The Most Significant Process in Arid Landscapes is the Accumulation of Soluble Minerals & Silicate Dust

- **Carbonates** *(calcite, Mg-calcite, dolomite)*

- **Sulfates** *(gypsum, bloedite, thenardite, mirabilite, hexahydrite, epsomite, konyaite, eugsterite, glauberite, anhydrite, bassanite,...)*

- **Chlorides** *(halite)*

- **Nitrates, Iodates, Chromates, Borates, Perchlorate*
Salt Minerals in Soils

- Can form in any parent material
- Common in arid and semi-arid environments
- Salt minerals can be both pedogenic and/or detrital
Why should we study soils with pedogenic salts?

White Sands Natl. Monument, NM
Identification of salt minerals is important for:

- Natural Water Quality

Three Rivers, NM
Identification of salt minerals is important for:

Interpreting Paleoclimate

Northern Jordan
Identification of pedogenic salt morphology is important for:

- Age/development of landforms
- Tectonics (earthquake recurrence intervals)

Eastern Spain
Identification of salt minerals is important for:
- Agriculture
Gypsum: Normally used for soil remediation

New Application: Gypsum paleosols: A New Technique for Petroleum Exploration
Salt Mineralogy is important to identify Health Hazards:

- Heavy Metals
- Increase mobility of radioactive elements
Identification of salt minerals is important for Urbanization

- Changing land use and the resulting effect on water quality and soils
- Soils effects on infrastructure/land-use planning
Identification of salt mineralogy is important for:

- Engineering-land use planning
Background on Arid Soils

- Calcium Carbonate

\[
\text{Ca}^{+2} + \text{H}_2\text{O} + \text{CO}_2 \leftrightarrow \text{CaCO}_3
\]

(dust, rain, wx minerals) (precipitation) (plant respiration)

Jordan Chile
Background on Arid Soils

• Gypsum (other sulfates), halite, borate, etc.

\[
\text{Ca}^{+2} + \text{H}_2\text{O} + \text{SO}_4^{2-} \leftrightarrow \text{CaSO}_4\cdot 2\text{H}_2\text{O}
\]

1. Original sediment,
2. Eolian/fluvial input,
3. Sea spray
4. Weathering of sulfide minerals
5. Volcanic gases
6. Industrial pollution
7. Atmospheric reactions
What controls mineral variability/amounts?

Soil Mineralogy

Climate (Water)

Parent Material & Dust & Atm processes

Life/Biota

TIME

Salt Minerals need a source of $\text{SO}_4$, $\text{Cl}$, $\text{NO}_3$....

CaCO$_3$ needs plant respiration (Rech et al., 2003)
How does Soil Mineralogy vary across Arid Landscapes? At what scale?
Amount & Type of Soluble minerals can vary greatly. Controlled by climate, topography, biota, time (geomorphic stability), parent material.
Climate change can either ‘erase’ previous minerals (if wetter) or overprint new minerals (if drier).
At the landscape scale

**Key: WATER**

Salts and carbonate record water movement.

Most arid landscapes have become more arid since late Pleistocene thus these minerals hold valuable paleoclimate records.
Pleistocene Lake (wet) = CaCO3 accumulation in alluvial fan soils

Overprinted by salts (gypsum, glauberite, halite, bornite..) in Holocene (shallower)

This system is complicated by internal controls. ex: desert pavements & Av (vesicular) -- mostly developed in Holocene -- decreases depth of wetting
Salt minerals record water movement: climate (precipitation, prevailing wind directions), geomorphology/landscape evolution, time/tectonic stability/earthquake hazards.
Mineralogy

Climate (Water)

Atmospheric Processes: DUST

Biota

TIME

Humans

Topography

Mineralogy

Soil Architecture (macro & micro scales)

Atmospheric Processes: DUST

Biota

TIME

Humans

Topography

Mineralogy

Soil Architecture (macro & micro scales)
Soil Architecture (macro & micro scales)

Climate (Water)

Mineralogy

Atmospheric Processes: DUST

Biota

Humans

Topography

TIME

Atmospheric Processes: DUST

Mineralogy

Humans

Topography

TIME

(landform stability = geomorphic processes)
For soils whose PM does not contain salt - it is brought in via dust, water (run-on), atm processes (fog, pollution, volcano, ozone..)

Carbonate and gypsum accumulate in soils with time through successive morphologic stages

Gile et al., 1966; Buck and Van Hoesen, 2002
Non-salt parent material:

Carbonates and sulfates accumulate in soils with time through successive morphologic stages.

