See Pocket 3 for encl.

101.2

101.1/RJW/84/07/09/0

Distribution
WM s/f 101.1
WMRP r/f
NMSS r/f
CF
REBrowning
MJBell
PAltomare
LBHigginbotham
MRKnapp
HJMiller
LBarrett
RRBoyle
SMCoplan
JLinehan
JKennedy
JStarmer
FRCook
DBrooks
WRehfeldt
RJWright & r/f
PDR
101.2

Mr. O. L. Olson
U. S. Department of Energy
Richland Operations Office
BWIP Project Office
P. O. Box 550
Richland, Washington, 99352

JUL 13 1984

Dear Mr. Olson:

I am writing with respect to open item number 1 in the summary meeting notes of the January 9-12, 1984 workshop on geochemistry:

> "1. NRC will study Attachment 4 and will request, by letter to DOE, any back-up material, reference citations or other items needed for an understanding of Attachment 4 material."

Attachment 4 to the summary meeting notes comprises the viewgraphs presented at the meeting. A review of these indicates that a large number do not provide background information on the origin of the data and references where the data can be examined. Our geochemical reviewers need this information to complete their review.

Accompanying this letter is a group of viewgraphs from Attachment 4. For each of these we request the following information:

1. SOURCE: Name of DOE organization that did the work, or citation to work published by other investigators. Designate whether or not data collection is complete or is continuing.

2. REFERENCES: Released reports (title and reference number), or for reports in progress (expected title, reference number and release date) that present or discuss the data.

Would you please advise me when this information will be made available.

WM Record File 101.2
WM Project 10
Docket No.
PDR ✓
LPDR ✓
Distribution:
(Return to WM, 623-SS)

8408010123 840713
PDR WASTE
WM-10 PDR

OFC	WMRP	WMRP					
NAME	RJWright	HJMiller					
DATE	7/13/84	7/13/84					

WRR for

909

If there are any questions about this letter, please contact David Brooks (FTS 427-4603).

Sincerely,

"ORIGINAL SIGNED BY"

Robert J. Wright
Senior Technical Advisor
Repository Projects Branch
Division of Waste Management

Enclosure:
Selected Viewgraphs from Attachment 4

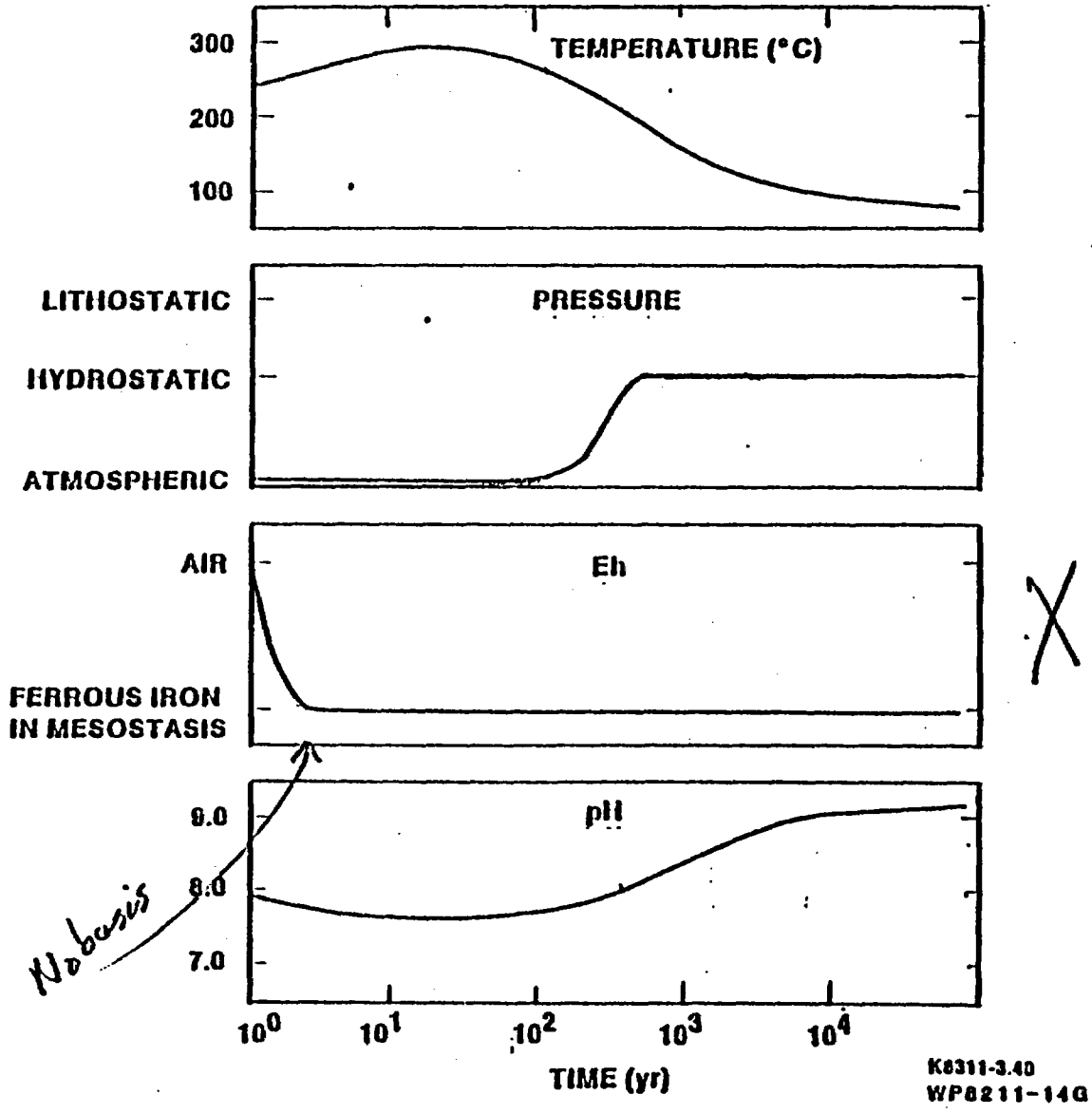
OFC	WMRP	WMRP					
NAME	RJWright	HJMiller					
DATE	7/ /84	7/ /84					

See Mr. Olson
from Wright 7-13-84

101.2
WM-10

OVERVIEW

PREDICTED VARIATION OF GEOCHEMICAL PARAMETERS WITH TIME



K8311-3.40
WP8211-14G

MAJOR PROCESSES AFFECTING CONTAINMENT OF NUCLEAR WASTE

ENGINEERED BARRIER SYSTEM	• SATURATION • CORROSION • PACKING MATERIALS - WATER-AIR REACTION • GAMMA RADIOLYSIS
DISTURBED ROCK ZONE	• BASALT-WATER-AIR REACTION • GAMMA RADIOLYSIS
SITE	NA

WP8401-148

PLANS FOR RESOLUTION OF U.S. NUCLEAR REGULATORY COMMISSION GEOCHEMISTRY CONCERNS

?
IN-SITU

RESOLUTION / ISSUE	EMPLACEMENT ENVIRONMENT CHARACTERIZATION				BARRIER MATERIALS TESTING			DRILLING AND TESTING
	ROCK	GROUNDWATER	WATER/ ROCK REACTIONS	T, P	RADIONUCLIDE STEADY STATE CONC. TESTING	SORPTION TESTING	WASTE/ BARRIER/ ROCK REACTIONS	FIELD TESTS
Eh CONDITIONS	X	X		X			X	X
Eh BUFFERING CAPACITY	X	X	X	X			X	
RADIONUCLIDE STEADY STATE CONCENTRATION VERIFICATION		X		X	X		X	
RADIONUCLIDE SORPTION BEHAVIOR	X	X		X		X		X ?
COLLIOD FORMATION AND TRANSPORT		X	X	X	X	X	X	
FRACTURE FILLING STABILITY	X		X	X				X
RADIATION EFFECTS		X	X	X	X	X	X	
LONG-TERM BEHAVIOR			X	X			X	X

WP8308-175

IDENTIFICATION OF KEY RADIONUCLIDES

- INITIAL INVENTORY
- HALF LIFE > 20 YEARS
- INVENTORY GREATER THAN 0.1% OF EPA LIMIT
- PRELIMINARY CONTAMINANT TRANSPORT ANALYSIS
  - CONSERVATIVE HYDROLOGIC PROPERTIES
  - CONSERVATIVE SORPTION VALVES
  - CONSERVATIVE SOLUBILITY VALUES

WP0401-92

PRELIMINARY LIST OF KEY RADIONUCLIDES FOR A NWRB

(100 YEAR OLD CHLW OR SPENT FUEL)

ELEMENT	RADIONUCLIDE (PRIORITY 1)
CARBON	(^{14}C)*
IODINE	(^{129}I)*
SELENIUM	^{79}Se
TECHNETIUM	^{99}Tc
NEPTUNIUM	^{237}Np
PLUTONIUM	^{239}Pu, ^{242}Pu
TIN	^{126}Sn
*( )=SPENT FUEL ONLY	

ELEMENT	RADIONUCLIDE (PRIORITY 2)
STRONTIUM	(^{90}Sr)*
CESIUM	(^{135}Cs, ^{137}Cs)*
RADIUM	(^{226}Ra)*
CURIUM	^{243}Cm, ^{245}Cm, ^{246}Cm
PROTACTINIUM	^{231}Pa
NICKEL	^{59}Ni, ^{63}Ni
URANIUM	^{233}U, ^{234}U, ^{235}U
LEAD	^{210}Pb
ZIRCONIUM	^{93}Zr
PALLADIUM	^{107}Pd
THORIUM	^{229}Th, ^{230}Th, ^{232}Th
PLUTONIUM	^{238}Pu, ^{240}Pu, ^{241}Pu
AMERICIUM	^{241}Am, 24:
*( )=EXISTING DATA SUFFICI	

WP8:

PRELIMINARY LIST OF KEY RADIONUCLIDES FOR A NWRB
CONTINUED

PRIORITY 1=RADIONUCLIDES WITH SOLUBILITY OR SORPTION CHARACTERISTICS THAT MUST BE WELL UNDERSTOOD TO ASSURE ISOLATION PERFORMANCE

PRIORITY 2=RADIONUCLIDES WITH SOLUBILITY OR SORPTION CHARACTERISTICS THAT REQUIRE CONFIRMATORY DATA TO DETERMINE THEIR IMPACT ON ISOLATION PERFORMANCE

WP8302-102

TERFORMANCE ASSESSMENT

FAR FIELD GEOCHEMICAL MODEL DEVELOPMENT

- MODEL SCOPE
- DATA REQUIREMENTS
- CODES UNDER CONSIDERATION

WP8401-108

FAR FIELD GEOCHEMICAL MODEL SCOPE

- PROVIDE AN ASSESSMENT OF GROUNDWATER COMPOSITION/EVOLUTION AS A FUNCTION OF TIME AND SPACE TO SUPPORT HYDROLOGIC FLOW MODELING/ISOLATION PERFORMANCE. ASSESSMENT EFFORTS
- PROVIDE A QUANTITATIVE ASSESSMENT OF RADIONUCLIDE RETARDATION (SORPTION) BEHAVIOR IN BASALT FLOW TOPS AND/OR INTERBEDS AS A FUNCTION OF TIME
- BOTH MODELS MUST BE CAPABLE OF PROBABILISTIC AND DETERMINISTIC ANALYSIS
    - PARAMETER SENSITIVITY ANALYSIS
    - INPUT DATA UNCERTAINTIES

WP8401-109

DATA REQUIREMENTS

- GROUNDWATER COMPOSITION

  - LATERAL AND VERTICAL VARIABILITY
  - ISOTOPIC ANALYSIS
  - GAS ANALYSIS

- ASSOCIATED BASALT FRACTURE FILLING, FLOWTOP AND INTERBED MINERALOGY, PARTICULARLY SECONDARY MINERALS CHARACTERIZATION

- TEMPERATURE, PRESSURE

- RADIONUCLIDE SORPTION EQUATIONS INCLUDING SPECIATION/COMPLEXATION EFFECTS

- REDOX POTENTIAL (EH)

- WATER-BASALT INTERACTIONS

WP8410-110

CODES UNDER CONSIDERATION

MINTEQ EQ3/EQ6 MINEQL PHREEQE	GROUNDWATER COMPOSITION-CHEMICAL EVOLUTION
ACTIVITY KD's ISOTHERMS SURFACE COMPLEXATION MODEL	EMPIRICAL ADSORPTION EQUATIONS/MODELS

WP8401-111

WASTE PACKAGE PERFORMANCE MODEL SCOPE

THE MODEL PROVIDES:

- A MODEL OF THE PHYSICAL-CHEMICAL (ENVIRONMENTAL) CONDITIONS AS A FUNCTION OF TIME
- A MODEL OF THE ENGINEERED BARRIERS SYSTEM
  - WASTE PACKAGE AND ITS COMPONENTS
  - REPOSITORY SEAL SYSTEM AND ITS COMPONENTS
- A MODEL OF THE ENGINEERED BARRIERS SYSTEM DEGRADATION AND FAILURE MODES AS A FUNCTION OF TIME
- A MODEL OF RADIONUCLIDE RELEASE AND TRANSPORT THROUGH THE WASTE PACKAGE

WP8401-101

APPROACH TO EVALUATING LONG-TERM PERFORMANCE OF ENGINEERED BARRIER MATERIALS

- STABILITY OF BARRIER MATERIALS DOMINATED BY INTERACTION WITH GROUNDWATER:

  $GROUNDWATER_I$ + BARRIER MATERIALS INITIAL UNSTABLE SOLID PHASES $\longrightarrow$

  $GROUNDWATER_F$ + SECONDARY STABLE SOLID PHASES

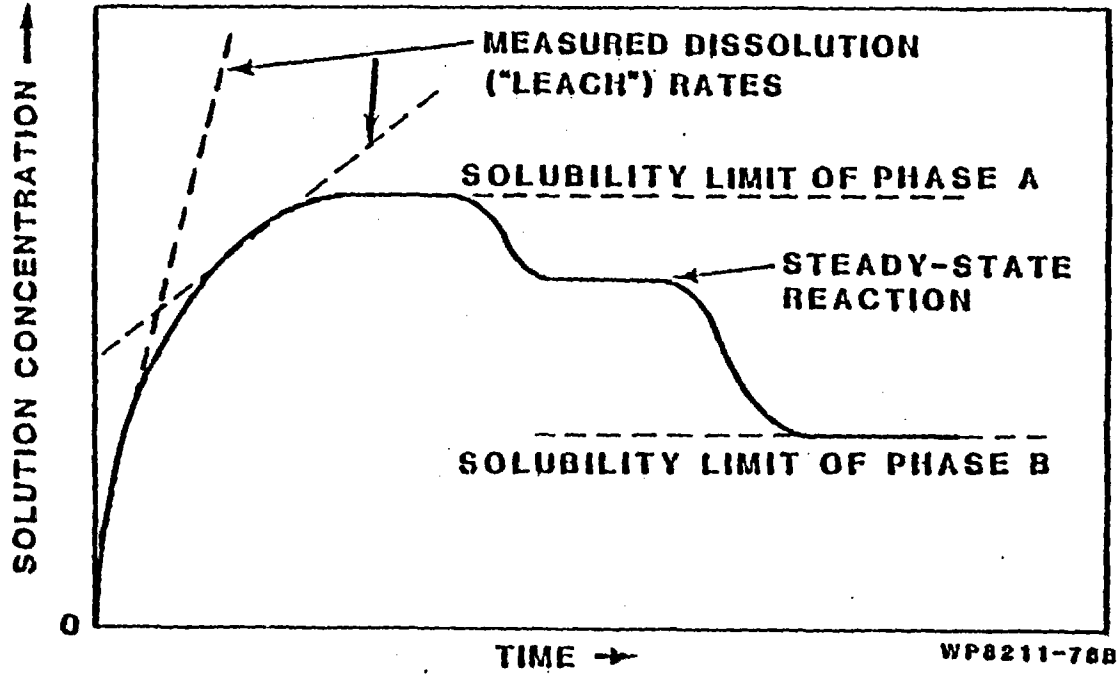
- TRANSITION FROM UNSTABLE TO STABLE PHASE(S) GENERALLY OCCURS THROUGH A SERIES OF INTERMEDIATE METASTABLE PHASES OF INCREASING THERMODYNAMIC STABILITY (OSTWALD STEP RULE)

- THE SOLUBILITY OF THE SOLID PHASE IS DIRECTLY RELATED TO ITS STABILITY;THE MORE STABLE THE PHASE IS, THE LESS SOLUBLE IT IS

- THEREFORE, EQUILIBIUM (STEADY-STATE) RADIONUCLIDE SOLUBILITY LIMITS CAN BE USED TO CONSERVATIVELY EVALUATE LONG-TERM RELEASE OF RADIONUCLIDES FROM FROM THE REPOSITORY

WP8401-104

SOLID DISSOLUTION BEHAVIOR AS A FUNCTION OF TIME



SUMMARY

- WASTE PACKAGE PERFORMANCE MODEL IS COMPRISED OF TWO SUBMODELS:
  - WASTE PACKAGE DEGRADATION SUBMODEL TO ESTABLISH CONTAINMENT FAILURE TIME
  - WASTE PACKAGE RADIONUCLIDE TRANSPORT/RELEASE SUBMODEL TO ESTABLISH RADIONUCLIDE FLUX FROM THE ENGINEERED BARRIER TO THE DISTURBED ROCK ZONE

WP8401-107

SUMMARY (CONTINUED)

- PRELIMINARY MODEL REQUIREMENTS HAVE BEEN IDENTIFIED AND A TESTING PROGRAM IS IN PLACE TO PROVIDE REQUIRED MODEL INPUT DATA
- CODES TO QUANTIFY IDENTIFIED SUBSYSTEM PROCESSES CURRENTLY BEING EVALUATED AND/OR DEVELOPED
- FY 84 GOAL IS TO COMPLETE DEVELOPMENT OF THE PRELIMINARY WASTE PACKAGE SUBSYSTEM PERFORMANCE MODEL

WP8401-107A

Basalt Characterization

TYPES OF MINERALOGICAL DATA ON HANFORD BASALT

- GENERAL COMPOSITION
  - BOREHOLE LOGGING; OBSERVATION OF SURFACE OUTCROPS
  - BULK CHEMICAL COMPOSITION Fe^{II}/Fe^{3+}
- PRIMARY MINERALOGY
  - OPTICAL IDENTIFICATION OF PHASES WITH PETROGRAPHIC MICROSCOPE (PRINCIPALLY ON CANDIDATE HORIZONS)
  - XRD IDENTIFICATION OF MAJOR PHASES (COHASSETT AND UMTANUM FLOWS)
  - ABUNDANCES BY POINT COUNTS (CANDIDATE HORIZONS)
  - MINERAL COMPOSITION BY ELECTRON MICROPROBE, STEM (COHASSETT, UMTANUM; OTHER CANDIDATE HORIZONS IN PROGRESS)
- SECONDARY MINERALOGY Bernard Tagna
  - IDENTIFICATION BY XRD, SEM (DC-2, DC-6; RRL-2, UMTANUM AND COHASSETT)
  - MEASUREMENTS OF FRACTURE FREQUENCY-BOREHOLE LOGGING, SURFACE MEASUREMENTS
  - MEASUREMENT OF FILLED FRACTURE WIDTHS HAND LENS, BINOCULAR MICROSCOPE
  - ESTIMATES OF RELATIVE PROPORTIONS OF FRACTURE FILLING MINERALS-BINOCULAR MICROSCOPE (UMTANUM AND COHASSETT FLOWS, OTHER CANDIDATE HORIZONS IN PROGRESS)
  - MINERAL COMPOSITION, (DC-6, DC-2)

CHEMICAL COMPOSITION OF MESOSTASIS GLASS

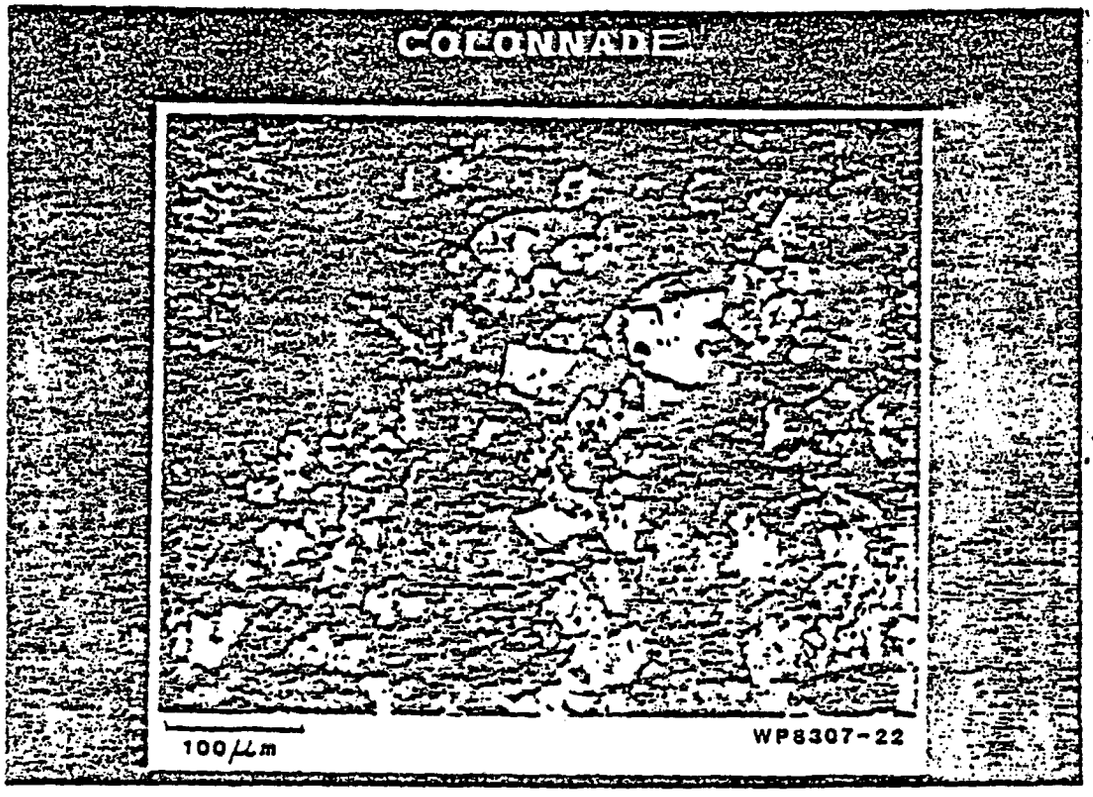
(OXIDE WT.%)

