U.S. DEPARTMENT OF ENERGY
OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT

PRESENTATION TO THE NUCLEAR WASTE TECHNICAL REVIEW BOARD

SUBJECT: MINERALOGICAL UNCERTAINTIES

PRESENTER: DR. DAVID L. BISH

PRESENTER'S TITLE AND ORGANIZATION:
TECHNICAL STAFF MEMBER
EARTH AND ENVIRONMENTAL SCIENCES DIVISION
LOS ALAMOS NATIONAL LABORATORY
LOS ALAMOS, NEW MEXICO

PRESENTER'S TELEPHONE NUMBER: (505) 667-1165

OCTOBER 8 - 10, 1991

U.S. DEPARTMENT OF ENERGY
OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT

PRESENTATION TO THE NUCLEAR WASTE TECHNICAL REVIEW BOARD

SUBJECT: MINERALOGICAL UNCERTAINTIES

PRESENTER: DR. DAVID L. BISH

PRESENTER'S TITLE AND ORGANIZATION: TECHNICAL STAFF MEMBER
EARTH AND ENVIRONMENTAL SCIENCES DIVISION
LOS ALAMOS NATIONAL LABORATORY
LOS ALAMOS, NEW MEXICO

PRESENTER'S TELEPHONE NUMBER: (505) 667-1165

OCTOBER 8 - 10, 1991

Scope

- Yucca Mountain and host rock mineralogy
- Effects of dehydration/rehydration and associated contraction/expansion of hydrous minerals
- Effects of heating on sorption properties
- Long-term stability of minerals near host rock

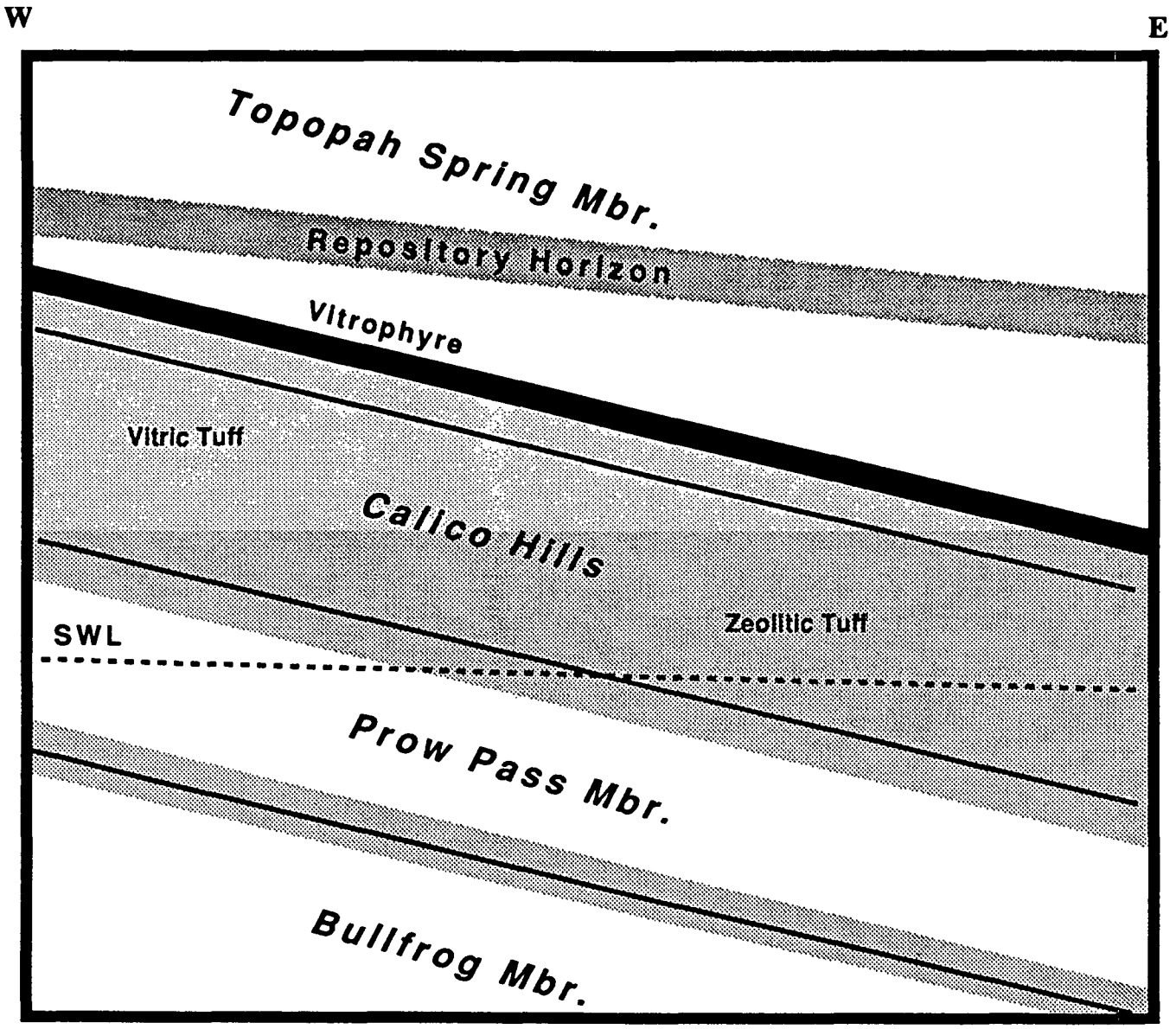
Mineralogy of Candidate Host Rock and Rocks Between Repository and Water Table

