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

PRESENTATION TO
THE NUCLEAR WASTE TECHNICAL REVIEW BOARD

SUBJECT: GEOCHEMICAL INTERACTIONS

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Waste Package Near-Field Chemistry and Mineralogy

This task defines the chemical conditions the waste package might experience

This information is required for

- Evaluation of candidate container materials
- Generation of source term
- Satisfying regulatory requirements

Organization

Ambient conditions

- Water chemistry

Perturbed conditions

- Types of processes
- Evaluation of processes

Modeling Activities

Summary

Ambient Conditions Affecting the Chemical Environment

- Unsaturated
- Slightly oxidizing
- Gas phase is primarily air
- Vadose water composition unknown but must approach equilibrium with Tpt

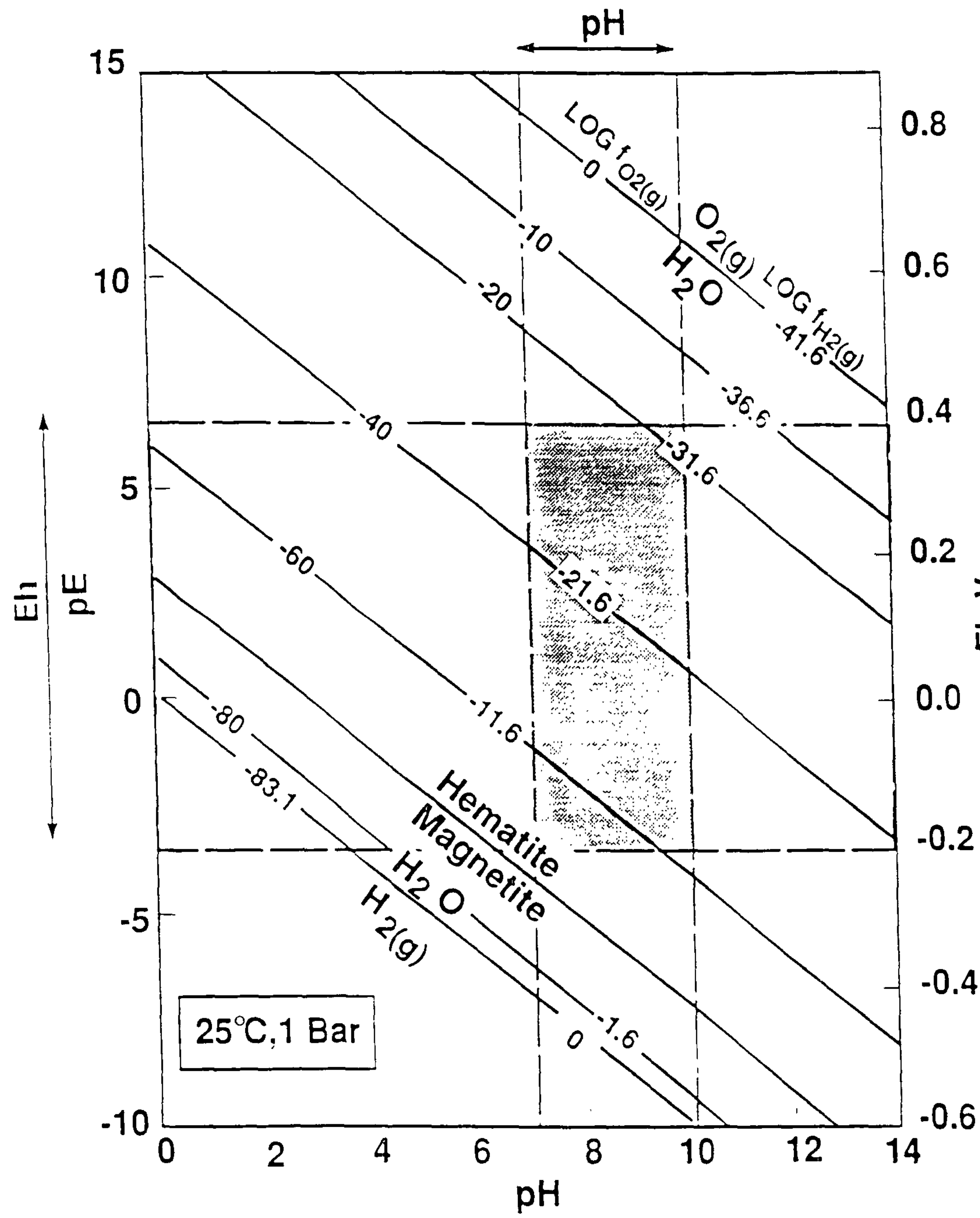
Chemical Composition (mg/l)