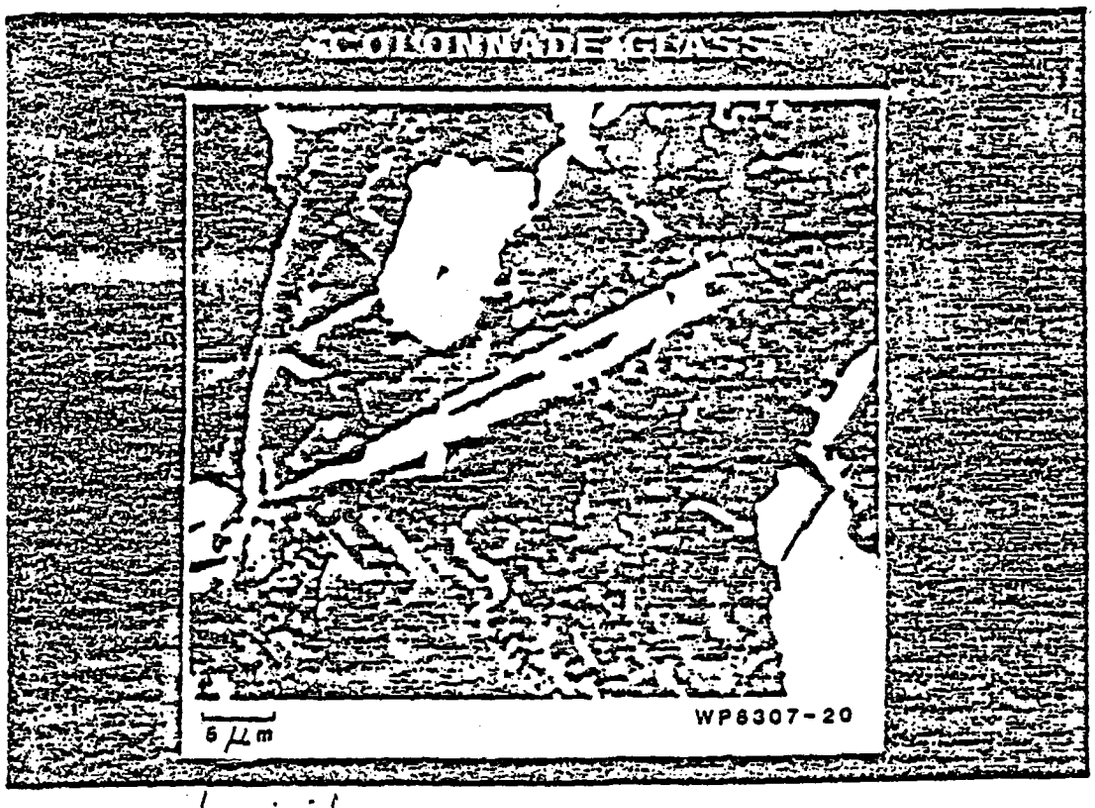
OXIDE	COHASSETT COLONNADE (RRL2-3173)		COHASSETT ENTABLATURE (RRL2-3134)	
SiO_2	77.1	± 4.7	60.4	± 2.7
TiO_2	0.6	± 0.3	2.1	± 0.7
Al_2O_3	10.8	± 2.7	13.6	± 1.7
FeO*	1.2	± 0.5	9.8	± 2.7
MnO	N.D.		0.2	± 0.1
MgO	0.1	± 0.1	0.5	± 0.3
CaO	0.4	± 0.5	4.4	± 0.8
Na_2O	3.0	± 0.8	4.1	± 0.5
K_2O	5.0	± 1.3	2.3	± 0.5
P_2O_5	N.D.		0.7	± 0.2
TOTAL	98.2	± 0.7	98.1	± 0.9
POINTS ANALYZED BY MICROPROBE	47		47	