- Relatively stable minerals
  - Quartz, Feldspar

- Minerals that dehydrate
  - Smectite, Clinoptilolite, Mordenite, Volcanic Glass

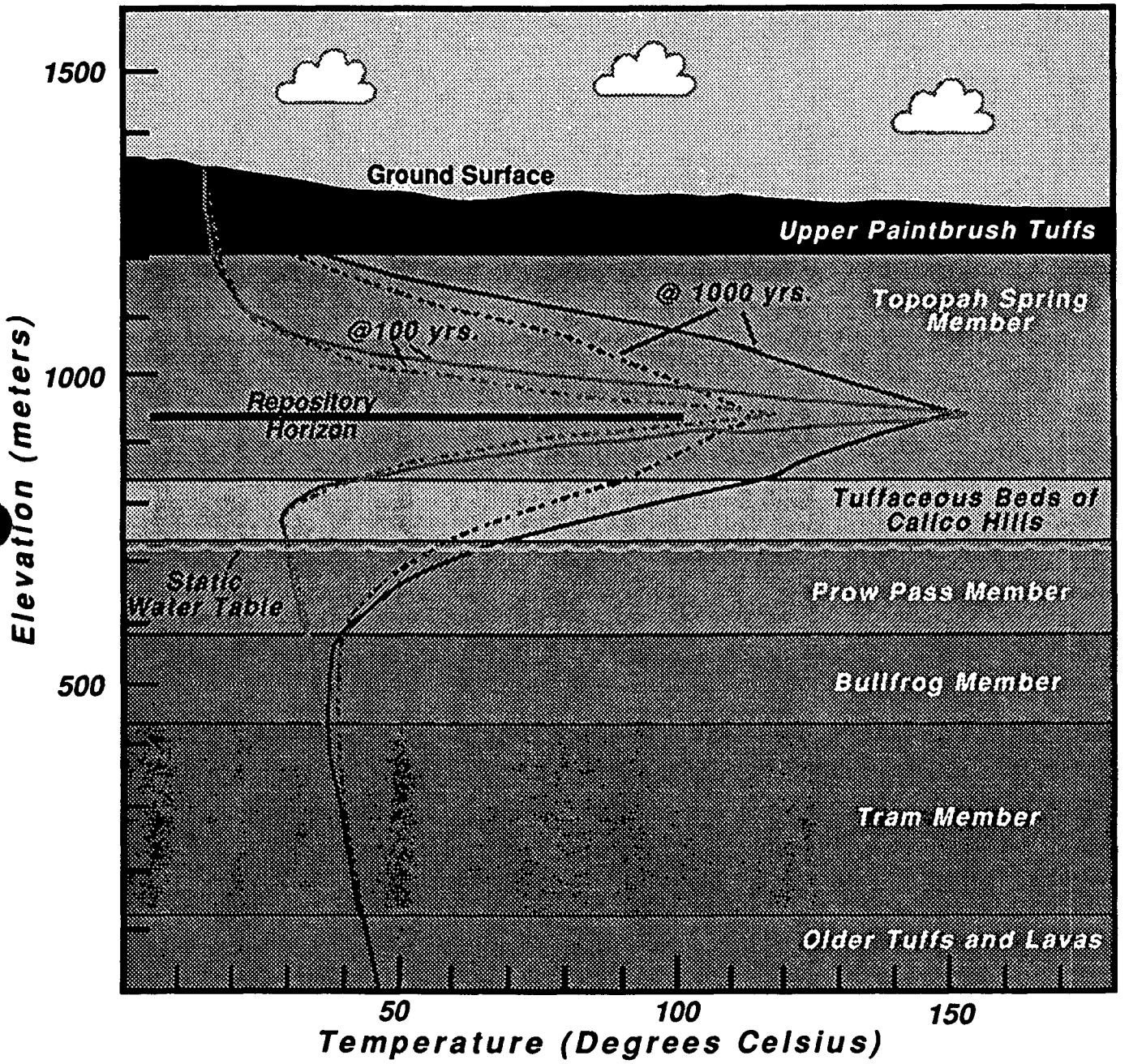
- Minerals that may transform or dissolve
  - Cristobalite, Tridymite, Opal-CT, Volcanic Glass
  - Smectite → Illite through Illite/Smectite
  - Clinoptilolite → Analcime
  - Mordenite → Analcime

