GAS-WATER-ROCK GEOCHEMISTRY

AT THE PROPOSED YUCCA MOUNTAIN REPOSITORY
UNDER VARIOUS THERMAL LOADS: RELATIONS TO FLUID FLOW

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KEY GEOCHEMICAL PROCESSES AND PARAMETERS
FOR THE REPOSITORY AT YUCCA MOUNTAIN

Gas-water-rock interactions affect repository performance through:

Containment:	Waste package degradation processes;
Source Term:	Waste form alteration and dissolution, Radioelement solubilities;
Transport:	Hydrologic and transport properties, Radioelement speciation, Distribution of radioelements (retardation).

Temperature affects equilibria and rates of chemical reactions.
Pressure affects liquid phase stability.
Materials control variations in phase compositions.
Oxidation state affects material stability, reaction rates and speciation.
Gas flow and gas-phase transport affect H_2O, CO_2, and O_2 pressures.
Liquid flow affects aqueous transport.
Evaporation (condensation) affects solution concentrations and
    precipitation (dissolution).
Vapor pressure lowering affects moisture distribution.

LIKELY GEOCHEMICAL EFFECTS OF HEATING AT YUCCA MT.

Volatilization and redistribution of CO_2 and H_2O:
With increasing temperature CO_2 and H_2O are strongly partitioned into the gas phase.

pH increase:
Due mainly to depletion in carbonic acid, increases in pH modify mineral stabilities, reaction rates and aqueous speciation.

Precipitation, then dissolution of calcite:
Temperature-retrograde and pH-dependent solubility and fast reaction rate of calcite lead to initial precipitation, then redissolution at long times.

Dissolution of feldspars, cristobalite, tridymite, and glass:
Increasing temperature and pH increase rates of reaction and solubilities.

Increase in sodium bicarbonate concentration:
Dissolution of feldspar and glass leads to increasing sodium bicarbonate concentrations.

Growth and ion exchange of zeolites and clay minerals (and quartz growth?):
Low solubility leads to precipitation of hydrated secondary alumino-silicates.
Changes in aqueous ion activity ratios and differing temperature effects on thermodynamics lead to ion exchange between solid and aqueous solutions.
Metastably supersaturated solutions may precipitate quartz lowering the silica activity.

Brine and salt formation and dissolution:
Drying at elevated temperatures leads to brine formation and precipitation of salts such as $NaHCO_3$ and $NaCl$. Vapor presure lowering over the salts stabilizes water at temperatures above the nominal boiling point. Rehydration dissolves preciptitated salts.

GEOCHEMICAL MODELING:
KEY CONCEPTS FOR THE YUCCA MOUNTAIN REPOSITORY

Staged modeling: Natural system -- Nonisothermal system -- Evaporative system

System components:
$(Na,K)AlSi_3O_8$ -- feldspar
SiO_2 -- cristobalite/quartz
H_2O/CO_2 -- liquid/vapor
$NaCl$ -- electrolyte
$CaCO_3$ -- calcite
$(Na_2,K_2,Ca)Al_2Si_{10}O_{24} \cdot 8H_2O$ -- clinoptilolite
$(Na_{.33},K_{.33},Ca_{.165})Al_{2.33}Si_{3.67}O_{10}(OH)_2$ -- smectite

Natural model:
Recharging water from the soil zone is saturated with calcite.
CO_2 gas pressure is buffered.
Feldspar/glass dissolution promotes clinoptilolite growth.

Nonisothermal model:
Temperature-time relations are derived from heat flow modeling.
Initial conditions are derived from ambient system modeling.
Variations in CO_2 gas fugacity are derived by gas flow and transport
modeling coupled with a local-equilibrium chemical model.
Reaction progress-time relations are derived from kinetic modeling.

Evaporative model:
Rayleigh fractionation versus CO_2 buffered systems models.
Equilibrium precipitation versus supersaturation models.
Vapor pressure lowering stabilizes liquid water at elevated
temperatures.