WP6401-35

*ALL Fe REPORTED AS FeO

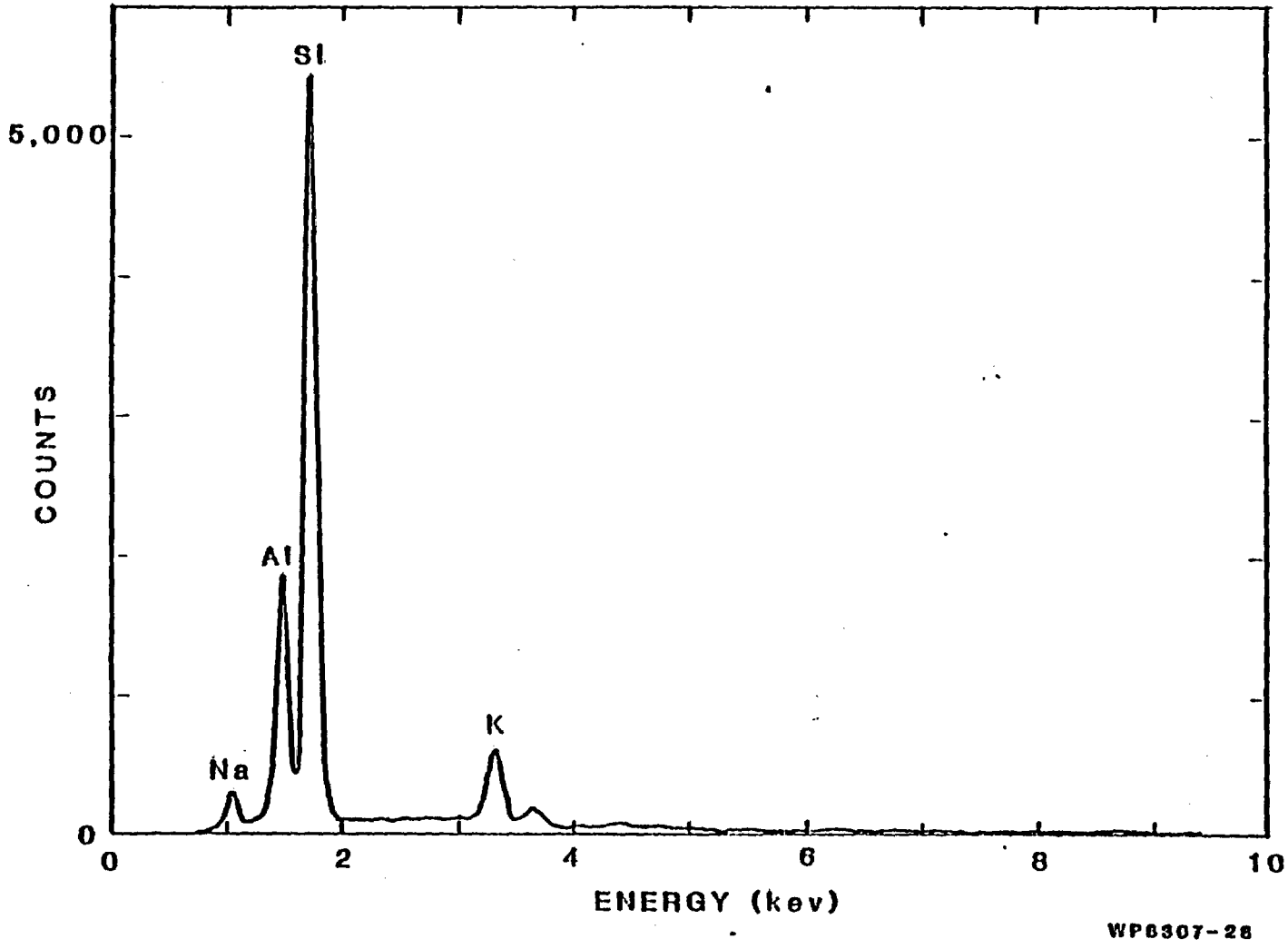
N.D. = NOT DETECTED

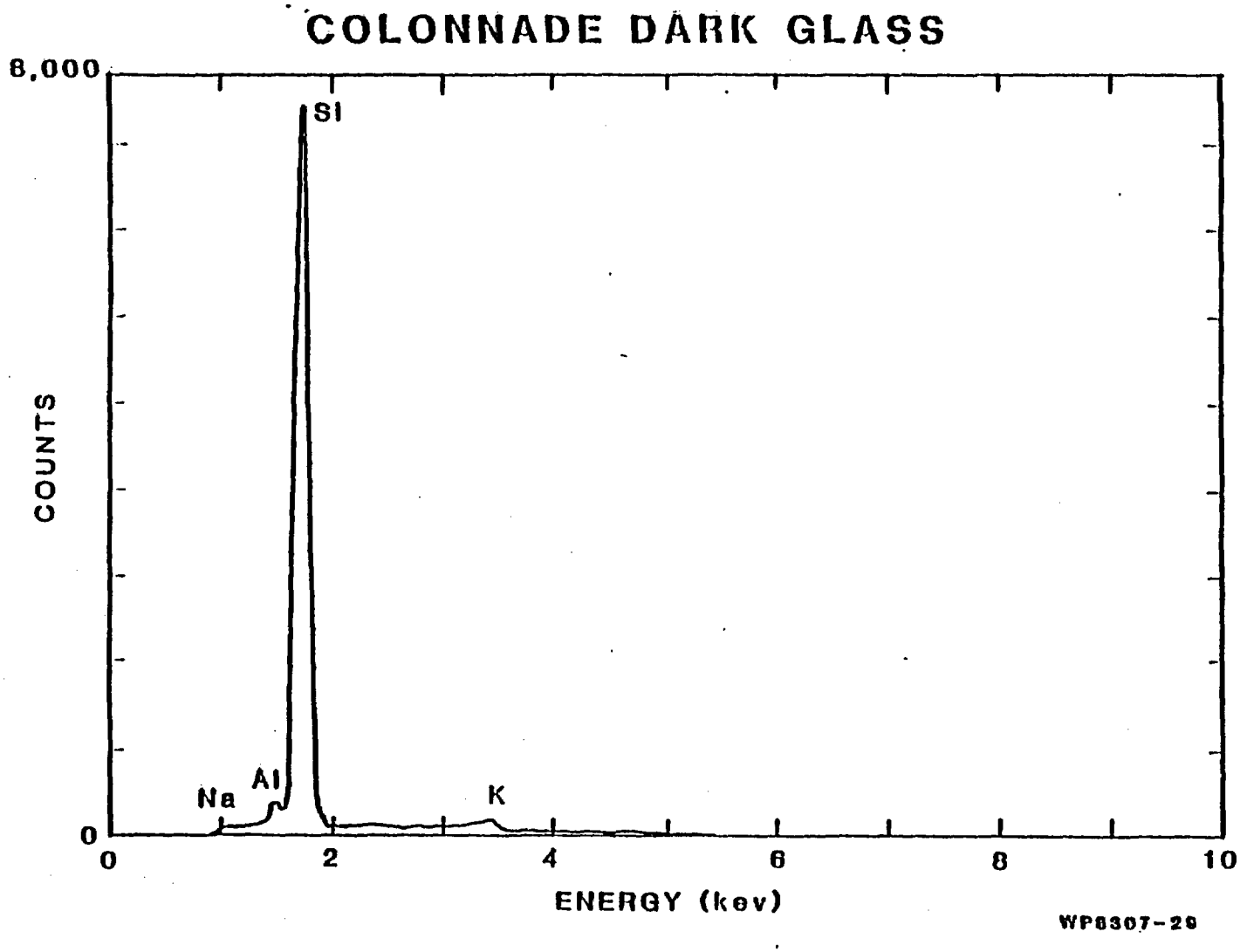


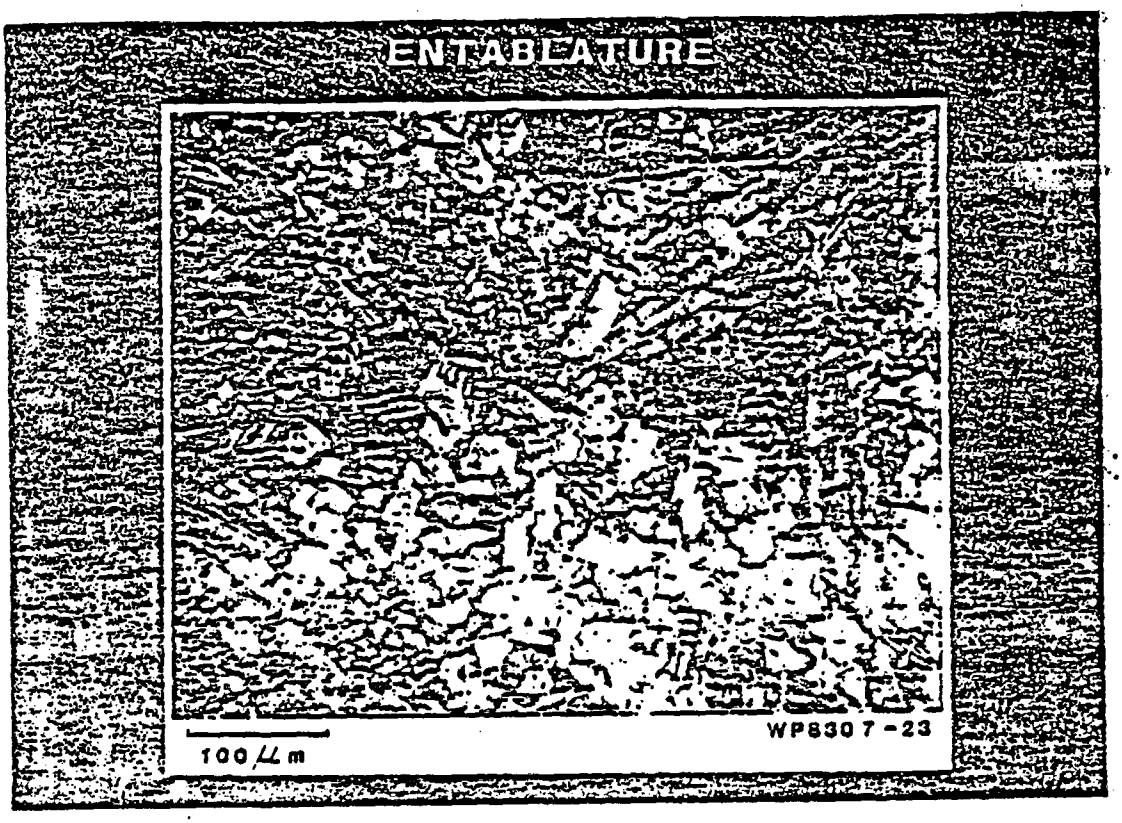


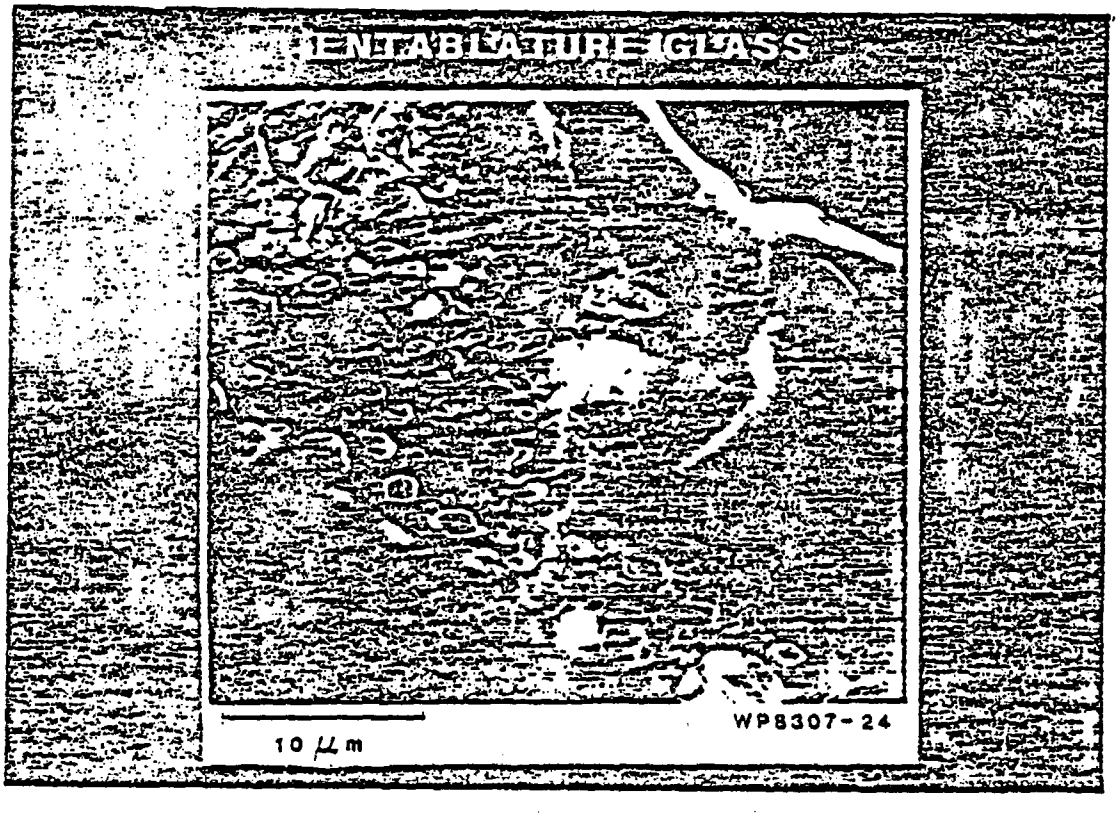
glass is inhomogeneous

COLONNADE LIGHT GLASS

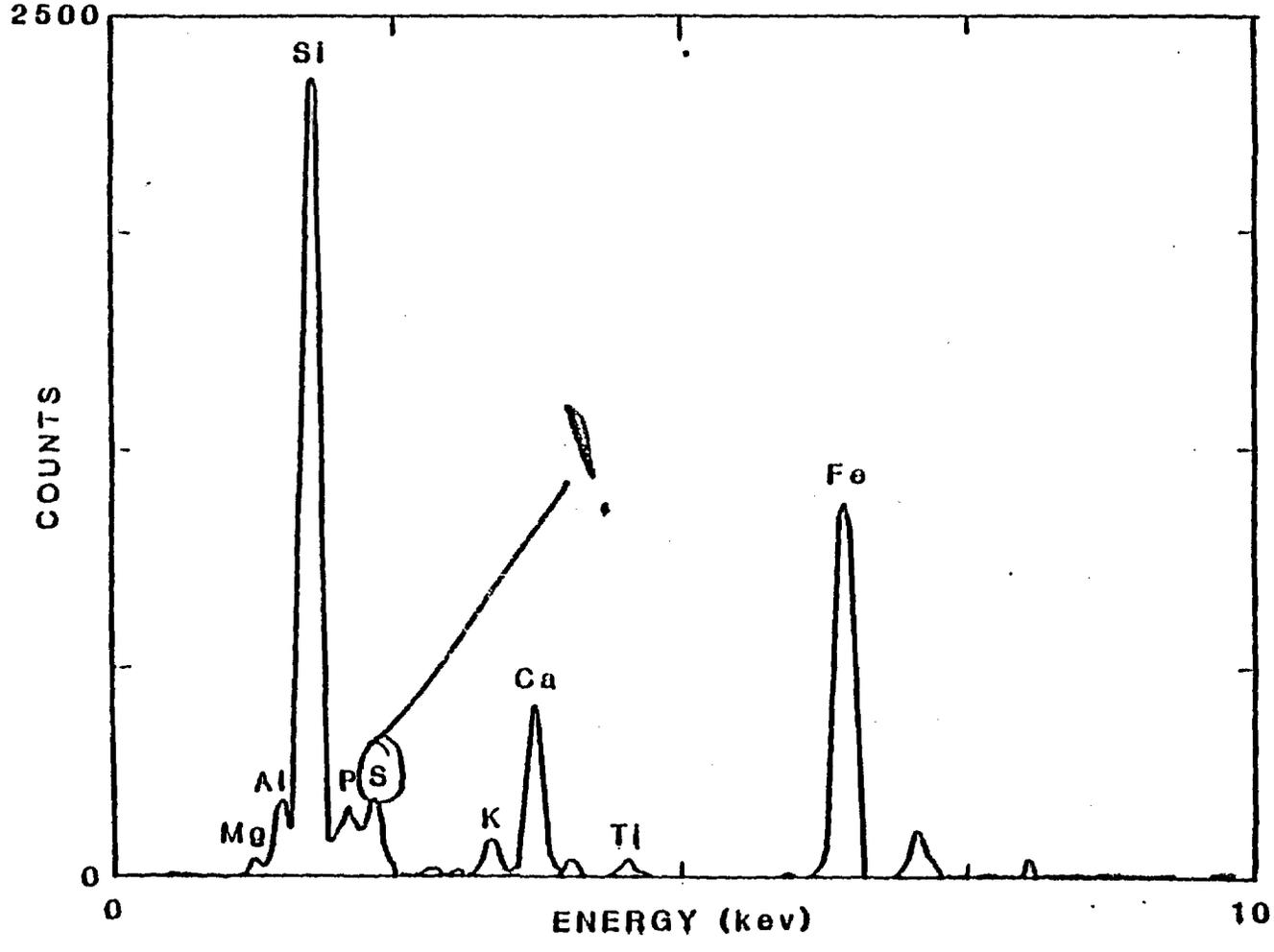



COLONNADE DARK GLASS
8,000
0
COUNTS
Si
Na
Al
K
0
2
4
6
8
10
ENERGY (kev)
WP6307-29


ENTABLATURE
100 μm
WP8307-23


ENTABLATURE GLASS
10 μm
WP8307-24

ENTABLATURE MICROCRYSTALLINE BLEB



WP6307-27

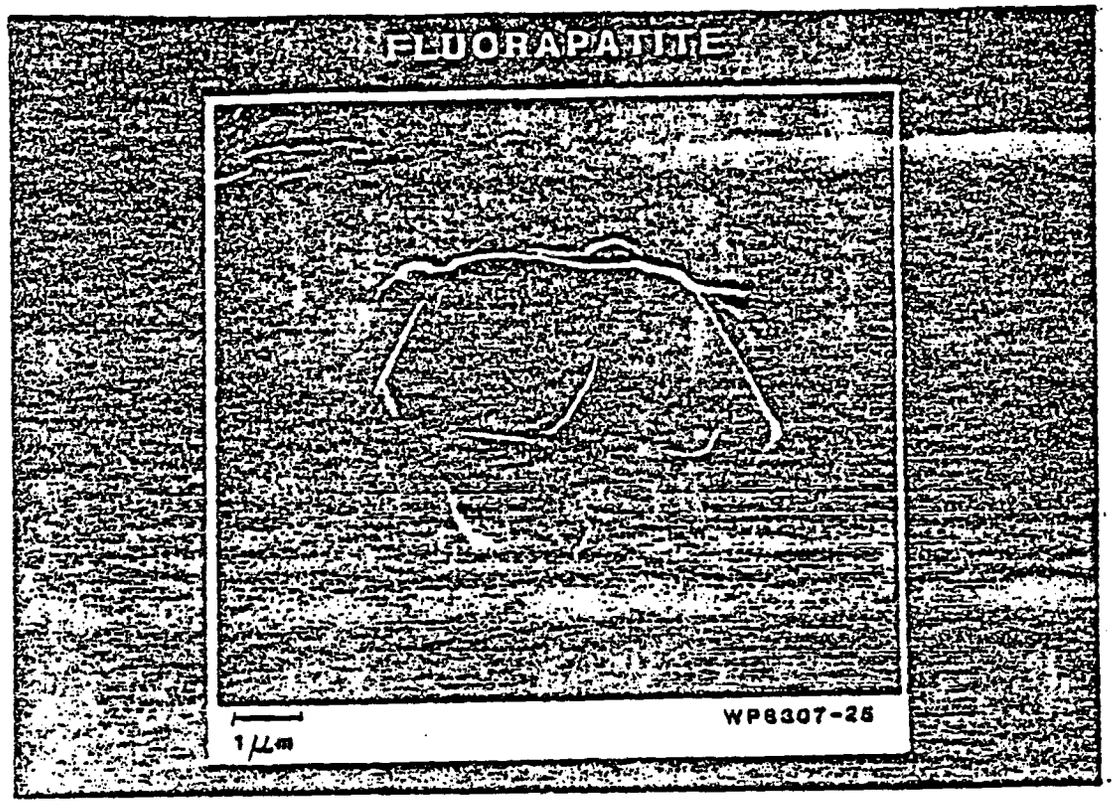
FLUORIDE CONTENT OF GRANDE RONDE BASALT

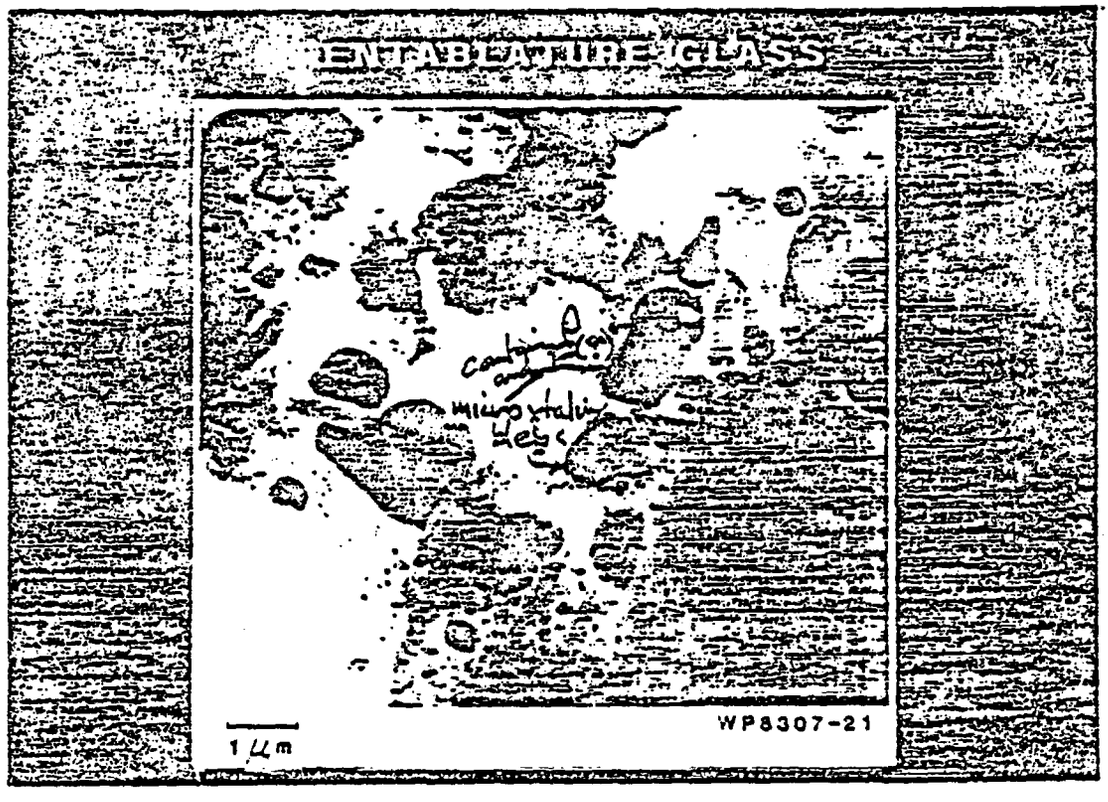
	(WEIGHT %)
BULK ROCK [a] (DC 15-3201)	0.054 ± 0.003
GLASS [b] (C8095)	0.08 ± 0.02
APATITE [b] (C9017)	3.1 ± 0.07
MICROCRYSTALLINE BLEBS [b] (RUE-1)	PRESENT

a DETERMINED BY ALKALI FUSION – SELECTIVE ION ELECTRODE TECHNIQUE

b DETERMINED BY MICROPROBE

WP8401-34


FLUORAPATITE
1 μm
WP8307-25


1 μm
WP8307-21

CHAPTER 6 (GEOCHEMISTRY)

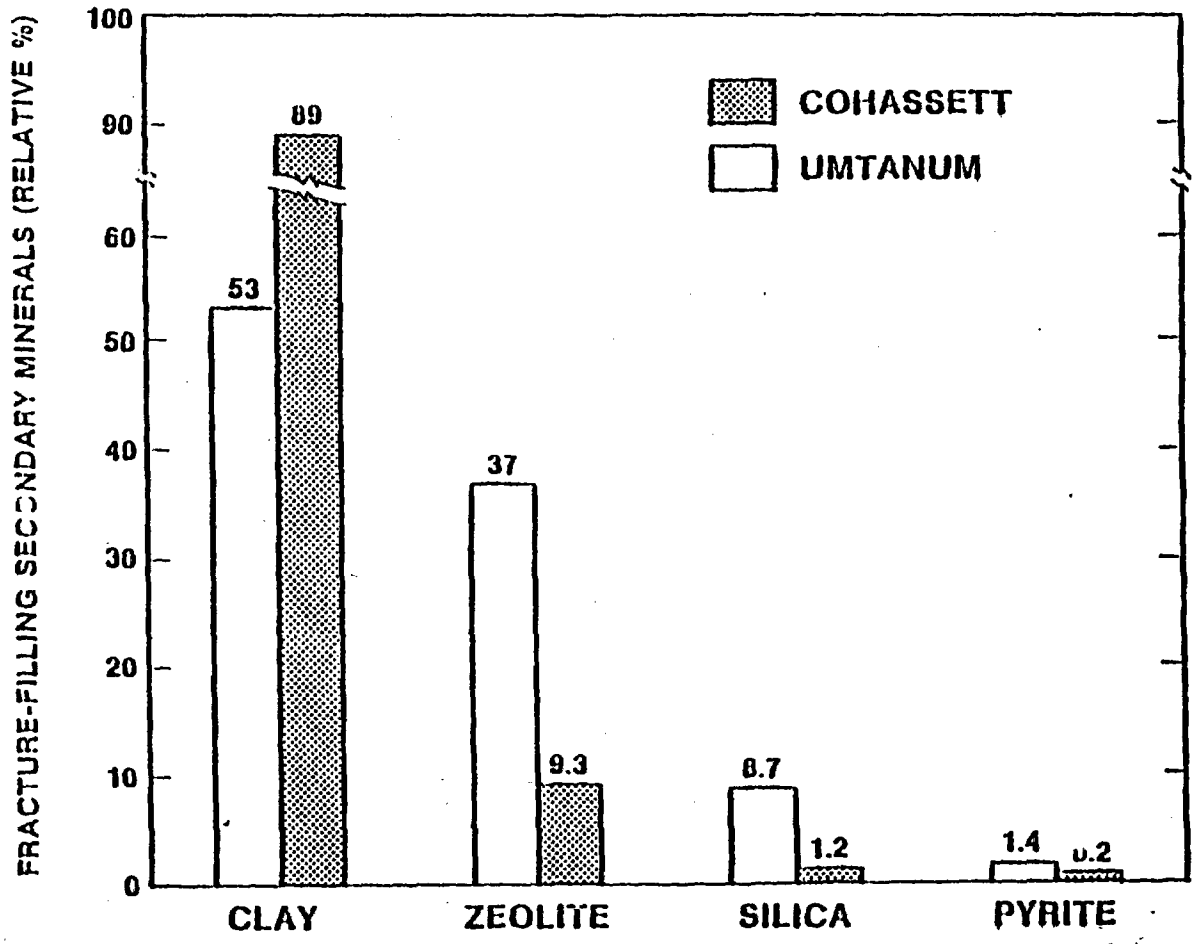
ITEM REFERENCE: SECTION 6.1.1, PAGE 6.0-1, PARAGRAPH 5.

NRC COMMENTS: "MINERAL FILLING OF TECTONIC FEATURES... THE COOLING JOINTS."/5, 16--"THESE MAY BE IMPORTANT IN CONSIDERING VERTICAL FLOW PATHS."

STATUS: AGREED

BWIP RESPONSE: A TECTONIC BRECCIA AND FRACTURES STUDY IS UNDERWAY. IT WILL BE INCLUDED IN AN EXPANDED FORM IN THE SCP, CHAPTER 5. IN PARTICULAR, THOSE FEATURES CONSIDERED IMPORTANT TO RADIONUCLIDE MIGRATION WILL BE INVESTIGATED.

RELATIVE PROPORTIONS OF SECONDARY MINERALS IN THE COHASSETT AND UMTANUM FLOWS IN BOREHOLE RRL2



WP0401-31

SECONDARY MINERALS IDENTIFIED IN GRANDE RONDE BASALT, PASCO BASIN

CLAY MINERALS

SMECTITES*		
MONTMORILLONITE	$(Ca,Na)_{0.66}(Al^{+3},Mg^{+2})_{4-6}(Si,Al)_8O_{20}(OH)_4 \cdot nH_2O$	DIOCTAHEDRAL
BEIDELLITE	$(Ca,Na)_{0.66}(Al^{+3})_{4-5}(Si,Al)_8O_{20}(OH)_4 \cdot nH_2O$	DIOCTAHEDRAL
NONTRONITE	$(Ca,Na)_{0.66}(Fe^{+3})_{4-6}(Si,Al)_8O_{20}(OH)_4 \cdot nH_2O$	DIOCTAHEDRAL
SAPONITE	$(Ca,Na)_{0.66}Mg_6(Si,Al)_8O_{20}(OH)_4 \cdot nH_2O$	TRIOCTAHEDRAL
ILLITES		
CELADONITE(?)	$(K,Na)\ (Al,Fe^{+3},Mg)_2(Al,Si)_4O_{10}(OH)_2$	DIOCTAHEDRAL

SILICA POLYMORPHS*

QUARTZ	SiO_2
TRIDYMITE	SiO_2
CRISTOBALITE	SiO_2
CHALCEDONY (INCLUDES OPAL)	$SiO_2 \cdot nH_2O$

(FROM AMES, 1980; BENSON AND TEAGUE, 1979)

*IDENTIFIES THE DOMINANT SECONDARY MINERALS

WP8401-33

SECONDARY MINERALS IDENTIFIED IN GRANDE RONDE BASALT, PASCO BASIN

(Continued)

ZEOLITES

HEULANDITE	$(Ca,Na_2)(Al_2Si_7O_{18})\cdot 6H_2O$
CLINOPTILOLITE*	$(Ca,Na_2,K_2)(Al_{1.5}Si_{7.5}O_{18})\cdot 6H_2O$
MORDENITE	$(Na_2,K_2,Ca)(Al_2Si_{10}O_{24})\cdot 7H_2O$
PHILLIPSITE	$(\frac{1}{2}\ Ca,Na,K)_3(Al_3Si_5O_{16})\cdot 6H_2O$
HARMOTOME	$Ba(Al_2Si_6O_{16})\cdot 6H_2O$
WAIRAKITE	$CaAl_2Si_4O_{12}\cdot 2H_2O$
CHABAZITE	$Ca(Al_2Si_4O_{12})\cdot 6H_2O$
ANALCIME	$Na_{16}[(AlO_2)_{16}(SiO_2)_{32}]\cdot 16H_2O$
ERIONITE	$(Na_2,K_2,Ca,Mg)_{4.5}(Al_9Si_{27}O_{72})\cdot 27H_2O$

MISCELLANEOUS SPECIES

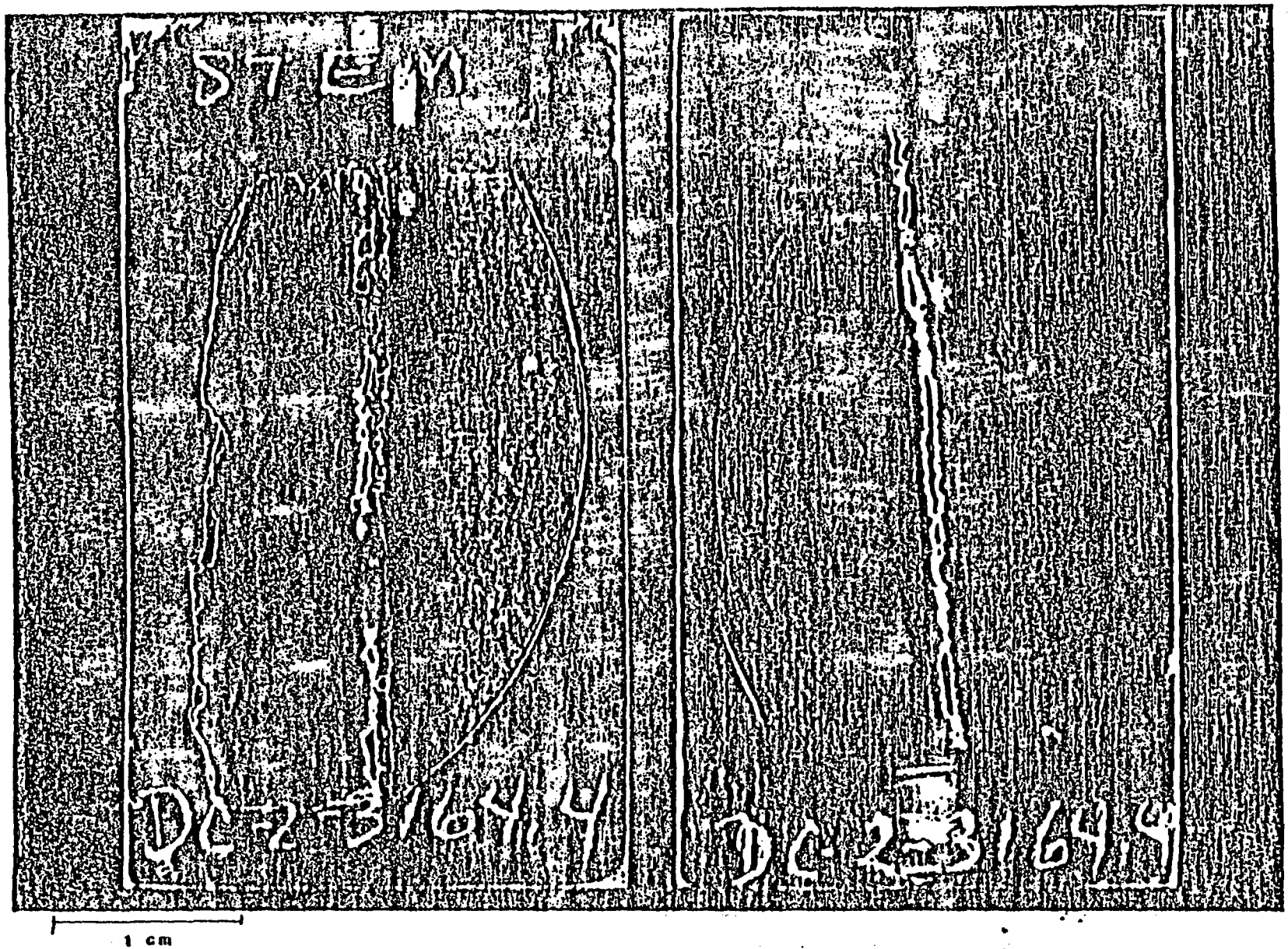
APATITE	$Ca_5(PO_4)_3(OH,F,Cl)$
GYPSUM	$CaSO_4\cdot 2H_2O$
CALCITE	$CaCO_3$
PYRITE	FeS_2

(FROM AMES, 1980; BENSON AND TEAGUE, 1979).

*IDENTIFIES THE DOMINANT SECONDARY MINERALS

WP8401-32

BASALT FRACTURE FILLING



1 cm

BASALT FRACTURE FILLING

0.5 mm

CONCLUSIONS

- CANDIDATE HORIZON FLOWS ARE SIMILAR IN TERMS OF PETROGRAPHY AND PRIMARY MINERAL COMPOSITION. DIFFERENCES BETWEEN COLONNADE AND ENTABLATURE WITHIN A SINGLE FLOW ARE AS GREAT AS THE DIFFERENCES AMONG FLOWS.

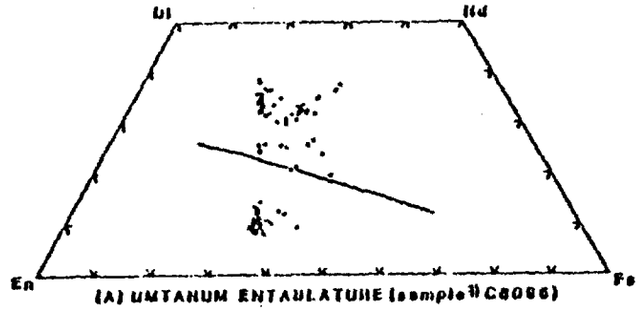
- THE GLASSY MESOSTASIS IS HETEROGENEOUS ON A MICRO-SCALE, AND DIFFERS SIGNIFICANTLY BETWEEN COLONNADE AND ENTABLATURE.

CONCLUSIONS (Continued)

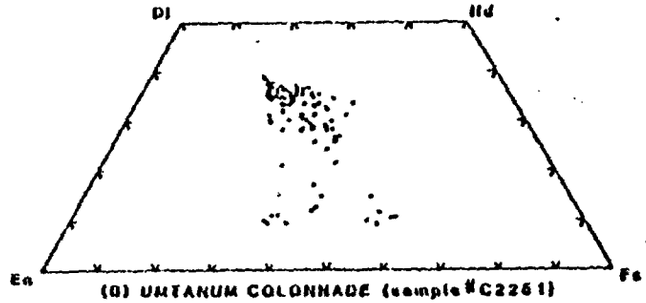
- FLUORIDE SINKS INCLUDE GLASS, APATITE, AND MICRO-CRYSTALLINE BLEBS.

- SECONDARY MINERALS, PREDOMINANTLY CLAY, ZEOLITE, SILICA, AND PYRITE, EXHIBIT CONSIDERABLE VARIATION IN RELATIVE PROPORTIONS BOTH WITHIN AND AMONG CANDIDATE HORIZON FLOWS.

WP8401-30



(A) UMTANUM ENTAULATURE (sample # C8086)



(B) UMTANUM COLONNADE (sample # C2261)

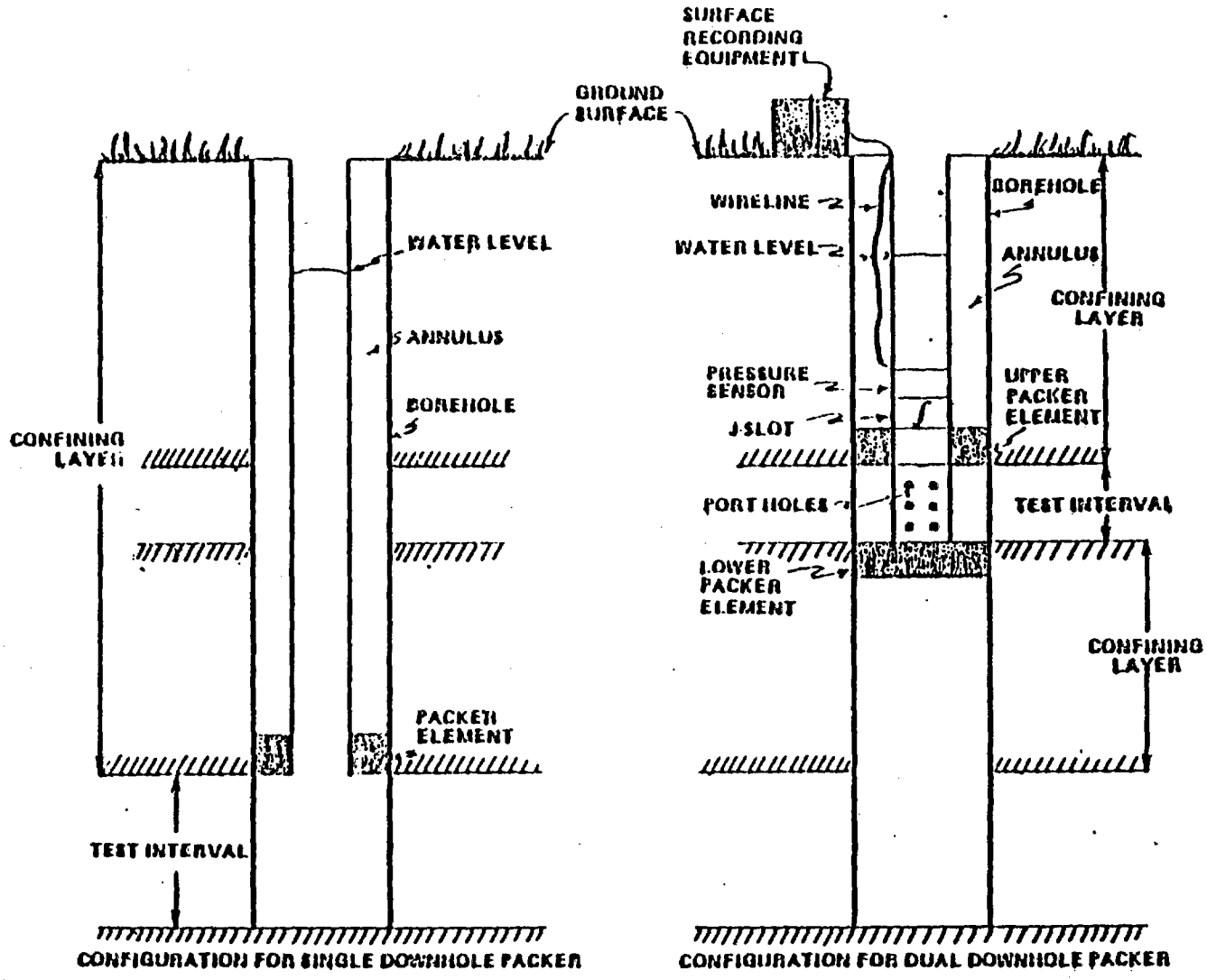
MINERALOGIC CHARACTERIZATION, F. Y. 1984

1. MABTON INTERBED, (10 SAMPLES)
2. COHASSETT FLOW TOP, (8 SAMPLES)
3. BASALT SAMPLES ASSOCIATED WITH HYDROCHEMICAL BREAKS (6 SAMPLES)
4. SULFIDE AND ASSOCIATED Fe-TI OXIDE GRAINS IN GRANDE RONDE (6 SAMPLES)
5. DETAILED CHARACTERIZATION OF PRIMARY AND SECONDARY MINERALS FROM CANDIDATE HORIZONS, (36 SAMPLES)
6. ESTIMATES OF VOLUME AND ABUNDANCE OF SECONDARY MINERALS IN CANDIDATE HORIZONS,(BASED ON 3200 FRACTURE WIDTH MEASUREMENTS)
7. DETAILED CHARACTERIZATION OF SELECTED SAMPLES OF GRANDE RONDE AND FRENCHMAN SPRINGS BASALT (6 SAMPLES)
8. POINT COUNTS ON ~25 ADDITIONAL BASALT SAMPLES.
9. GRAIN SIZE MEASUREMENTS ON ~10 ADDITIONAL BASALT SAMPLES.