Schematic Cross Section in Central Portion of Repository Block



RTMSDB5P.125.NWTRB/10-8/10-91

Heating of Tuffs in the Vicinity of Repository Due to Radioactive Decay of Waste

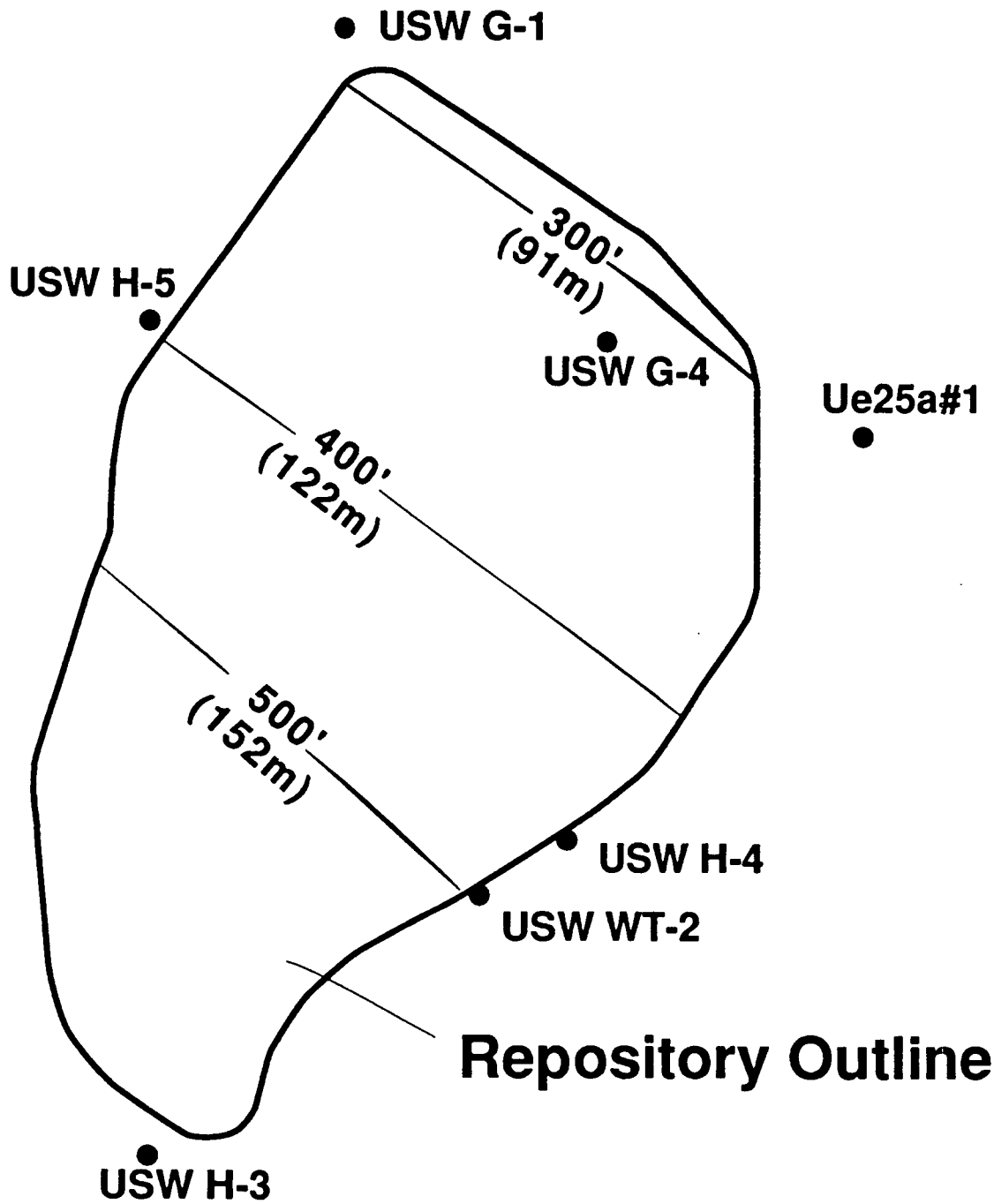


- - - - - - - -	APD = 57 kW/a
————	APD = 80 kW/a
APD = Areal Power Density	

Modified from Brandshaug (Figs. 6-1 and 6-2, SAND87-7079). Geologic contacts for USW G-4; position of repository and geotherms adjusted to stratigraphy in USW G-4.

