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

PRESENTATION TO THE NUCLEAR WASTE TECHNICAL REVIEW BOARD

SUBJECT: GEOCHEMICAL SIMULATION OF SPENT FUEL DISSOLUTION

PRESENTER: CAROL J. BRUTON

PRESENTER'S TITLE AND ORGANIZATION: GEOCHEMIST
LAWRENCE LIVERMORE NATIONAL LABORATORY
LIVERMORE, CALIFORNIA

PRESENTER'S TELEPHONE NUMBER: (415) 423-1936

AUGUST 28-29, 1990

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WHY USE GEOCHEMICAL MODELING?

- NUCLEAR WASTE REPOSITORY PERFORMANCE MUST BE EVALUATED OVER TIME PERIODS AS GREAT AS 10,000 YEARS IN RESPONSE TO CHANGES IN TEMPERATURE, FLUID FLOW AND OTHER CONDITIONS

- EXPERIMENTAL LIMITATIONS

  - LABORATORY TIME SCALE
  - NUMBER OF VARIABLES AND THEIR COMBINATIONS
  - EXTRAPOLATION TO MULTIPLE REPOSITORY SCENARIOS

EXPERIMENTS AND GEOCHEMICAL MODELING: A POWERFUL COMBINATION

- DEVELOPMENT OF QUANTITATIVE, PROCESS-ORIENTED MODELS OF REPOSITORY RESPONSE

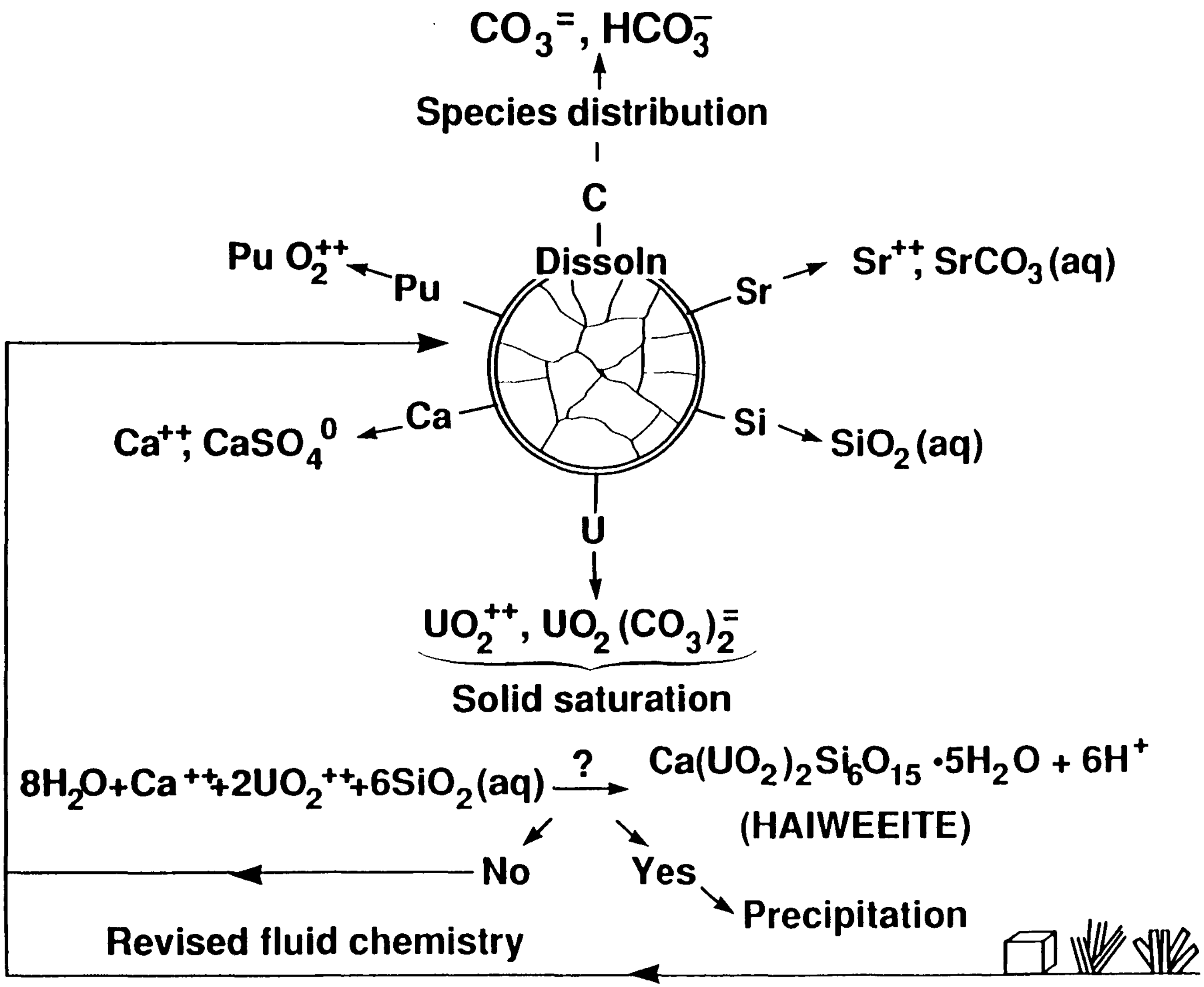
- SIMULATION OF THE COMPLEX INTERPLAY AMONG PROCESSES THAT CONTROL RATES OF WASTE FORM DEGRADATION