CHEMICAL PRINCIPLES AND COMPUTATIONAL METHODOLOGY

CARBON SYSTEM MODELS

Conductive heat flow
Averaged one-dimensional gas flow
CO_2 transport by advection
Local equilibrium among gas, aqueous, and calcite phases based on mass
conservation, electroneutrality, and mass action relations
Aqueous activity coefficients based on an extended Debye-Huckle formulation

Computations were performed with codes written by Codell, Goulet, and
Murphy and thermodynamic data from DATA0.COM (Johnson et al.).

PARTIAL EQUILIBRIUM REACTION PATH MODELS

Equilibrium among gas, aqueous, and secondary minerals based on mass
conservation, electroneutrality, and mass action relations
Aqueous activity coefficients based on an extended Debye-Huckle formulation
Dissolution and growth of feldspar and cristobalite based on rate expressions
Time obtained by integrating rate equations for increments of mass transfer
CO_2 gas fugacity controlled as a function of time and temperature

Computations were performed with the EQ3/6 software (Wolery et al.) and
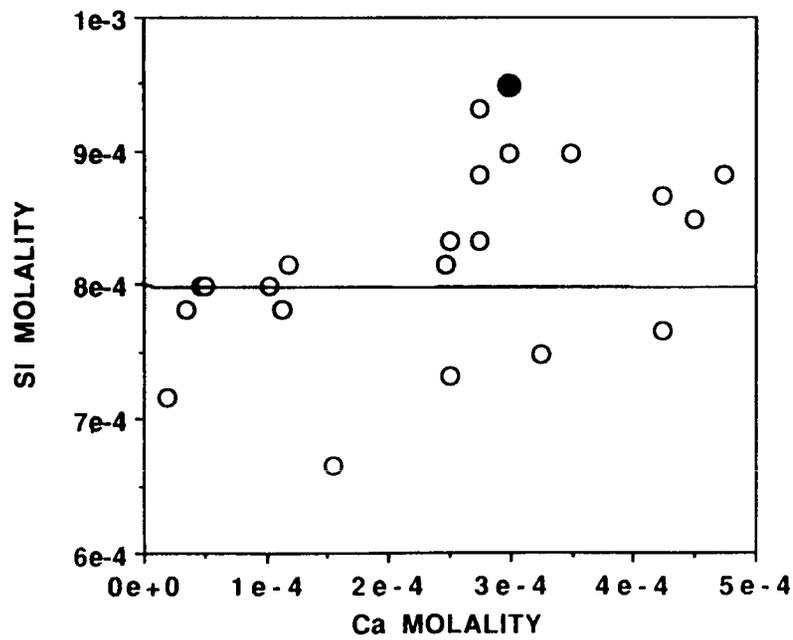modified DATA0.COM data.