RTMSDB5P.125.NWTRB/10-8/10-91

Contour Map of the Thickness Between Base of Repository and Top of Major Zeolite Horizons



RTMSDB5P.125.NWTRB/10-8/10-91

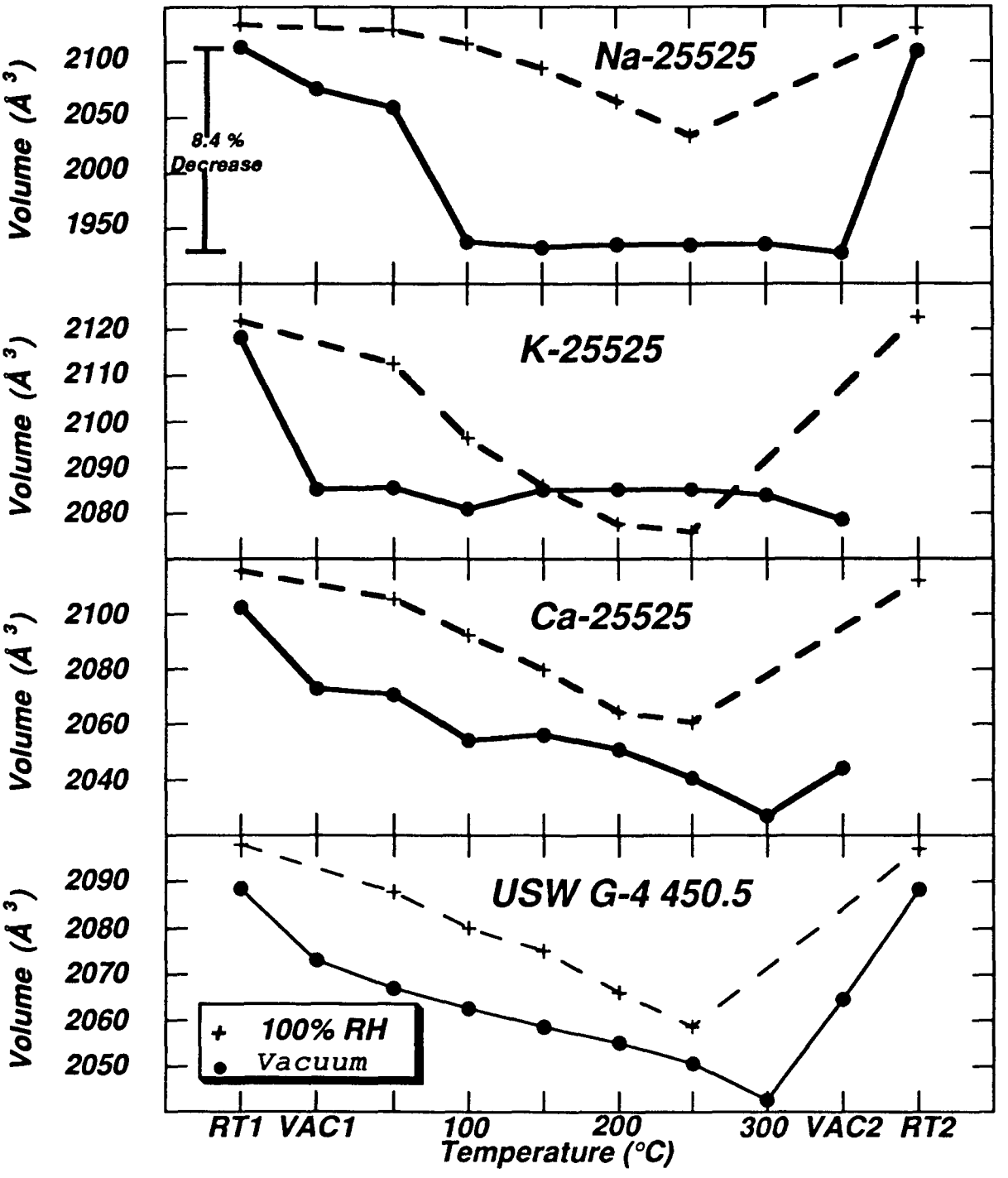
Dehydration/Rehydration

- Mineral hydration state will change whenever P_{H_2O} or temperature changes
- Most reactions are reversible, i.e., minerals will rehydrate as temperatures decrease
- Uncertainty is not strongly dependent on temperature
- Critical uncertainty is the vapor pressure of H_2O in the repository environment
- Requires coupled models