- PREDICTION OF CHANGES IN THE CHEMICAL ENVIRONMENT THROUGHOUT THE POST-CLOSURE PERIOD

EQ3/6 SOFTWARE PACKAGE FOR GEOCHEMICAL MODELING

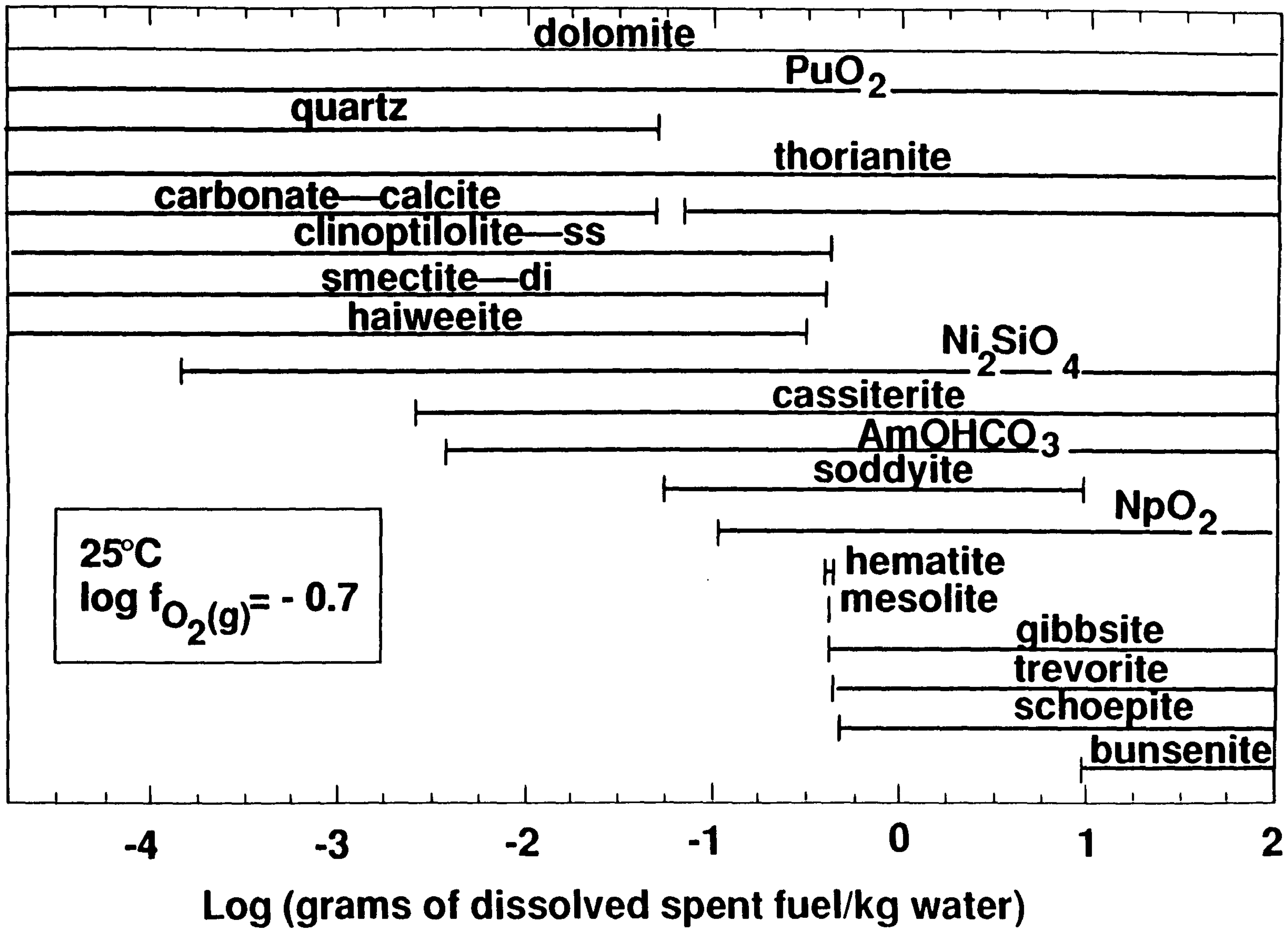
- EQ3 - AQUEOUS SPECIES DISTRIBUTION
- EQ6 - DYNAMIC SIMULATION OF INTERACTIONS AMONG HOST ROCKS, REPOSITORY COMPONENTS, AND FLUIDS
- THERMODYNAMIC DATA BASES - SOLIDS, GASES, INORGANIC AND ORGANIC AQUEOUS SPECIES