	J-13*	Extracted pore water**
Li	0.04 - 0.17	
Na	42 - 50	26 - 65
K	3.7 - 6.6	5 - 15
Mg	1.7 - 2.5	5 - 21
Ca	11.5 - 15	27 - 127
Sr	0.02 - 0.1	0.55 - 1.5
Fe	<0.01 - 0.16	<0.003 - 0.118
Al	0.008 - 0.11	
Si	26.6 - 31.9	72 - 100
NO_3	6.8 - 10.1	
F	1.7 - 2.7	
Cl	6.3 - 8.4	34 - 105
HCO_3	118 - 143	
SO_4	17 - 21	37 - 174
pH	6.8 - 8.3	

* Tables 4.1 and 4.2, Harrar et al., 1988.

** Triaxial - compression extractions from unsaturated tuff, Yucca Mt., Yang et al., 1988.

APPROXIMATE Eh-pH RANGES OF YUCCA MOUNTAIN WATERS (SHADED REGION)



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Radionuclide Behavior at Elevated Temperature

Strategy:

- Establish near-field flow and transport properties
- Identify solution composition entering and leaving container
  (Includes interactions with corrosion products)
- Establish solution-rock interaction, and flow and transport properties in near-field for released fluid

Require:

- Results of waste form-water interaction (in progress)
- Sorption and transport characteristics of near-field incorporated in code (in progress)

Will begin modeling and experimental/field studies when "in progress" work sufficiently advanced.

Conditions that Influence Chemical Environment after Waste Package Emplacement

- Thermal peak (~240°C) within ~40 years after emplacement followed by thousands of years of cooldown

- Vaporization of water in rock near boreholes with development of a saturation halo followed by slow rehydration

- Reaction products from radiolysis of moist air/steam in proximity to borehole wall

- Presence of man-made materials (concrete, shotcrete, human biological wastes, etc.)