Expansion/Contraction of Zeolites and Smectites

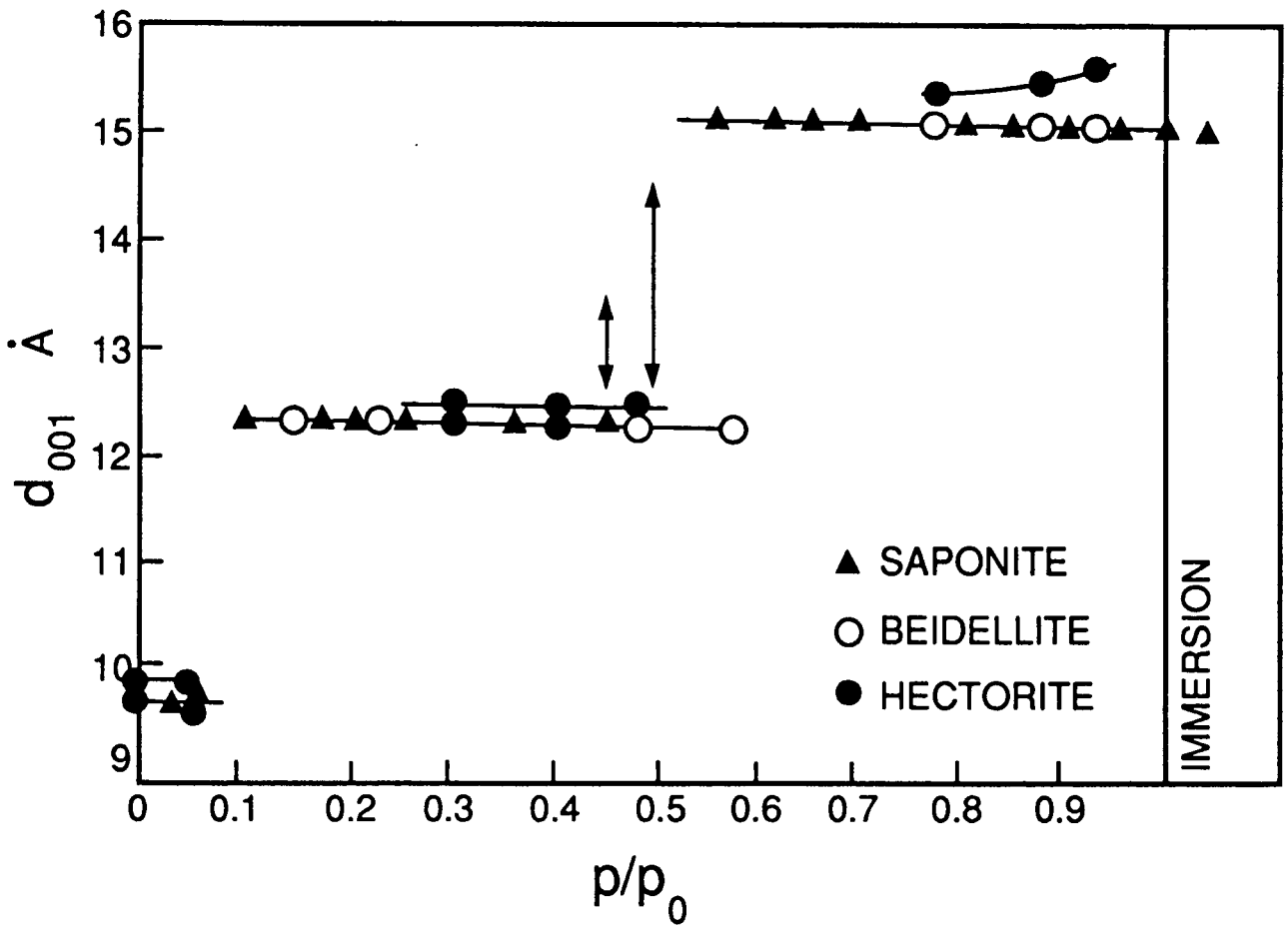
- Function of P_{H_2O} and temperature
- Minerals readily contract on dehydration
  - Zeolites by only several %
  - Smectites by a factor of 2 or more
- Potentially enlarge transport pathways
  - Pathways will probably return to original state when minerals rehydrate (based on volumetric data)
  - Gaseous transport may be more important when dehydrated
- Effects of expansive strains
  - Potential effect on rock strength
- Short-term contraction is reversible, but long-term contraction may not be easily reversible, particularly for clinoptilolite