EQ 3/6



$CO_3^{=}$, HCO_3^{-}
Species distribution
C
Dissoln
Pu O_2^{++}
Pu
Sr
Sr^{++}; $SrCO_3(aq)$
Ca
Ca^{++}; $CaSO_4^{0}$
Si
$SiO_2(aq)$
U
UO_2^{++}, $UO_2(CO_3)_2^{=}$
Solid saturation
$8H_2O + Ca^{++} + 2UO_2^{++} + 6SiO_2(aq) \xrightarrow{?} Ca(UO_2)_2Si_6O_{15} \cdot 5H_2O + 6H^{+}$
(HAIWEEITE)
No
Yes
Precipitation
Revised fluid chemistry

SPENT FUEL WASTE FORM / J-13 WATER-SIMULATION RESULTS



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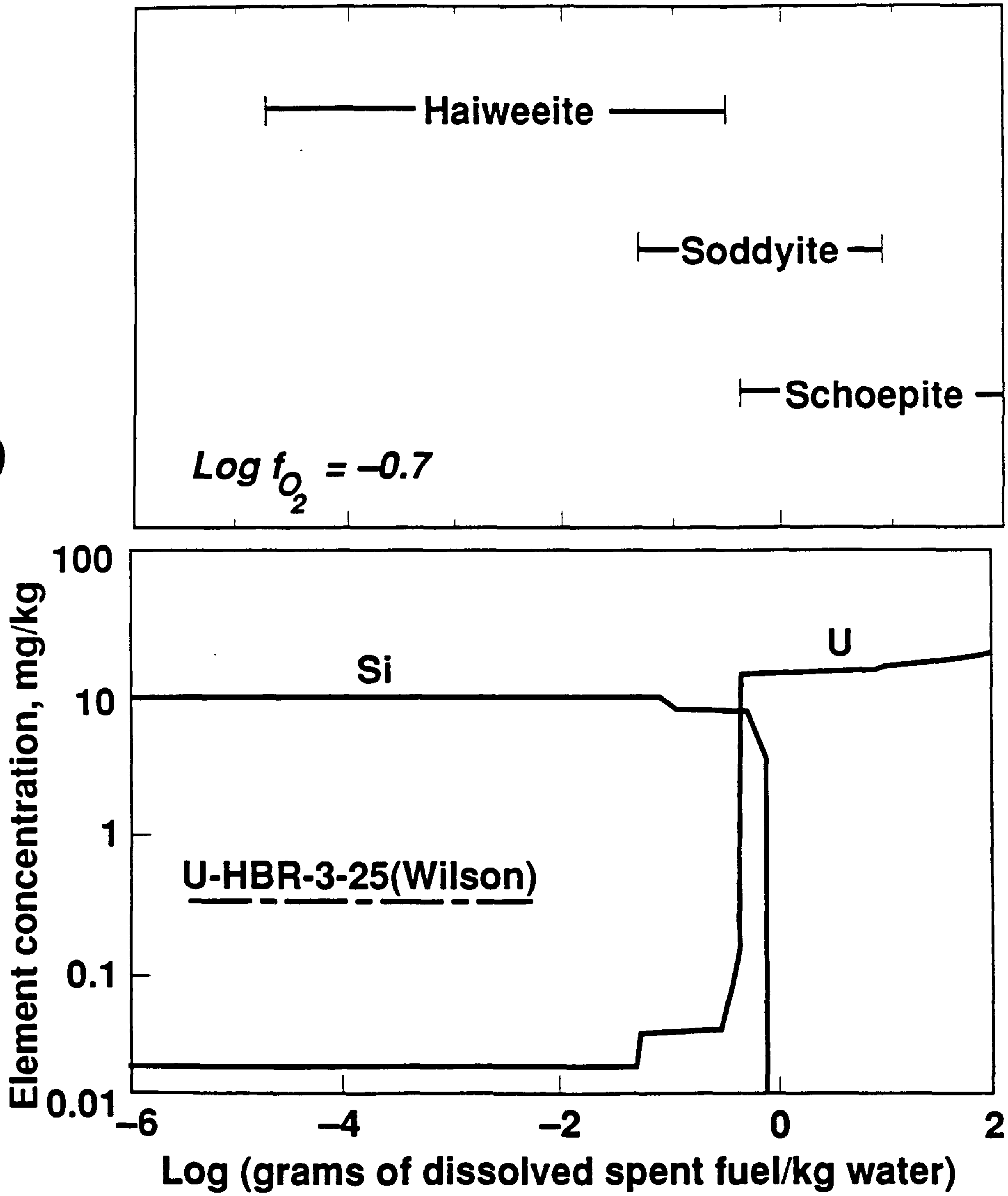
MINERAL NAMES AND FORMULAS