Sulfate morphology alone cannot be used as an indicator of geomorphic age.

Gile et al., 1966; Buck and Van Hoesen, 2002
Morphology of Pedogenic Calcite

- Stage I filaments

From Van Hoesen, 2000
Morphology of Pedogenic Gypsum

• Snowball Morphology:

Sulfate salts precipitate and accumulate in small (1-3 mm) spherical ‘snowballs’

Spherical masses are a special characteristic of sulfate minerals (Buck and Van Hoesen, 2002; Buck et al., 2006)
Snowball Morphology: Distinct from Stage II (order of magnitude smaller in size)
Snowballs in NM
100% had associated organics
63% *Actinomyces*

*Actinomyces* colony

Buck and Van Hoesen, 2002
Snowball Morphology
Do the organisms create/cause the snowball morphology by creating a framework in which the gypsum precipitates?

Actinomyces coating tabular crystal

Buck and Van Hoesen, 2002
Snowball morphology in Las Vegas Wash
Test hypothesis that snowball morphology controlled by biota/gypsum/water interactions
• **Minerals forming Snowball Morphology in Las Vegas Wash:**

  - Gypsum \( \text{CaSO}_4\text{2H}_2\text{O} \)
  - Bloedite \( \text{Na}_2\text{Mg}((\text{SO}_4)\text{2H}_2\text{O} \)
  - Hexahydrite \( \text{MgSO}_4\text{6H}_2\text{O} \)
  - Eugsterite \( \text{Na}_4\text{Ca}((\text{SO}_4)\text{3H}_2\text{O} \)
  - Mirabilite \( \text{Na}_2\text{SO}_4\text{10H}_2\text{O} \)
  - Thenardite \( \text{Na}_2\text{SO}_4 \)

1st study in which *minerals other than Gypsum were found to form the Snowball morphology.*
Snowball morphology in Las Vegas Wash: cannot distinguish specific sulfate minerals in hand sample

“sugary” texture
0% of Las Vegas Wash snowballs had evidence of biota

Snowball morphology commonly forms w/out biological interaction

….still no answer as to why sulfate minerals form snowball morphology

Buck et al., 2006
Minerals now known to form Snowball

**Morphology:**

- Gypsum: $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
- Bloedite: $\text{Na}_2\text{Mg(SO}_4\text{)}_2 \cdot 4\text{H}_2\text{O}$
- Hexahydrite: $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$
- Eugsterite: $\text{Na}_4\text{Ca(SO}_4\text{)}_3 \cdot 2\text{H}_2\text{O}$
- Mirabilite: $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
- Glauberite: $\text{Na}_2\text{Ca(SO}_4\text{)}_2$
- Thenardite: $\text{Na}_2\text{SO}_4$
- Barite: $\text{BaSO}_4$
- Celestine: $\text{SrSO}_4$

**ALL SULFATES!**
Lenticular gypsum
Gypsum: star trek voyager
Mirabilite

$\text{Na}_2\text{SO}_4\text{10H}_2\text{O}$
Aggregates of bloedite, thenardite (+/- mirabilite)

Thenardite
Thenardite   \( \text{Na}_2\text{SO}_4 \)
Barite $\text{BaSO}_4$
Barite ‘Snowball’
Hexahydrite
\[ \text{Mg(SO}_4\text{)} \ 6\text{H}_2\text{O} \]
Bloedite

$\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$
Bloedite & Eugsterite
Eugsterite - previously thought to be RARE
\[ \text{Na}_4\text{Ca(}\text{SO}_4\text{)}_3\text{2H}_2\text{O} \]
Glauberite - $\text{Na}_2\text{Ca(\text{SO}_4)}_2$
Las Vegas Wash Surface Crust in July
Bloedite ‘micro-snowballs’
Bloedite ‘microsnowballs’
Bloedite ‘microsnowballs’
Kinetic effects during rapid supersaturation and ppt. under high temperatures
Halite NaCl
often found w/sulfate minerals, but **NEVER** found to form snowball morphology alone
Other minerals found with *Sulfates* in snowballs:

Fluorite
Conclusions

Snowball Morphology *independent* of biology

Snowball Morphology *dependant* on mineralogy

– *Pedogenic SULFATE minerals*
Sulfate Morphology

Non-salt parent material:

Gile et al., 1966; Buck and Van Hoesen, 2002
Bloedite Snowballs
Na$_2$Mg(SO$_4$)$_2$ • 4H$_2$O

Las Vegas Wash, NV
Sulfate Salts:
Stage 1 filaments

snowballs
Gypsum Snowballs

04-21cm DV7, Death Valley

2 mm
Stage I snowballs composed of pseudohexagonal tabular bloedite crystals.