Assumptions Necessary to Conduct Modeling of Long-Term Behavior

- Chemical equilibrium is approached but not attained

    ∴ Reaction <u>kinetics</u> important

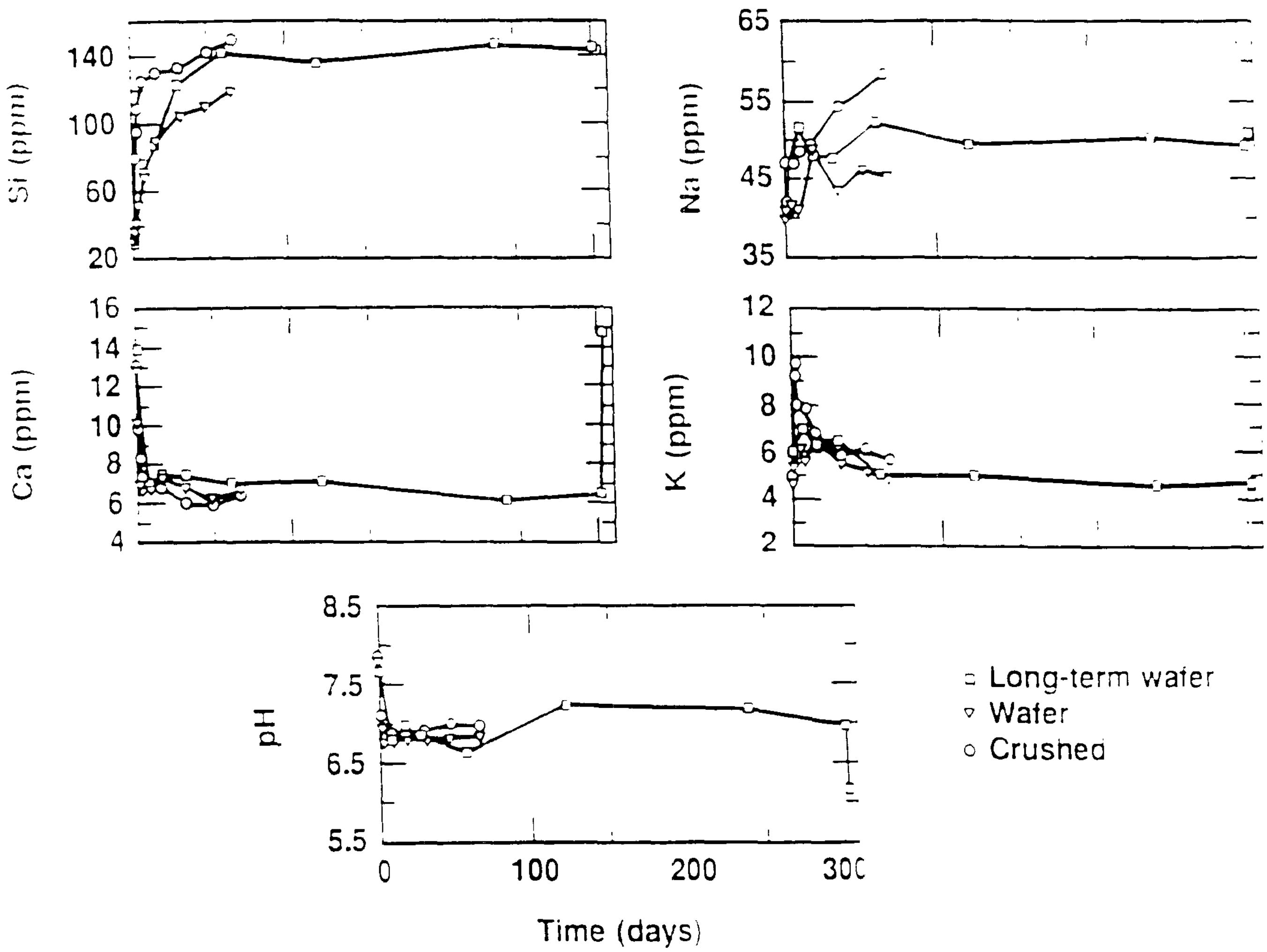
- Thermal stability of minerals is a function of composition

    ∴ <u>Solid solution</u> models must be available

- Interaction of pore water with man-made materials (concrete, paint, human biological wastes, etc.) will modify water composition

    ∴ Effects of <u>man-made materials</u> on water–rock interaction must be established

ROCK-WATER INTERACTION AT 150° C



Thermal Stability of Minerals

Near field studies concerned with high temperature range ($25^{o}C \sim 250^{o}C$) at variable saturations

