexico, and from two attics and a BSNE dust sampler in Big Spring, Texas.

Sample organic content was estimated using Loss-On-Ignition (LOI) at 360 °C to combust organic carbon without loss of mineralogic water or CO<sub>2</sub>. The citrate-bicarbonate-dithionite (CBD) method was used to dissolve Fe oxides and oxyhydroxides, creating two sample fractions: the extracted supernatant and a solid pellet. If Pu is partitioned with Fe oxides and oxyhydroxides, then both should be removed from the pellets and concentrated in the supernatants. Major and trace element concentrations of supernatants, bulks and pellets were measured using ICP-AES at Texas Tech University. Activity concentrations of <sup>239,240</sup>Pu were measured in each sample fraction by alpha spectrometry at Carlsbad Environmental Monitoring and Research Center; Pu concentrations were also measured in bulks and pellets using TIMS at Los Alamos National Laboratory.

Fe, Mn, Ca, Sr, Ba, V, Cr, and Zn are preferentially partitioned into the supernatant by the CBD treatment; Al, Mg, and Ti remain in the pellet. Petrographic and SEM analysis shows CBD reduced coatings on individual grains in the pellets compared to bulks. Alpha spectrometry data reveal depletion of Pu activity in pellets relative to bulks and Pu enrichment in supernatants. TIMS analysis of bulks and pellets permits the calculation of <sup>240</sup>Pu/<sup>239</sup>Pu ratios. Bulk sample ratios indicate mixtures of two fallout types: global fallout and low-ratio tropospheric fallout, with the former preferentially extracted from pellets by CBD. Organic content effect on Pu sorption was not investigated; however, bulk samples had low (0.17–8.09) LOIs, therefore Pu sorption to soil and dust particles is attributed to Fe oxide and oxyhydroxide coatings.