Effects of Temperature and P_{H_2O} on Clinoptilolite Unit Cell Volume



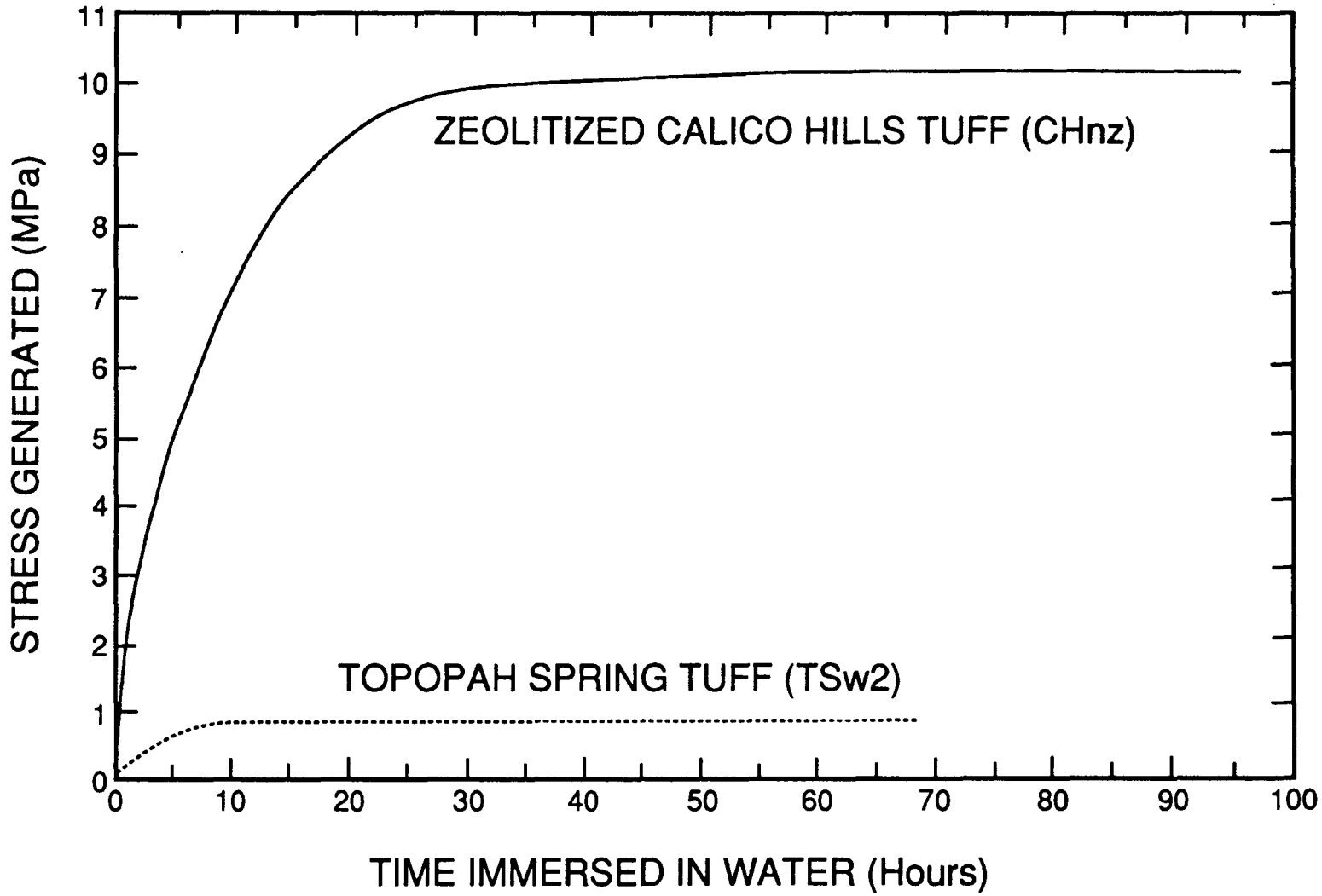
RT1 & RT2 data obtained at 23°C in air.
VAC1 & VAC2 data obtained at 23°C in vacuum.