dolomite	$CaMg(CO_3)_2$	hematite	Fe_2O_3
quartz	SiO_2	mesolite	$Na_{0.68}Ca_{0.66}Al_{1.99}Si_{3.01}O_{10}\cdot2.647H_2O$
thorianite	ThO_2	gibbsite	$Al(OH)_3$
carbonate-calcite*	$(Ca,Mg,Fe,Sr)CO_3$	trevorite	$NiFe_2O_4$
haiweeite	$Ca(UO_2)_2Si_6O_{15}\cdot5H_2O$	schoepite	$UO_3\cdot2H_2O$
cassiterite	SnO_2	bunsenite	NiO
soddyite	$(UO_2)_2SiO_4\cdot2H_2O$		
clinoptilolite-ss*	$(Na,K,Cs,Ca_{0.5}Sr_{0.5}Ba_{0.5})_{3.467}Al_{3.45}Fe_{0.017}Si_{14.533}O_{36}\cdot10.922H_2O$		
smectite-di*,**	$(Na,K,Ca_{0.5},Mg_{0.5})_{0.33}(Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH)_2$		

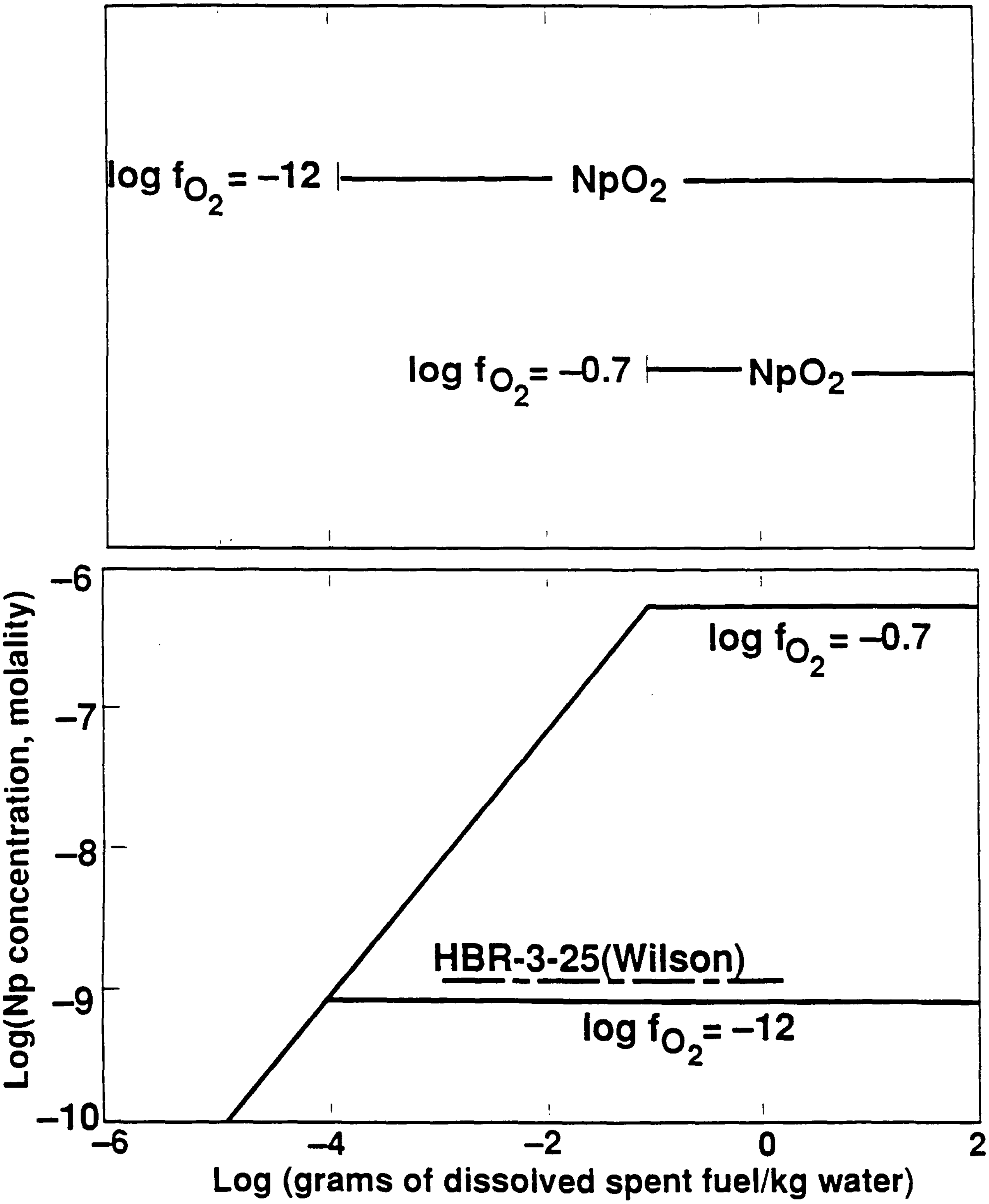
* denotes solid solution

** di = dioctahedral

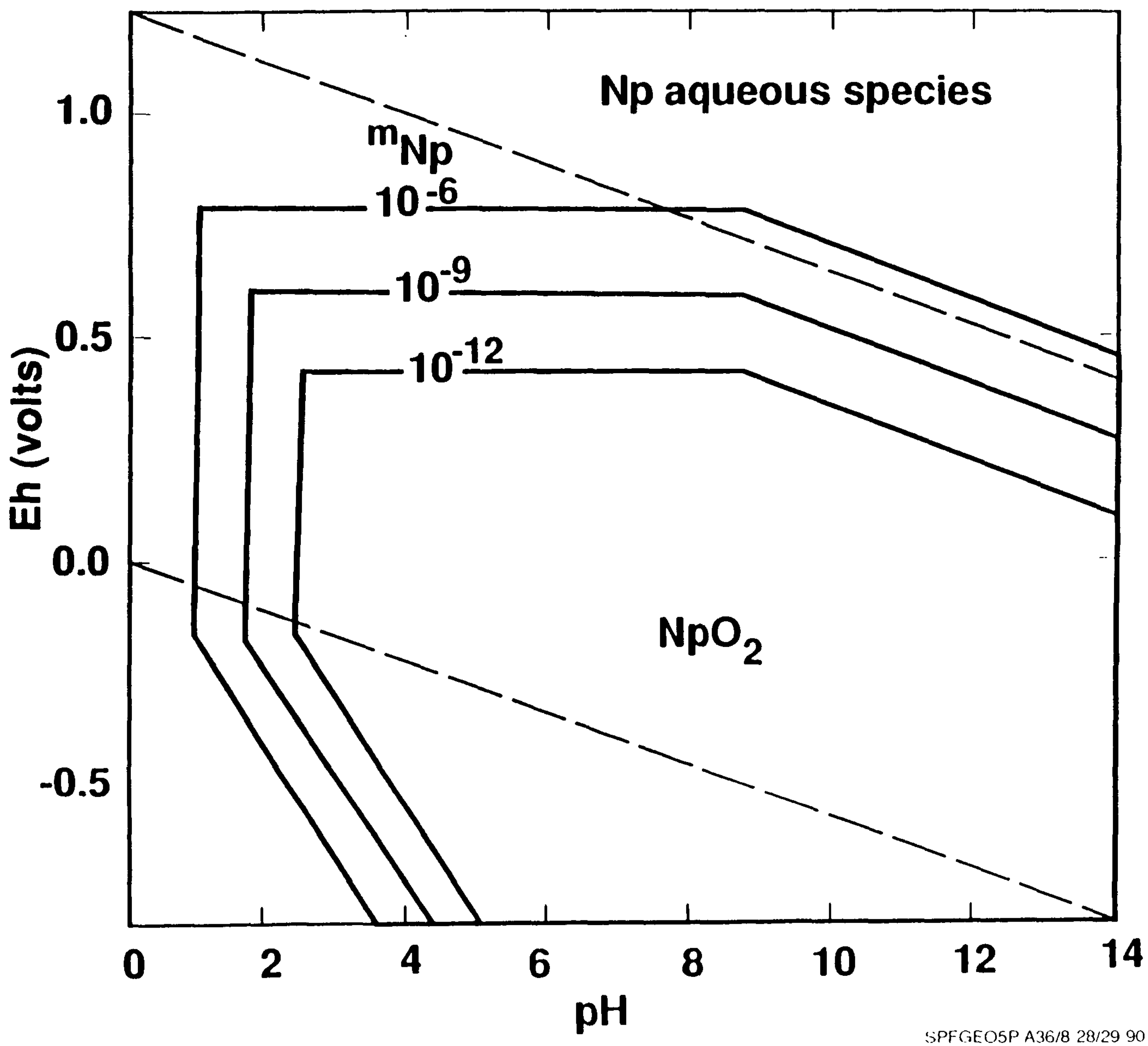
SPENT FUEL 25°C