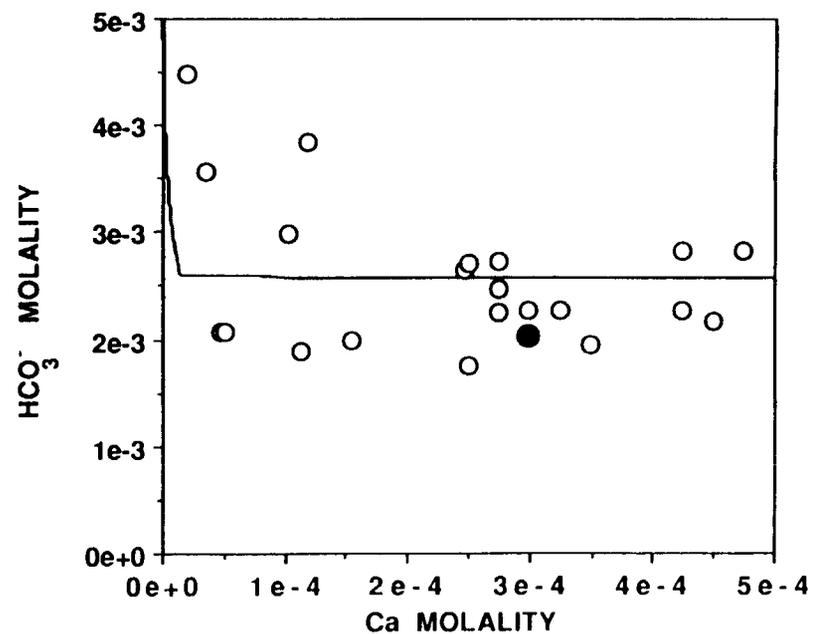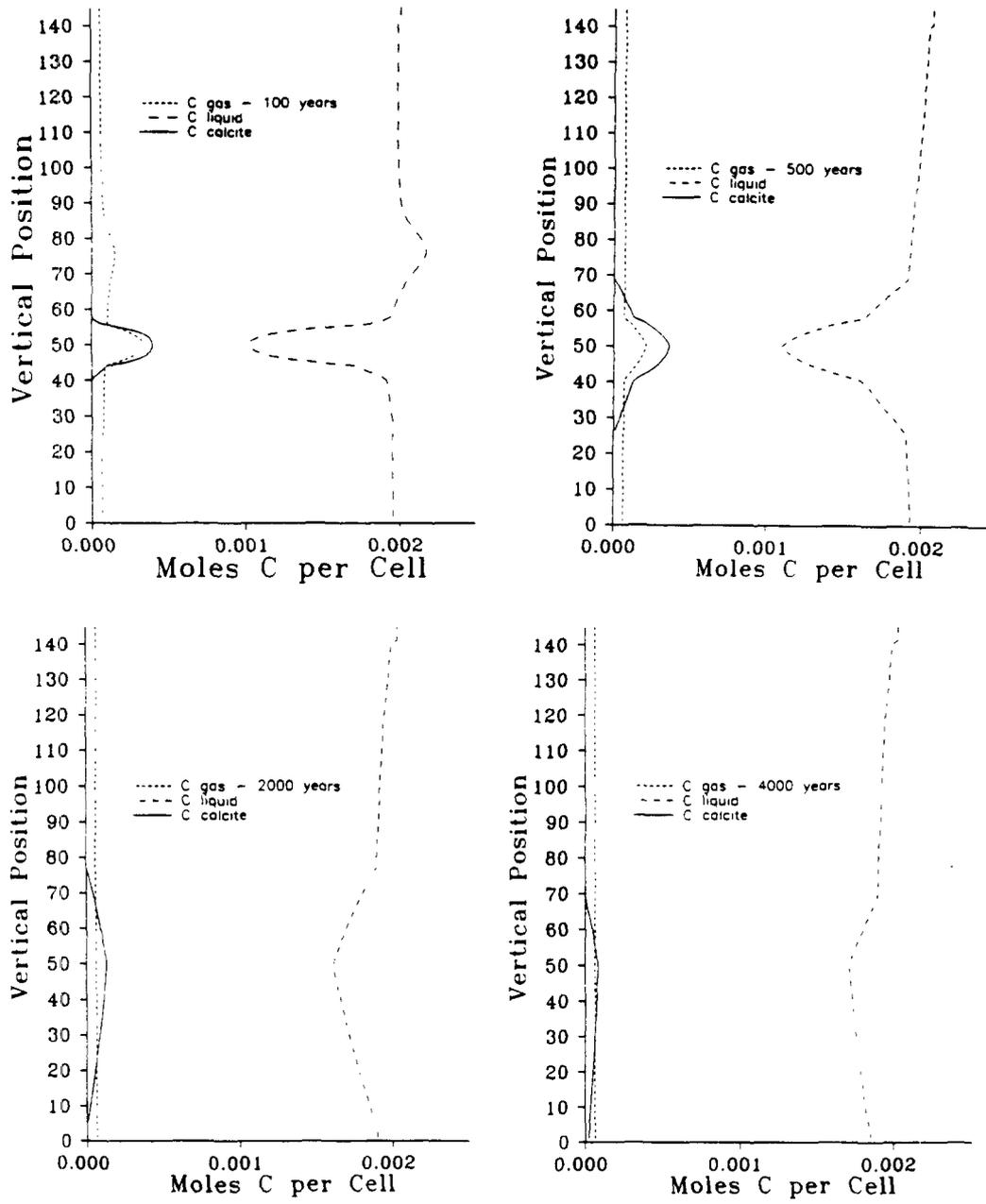LINES: 25°C REACTION PATH MODEL; CIRCLES: YUCCA MOUNTAIN GROUNDWATER DATA
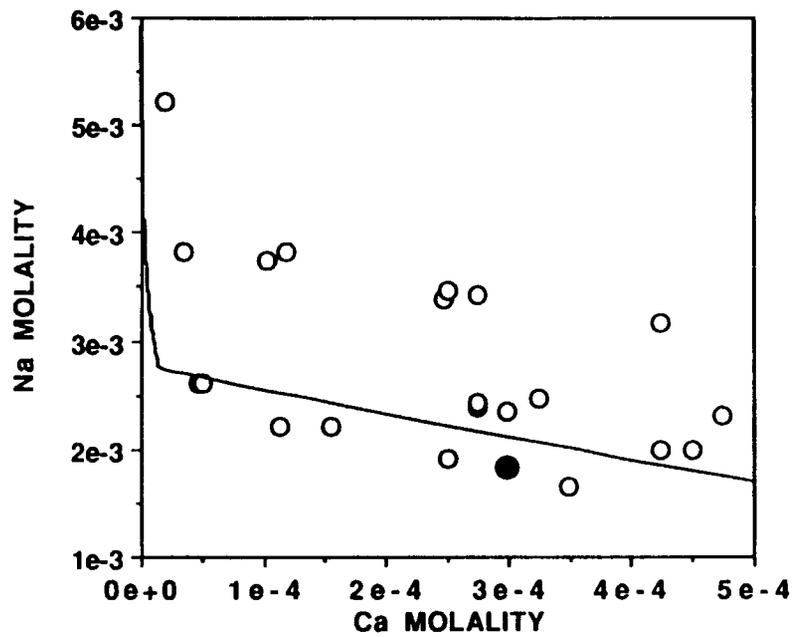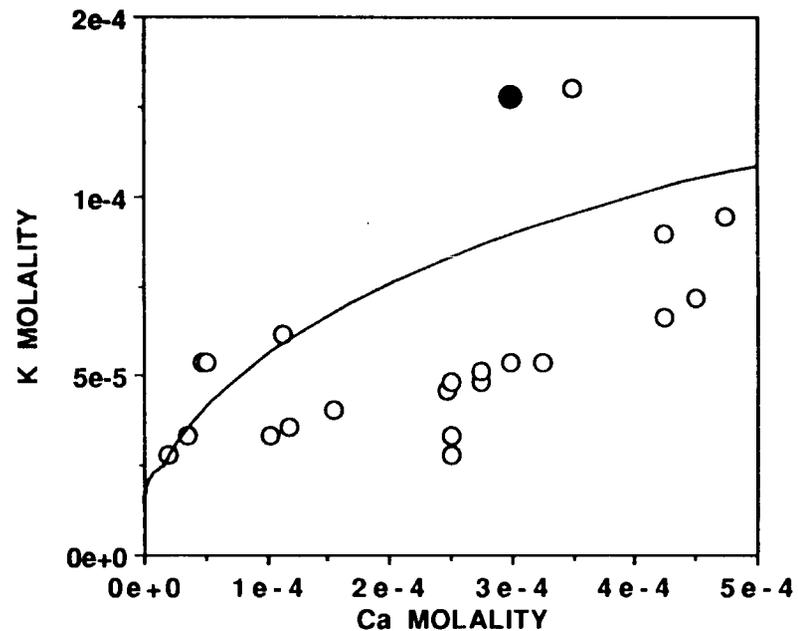
