Near-Field Corrosion Processes Evaluation

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The State of Nevada analytical and experimental program for near-field EBS corrosion processes evaluation focuses on the:

1. **Prediction of the range of service environments**

2. **Determination of corrosion behavior within that range**

Range of Service Environments - Aqueous State

- Dry Environments (during ventilation)
- Moist Dust/Scale/Bacterial Environments*
- Aqueous (Aqueous-Dryout) Environments:
  - Episodic Drip
  - Episodic Flow
  - Surface Condensate from Humidity
  - Surface Condensate Associated with Hydroscopic Salts
  - Standing Near-Field Water in Rockfall Metal Depression
  - Standing Near-Field Water at the Invert-Rail System
  - Standing Near-Field Water Inside a Breached Canister

* rock dust & fragments, precipitated minerals, EBS corrosion products, biofilms

Range of Service Environments - Aqueous Geochemistry

1. **Vadose Fracture Water** (assumed to be an immature*, near-neutral mildly alkaline calcium bicarbonate water)
2. **Vadose Matrix Pore Water** (a submature* water that ranges from calcium bicarbonate to calcium-chloride-sulfate in composition)
3. **Dead-End Fracture Water** (unknown compositions)
4. **Perched Water** (a submature* sodium bicarbonate water)
5. **Condensate** (dilute to concentrated brines)
6. **Vadose Biotic Transfer Water** (very low nitrate & phosphate content)
7. **Mixtures** (any and all combinations of the above, and their evaporative concentrates)

* Water Maturity: mature and submature waters are more equalibrated with the host rock than immature water. Oil field brines are considered to be mature waters.

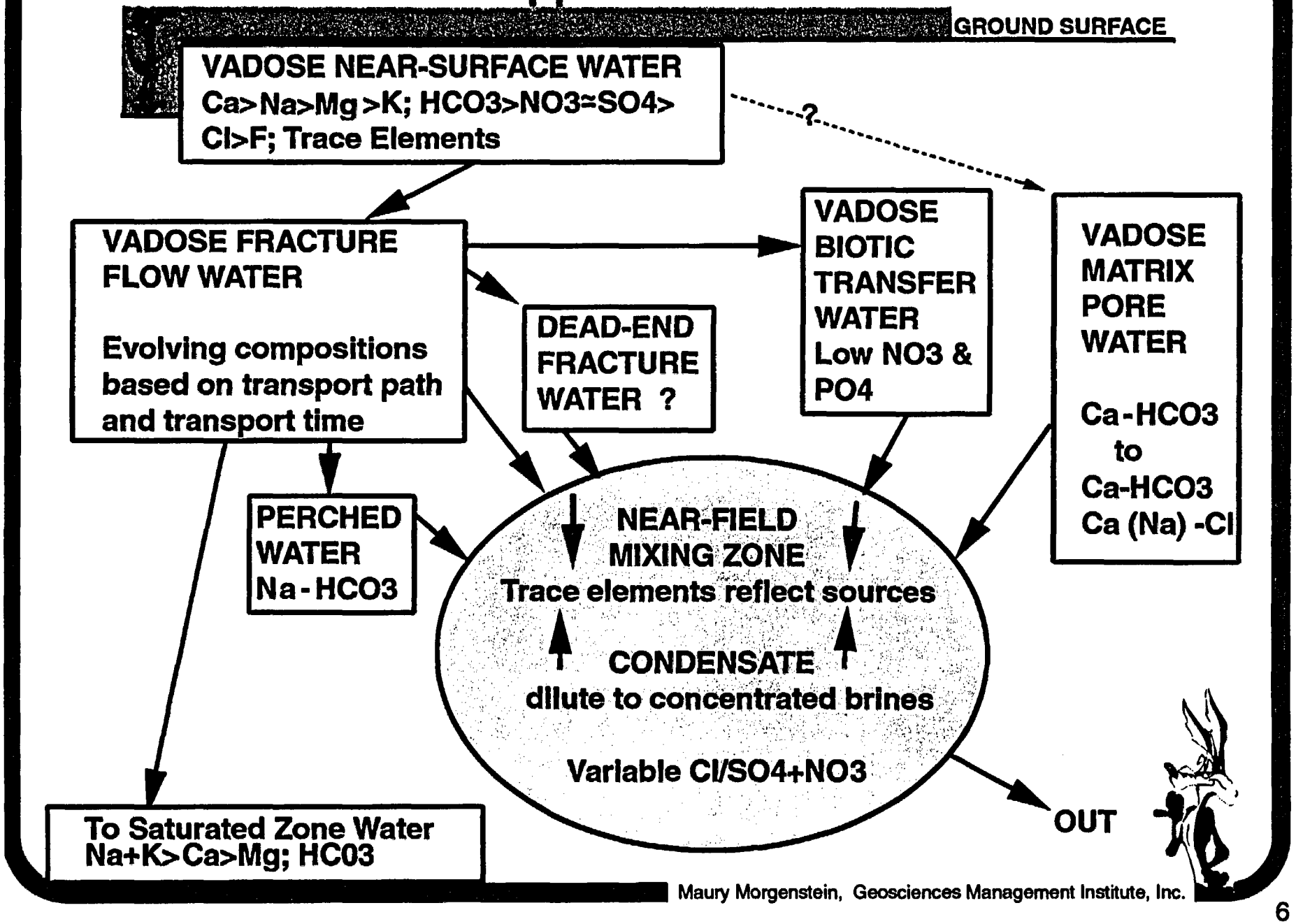
Evolution of Natural Waters - Yucca Mountain