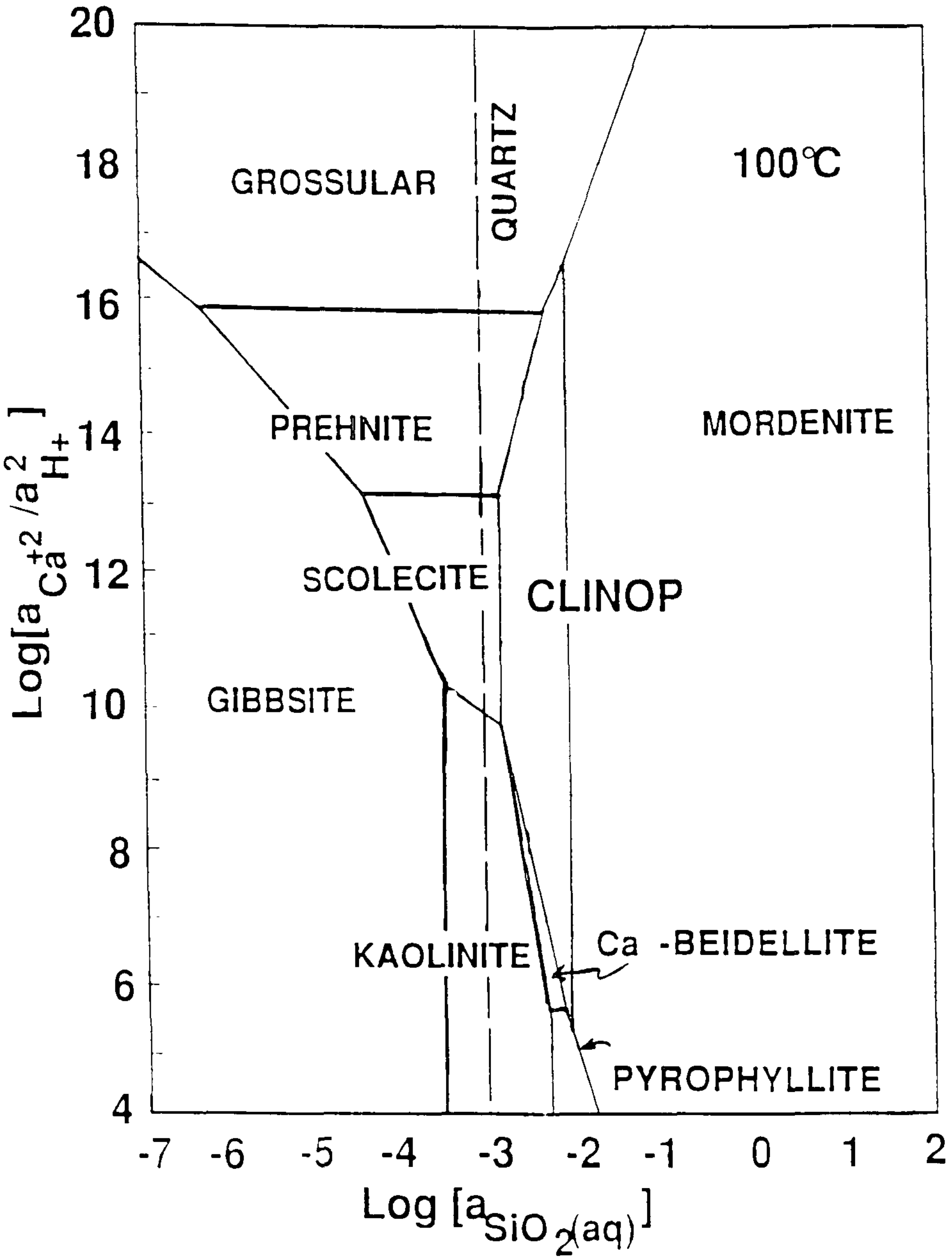
Strategy:

- Establish composition isotherms and thermodynamic properties

- Compare results with laboratory experiments at variable temperature and water chemistry

- Define stability fields as a function of temperature, fluid composition and rock mineralogy