Las Vegas Wash, NV
Stage I barite snowball, Jordan

2 mm
Barite filling root trace (Jordan)
Stage II gypsum nodules

5 cm
Salt pendants, base of clasts
Petrogypsic, Stage III

Drygyp, Lake Mead, Nevada
Note that Harden et al. 1991 developed stages of gypsum accumulation for gravelly soils - up to stage IV - but no laminae as in carbonates.

See Table A1.7 in Appendix of Birkeland’s textbook.
Atacama Desert, Chile

Stage III + Petrosalic horizons

Petrosalic Horizon: halite, Na-nitrate (glauberite, anhydrite)
How much salt? Controlled by INPUTS & TIME

Pedogenic processes concentrate salt minerals in B (or A) horizons, some horizons can be up to 99% salt minerals (even in non-salt parent materials)
What about Paleosols?
Snowball Morphology: Numerous applications, useful for modern and Holocene-Late Pleistocene soils.

Snowballs probably can’t survive into the rock record.
La Popa Salt Weld/Diapir

Salt Diapirs are the #1 geologic phenomenon associated with petroleum deposits. Nearly all are subsurface features.
Carroza Formation

- at least 805 m thick
- interbedded red and less commonly green, shale (47%), siltstone (4%), and sandstone (48%)
- represent an arid, low-gradient, ephemeral fluvial system (channel, crevasse splay, levee) with associated overbank deposits (floodplain, pond).
Ephemeral streams with localized riparian environments
Mudcracks
DC unit 5
Hypothesis: Paleosols can be used to interpret salt tectonics

Evidence for primary sulfate and chloride minerals when diapir is exposed

Common-ion effect decreases solubility of CaCO3, hinders calcic soil formation
Hypothesis:
Carbonate paleosols when diapir is not exposed
Hypothesis:
Paleosols can be used to measure salt tectonics through time.
Where to Test?

Devil’s Anus (best exposure)
Dripping, Oozing, Bad-Smelling, *Nasty-Tasting* diapir contact: Devil’s Anus
BREAKING NEWS!

DEVIL’S ANUS CONTAINS SNOWBALLS
Snowball morphology in Paleosols

- S-isotopic signature same as that of gypsum in diapir
Paleosols with other Diapir Salts:
Barite
Paleosols with other Diapir Salts

Barite
Halite Casts = Salic Horizon

Paleosols with other Diapir Salts:

Halite
Soil structure types

- Crumb or granular
- Platy
- Blocky
- Prismatic or columnar
Columnar soil structure = Evidence of Na$^+$

Source of Na$^+$ = NaCl from exposed diapir
Fossil Ant Nests in Paleosols
Paradox Basin, UT
World’s oldest gypsic paleosols

Lawton and Buck, 2006
Stage II gypsum, Moenkopi Fm, Utah (Triassic)
Indicator of Salt Tectonics (Lawton and Buck, 2006).
Important Points

1. It’s not just gypsum

Rarely is gypsum found alone without other salt minerals
(Except in areas where gypsum is the parent material)
Important Points

2. Salt minerals are transitory

A single major geomorphic event can initiate the addition or removal of salt from soils, thus changing taxonomy, land management, vegetation, etc.
Hexahydrite Today, Gypsum Tomorrow: Dynamics of Salt Minerals in Soils

Brenda J. Buck

Department of Geoscience, University of Nevada Las Vegas, 4505 Maryland Parkway, Las Vegas NV 89154, USA.
Lower Las Vegas Wash 1950’s

Perennial flows were not observed until 1955 -
Caused by increased urbanization

Image - July 3, 1950
Increased flow transformed floodplain vegetation from a mainly sparse, desert-shrub community to a greenbelt that included ponds and swampy wetlands. This vegetal transition took place over about half a century.
Creation of the Wetlands by Urbanization

Photo credit: Vern Bostick
Loss of the Wetlands: Flashfloods from Urbanization
Loss of the Wetlands

1974 floodplain

1985 Floodplain
Response of Salt Minerals:

Lowering water tables stops the surficial accumulation of soluble salts.