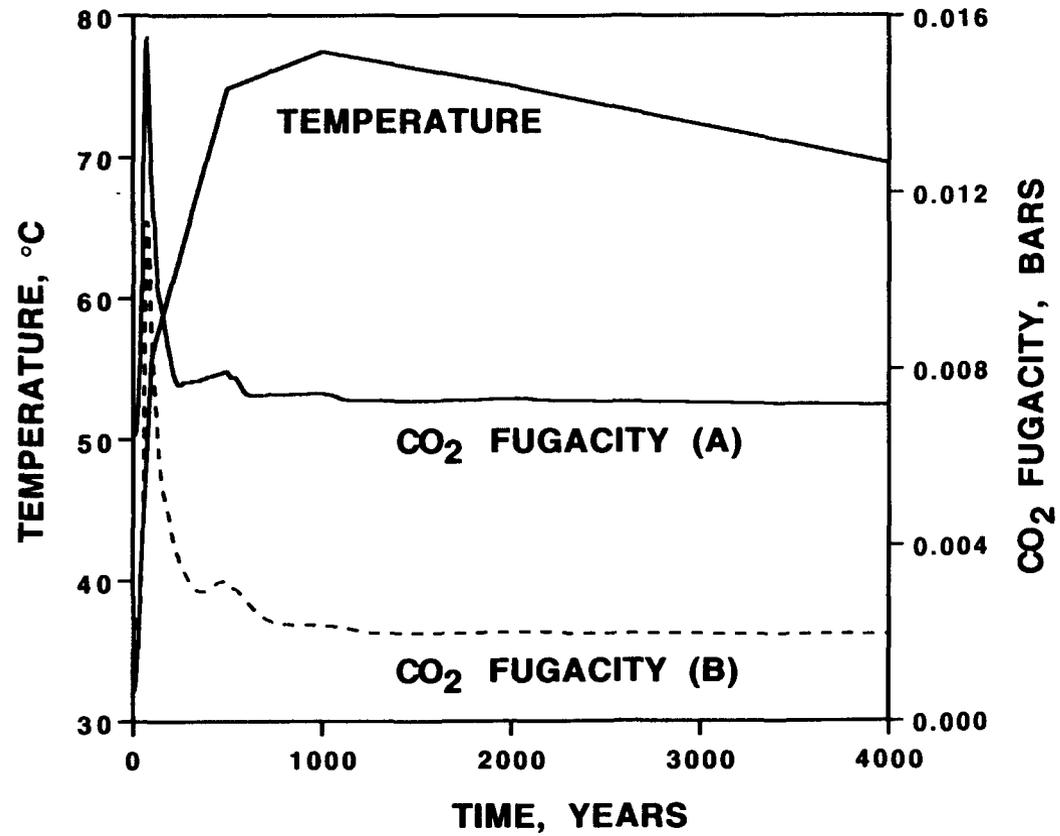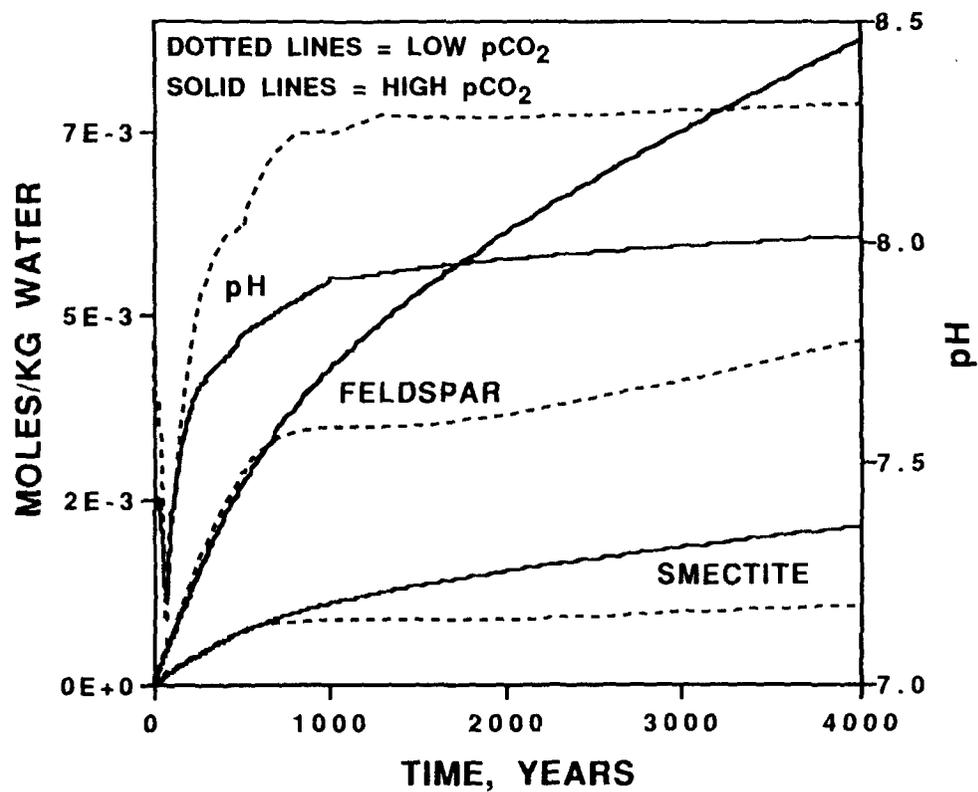Figure 5 - Carbon content of