Mechanism	Reactions
CEC - zeolites and clays	Na and K mobilized Ca and Mg into phyllosilicates
Hydration-base-exchange of volcanic glass	Na and K mobilized, amorphous silica formed, phyllosilicates formed, ferromanganese oxyhydroxides formed
Weathering of:	
plagioclase & pyroxenes	mobilized alkali, silica, transition metals
mineral oxides, magnetite	mobilized transition metals
Change in pCO_2	precipitation of calcite & low Mg calcite
Evaporation - near surface, and in fault zone fractures	precipitation of gypsum-selinite & other salts, and amorphous silica

Evolution of Vadose Water in Perturbated Yucca Mountain Environments

Mechanism	Reactions
Refluxing of aqueous fluids	precipitation of amorphous silica, carbonates and sulfates, change in aqueous compositions
Condensation of vapor above the emplacement drift	rock dissolution and the formation of condensates of variable pH, mixing waters from various sources and compositions
Condensation of vapor from canisters	highly acidic condensate reacts with drip shield, support pedestals, rock bolts and wall rock
Formation of perched zones above the repository due to heat flux and silica cap	fluids evolve to brines, then after the thermal pulse become less concentrated
Formation of incubator zones in Tiva Canyon and Topopah Springs tuff fault and fracture zones (about 45°C)	dentrifier bacteria and fungi metabolism with near-surface organics or manganese oxyhydroxides and apatite substrates on conduit fracture walls - lose vadose water nitrates and phosphates

The State of Nevada Approach: Evolution of YM Waters



State of Nevada Soil-Water Project

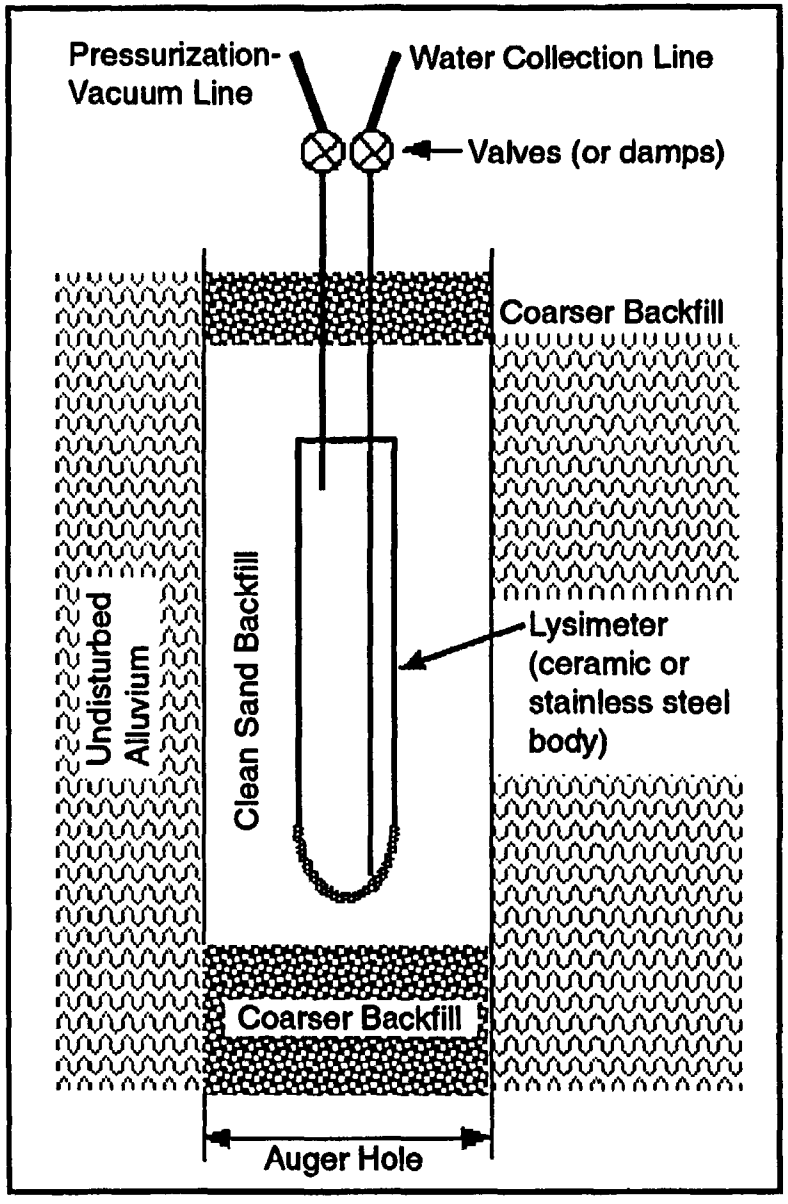
In December 2001, two lysimeter holes were augered in Area 25 of NTS:

1. Midway Valley (just off WT-6 pad):
   4 lysimeters emplaced
2. Coyote Wash:
   1 lysimeter at about 7 foot depth

Purposes: 1. sample near-surface vadose zone water
2. sample precipitation and surface run-off