A lower water table facilitates removal of soluble salts from the upper portion of the profile.
Response of Salt Minerals

Movement of salt minerals can change soil classification.

Soils originally mapped as Land Series (Typic Aquisalids) in 1977.

Now some areas are Typic Haplogypsids and Gypsic Haplosalid.
Important Points

3. Salt minerals are active geomorphic agents
Salt Weathering, Salt Heave, Salt Corrosion are some of the most expensive urban problems faced by humans
Las Vegas Valley Water District

Salt Corrosion (also salt collapse, salt heave) causing increased pipe failure rates:

$2 Billion in replacement of current piping assets
Worldwide: Salt Corrosion of Art, Buildings
Salts: Active Geomorphic agents
Salt Damage caused by:
1. Precipitation (force of crystallization)
2. Hydration/Dehydration (dissolution/precipitation)
3. Differential thermal expansion.

Mirabilite $\text{Na}_2\text{SO}_4\cdot10\text{H}_2\text{O}$  Thenardite $\text{Na}_2\text{SO}_4$
Important Points
Salt minerals as health hazards

1. Heavy Metals
2. Increase mobility of Cs$^{137}$
Landscaping Rocks and Salt

- **Xeroscaping** is a popular form of landscaping.
- Crushed rock products are being used extensively.
- Some react unfavorably - salt crusts are formed.
- Currently there are no regulations controlling the mineralogy of landscaping rocks.
Project initiated:
Green, acidic crust on new school grounds - one child burned
• Three sites in Las Vegas:
  Del Sol High School,
  Canyon Springs High School
  Ed Fountain Park
• 58 additional locations w/Clark County School District.
What are these crusts? What processes are causing their formation? Are they harmful?
Particle-size Results

Over two-thirds (weight %) of the material at each site is finer than gravel.

Crushed rock: too small = dust pollution;
               too large = projectile weapons
Results

All three sites contain at least 8 cm (ground cover) of crushed decorative rocks.

High levels of acidity were measured (pH 3.91-4.10) prior to and directly after landscaping rocks were emplaced.
ICP Results: Salt Crusts

Elemental Abundance (wt %)

Site 1        Site 2        Site 3

Al  Cu  Fe  Mg  Zn

Bar chart showing the elemental abundance (wt %) for Sites 1, 2, and 3.
XRD Results: Salt Crusts

Pentahydrite (MgSO$_4$·5H$_2$O)
Hexahydrite (MgSO$_4$·6H$_2$O)
Epsomite (MgSO$_4$·7H$_2$O)

Bloedite (Na$_2$Mg(SO$_4$)$_2$·4H$_2$O)
Halite (NaCl)

Tamarugite (NaAl(SO$_4$)$_2$·6H$_2$O)
Polyhalite (K$_2$Ca$_2$Mg(SO$_4$)$_4$·2H$_2$O).
EDS analyses identified copper phases in 40.3% of all observed sulfate minerals and 25.9% of all chlorides.

EDS analyses yielded elemental copper concentrations ranging from 6.6 to 83.0% in all sulfate minerals.
Elemental Analyses indicate Copper-Sulfate
Copper Sulfate is a Mutagen & a Teratogen
(regulated by OSHA, cited by NIOSH, ACGIH, DOT, DEP, and EPA)
Copper Sulfate is **HIGHLY SOLUBLE & EASILY INJECTED** (either through dust inhalation or drinking water).

*Should not be handled without protective clothing.*
SEM data indicate the presence of Copper Chloride. Copper Chloride is also on the Hazardous Substance List (regulated by OSHA and cited by ACGIH, DOT, NIOSH, DEP and EPA.)
ICP Results: Runoff

Exceeds the EPA’s standard of 1.3 ppm Cu for drinking water by 4.1 ppm (Environmental Protection Agency, 1974).
Parking lot runoff will be diluted downstream, but continued use of these decorative rock products will increase the unnecessary pollution of LV Wash, underground aquifers, and Lake Mead.
Total elemental analyses were performed on foliage samples taken from four plant species in 2004 and 2005. Results indicate several metals that were extremely low, or not detectable, in leaf tissue in 2004 have significantly increased, 2 to 20 times in just under a year - and base cations have decreased.
Arsenic has increased by a factor of 14 in one species at Del Sol high School and copper by a factor of 16 at Ed Fountain Park. Lead has increased by a factor of 7.6 to 19 across all species.
Copper and other metals present in:
- Parking lot runoff
- Salt Crusts
- Vegetation