Basal Spacing/Vapor Pressure Relations for NA-smectites



RTMSDB5P.125.NWTRB/10-8/10-91

Yucca Mountain Tuff
Axially Confined Hydration



RTMSDB5P.125.NWTRB/10-8/10-91

Effects of Heating on Sorption Properties

- Little or no effects on smectite unless transformed to illite/smectite or illite
- Little or no effects on zeolites, even when irreversibly collapsed

Sorption Ratios (R_D)[1] for Heated and Unheated Clinoptilolite

	Unheated	105° C[2]	200° C[2]
Sr	19100 (9000)[3]	17000 (1800)	29000 (5200)
Cs	13700 (100)	22700 (1700)	37000 (2000)
Ba	433000 (8000)	418000 (65000)	244000 (31000)
Eu	1950 (100)	2800 (300)	2400 (100)

[1] $R_D = \frac{\text{activity on solid phase per unit mass of solid}}{\text{activity in solution per unit volume of solution}}$ (measured at 23°C)

[2] All heatings for 385 days, dry

[3] Values in parentheses are estimated standard deviations

Long-Term Stability of Minerals Near Candidate Host Rock

- Clinoptilolite
  - Appears stable in saturated rock to ~100°C, may react to mordenite or analcime [f (a_{SiO_2})?]
- Mordenite
  - Appears stable in saturated rock to at least 130° C
- Glass
  - May alter at low temperatures in saturated rock to silica phases, smectite, or zeolites
  - Non-welded vitric tuffs will probably alter to clinoptilolite and smectite when in contact with hot condensate

Long-Term Stability of Minerals Near Candidate Host Rock

(Continued)

- Cristobalite/Tridymite
  - Can react to quartz at low temperatures (<100° C) through a solution/reprecipitation reaction ($\Delta V_{cr\text{-}q}$ = -3.24 cm^3/mol, -12.5%) (10-20% cristobalite in TSw2)
- $\alpha \rightarrow \beta$ cristobalite @ 230 $\pm$ 20° C, ΔV = +4.0%
- Smectite
  - Progressively reacts through illite/smectite series with increasing temperature under saturated conditions
  - Requires temperatures above 100° C for times in excess of 10^6 years
- Increasing temperature improves predictability-partially mitigates kinetic problems

Vitrophyre Alteration

- Transition zone between Topopah Spring devitrified tuff (TSw2) and vitrophyre (TSw3) a potential natural analog to repository- induced alteration
  - State of saturation uncertain and spatially variable
- Alteration dynamic, concentrated around fractures
- Natural alteration assemblage suggests vitrophyre alteration to clinoptilolite, smectite, and silica phases between 40 and 100° C (oxygen isotope geothermometry)

Isotopic Compositions and Temperatures of Secondary Quartz Formation

Sample	$\delta^{18}O$ (‰ , SMOW)	T_A (°C)	T_B (°C)
VH2-3545-q	13.0	65	95
VH2-3565a	11.9	70	100
YF-4-q	17.8	40	70

T_A Calculated from Clayton & others (1972)
T_B Calculated from Bottinga & Javoy(1973)
$\delta^{18}O$ of -13.5‰ assumed for the water
Analyses reproducible to $\pm$0.1‰

Summary

- Significant amounts of volcanic glass, zeolites, and smectites occur in proximity to the repository horizon (beneath)
- Hydration state of zeolites and clays will change whenever temperature or P_{H_2O} changes
  - Volume decreases-reversible
  - Creation of fractures, differential stresses
- Sorptive properties are little affected by dehydration or collapse
- Temperatures of ~100° C and long times (> 10^5 years?) are required to transform the zeolites or smectites to other less sorptive phases

Summary

(Continued)

- Volcanic glass may transform to zeolites and/or smectite at temperatures as low as 40° C in the presence of H_2O
- Increasing temperature generally improves predictability because of kinetic problems at lower temperatures
- Some of the thermal reactions, e.g., glass to zeolite and smectite, may be beneficial although they will cause a modification of flow paths

Mineralogical Uncertainties

- Benefits to lower thermal loading (smaller rock volume affected, lower intensity alteration) probably outweigh those of higher thermal loading (larger rock volume dried)