Groundwater

EVALUATION OF BOREHOLE DEVELOPMENT FOR HYDROCHEMICAL SAMPLING

D.L. GRAHAM



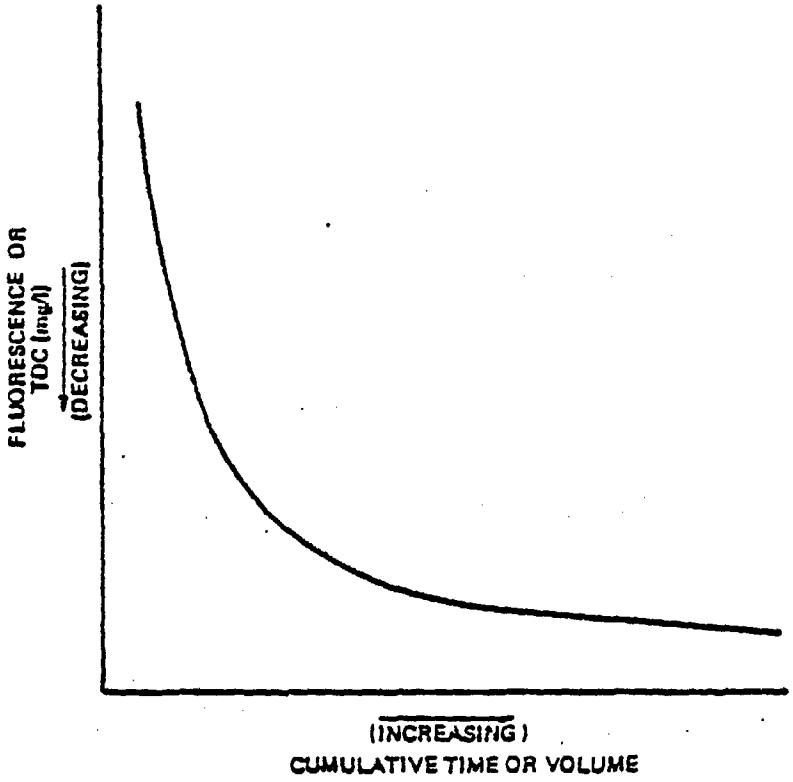
TYPICAL DOWNHOLE PACKER INSTALLATIONS

DRILLING FLUID TRACERS USED BY BWIP TO ASSESS BOREHOLE DEVELOPMENT

- FLUORESCEIN DYE
- TOTAL ORGANIC CARBON
- TRITIUM

Col. R. 10^{-80} tu

basalt = 0



IDEALIZED CURVE FOR BOREHOLE TRACERS USED TO MONITOR BOREHOLE DEVELOPMENT.

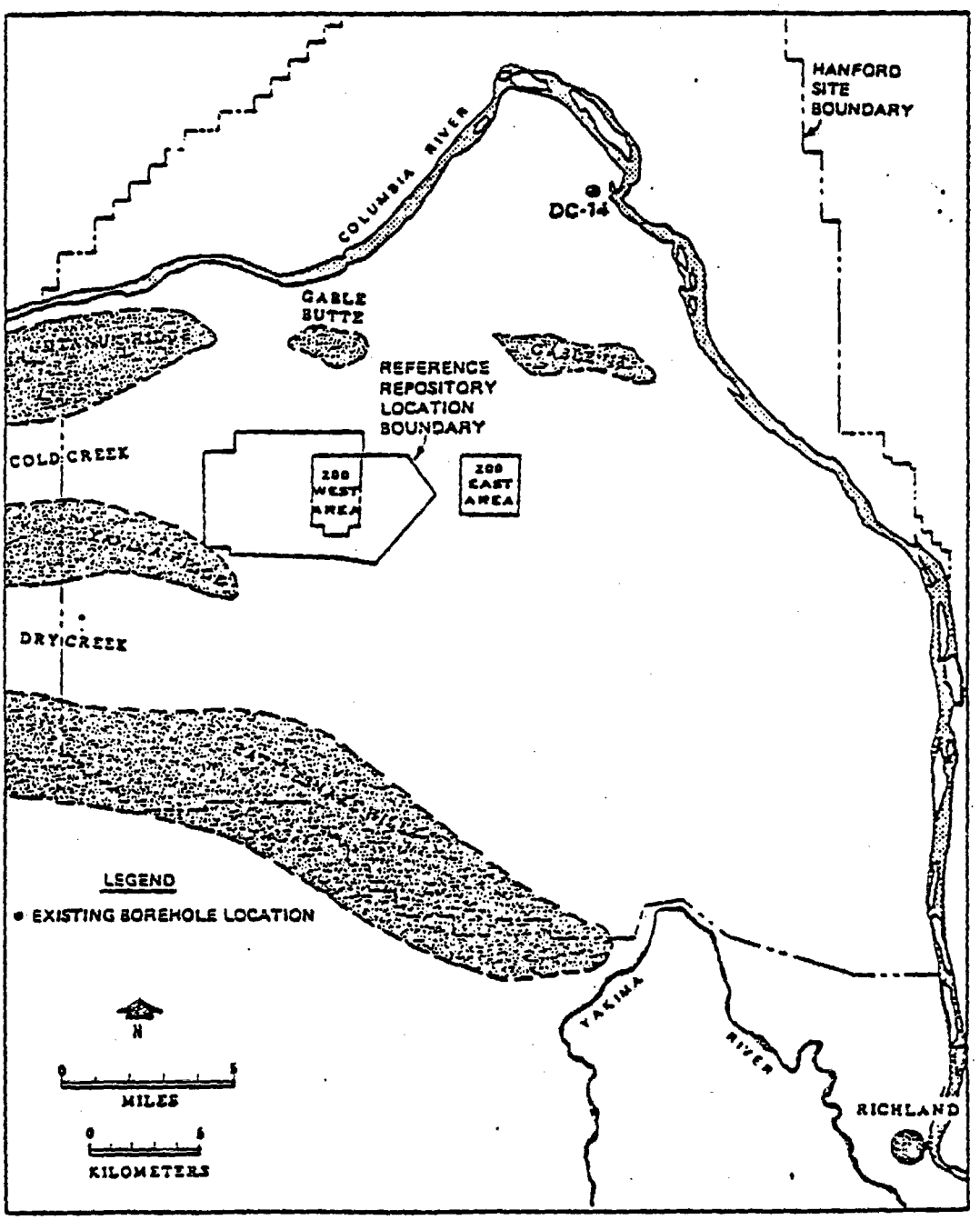
DC-14 DRILLING FLUID TEST

PURPOSE

- TO ASSESS THE AFFECTS OF DRILLING FLUIDS ON THE REPRESENTATIVENESS OF GROUNDWATER HYDROCHEMICAL SAMPLES

OBJECTIVES

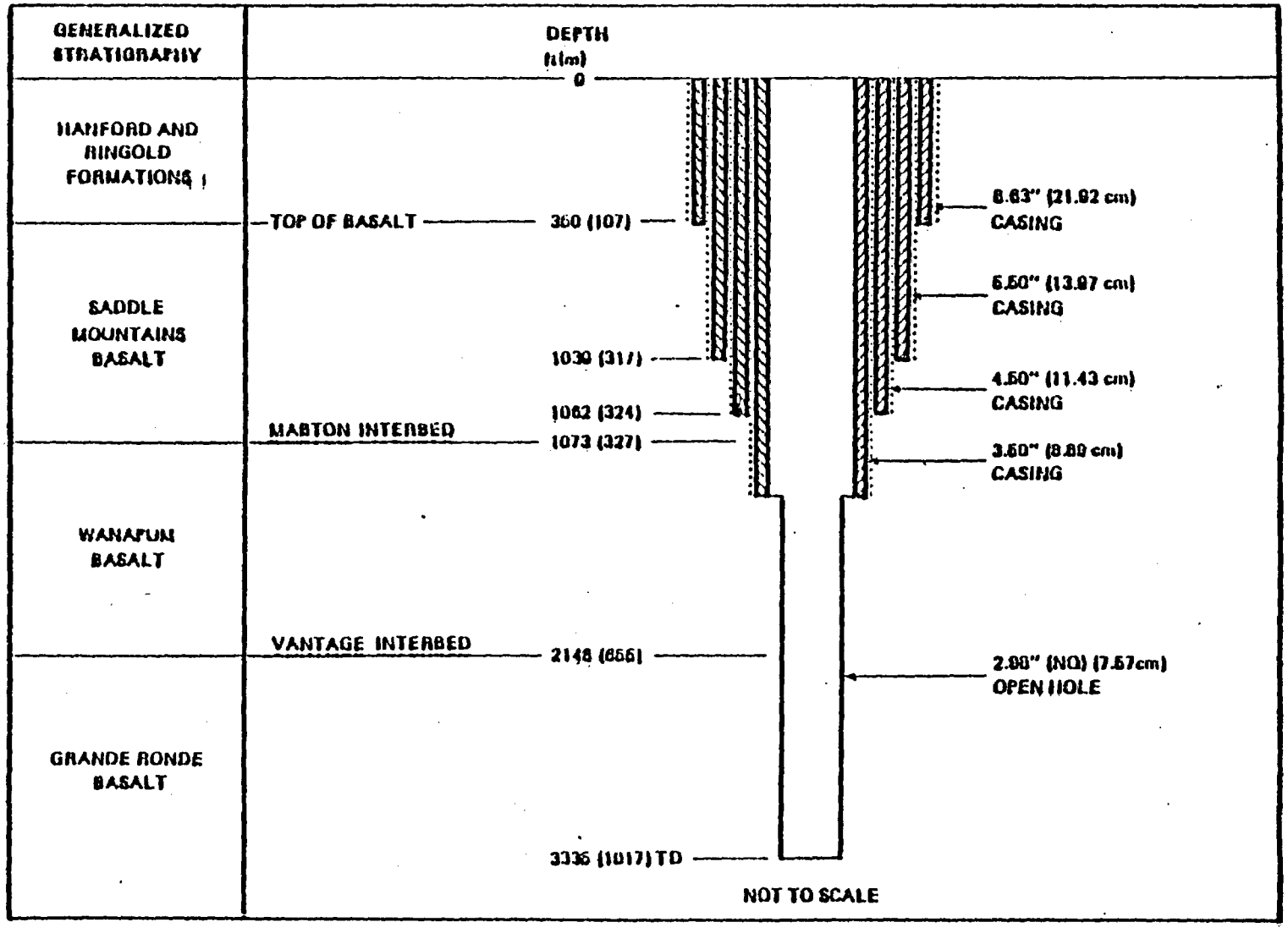
- PROVIDE CRITERIA FOR EVALUATING EXISTING DATA
- PROVIDE GUIDELINES FOR COLLECTION OF FUTURE SAMPLES



LOCATION OF BOREHOLE DC-14

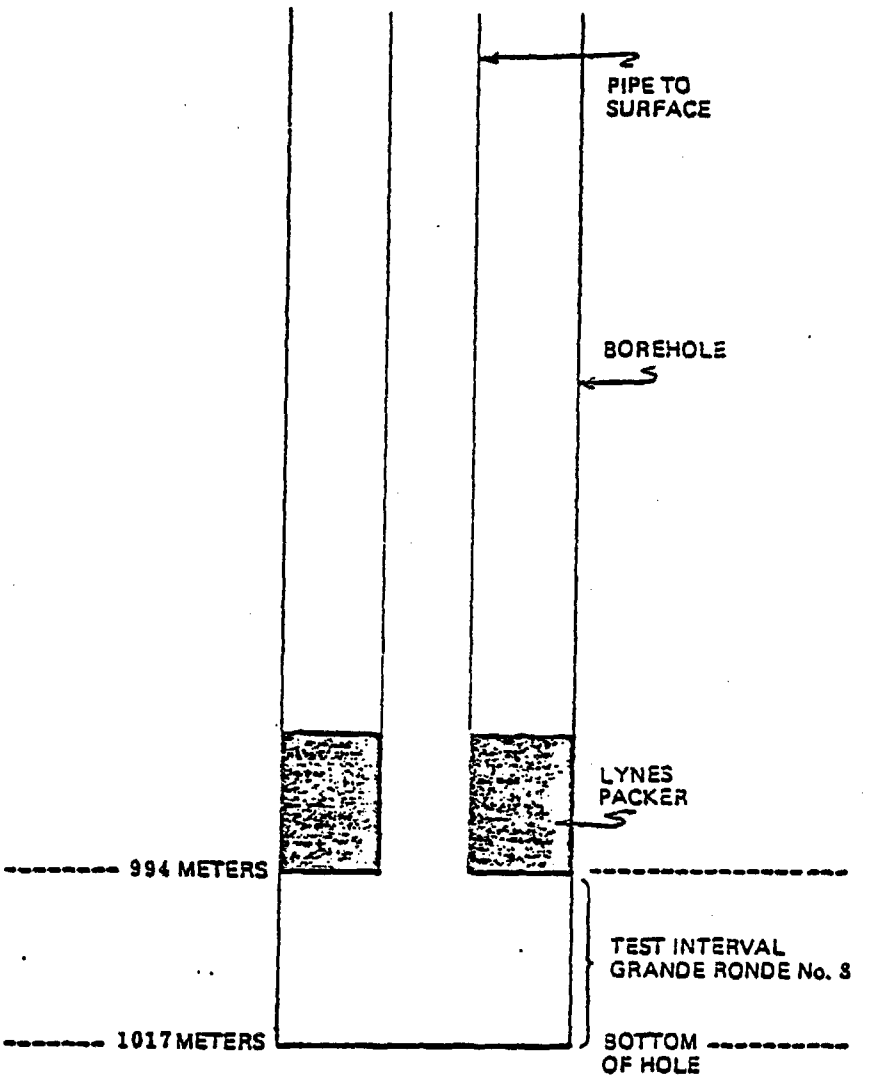
RATIONALE FOR SELECTING BOREHOLE DC-14

- IT IS A FLOWING ARTESIAN WELL REQUIRING NO PUMPING EQUIPMENT FOR DEVELOPMENT ACTIVITIES
- NO HYDRAULIC TESTING ACTIVITIES SCHEDULED IN THIS BOREHOLE DURING THE DURATION OF TEST
- THE ZONE TO BE USED (GRANDE RONDE #8) HAS BEEN FLOWING FOR ~1 YEAR AND SHOULD BE CLOSE TO NATURAL BACKGROUND LEVELS 4 gal/min
- HISTORICAL DATA, BOTH CHEMICAL AND HYDRAULIC, ARE AVAILABLE FOR THIS ZONE



AS-BUILT DIAGRAM FOR BOREHOLE DC-14.

DLG 2/2/83



CONFIGURATION OF PACKER IN BOREHOLE.

INJECTION OF DRILLING FLUID

- APPROXIMATELY 10,000 GALLONS OF FLUID INJECTED INTO ZONE

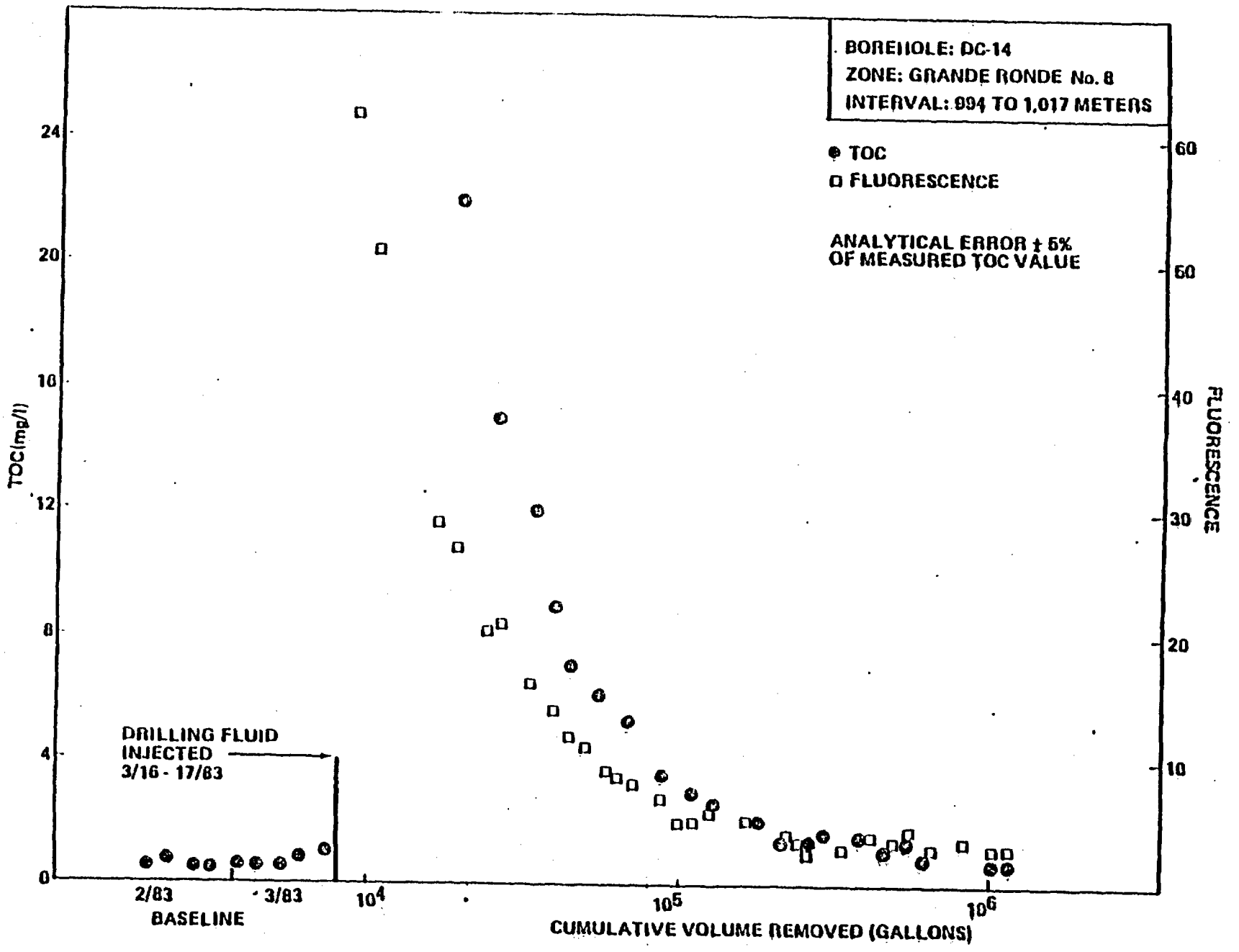
PRIMARY CONSTITUENTS IN DRILLING FLUID

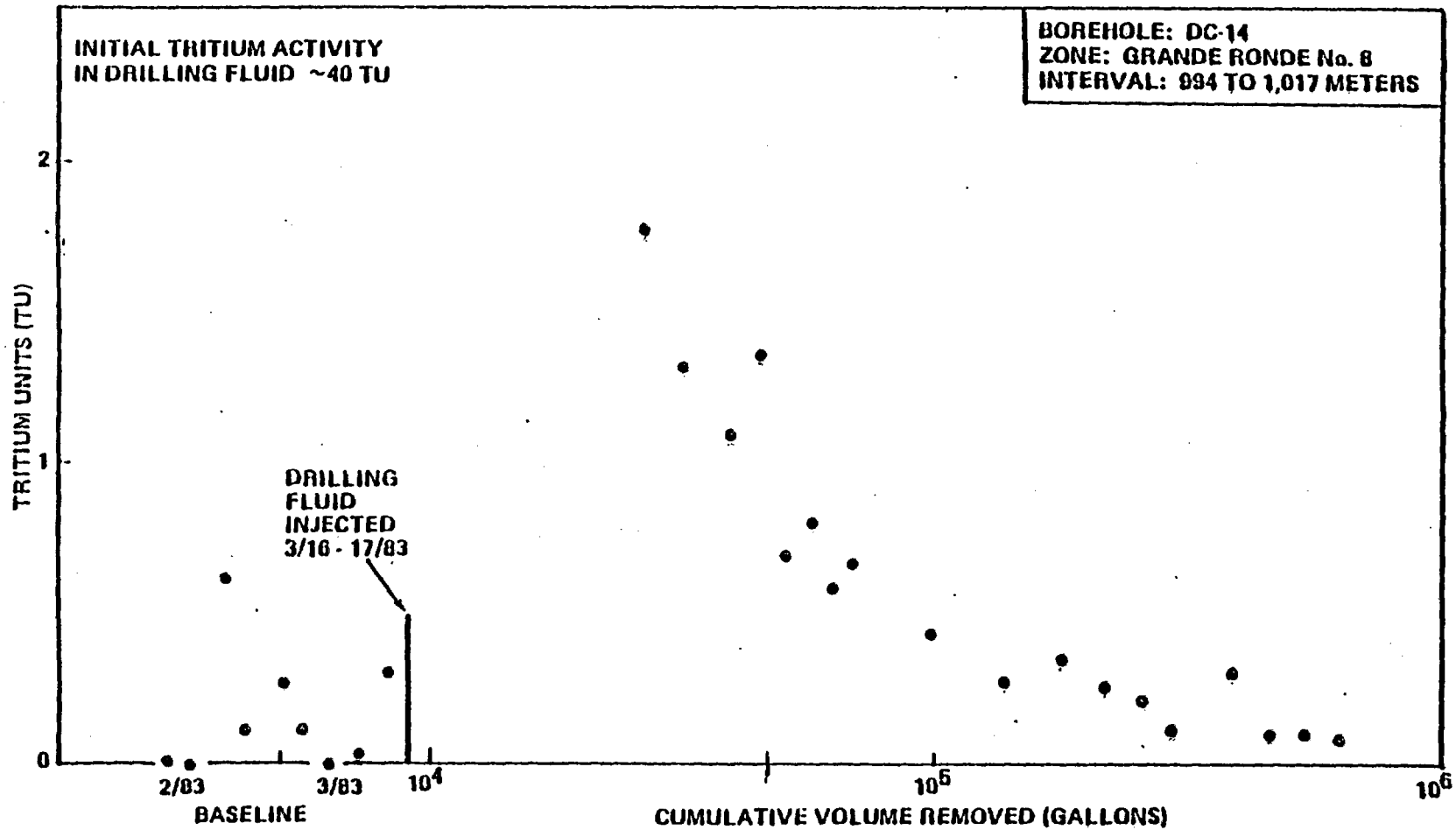
- NA BENTONITE
- SODA ASH (NA_2CO_3)
- CAUSTICIZED LIGNITE
- ORGANIC POLYMER
- COLUMBIA RIVER WATER