What is the origin of these metals?
Results

Thin section analyses of landscaping rock identified hydrothermally-altered granite: dominated by Quartz & Feldspar or Clays and Fe-oxides (depending upon degree of alteration).
Results

XRD analyses of Landscaping Rock:

- Quartz
- Biotite
- Muscovite
- Albite
- Anorthite
- Sodalite
- Berlineite
- Ankerite
- Microcline
- Calcite
- Kaolinite
- Illite

**Pyrite. (up to 4% in point counts; up to 10% in hand specimens)**
oxidation of sulfide minerals (pyrite) creates urban acid-mine drainage

$$\text{FeS}_2(s) + \frac{15}{4} \text{O}_2(aq) + \frac{7}{2} \text{H}_2\text{O}(l) \rightarrow \text{Fe(OH)}_3(s) + 2 \text{H}_2\text{SO}_4(aq)$$
ICP Results: Rock and Soil

Elemental Abundance (ppm)

Site 1 (rock)  Site 1 (soil)  Site 2 (rock)  Site 2 (soil)  Site 3 (rock)  Site 3 (soil)

- Mo
- Zn
- Cu
Copper levels in decorative gravels: 196-377 ppm
Copper levels in underlying soils: 6-21 ppm

Copper salts are a **DIRECT RESULT** of the decorative rock/gravels and **NOT** from underlying soils.
• The source of the heavy metals is the crushed landscaping rock.
• The metals are liberated through the acid generated by oxidation of pyrite.
Salt Crusts result from watering of vegetation planted in decorative rock gravel/sand, wicking up of water and evaporation.
Acid drainage and heavy metal (copper) contamination will also eventually cause vegetation to sicken and die (increased costs)
Conclusions:

Material should not be used

- High Copper Levels (in toxic forms)
  - Highly soluble, hazardous salts (copper sulfates & copper chlorides) - should not be touched/handled.
  - Contaminate run-off water downstream and/or to aquifers
  - Can be inhaled through dust to downwind inhabitants

- If ingested will taste like table salt - therefore possible that children will unknowingly eat it.
Conclusions: Material should not be used

- Creates Acid Mine Drainage in Urban Area
  - Detrimental to plants (will add additional costs to landscaping through time)
- Detrimental to curbs/infrastructure through salt damage (will add additional costs)
- Unattractive green salt crusts
These hazardous substances are a direct result of imported decorative rock materials that do not naturally occur in the LV urban environment and therefore human exposure is preventable.
Solution to Problem

- Discontinue use of products containing sulfide minerals (pyrite).

- Develop standards for decorative rock products.
Problem Continues:
• Thousands of tons of new materials continues to be placed.
• New quarry sites at different locations
• $$$ = accusations of “junk science”
Important Points

4. Salt = Life

In the most extreme environments, salt may be a reservoir of life.
Algae in Jordan (Av horizon)
El Papolote Mexico, Nuevo Leon
(100 km N of Monterrey)
petrogypsic soil, yucca & cactus vegetation
~ 250 mm precipitation/yr;
~ 22°C mean annual temperature
El Papolote, Mexico
Mojave Desert, NV
Loamy, gypsic, hyperthermic Typic Petrogypsid
147 mm precip/yr; temp ranges 3-48°C, average 20°C
Mojave Desert, NV
nearly pure gypsum, highly indurated
patchy vegetation: Fremont's dalea, Parry's sandpaper plant,
catclaw acacia, desert trumpet
Al-Jafr Basin, Jordan  
no vegetation, ~ 50 mm precip/yr, surficial clasts of gypsum and artifacts
Jafr Basin, Jordan

gypsum distribution is (clasts of gypsum blocks), extremely variable.
Typical Atacama Petrogypsic soil (Gypsum/Anhydrite) with minor carbonate
No vegetation
Atacama Desert, Chile
Cyanobacteria
Atacama
Jordan
Jordan
Mexico
Atacama
Controlling mechanism for life might be the location and presence of gypsum near the surface to attract atmospheric water vapor.
Biota in Gypsum: implications for the search for extraterrestrial life?

Atacama Desert, Chile
Jordan Badia
Mojave Desert, NV
Chihuahuan Desert, MX

Cyanobacteria
Do they also have implications for land management?

Dong et al., 2007
Salt = Life?
The Buck Stops Here