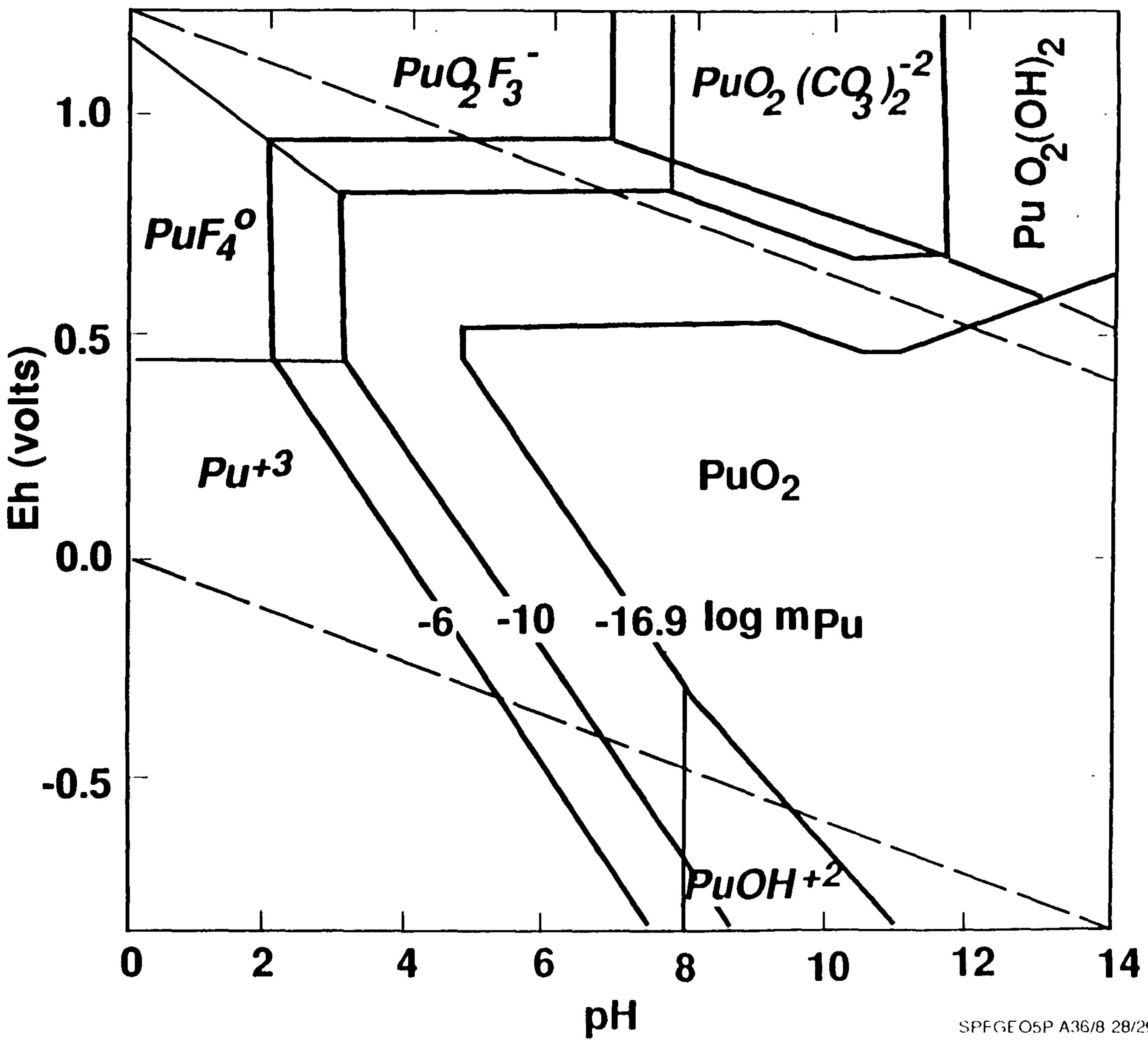
SPENT FUEL 25°C



Np / LEMIRE (1984) GROUNDWATER #1-25°C



Pu CONCENTRATION / J-13 WATER - 25°C



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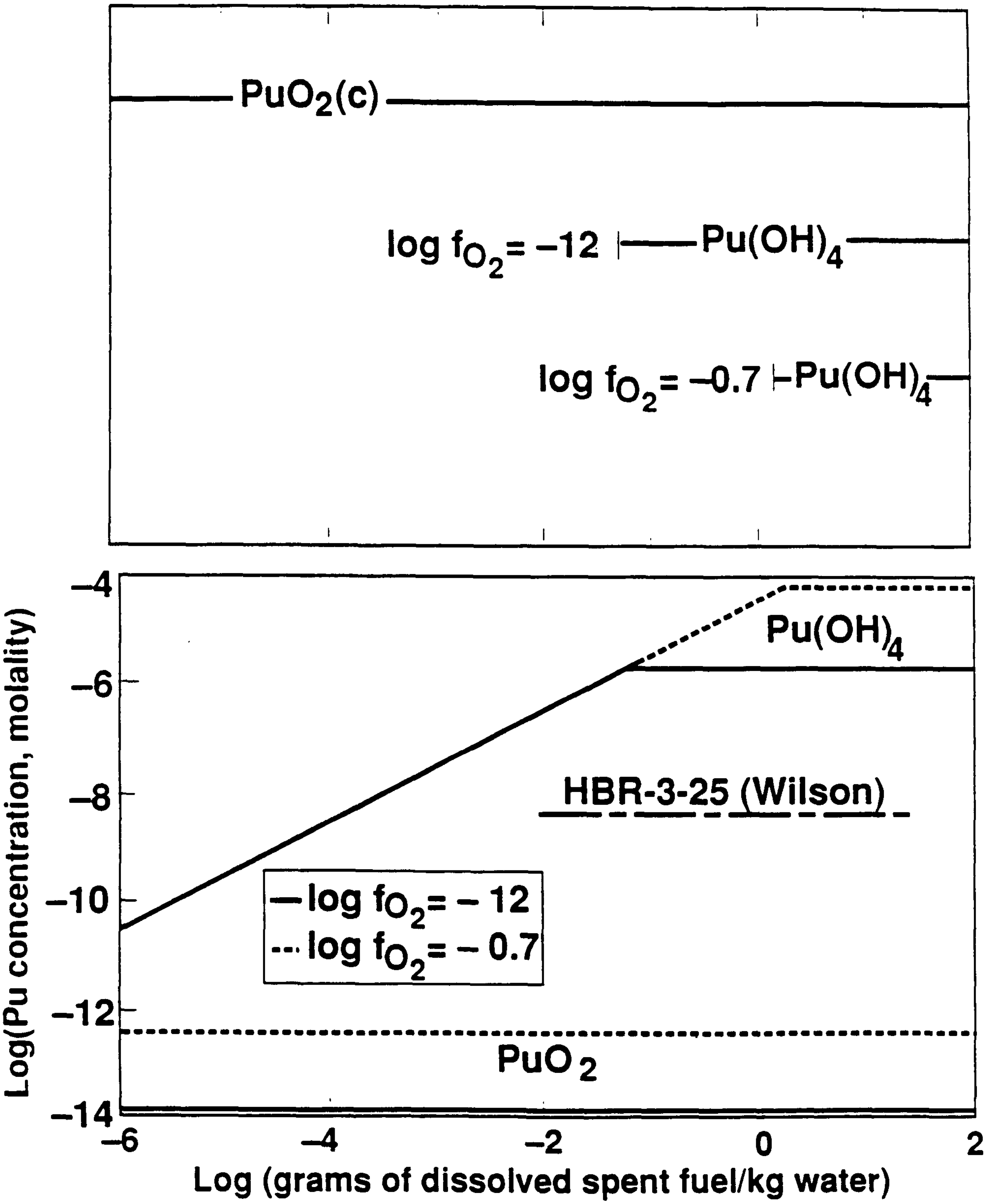
SPENT FUEL 25°C