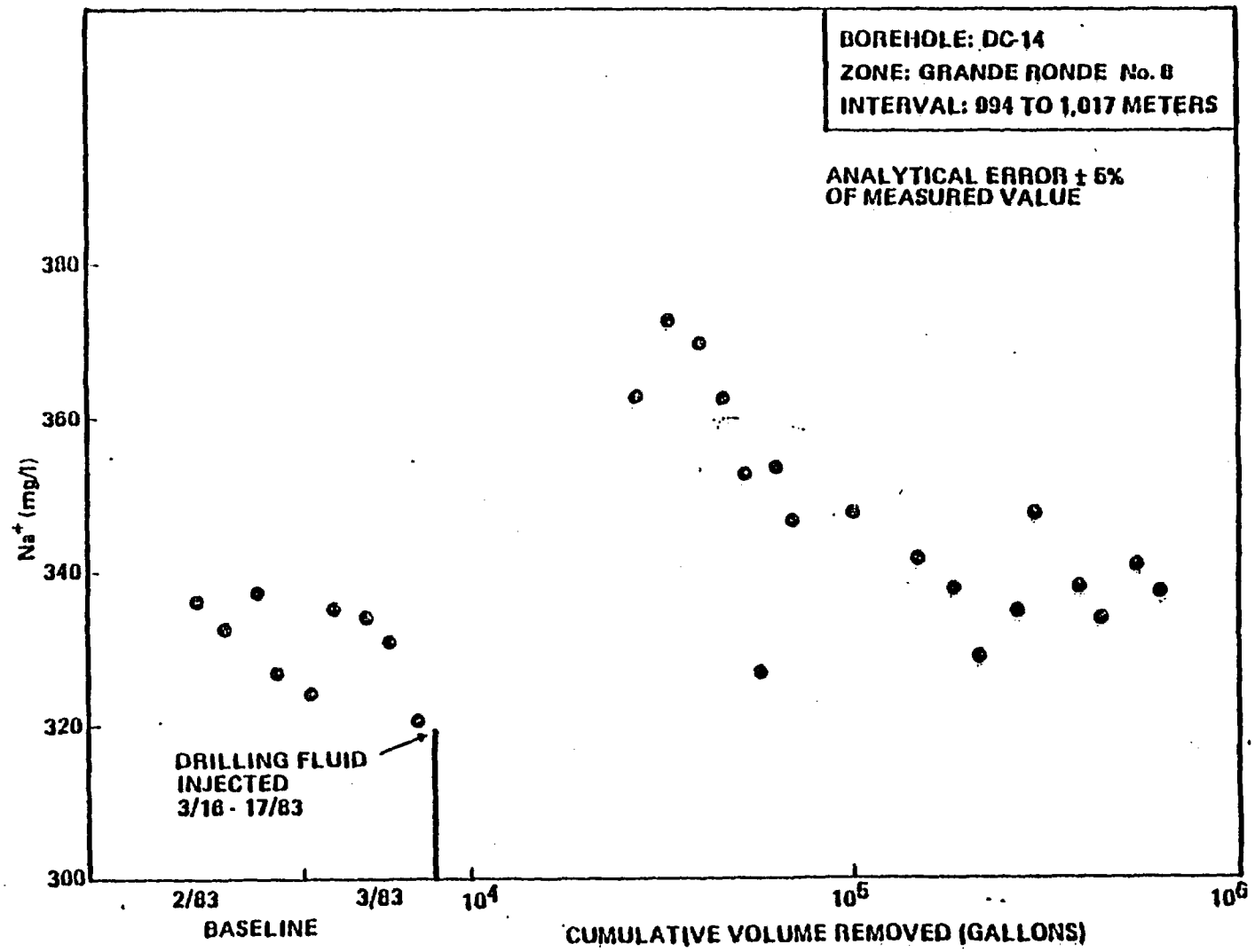
lignin sulfonates
paper mill pulp liquor

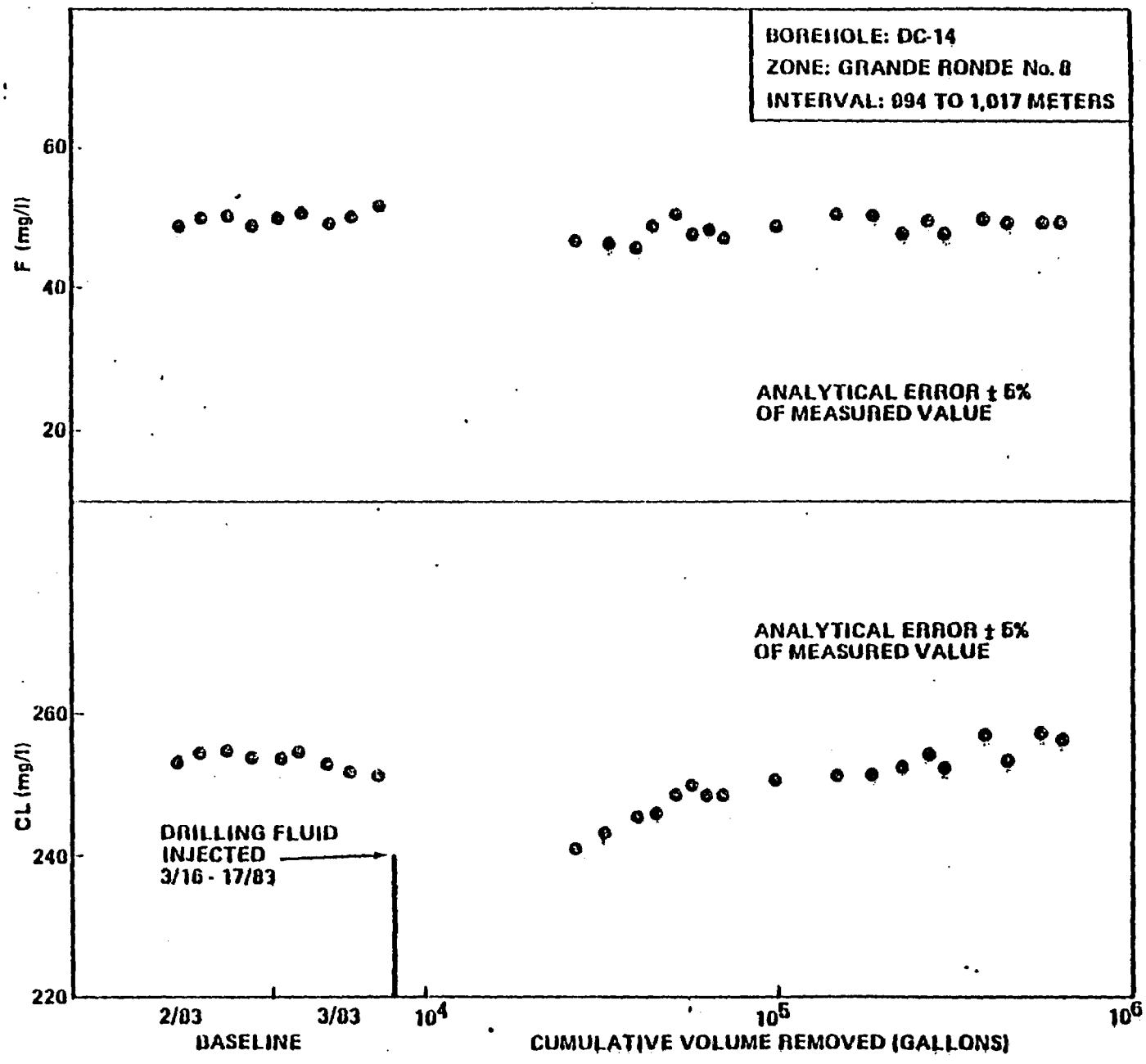
SAMPLES ARE BEING COLLECTED AND ANALYZED FOR:

- MAJOR INORGANICS
- TRACE ELEMENTS
- DISSOLVED GASES
- STABLE ISOTOPES
- RADIOACTIVE ISOTOPES

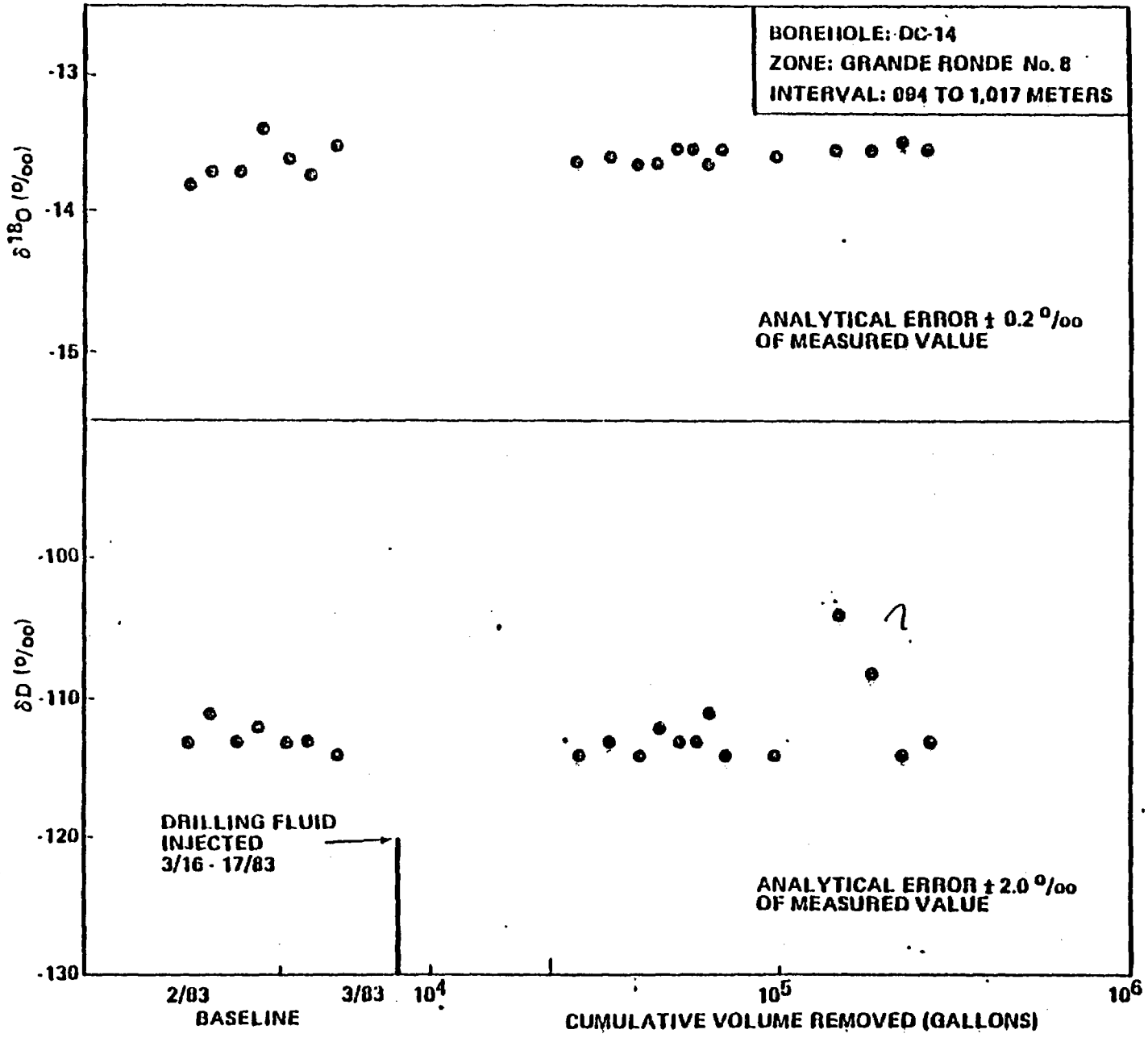

BOREHOLE: DC-14
ZONE: GRANDE RONDE No. 8
INTERVAL: 994 TO 1,017 METERS
TOC
FLUORESCENCE
ANALYTICAL ERROR ± 5%
OF MEASURED TOC VALUE
DRILLING FLUID
INJECTED
3/16 - 17/83
TOC(mg/l)
FLUORESCENCE
0
4
8
12
16
20
24
10
20
30
40
50
60
2/83
3/83
BASELINE
10^4
10^5
10^6
CUMULATIVE VOLUME REMOVED (GALLONS)

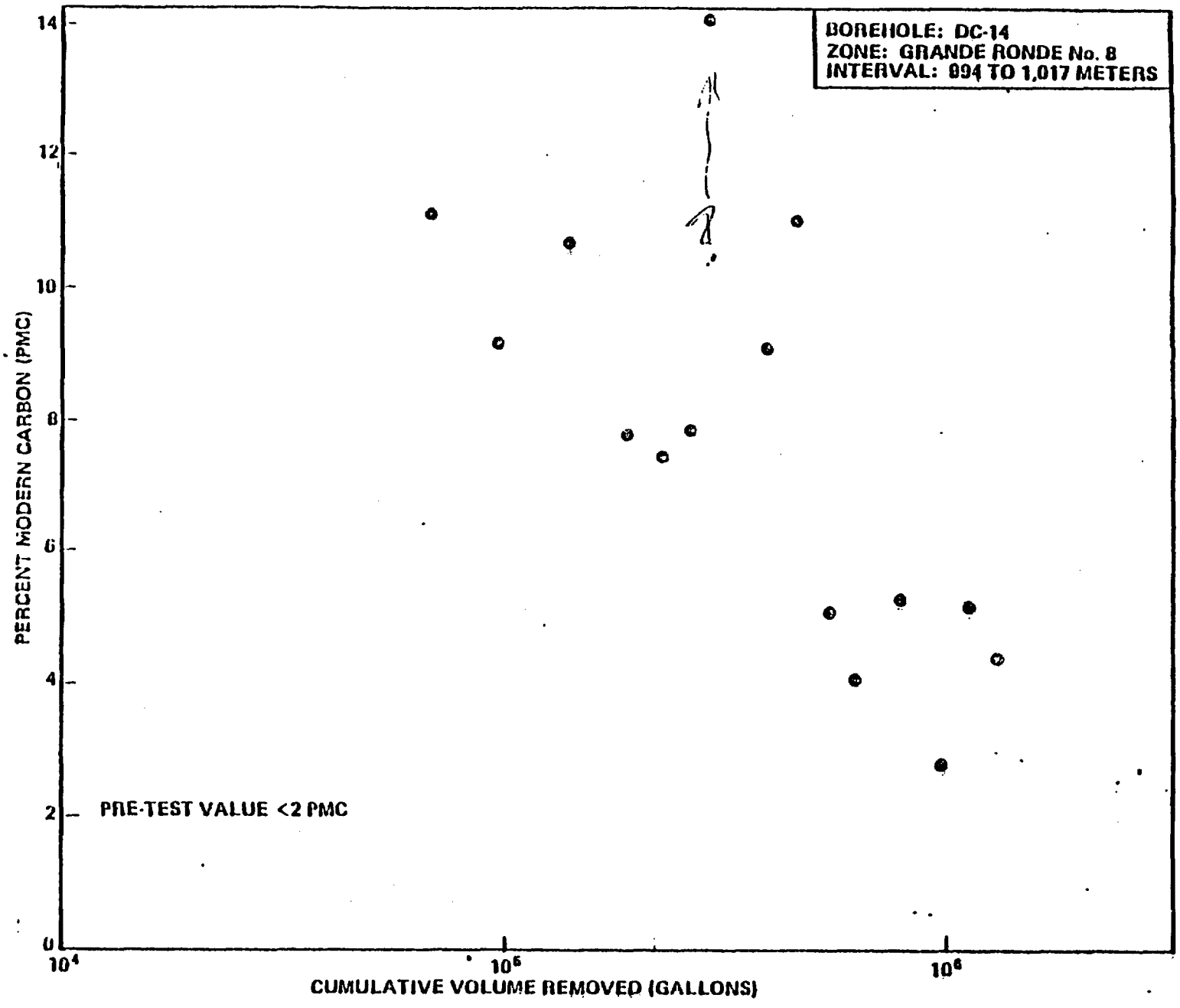

INITIAL TRITIUM ACTIVITY
IN DRILLING FLUID ~40 TU
BOREHOLE: DC-14
ZONE: GRANDE RONDE No. 8
INTERVAL: 994 TO 1,017 METERS
TRITIUM UNITS (TU)
2
1
0
DRILLING
FLUID
INJECTED
3/16 - 17/83
2/83
3/83
BASELINE
10^4
10^5
10^6
CUMULATIVE VOLUME REMOVED (GALLONS)


BOREHOLE: DC-14
ZONE: GRANDE RONDE No. 8
INTERVAL: 994 TO 1,017 METERS
ANALYTICAL ERROR ± 5%
OF MEASURED VALUE
380
360
340
320
300
Na^+ (mg/l)
DRILLING FLUID
INJECTED
3/16 - 17/83
2/83
3/83
BASELINE
10^4
10^5
10^6
CUMULATIVE VOLUME REMOVED (GALLONS)


BOREHOLE: DC-14
ZONE: GRANDE RONDE No. 8
INTERVAL: 994 TO 1,017 METERS
F (mg/l)
60
40
20
ANALYTICAL ERROR ± 5%
OF MEASURED VALUE
CL (mg/l)
260
240
220
ANALYTICAL ERROR ± 5%
OF MEASURED VALUE
DRILLING FLUID
INJECTED
3/16 - 17/83
2/83
3/83
BASELINE
10^4
10^5
10^6
CUMULATIVE VOLUME REMOVED (GALLONS)

dilution


BOREHOLE: DC-14
ZONE: GRANDE RONDE No. 8
INTERVAL: 094 TO 1,017 METERS
-13
-14
-15
δ18O (°/oo)
ANALYTICAL ERROR ± 0.2 °/oo
OF MEASURED VALUE
-100
-110
-120
-130
δD (°/oo)
DRILLING FLUID
INJECTED
3/16 - 17/83
ANALYTICAL ERROR ± 2.0 °/oo
OF MEASURED VALUE
2/83
BASELINE
3/83
10^4
10^5
10^6
CUMULATIVE VOLUME REMOVED (GALLONS)


BOREHOLE: DC-14
ZONE: GRANDE RONDE No. 8
INTERVAL: 994 TO 1,017 METERS
PRE-TEST VALUE <2 PMC
PERCENT MODERN CARBON (PMC)
0
2
4
6
8
10
12
14
10^4
10^5
10^6
CUMULATIVE VOLUME REMOVED (GALLONS)

SUMMARY

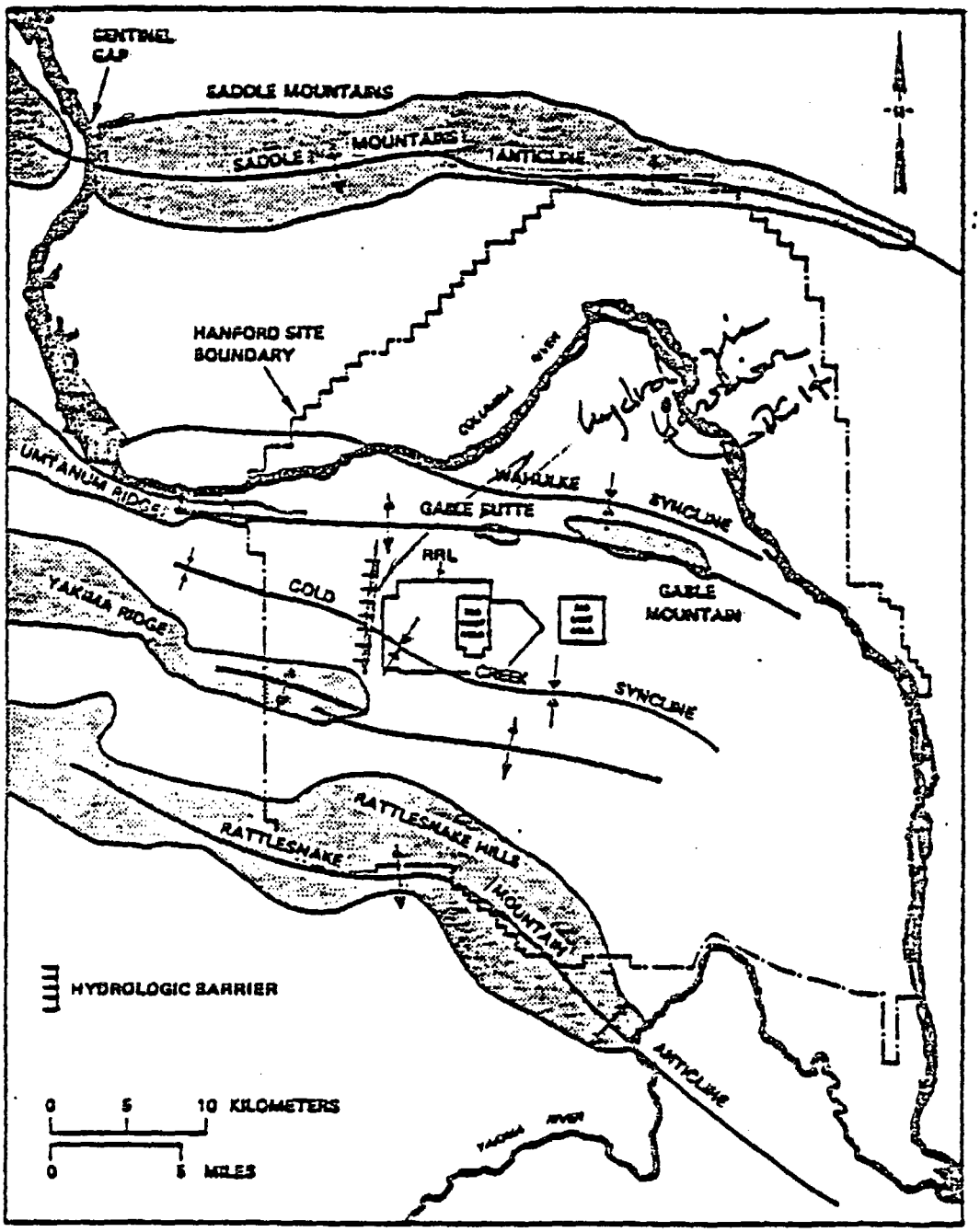
- DRILLING FLUID AFFECTS GROUNDWATER CHEMISTRY
  - CONCENTRATIONS ELEVATED, I.E. Na^+
  - CONCENTRATIONS DILUTED, I.E. Cl^-, F^-
- DRILLING FLUID TRACERS USED BY THE BWIP ALLOW BOREHOLE DEVELOPMENT TO BE MONITORED PRIOR TO FINAL SAMPLE COLLECTION
- TEST PERFORMED AT DC-14 SUPPORTS PREVIOUS DATA
- TEST RESULTS FROM DC-14 WILL ALLOW EVALUATION OF EXISTING DATA
- EFFECTS OF OTHER DRILLING TECHNIQUES (I.E. AIR ROTARY) ARE BEING EVALUATED