THERMAL STABILITY OF MINERALS AT ELEVATED TEMPERATURES: AN EXAMPLE FROM THE $CaO-Al_2O_3-SiO_2-H_2O$ SYSTEM



Dissolution and Precipitation Kinetics Data

Dissolution

ALBITE*
CRISTOBALITE*
GIBBSITE
HEULANDITE
KAOLINITE
QUARTZ*

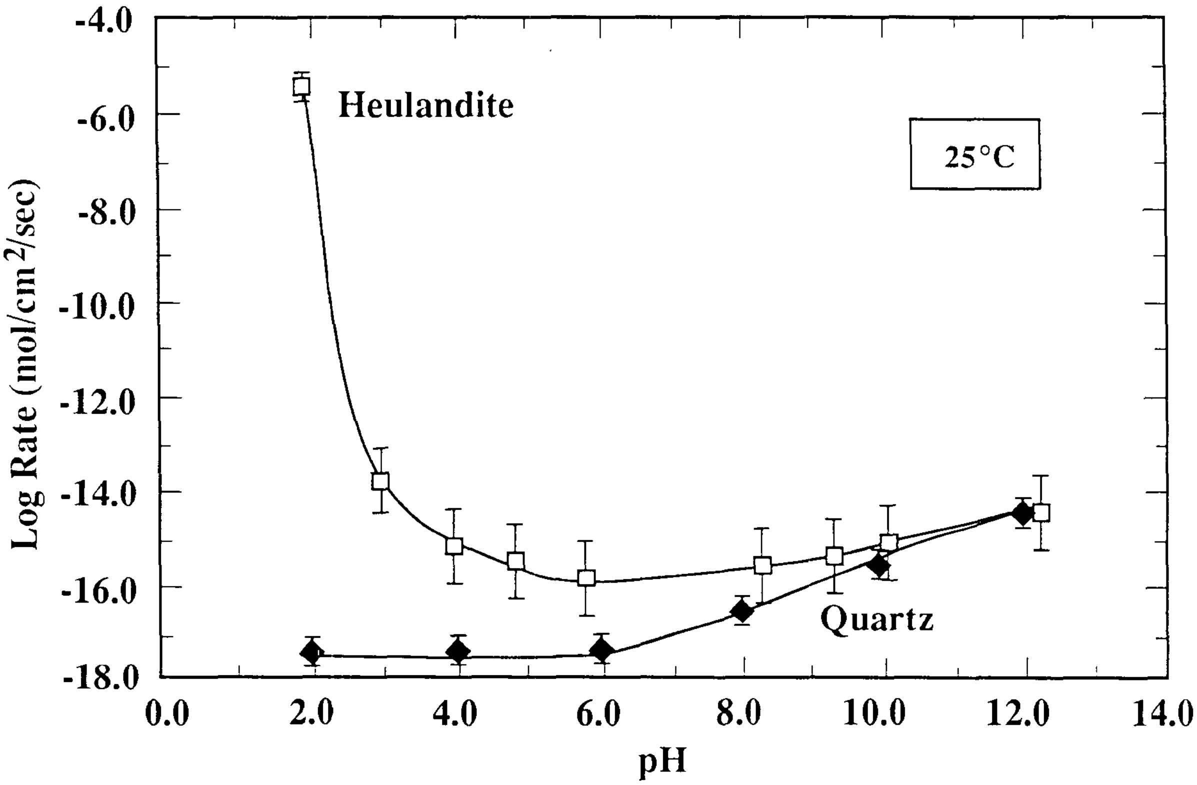