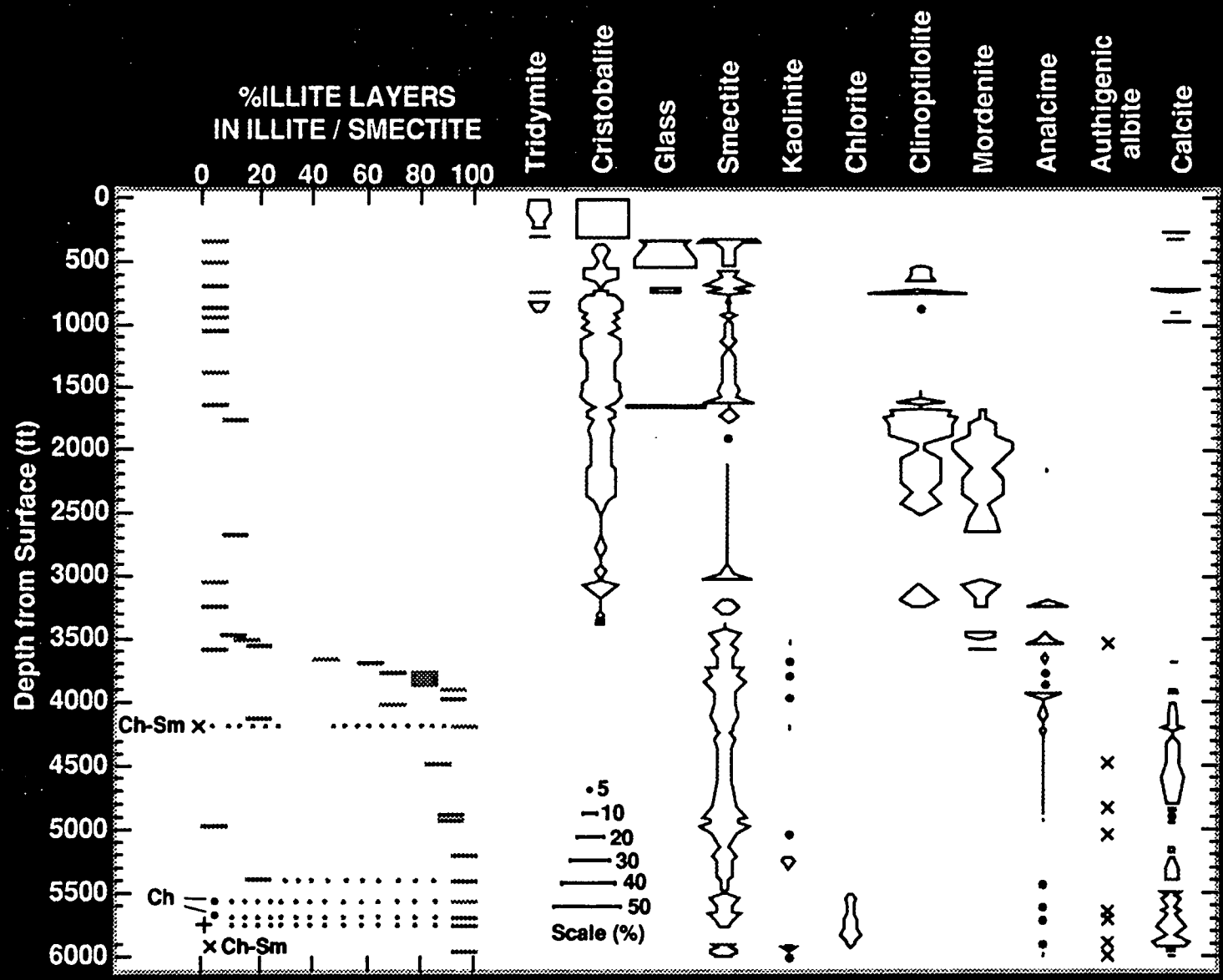
- Potential mineralogical problems associated with higher loading (alteration of zeolitized tuff) are greater than those associated with lower loading

- Uncertainties in mineral alteration
  - time - temperature - saturation information
  - kinetics of low-temperature mineral reactions

- Resolution of uncertainties
  - Experimental data
  - Natural analog - field data
  - Consider mineralogic reactions in modeling

Conclusions

- Changing the thermal load will probably only modify the <u>extent</u> of the above reactions, <u>not</u> <u>eliminate</u> them
- Understanding of thermal effects will require coupled models and some additional experimental data


%ILLITE LAYERS
IN ILLITE / SMECTITE
0
20
40
60
80
100
Depth from Surface (ft)
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
5500
6000
Ch-Sm
Ch
Ch-Sm
Tridymite
Cristobalite
Glass
Smectite
Kaolinite
Chlorite
Clinoptilolite
Mordenite
Analcime
Authigenic albite
Calcite
5
10
20
30
40
50
Scale (%)