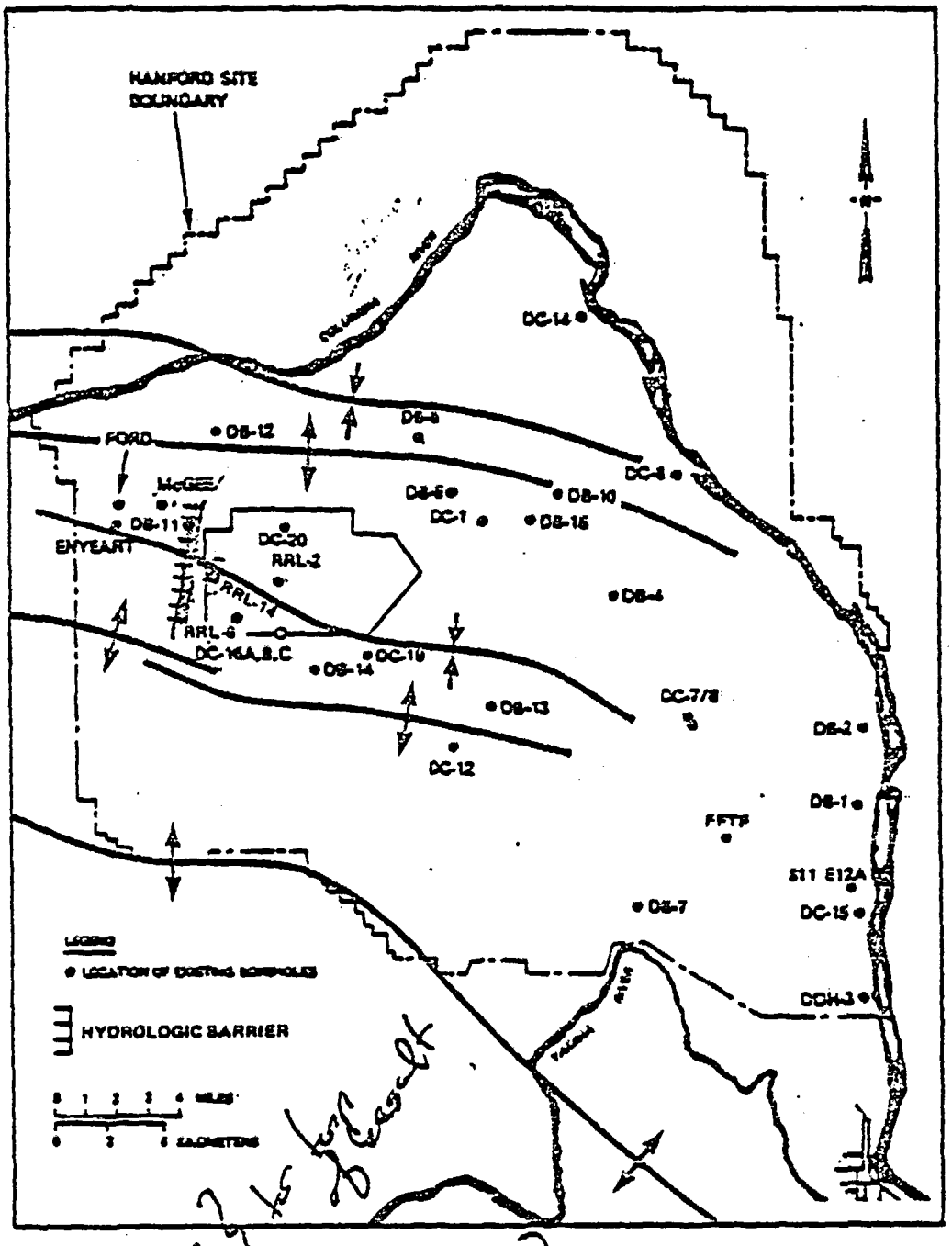
HYDROCHEMICAL CHARACTERISTICS OF GROUNDWATER AND THE INTERPRETATION OF AVAILABLE DATA

T. O. EARLY

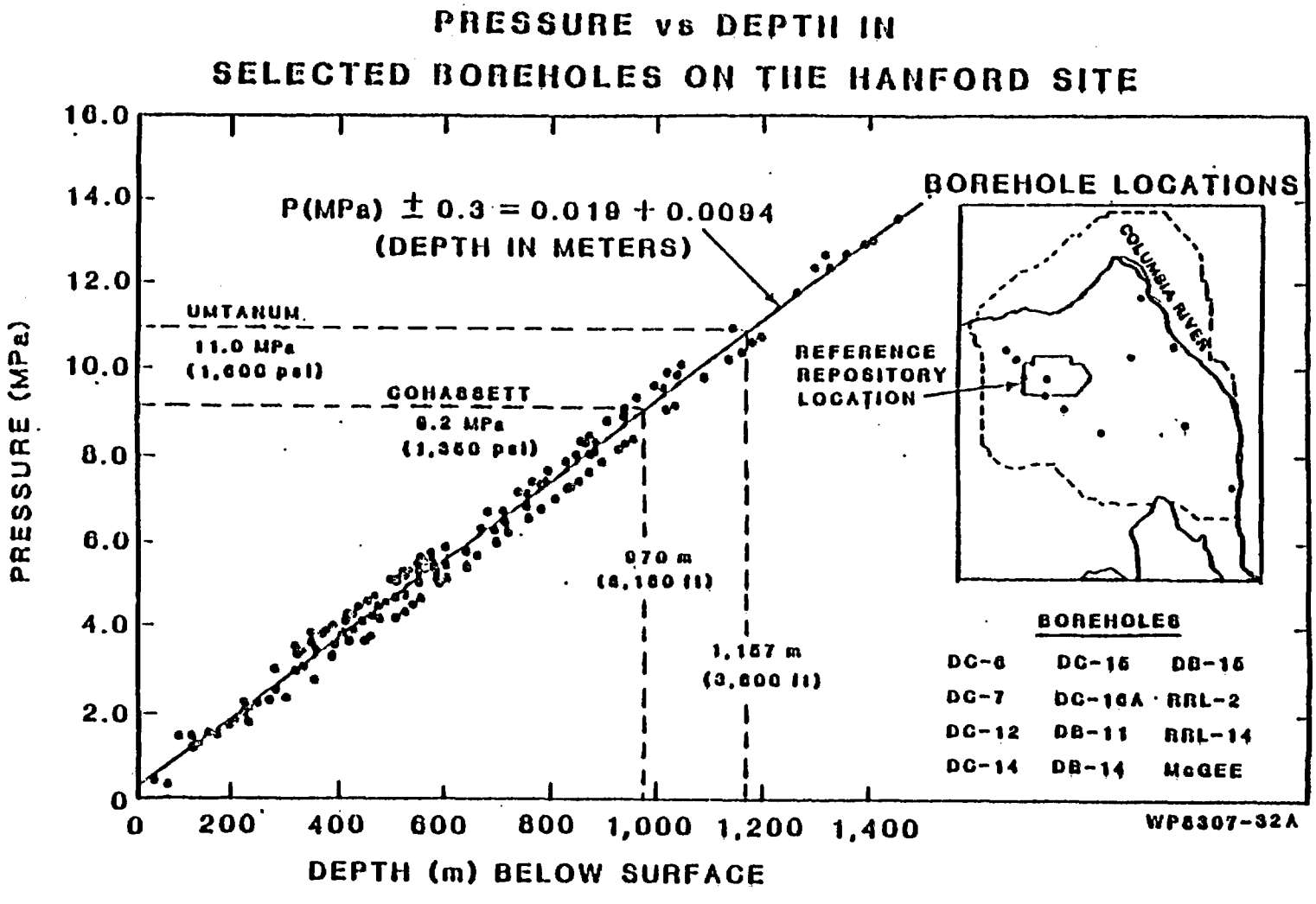
PRESENTATION OUTLINE

- EXAMINATION OF MAJOR ELEMENT CHEMISTRY OF HANFORD GROUNDWATERS AS A FUNCTION OF DEPTH.
- EVALUATION OF ROCK/WATER INTERACTION IN GEOCHEMICAL DEVELOPMENT OF SHALLOW HANFORD GROUNDWATERS.
- EVALUATION OF GEOCHEMICAL EVIDENCE FOR VERTICAL MIXING OF GROUNDWATERS UNDERLYING THE HANFORD SITE.

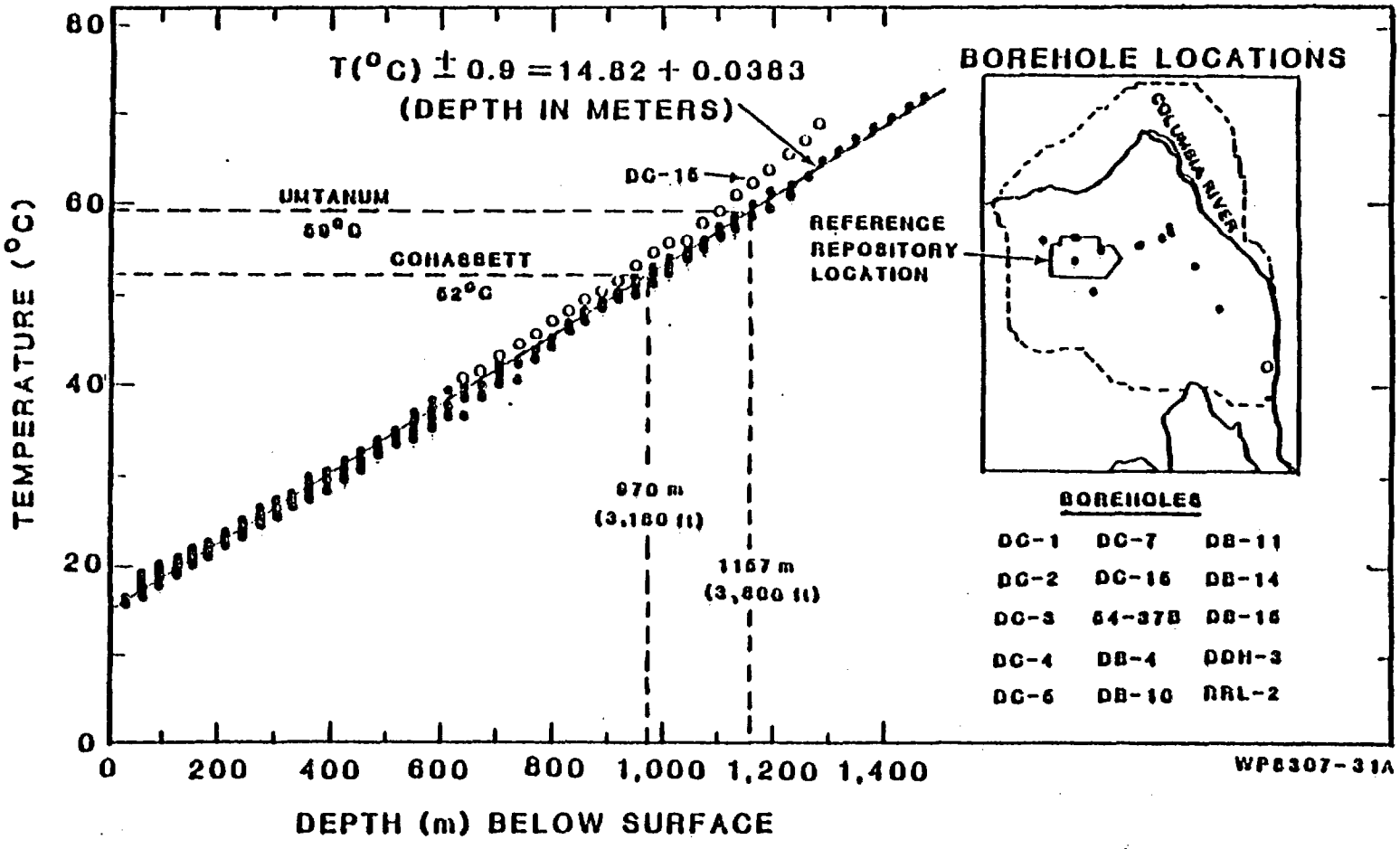

CENTINEL GAP
SADDLE MOUNTAINS
SADDLE MOUNTAINS ANTICLINE
HANFORD SITE BOUNDARY
COLUMBIA RIVER
UMTANUM RIDGE
WAHLUKE
GABLE BUTTE
SYNCLINE
RRL
COLD
CREEK
YAKIMA RIDGE
GABLE MOUNTAIN
SYNCLINE
RATTLESNAKE HILLS
RATTLESNAKE MOUNTAIN
ANTICLINE
YAKIMA RIVER
HYDROLOGIC BARRIER
0 5 10 KILOMETERS
0 5 MILES

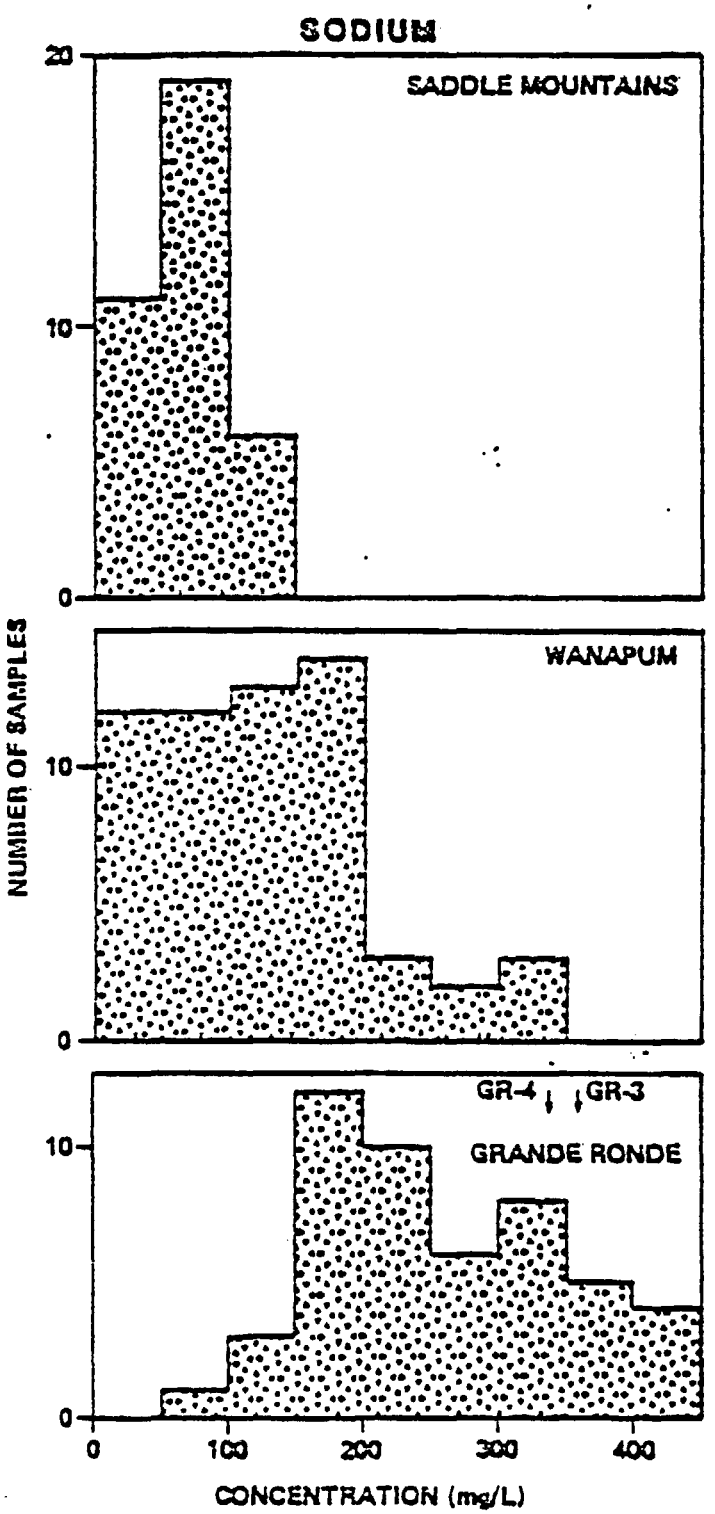


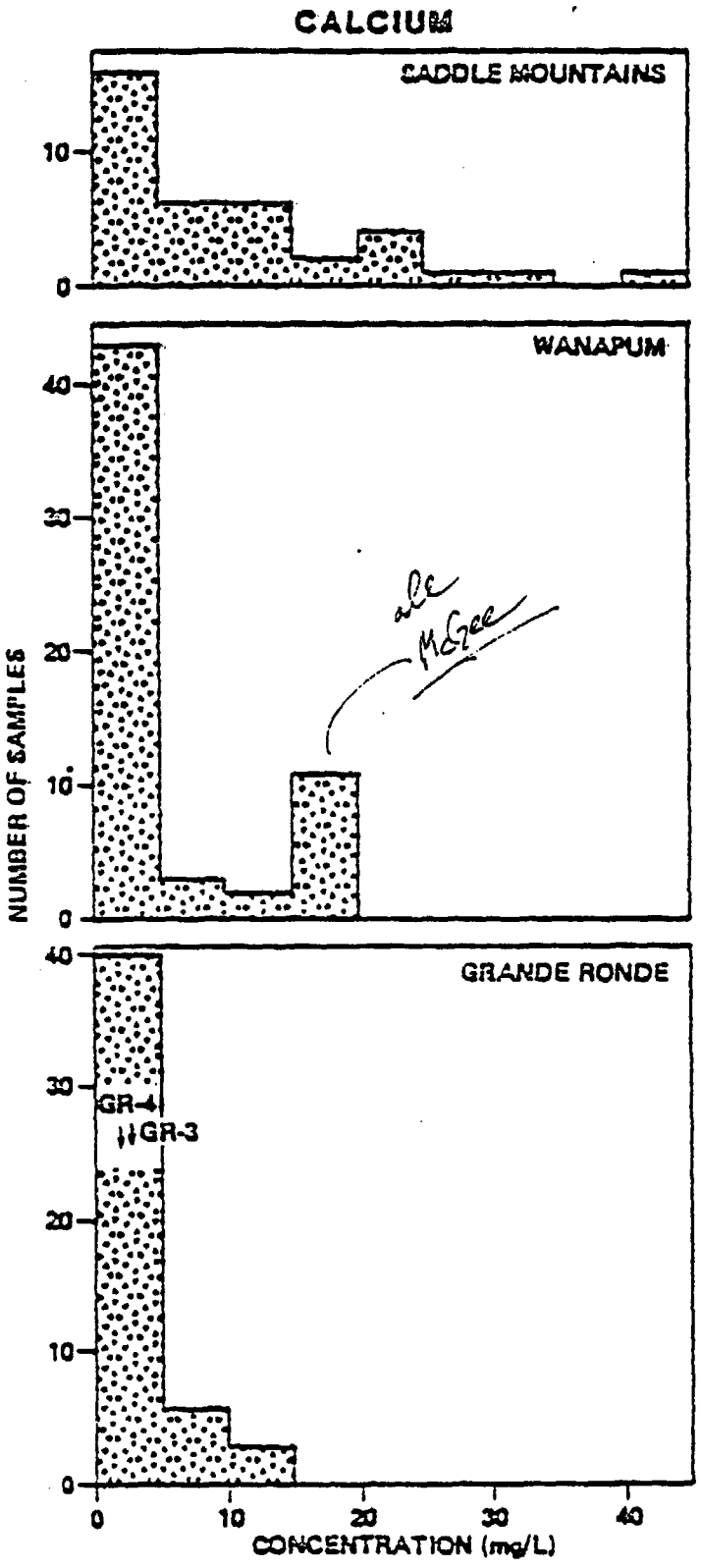
DB 27 ? to top of basalt
DB 28
• strat
• channeling
• monoclinic (relief ~200')
• faulting

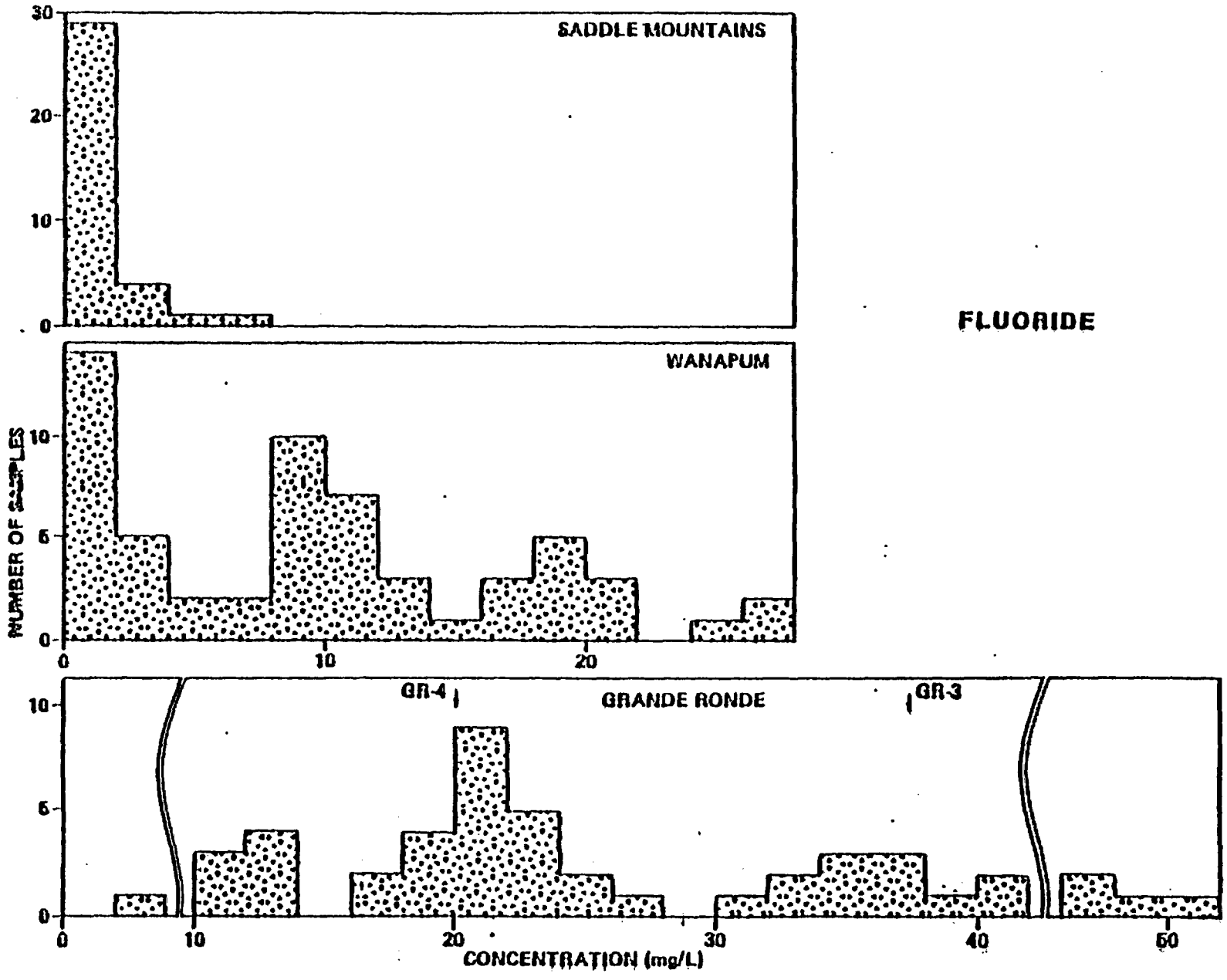

PRESSURE vs DEPTH IN
SELECTED BOREHOLES ON THE HANFORD SITE
P(MPa) ± 0.3 = 0.019 + 0.0094
(DEPTH IN METERS)
BOREHOLE LOCATIONS
UMTANUM
11.0 MPa
(1,600 psi)
COHASSETT
9.2 MPa
(1,350 psi)
970 m
(3,180 ft)
1,157 m
(3,800 ft)
REFERENCE
REPOSITORY
LOCATION
COLUMBIA RIVER
BOREHOLES
DC-6
DC-15
DB-15
DC-7
DC-16A
RRL-2
DC-12
DB-11
RRL-14
DC-14
DB-14
McGEE
PRESSURE (MPa)
DEPTH (m) BELOW SURFACE
0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
200
400
600
800
1,000
1,200
1,400
WP8307-32A