pH 2–12

TEMP $25^{O}C–240^{O}C$

Precipitation

AMORPHOUS SILICA
CRISTOBALITE
QUARTZ
KAOLINITE

QUARTZ AND HEULANDITE (Si) DISSOLUTION RATES



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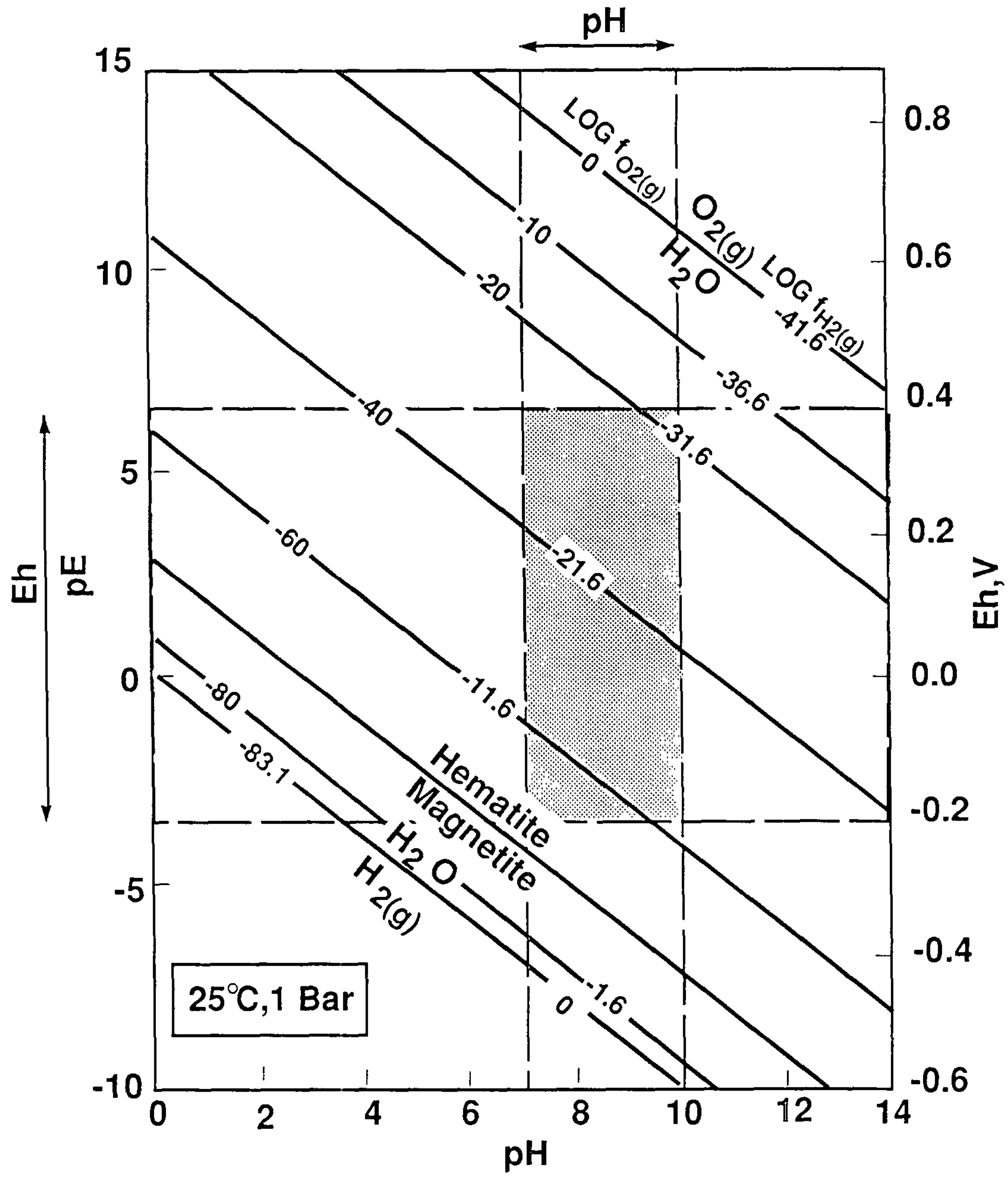