gas, liquid and solid phases
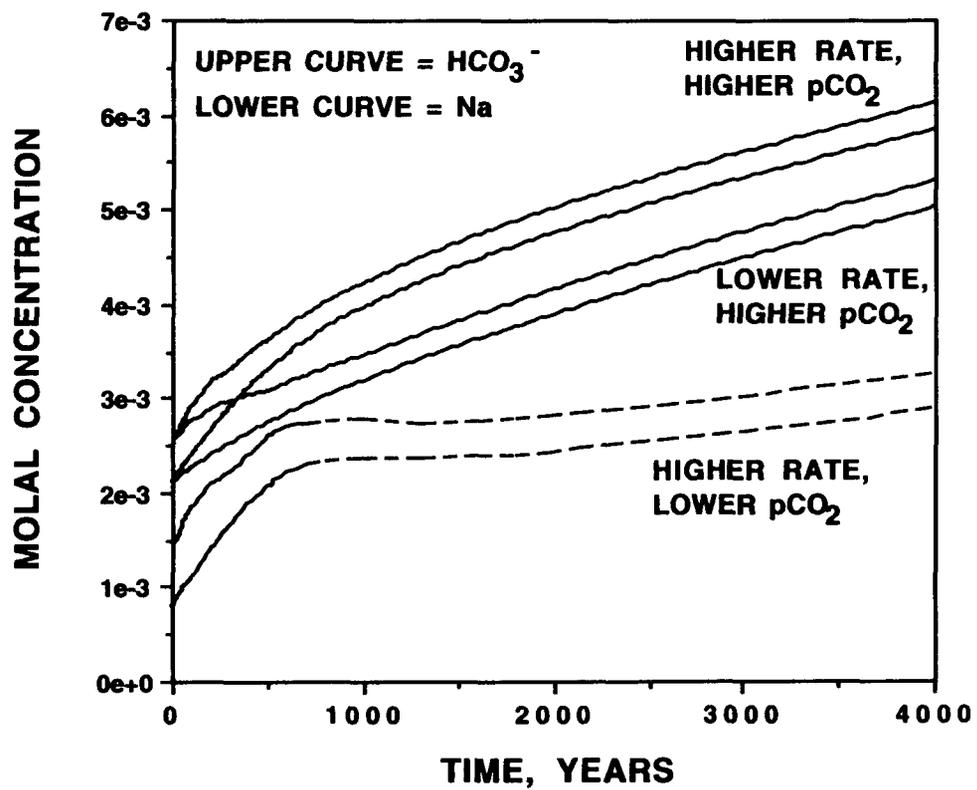between the water table and the ground surface