MEASURED FLUID TEMPERATURE vs DEPTH IN SELECTED BOREHOLES ON THE HANFORD SITE

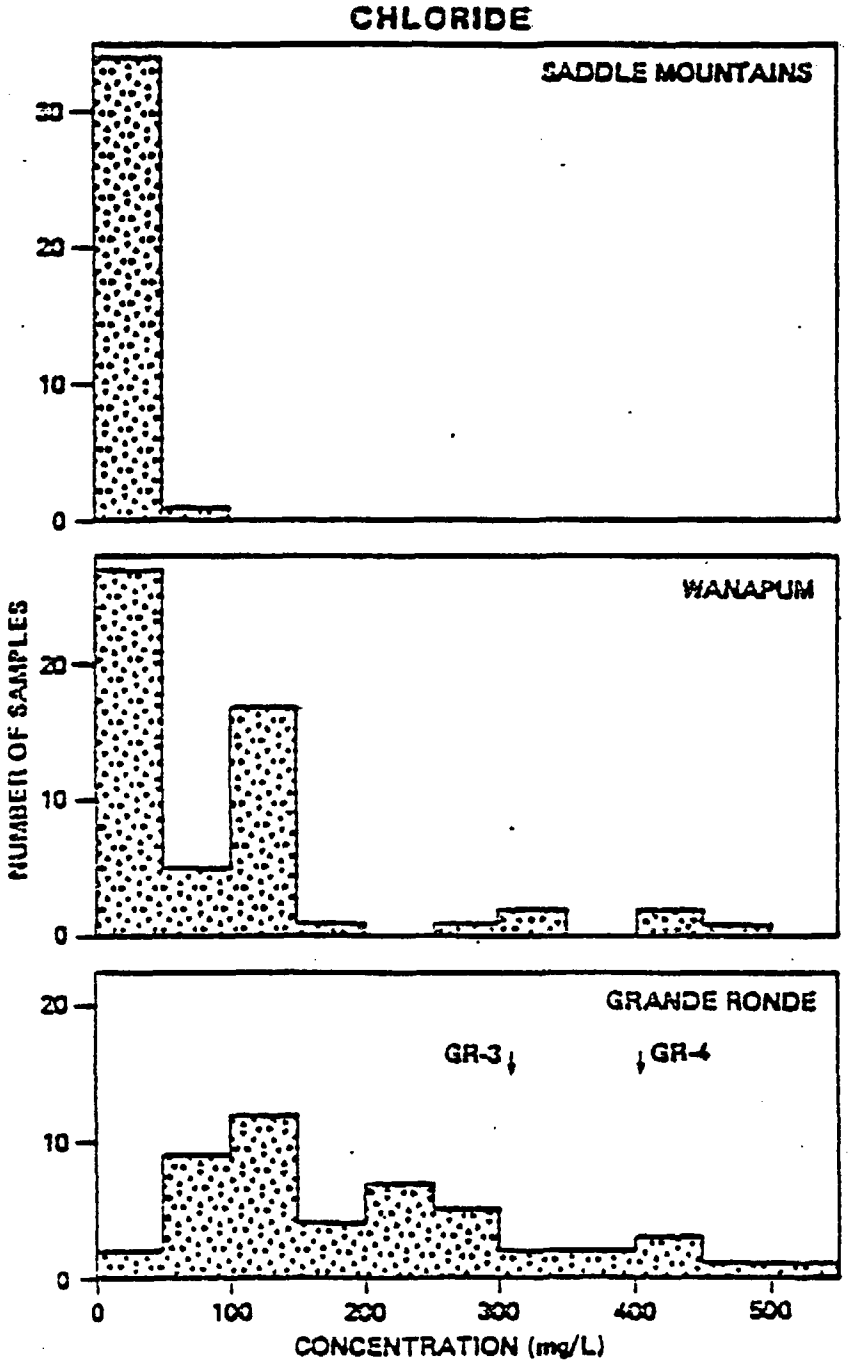


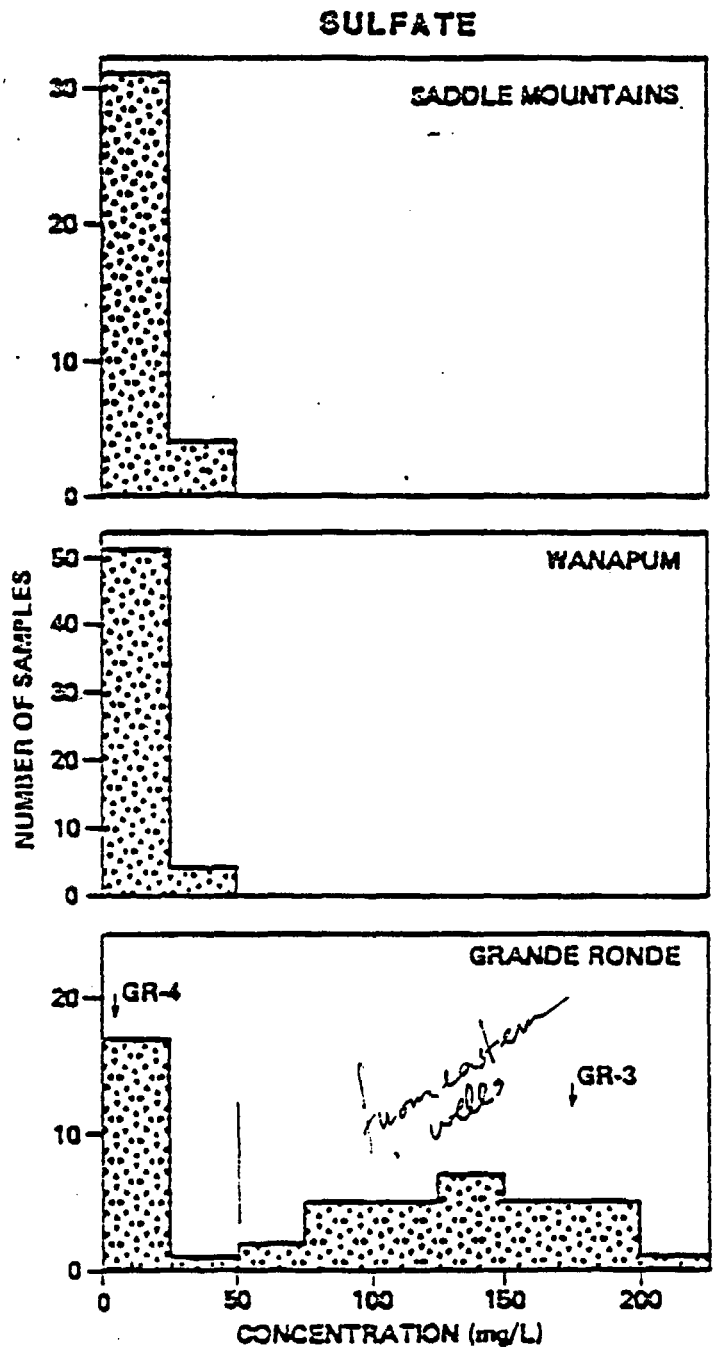

SODIUM
SADDLE MOUNTAINS
WANAPUM
GR-4
GR-3
GRANDE RONDE
NUMBER OF SAMPLES
CONCENTRATION (mg/L)
0
10
20
100
200
300
400

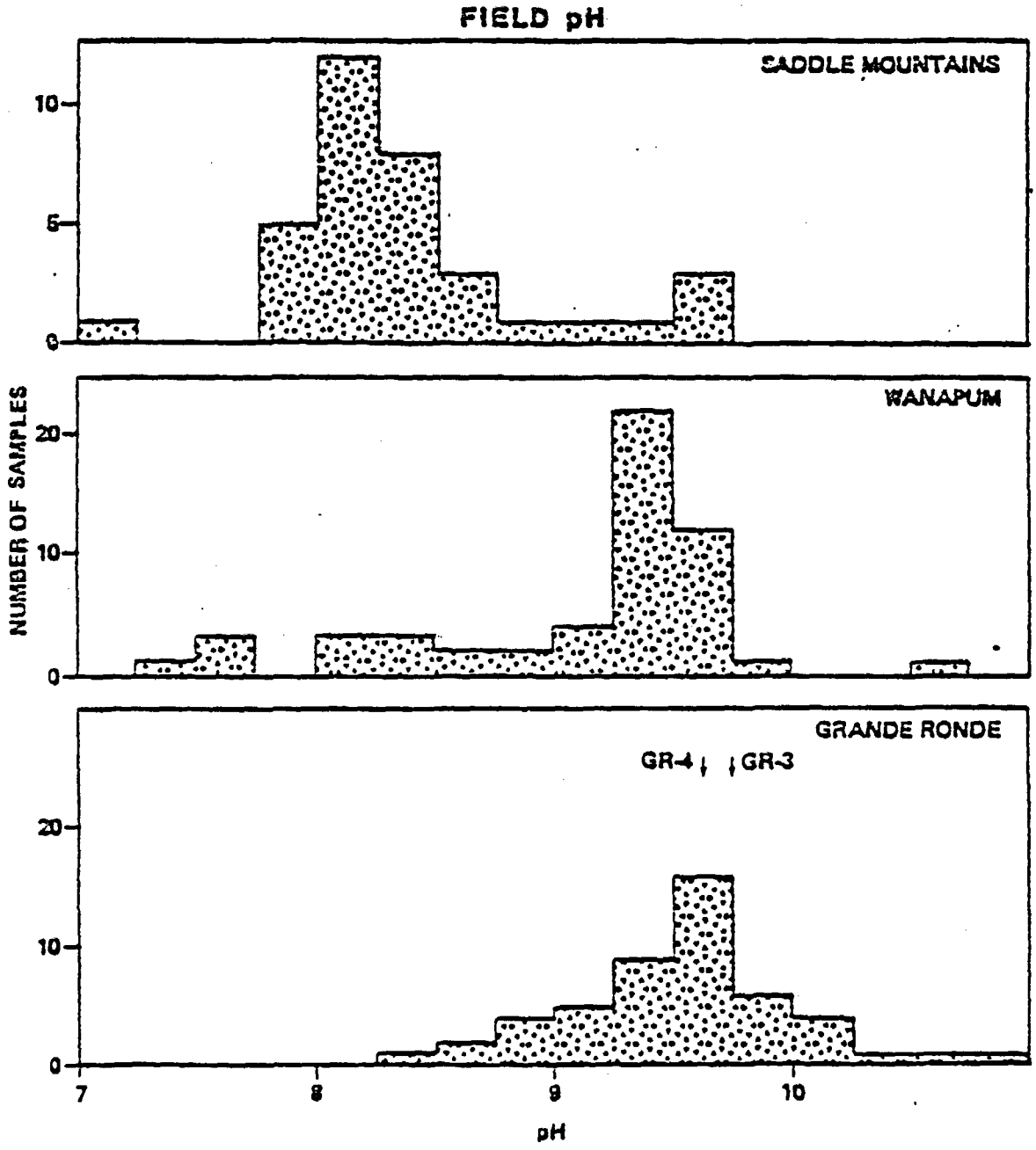

CALCIUM
CADDLE MOUNTAINS
WANAPUM
GRANDE RONDE
GR-4
GR-3
NUMBER OF SAMPLES
CONCENTRATION (mg/L)
0
10
20
30
40

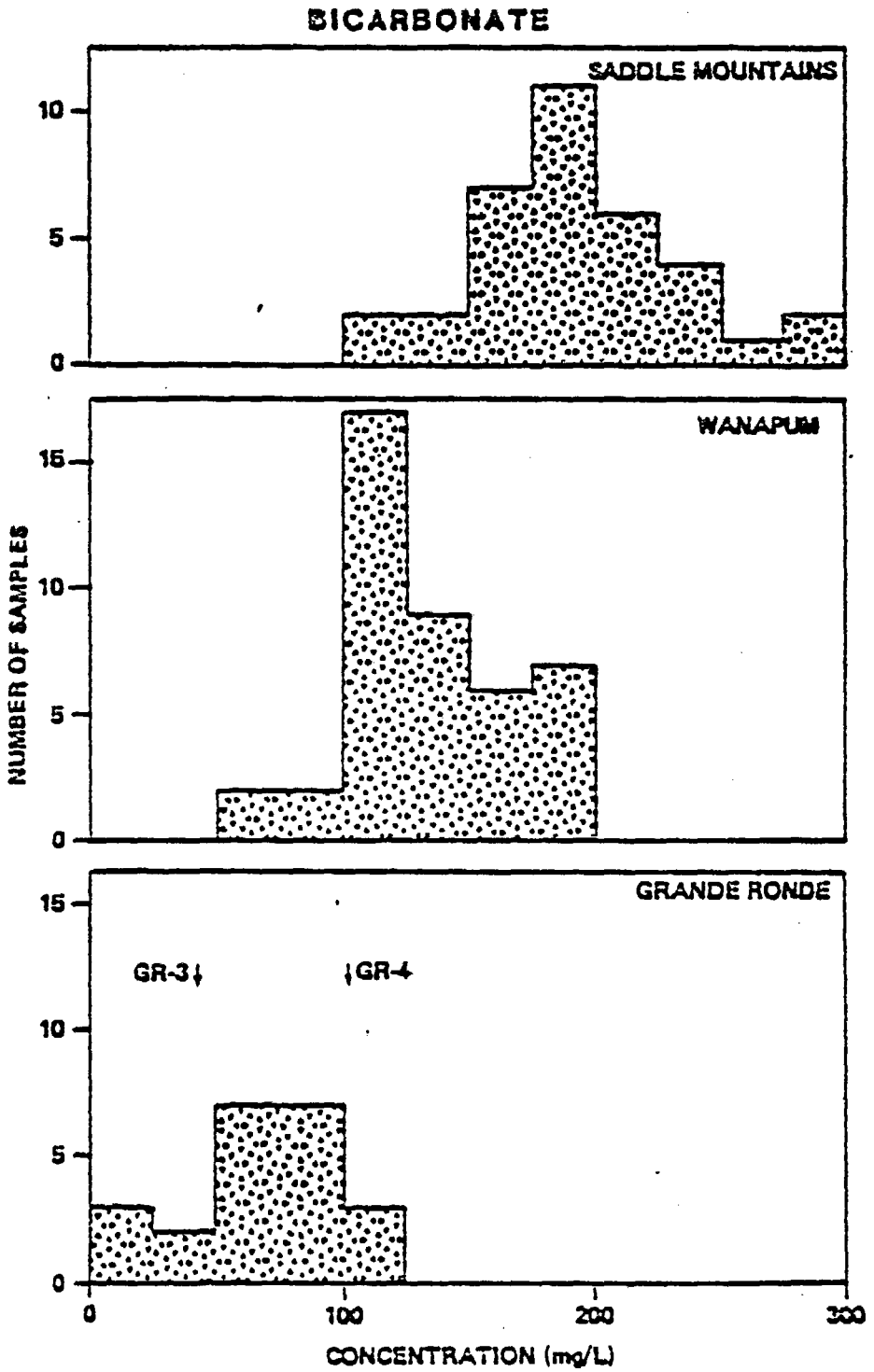

SADDLE MOUNTAINS
WANAPUM
GRANDE RONDE
GR-4
GR-3
NUMBER OF SAMPLES
CONCENTRATION (mg/L)
0
10
20
30
40
50
5

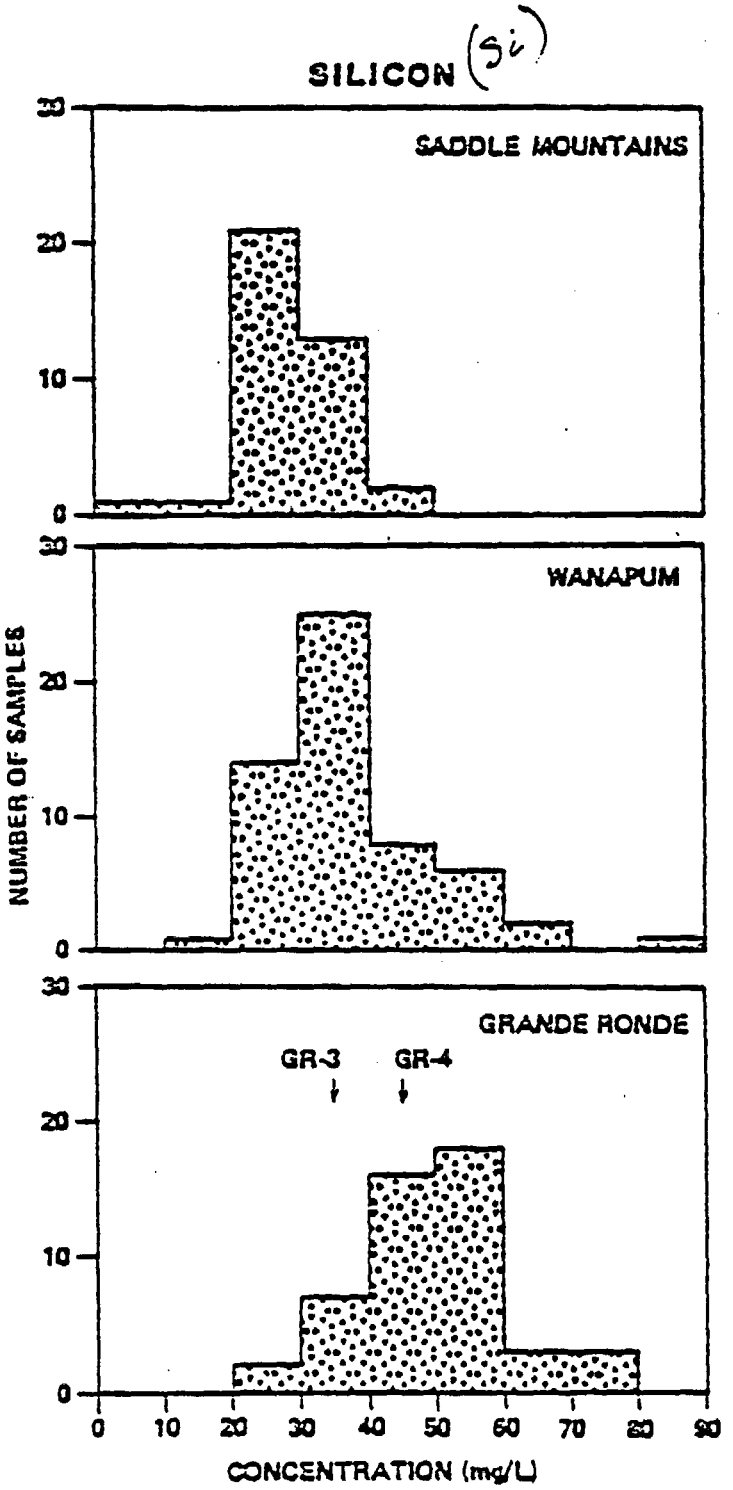
FLUORIDE


CHLORIDE
SADDLE MOUNTAINS
WANAPUM
GRANDE RONDE
GR-3
GR-4
NUMBER OF SAMPLES
0
10
20
30
0
100
200
300
400
500
CONCENTRATION (mg/L)

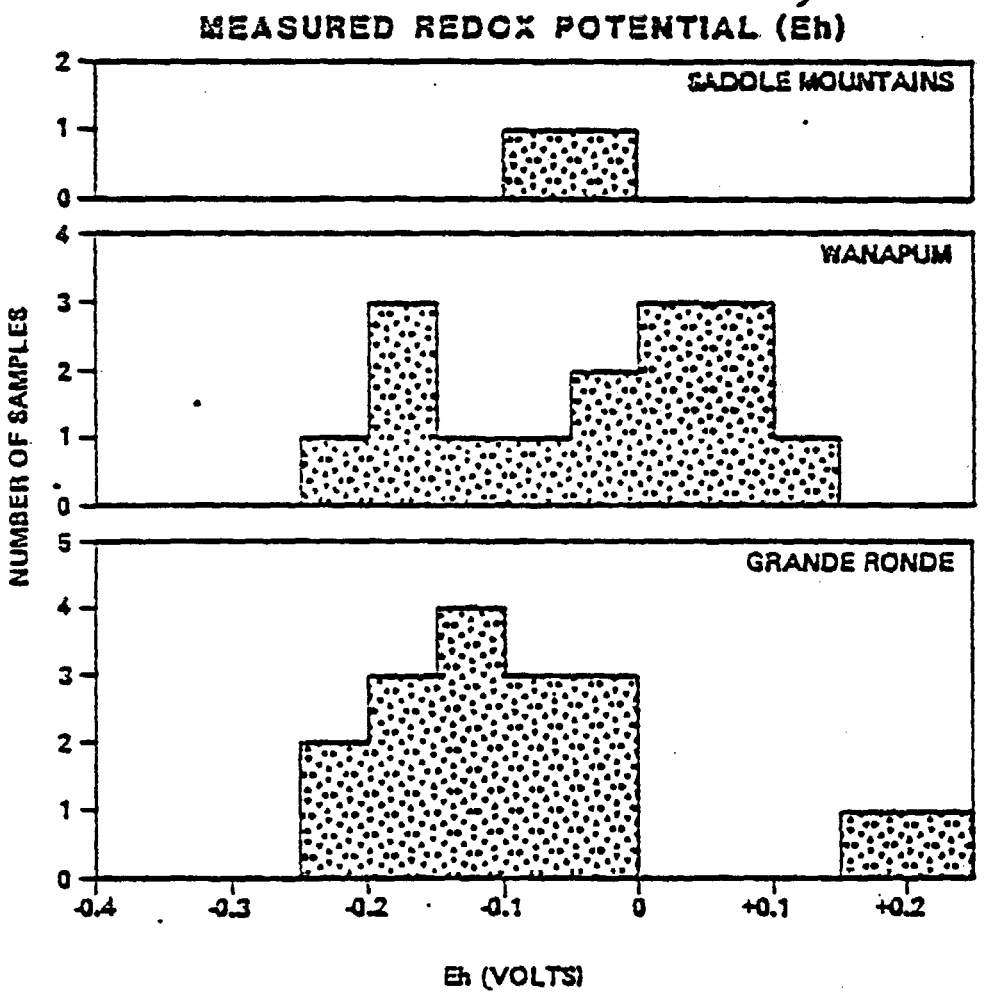

SULFATE
SADDLE MOUNTAINS
WANAPUM
GRANDE RONDE
GR-4
GR-3
from eastern wells
NUMBER OF SAMPLES
CONCENTRATION (mg/L)
0
10
20
30
40
50
100
150
200