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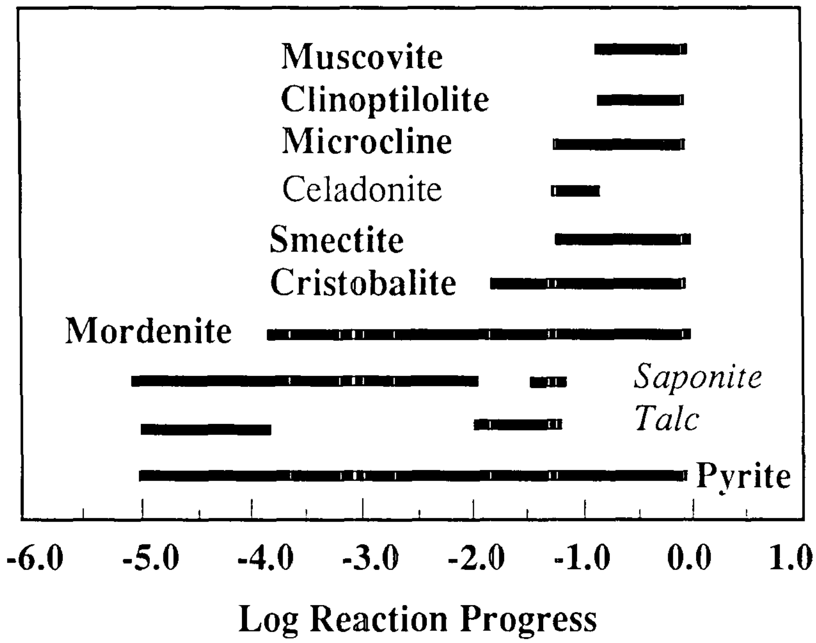
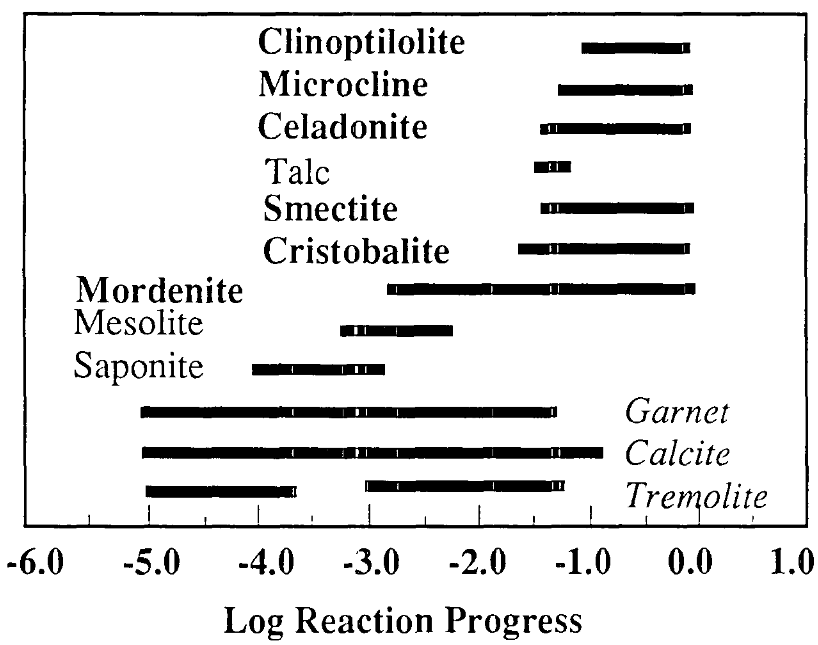
PARAGENETIC SEQUENCES IN SIMULATED WATER-ROCK INTERACTIONS (25° TO 90° C)