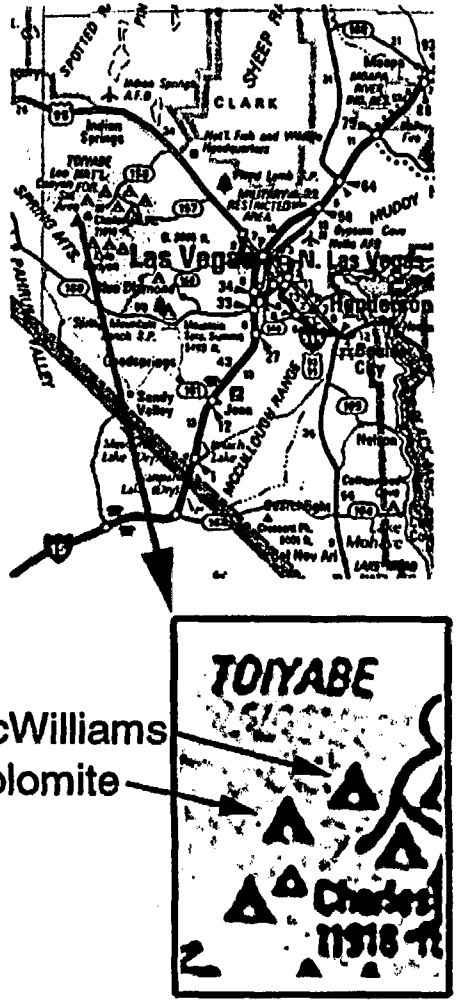
Analyses: general chemistry, trace elements, isotopes

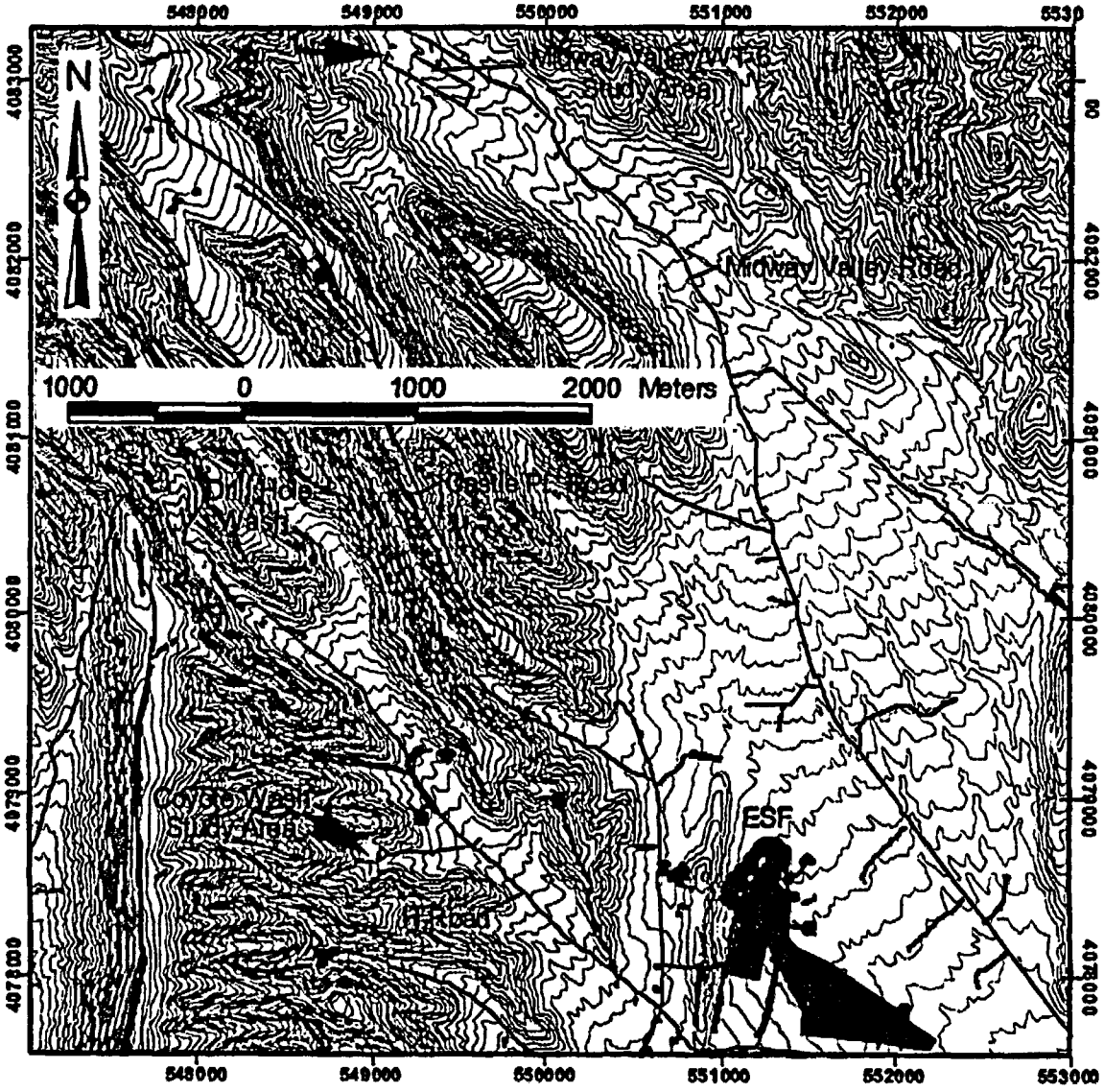
Goal: Characterize water entering Yucca Mountain system