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	

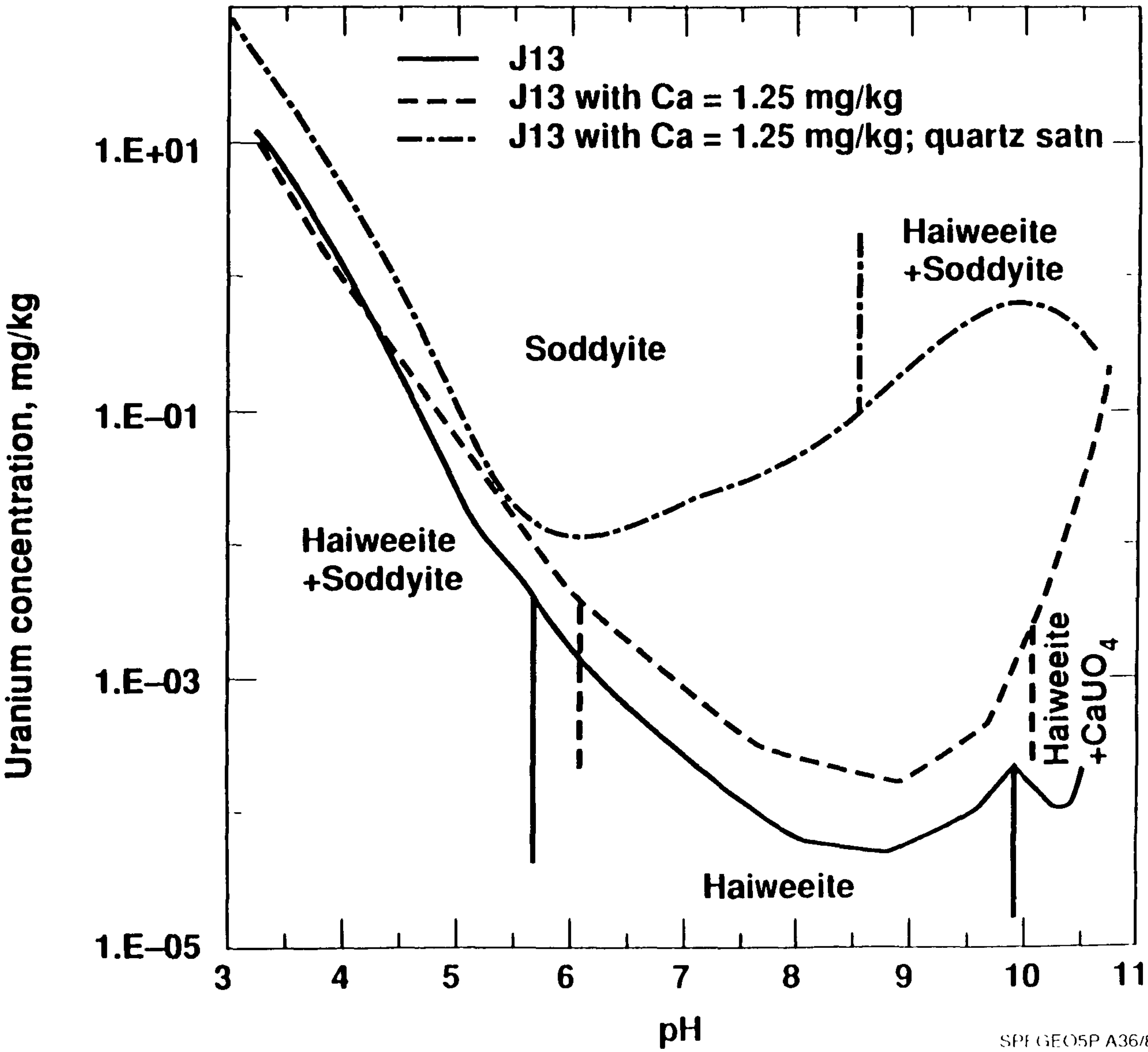
* Tables 4.1 and 4.2, Harrar et al., 1988.

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

INTERACTIONS THAT COULD ALTER WATER CHEMISTRY

Water interaction with:	Effect on pH?	Effect on Eh?	Effect on major/minor components of water?
Host rock (under study)	Yes	Yes	Ppt, sorption
Metal corrosion	Yes	Decrease	Ppt, sorption
Cement	Increase	Yes	Ppt, sorption
Organics	Organic acids	Yes	Ppt, sorption, complex fm
Partial liner, man-made components	Yes	Yes	Ppt, sorption
Radiation field	Decrease	Increase	Ppt, sorption

IMPACT OF WATER CHEMISTRY ON URANIUM CONCENTRATIONS IN SOLUTIONS



CONCLUSIONS

- **ACTINIDE CONCENTRATIONS IN SOLUTION CAN VARY SIGNIFICANTLY WITH CHANGES IN Eh, pH, SOLUTION COMPOSITION, AND THE NATURE OF THE ACTINIDE-BEARING PRECIPITATE**

	Ca	Si	HCO_3	pH	Eh
U	X	X	X	X	X
Np	O	O	O	X	X
Pu	O	O	O	X	X
Am	O	O	X	X	X

X = significant impact O = little impact

- **SOLUTION CHEMISTRY MUST CHANGE BY ORDERS OF MAGNITUDE TO IMPACT ACTINIDE BEHAVIOR**

CONCLUSIONS
(CONTINUED)

- OBSERVED VARIATIONS IN THE CHEMISTRY OF J-13 WATER AND EXTRACTED PORE WATERS FROM THE UNSATURATED ZONE DO NOT SEEM LARGE ENOUGH TO AFFECT ACTINIDE CONCENTRATIONS

- INTERACTIONS AMONG THE WASTE FORM, REPOSITORY COMPONENTS AND HOST ROCK CAN RESULT IN ORDER-OF-MAGNITUDE CHANGES IN SOLUTION CHEMISTRY. SUCH INTERACTIONS MUST BE CONSIDERED IN ORDER TO PREDICT RADIONUCLIDE CONCENTRATIONS THROUGH TIME