Initial Conditions:
-200 mV
7.0 pH



Initial Conditions:
+400 mV
10.0 pH

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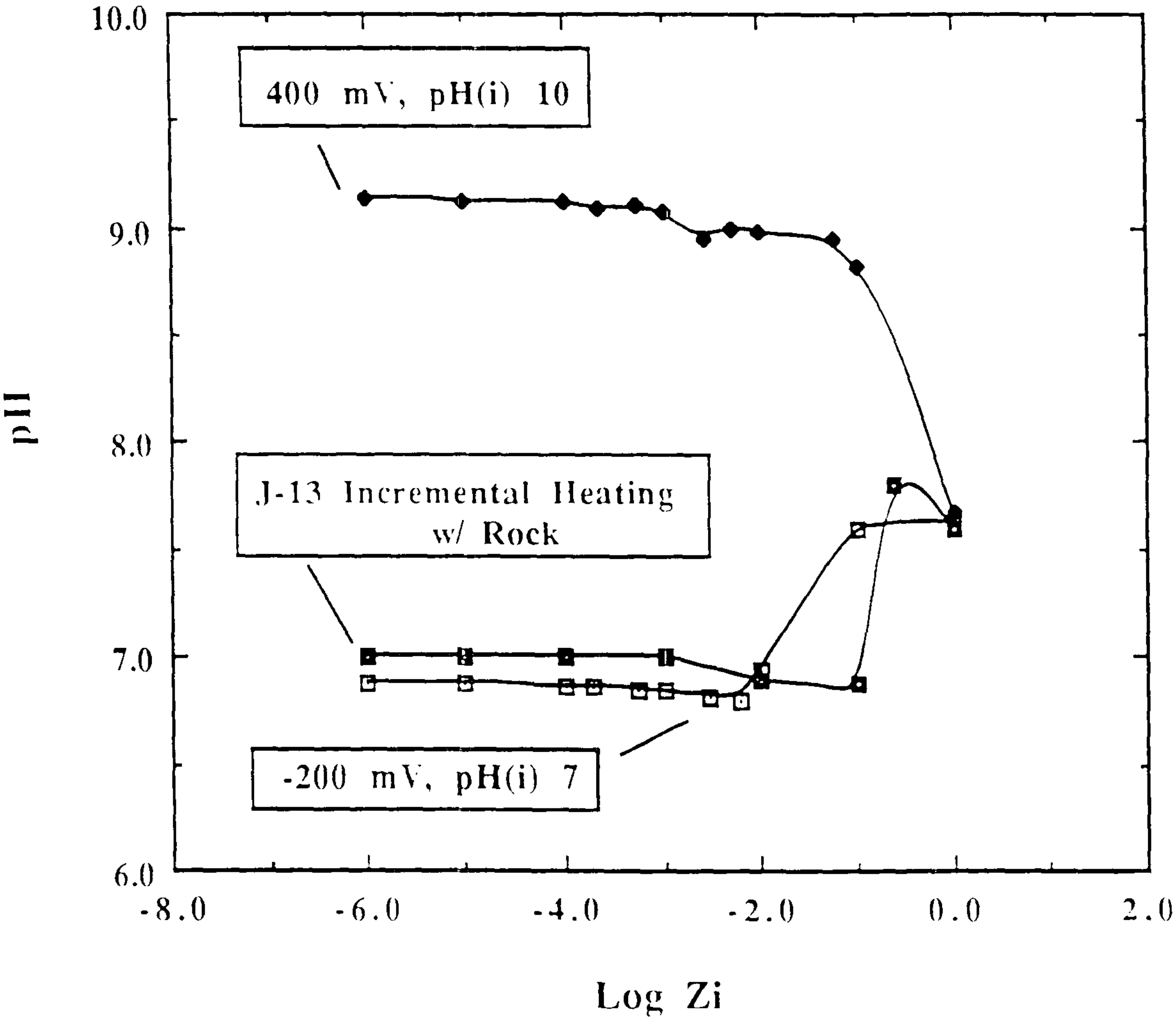
pH PROGRESS DURING SIMULATED WATER-ROCK INTERACTION (25 TO 90° C)



Summary

Reaction rates (kinetics) are being established

- Water–rock
- Dissolution precipitation

Thermal stabilities of phases are being established

- Solid solution models

Effects of man-made materials will be determined e.g cement can have high ph

Modeling is proceeding with available data

- Validation planned using lab, field, and natural analog systems