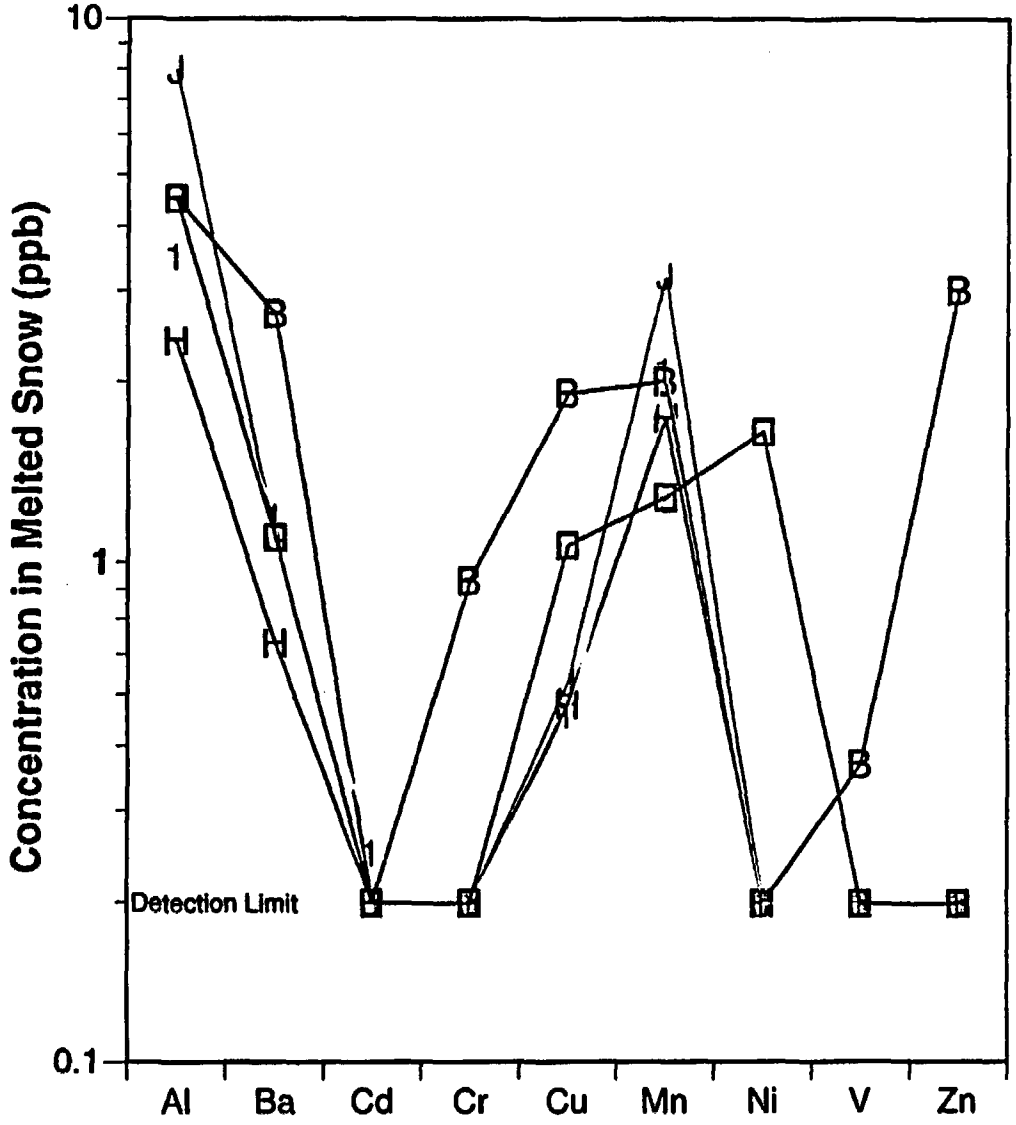
Location of NTS Lysimeter Holes

Location of Most Snow Samples





Analysis of Snow Samples by EPA method 200.8 (ICP-MS)



Campground Samples

- B — Dolomite 11-27-01
- J — Dolomite#5 3-7-02
- H — Dolomite#5 3-20-02
- 1 — Dolomite#5 3-20-02 dup
- □ — McWilliams#14 2-19-02