VARIATION IN TEMPERATURE AND CO_2 FUGACITY
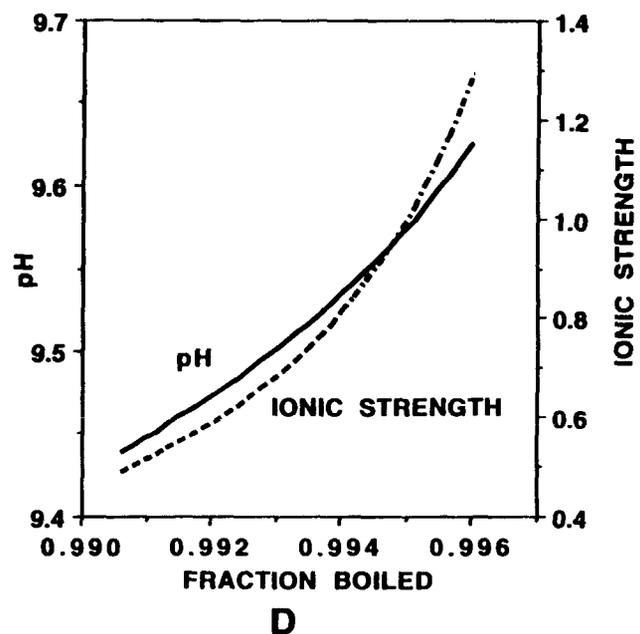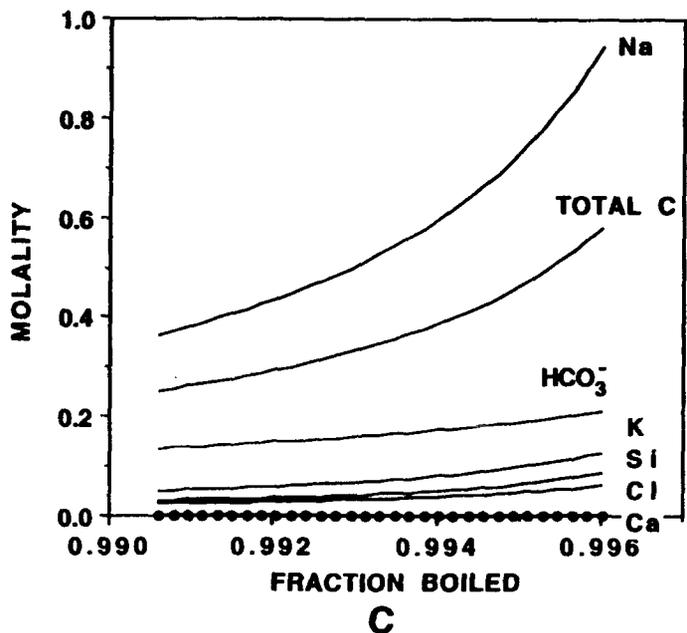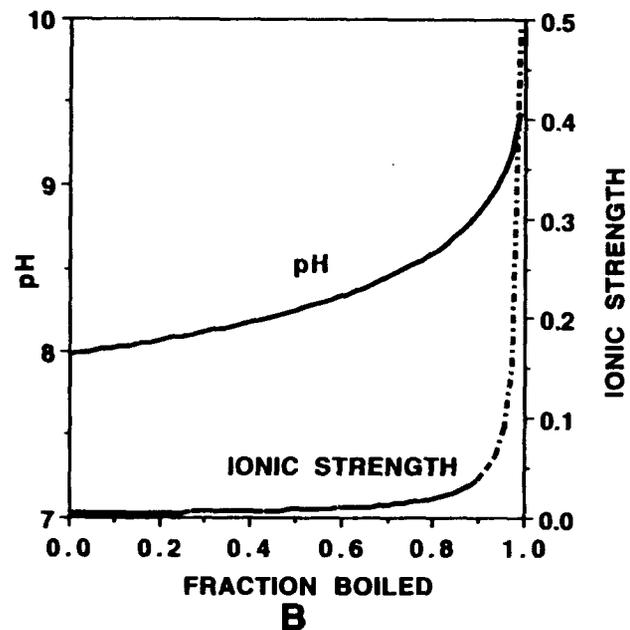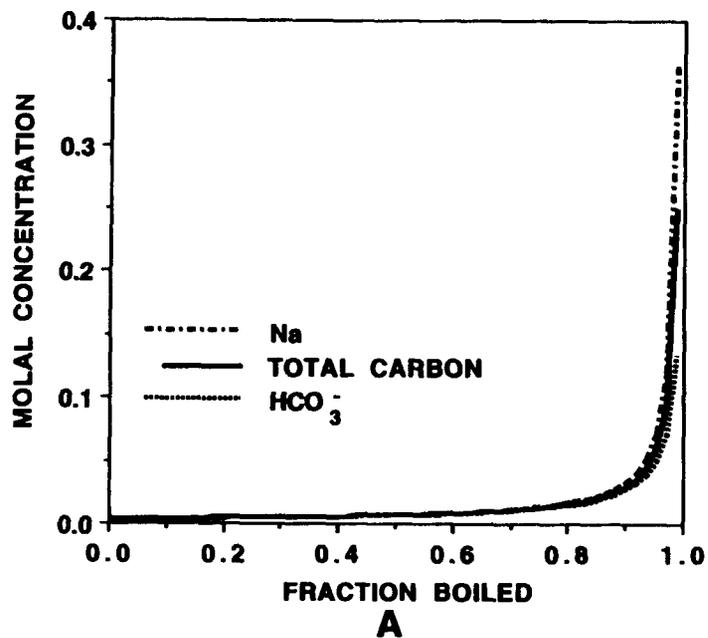75 METERS ABOVE THE REPOSITORY HORIZON