State of Nevada: Soil-Water Project

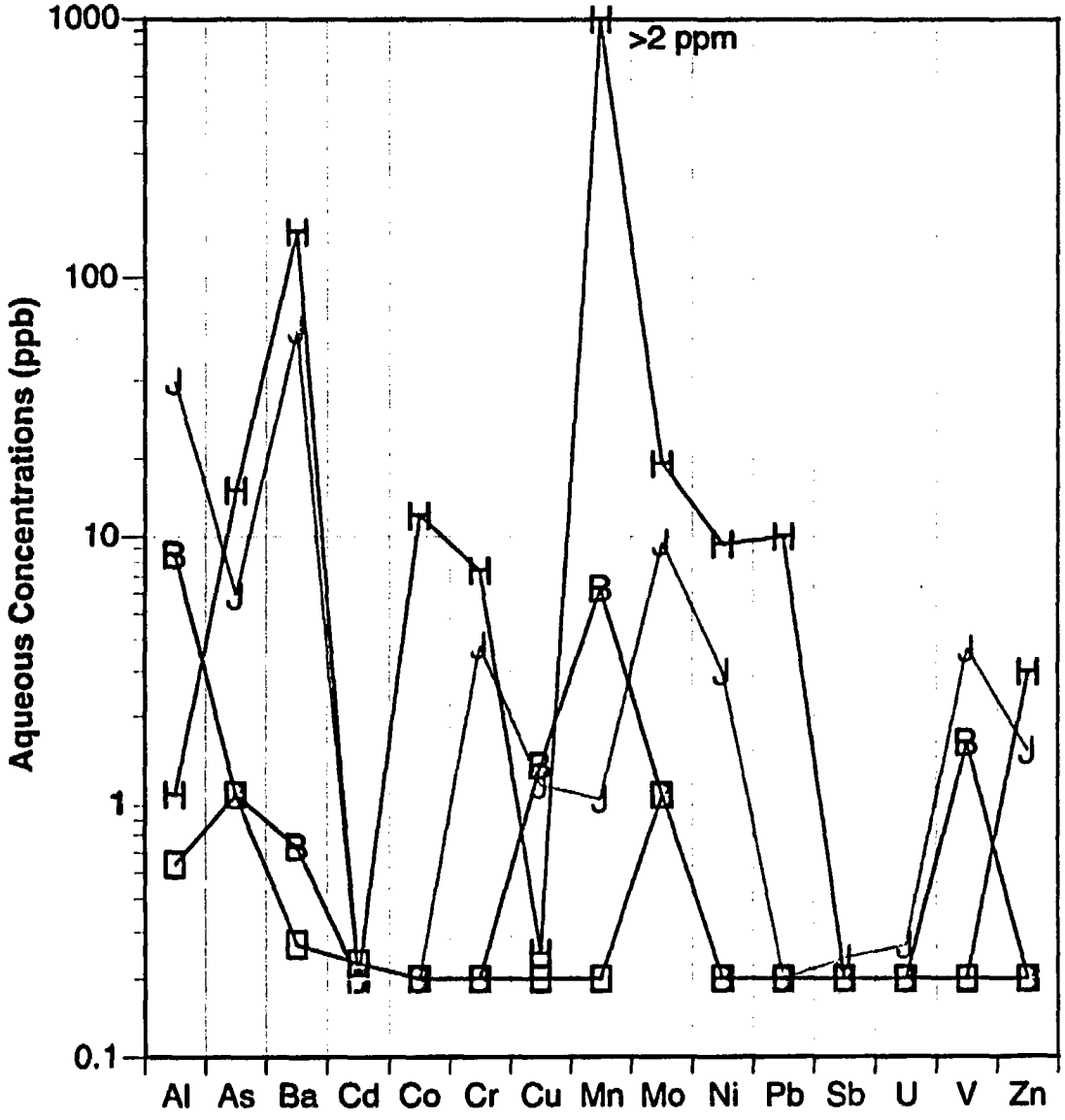
Location of Samples:
Campgrounds in Lee Canyon, Toiyabe Nat. Forest, Clark Co., NV

First "Dolomite" campground sample is within 10 meters of Hwy. 156, remainder more than 100m upslope from road.

Samples were filtered thru 0.45 micron cellulose acetate filters, then acidified.

Additional elements analyzed, but all below detection limit, include: Ag, Be, Co, Mo, Pb, Sb, Se, Tl, and U.

Analysis of Snow and Soil Leachate Samples by EPA method 200.8 (ICP-MS)



- Coyote Wash: 1-31-02
- CW1-reacted
- CW2-reacted
- Distill.Drink.Water
- Filter Blank

State of Nevada: Soil-Water Project

Coyote Wash samples located on NTS, just south of Meteo. Station (<5m).

CW1- and CW2-reacted samples were melted snow reacted with soil samples for almost 2 months at ambient temperatures.

All water samples were filtered thru 0.45 micron cellulose acetate filters and acidified.

Additional elements analyzed, but all below detection limit, include: Ag, Be, Se, and Tl.

Classification of Snow Samples

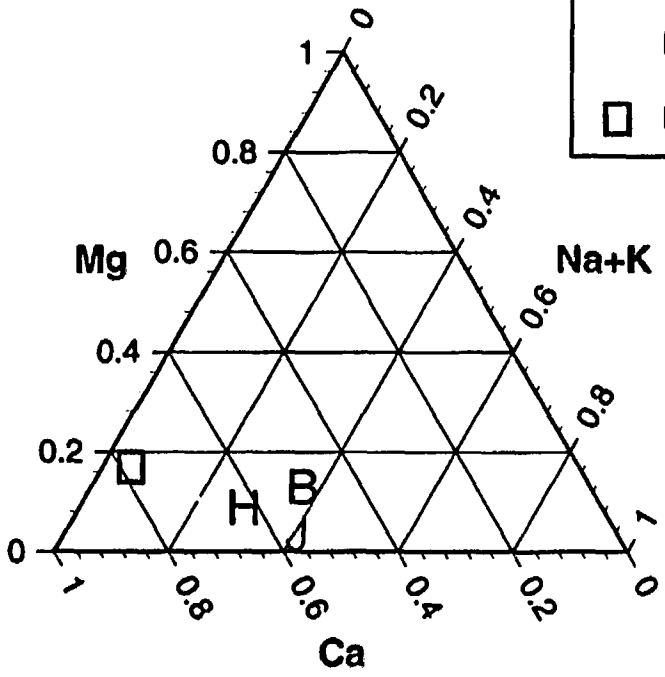
B Coyote Wash, 1-31-02

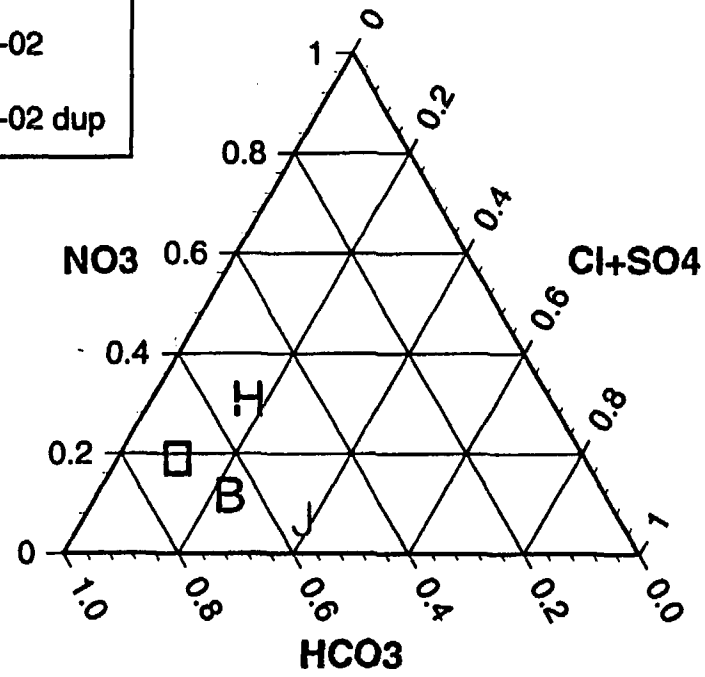
J McWilliams#14, 2-19-02

H Dolomite#5, 3-7-02

Dolomite#5, 3-20-02

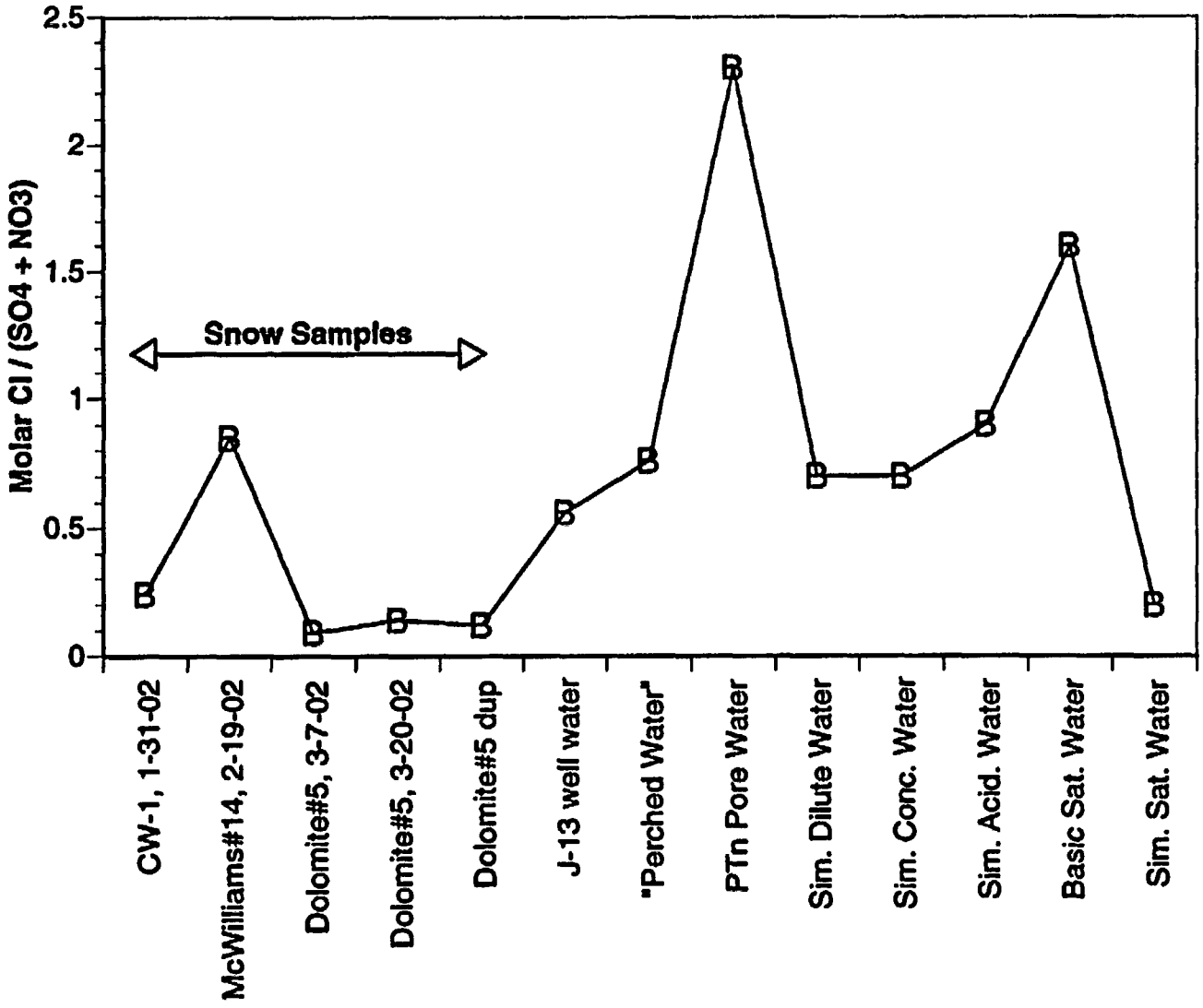
□ Dolomite#5, 3-20-02 dup





CONCLUSION: All of these snow samples are dilute Ca-HCO3 type waters, with significant nitrate.