VARIATION IN pH, FELDSPAR DISSOLUTION, AND SMECTITE PRECIPITATION 75 METERS ABOVE THE REPOSITORY HORIZON

VARIATION IN MAJOR SOLUTION COMPONENTS
75 METERS ABOVE THE REPOSITORY HORIZON

UPPER CURVE = HCO_3^-

LOWER CURVE = Na

HIGHER RATE, HIGHER pCO_2

LOWER RATE, HIGHER pCO_2

HIGHER RATE, LOWER pCO_2

ECTS OF BOILING ON WATER CHE. TRY WITH MINERAL PRECIPITATION AT 100°C AND CO_2 PRESSURE AT $10^{-2.14}$ BAR.

YUCCA MOUNTAIN REPOSITORY GEOCHEMISTRY: RELATIONS TO THERMAL LOADING AND FLUID FLOW

FLUID FLOW:

Redistribution of H_2O and CO_2 by gas phase flow would affect aqueous solution properties on a large (e.g., mountain-sized) scale.

Zeolitization of bedded vitric tuffs could affect hydraulic properties.

Precipitation of calcite (or other minerals) could affect hydraulic properties.

Most chemical reactions would occur in the matrix, where the water is, and most flow of significance to repository performance would be in the fractures. However, alteration of fracture lining minerals could affect flow and transport.

INCREASED THERMAL LOADING:

Time and space scales of thermal effects would increase with increasing thermal loading.

At elevated temperature and decreased H_2O vapor pressure, hydrated minerals could dehydrate and smectites could alter to illite, which could affect sorption or hydraulic properties.

Heating could affect near-field materials, e.g., dehydration or cracking of grout and corrosion of rock bolts.