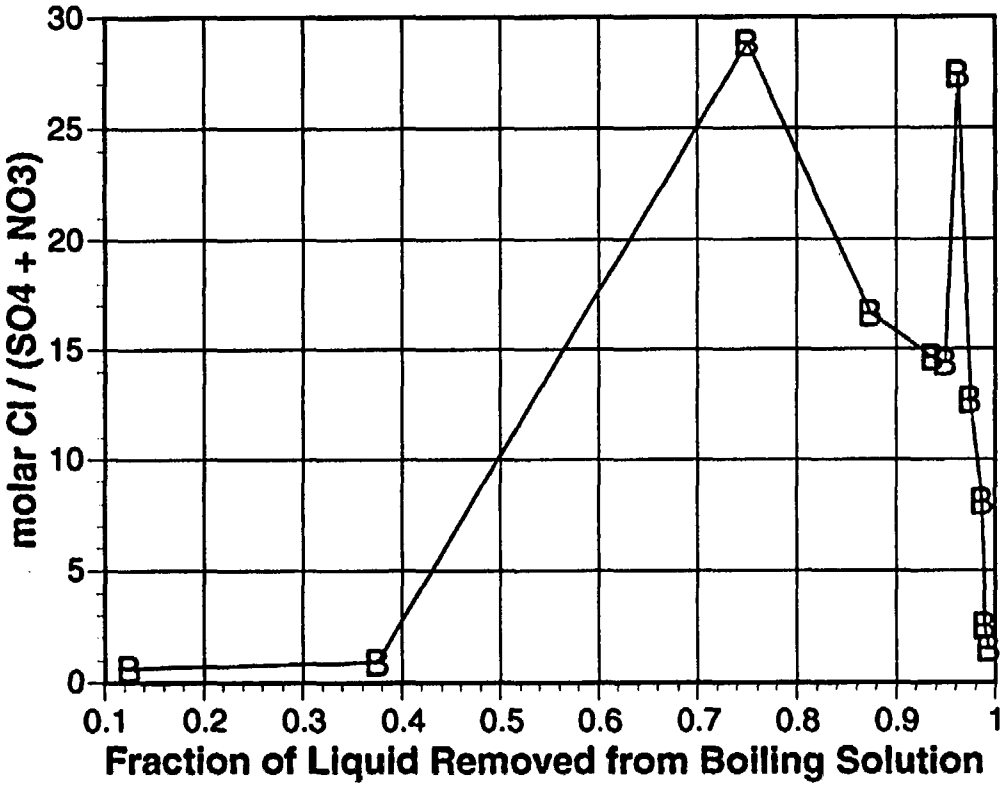
Comparison of Molar Cl/(SO4+NO3) Ratios for Various Waters

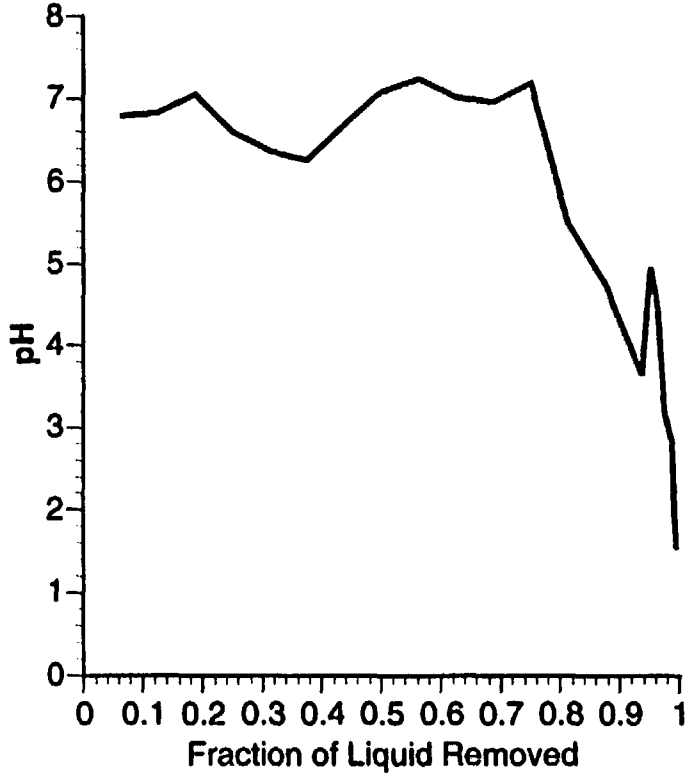


The mostly low ratios observed in snow samples will evolve by contact with soil zone: NO3- will be utilized by plants and microbes, Cl- and SO4-- will increase due to evaporative concentration and additions by dissolution.

Ratios in water contacting canisters will not be static, but will increase as evaporation and precipitation of sulfates occurs; microbes may further reduce [SO4--] and [NO3-] by reduction.

Composition of Increments (10-50 mL) of Condensate Collected from Boiling Pore Water

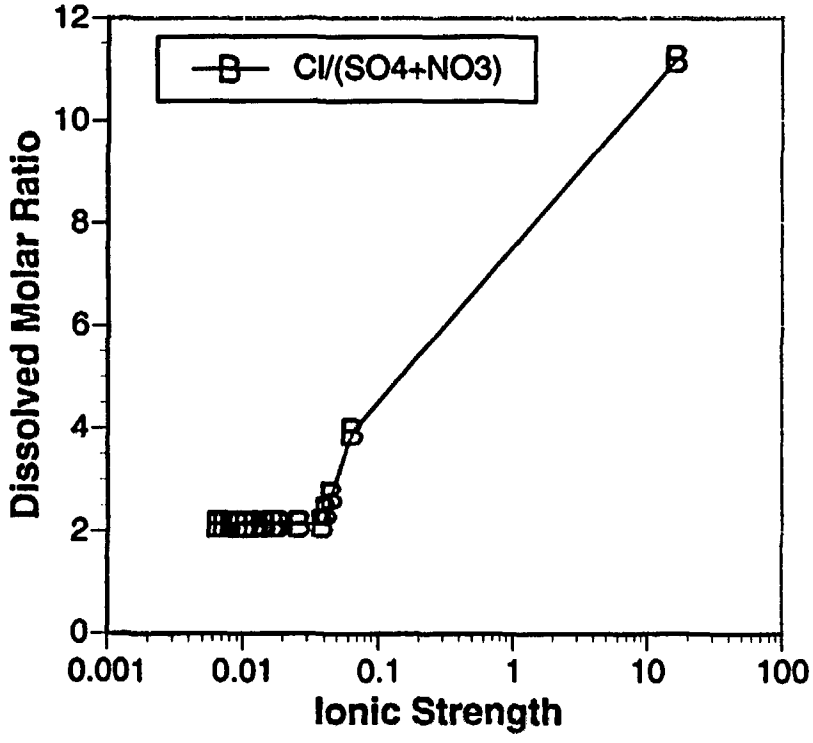


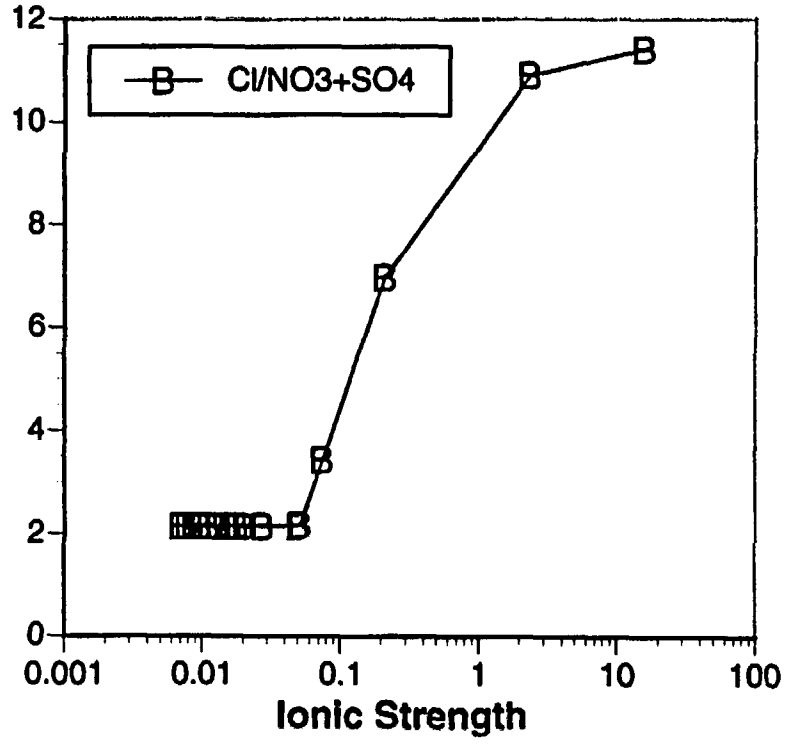


Solutions would be boiled by contact with surface of drip shields and canisters. Condensate collects on cooler surfaces, such as inside of drip shields, canister support pedestals, inverts, steel sets, and drift wall rocks.
Data collected by Dr. A. Pulvirenti, Chem. Dept., Catholic University of America.

Variation of molar Cl/(SO4+NO3) in UZ Pore Water during Evaporation

(modeled with Geochemists' Workbench v. 3.1)





UZ pore water evaporated at 95°C.

UZ pore water simultaneously heated and evaporated from 25 to 95°C.

Conclusion: Ratio is not static, but varies during heating and evaporation.

Alloy C-22 Corrosion Rate (µm/yr) as a Function of pH

Test Conditions: C-22 Discs in Simulated 1000xJ13 with 5000 ppm F^- added; 160°C, 14 days

	Oxidizing Conditions		Reducing Conditions	
pH	By Weight	By Ni ion	By Weight	By Ni ion
1.0	1333	1075	1390	999
2.0	61	55	67	64
3.0	50	40	86	82
4.0	4	8	1	11
7.0	4	0	2	0

CONCLUSIONS

- Important water compositions relative to corrosion are: Condensate, Vadose Fracture Flow, Refluxed Vadose Matrix Water, Biotic Transfer Water (solely as a function of the repository), and Mixtures. Saturated zone water is not a good starting composition for corrosion studies because it occurs below the repository.
- Based upon only 5 samples of snow the input vadose water signal is a Calcium Bicarbonate Water.
- Trace elements in the snow samples suggest a desert varnish particulate input.
- Human activities can influence the hydrogeochemistry of the soil zone waters.
- Cl/(SO4+NO3) ratio used in 'YM Project' studies are low.
- Cl/(SO4+NO3) ratios can vary with evaporation by water contacting hot surfaces. Condensates can have rather extreme ratios and pH values.
- General corrosion of C-22 appears to be greatly influenced by pH and fluoride. This observation differs from the chloride/(sulfate+nitrate) model used by the 'YM Project'.