FIELD pH
SADDLE MOUNTAINS
WANAPUM
GRANDE RONDE
GR-4
GR-3
NUMBER OF SAMPLES
0
5
10
20
7
8
9
10
pH


BICARBONATE
SADDLE MOUNTAINS
WANAPUM
GRANDE RONDE
GR-3
GR-4
NUMBER OF SAMPLES
CONCENTRATION (mg/L)
0
5
10
15
100
200
300

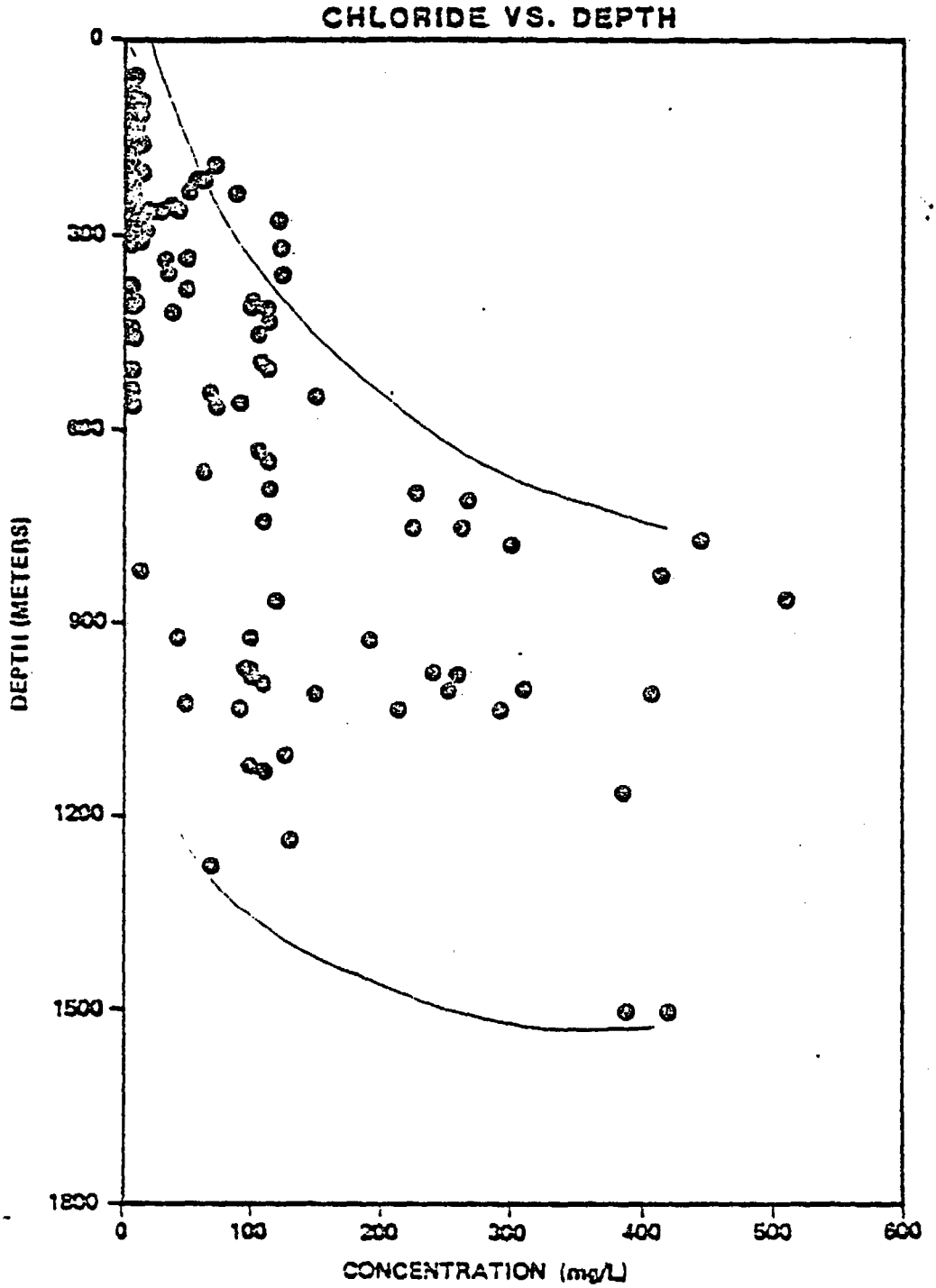

SILICON (Si)
SADDLE MOUNTAINS
WANAPUM
GRANDE RONDE
GR-3
GR-4
NUMBER OF SAMPLES
CONCENTRATION (mg/L)
0
10
20
30
40
50
60
70
80
90

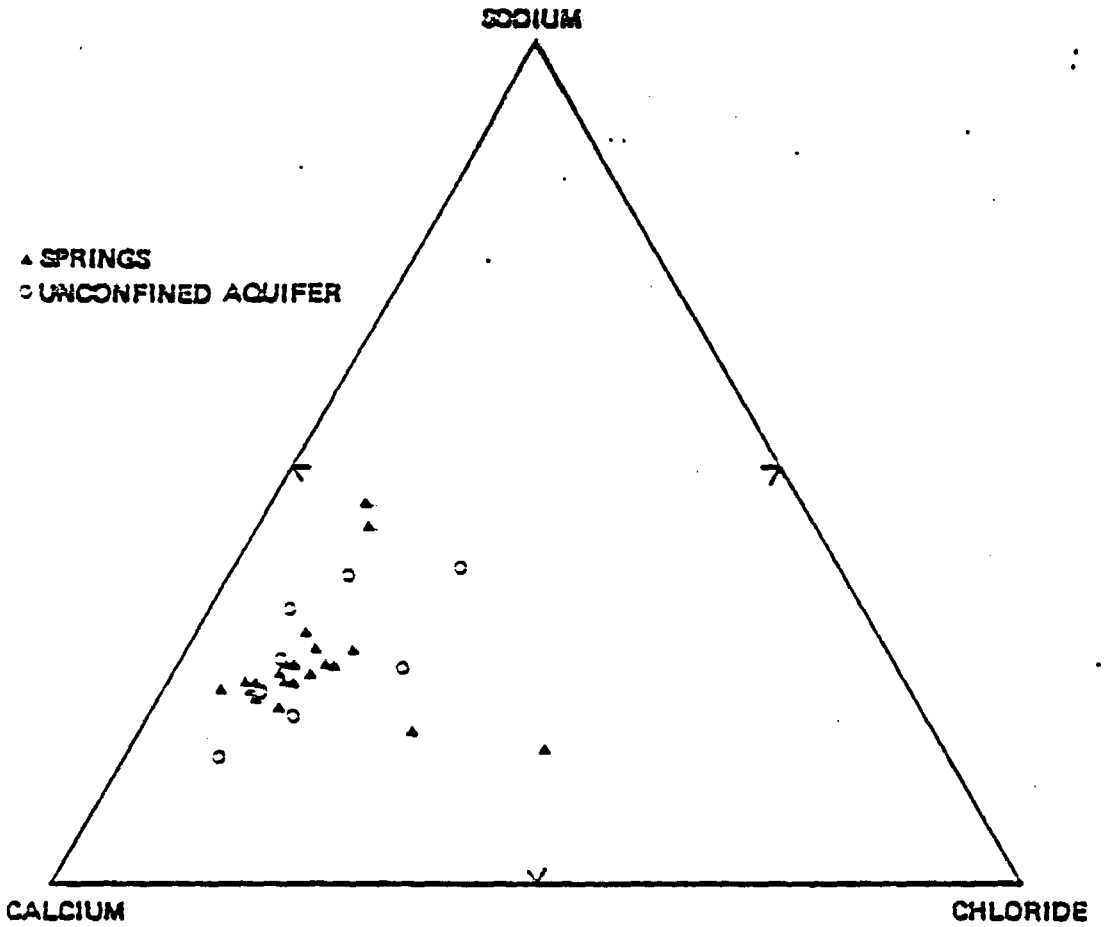
ref. to H^+

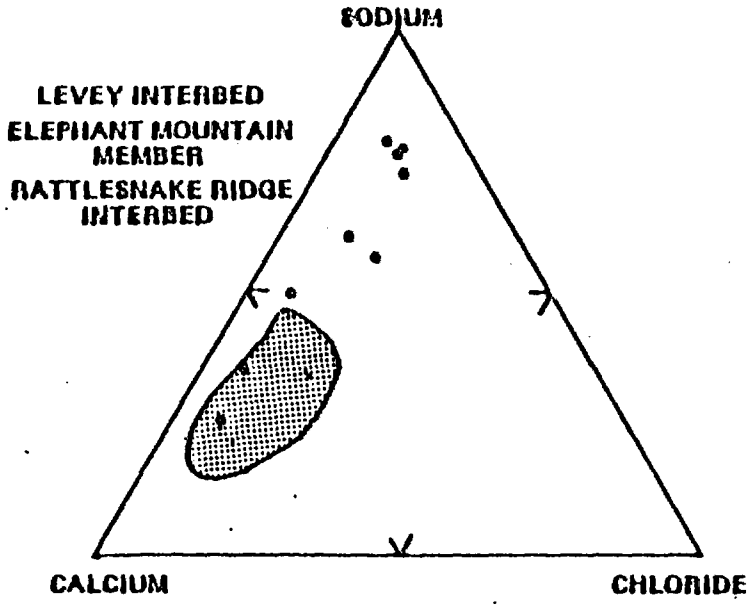

MEASURED REDOX POTENTIAL (Eh)
SADDLE MOUNTAINS
WANAPUM
GRANDE RONDE
NUMBER OF SAMPLES
0
1
2
3
4
5
-0.4
-0.3
-0.2
-0.1
0
+0.1
+0.2
Eh (VOLTS)

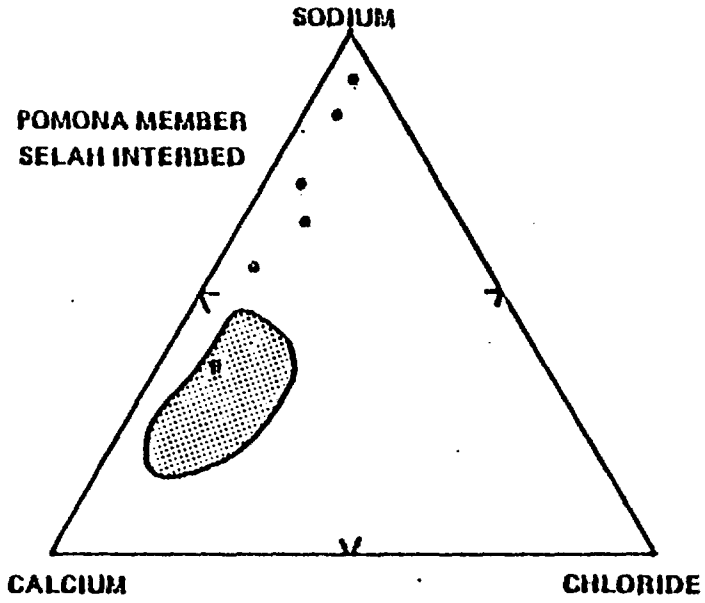
FUTURE PLANS - SITE HYDROCHEMICAL CHARACTERIZATION

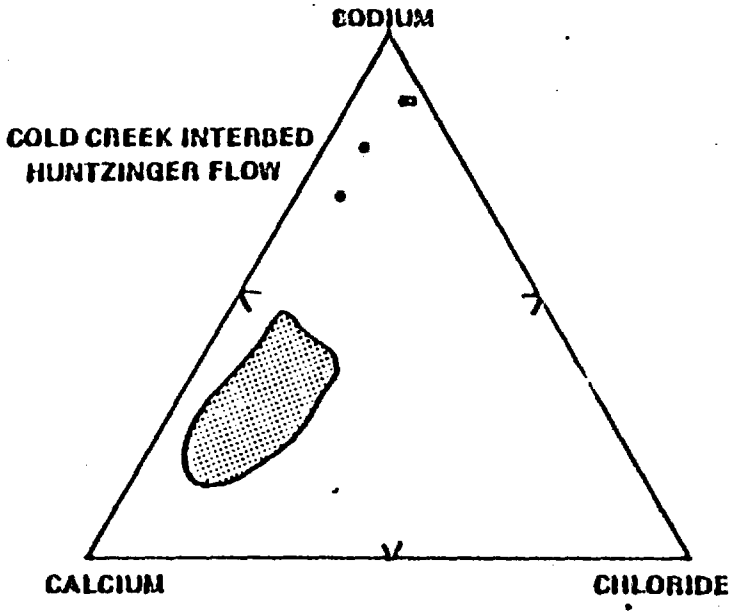
- CONTINUE ANALYSES OF GROUNDWATER FROM EVERY TESTED HORIZON IN NEW BOREHOLES.
- RESAMPLE SEVERAL HORIZONS IN SELECTED BOREHOLES TO PROVIDE INCREASED RELIABILITY OF ANALYSES.
- CONSIDER DRILLING ADDITIONAL BOREHOLES IN AREAS WITH SPARSE DATA !
- COLLECT AVAILABLE REGIONAL HYDROCHEMICAL DATA (eg. USGS).

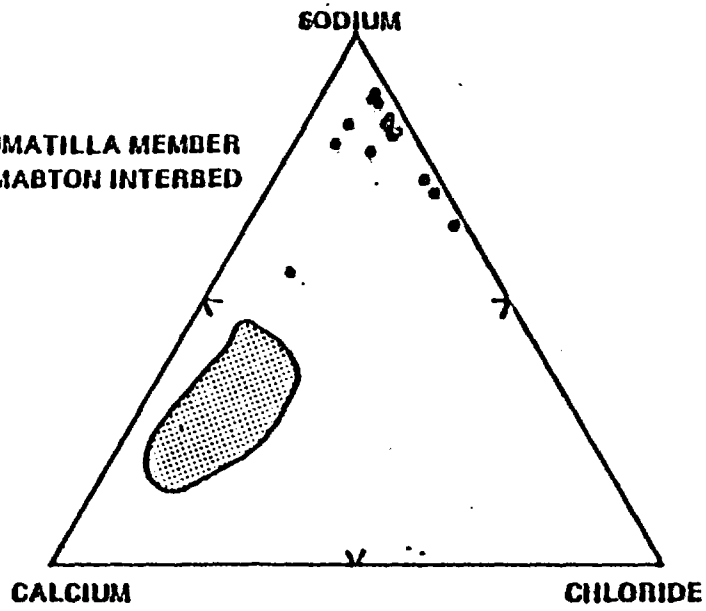

CHLORIDE VS. DEPTH
DEPTH (METERS)
0
300
600
900
1200
1500
1800
0
100
200
300
400
500
600
CONCENTRATION (mg/L)

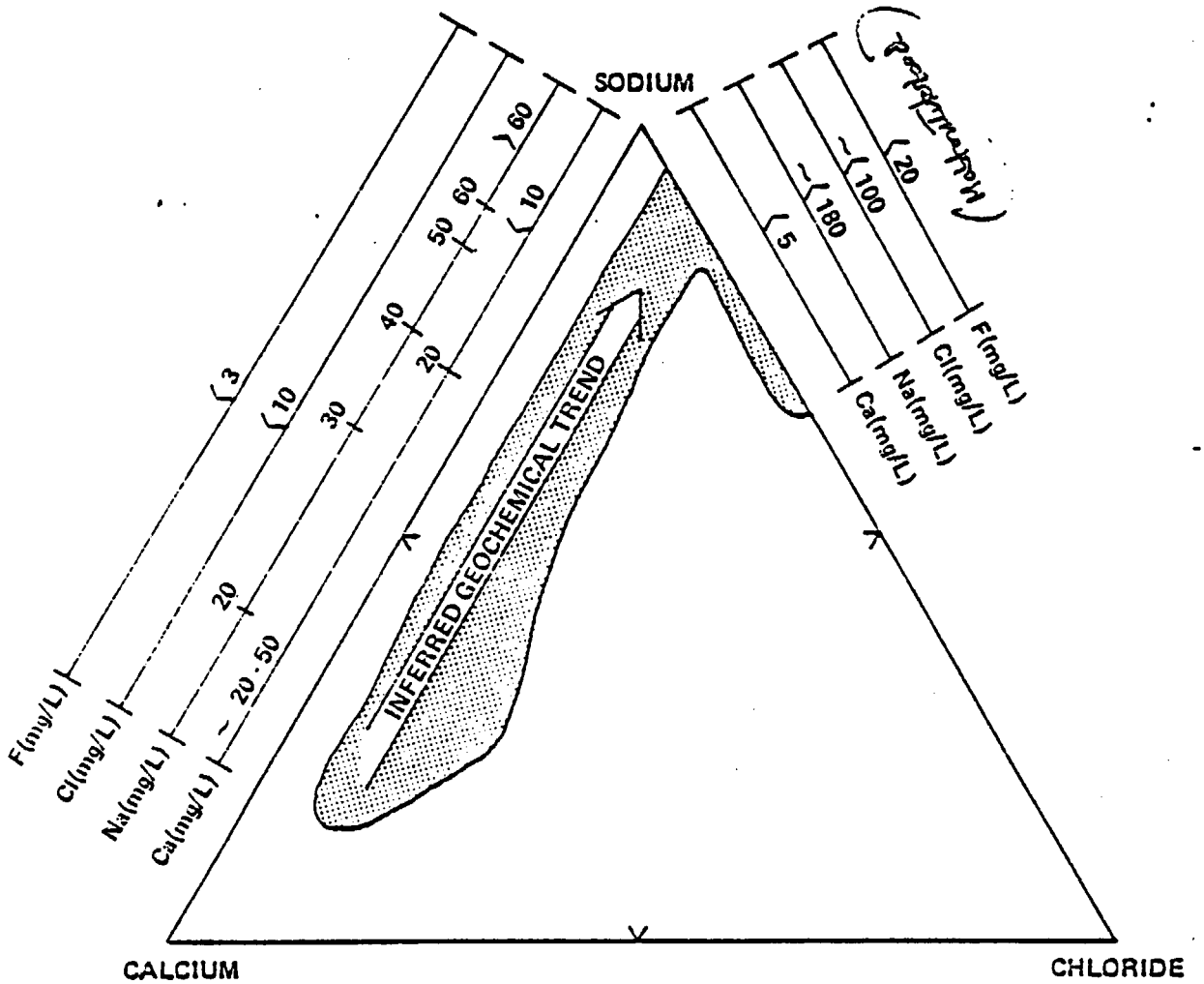

SODIUM
▲ SPRINGS
○ UNCONFINED AQUIFER
CALCIUM
CHLORIDE


SODIUM
LEVEY INTERBED
ELEPHANT MOUNTAIN MEMBER
RATTLESNAKE RIDGE INTERBED
CALCIUM
CHLORIDE

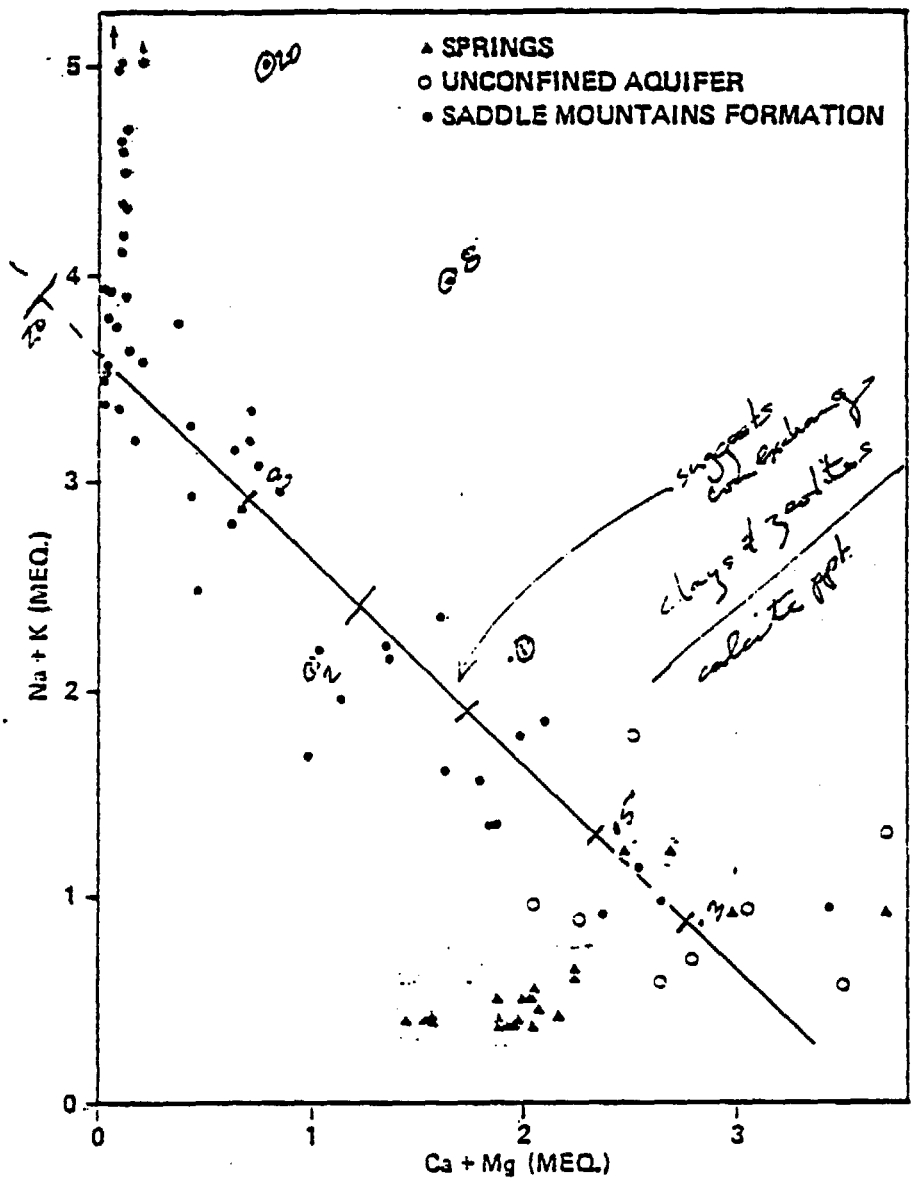

SODIUM
POMONA MEMBER
SELAH INTERBED
CALCIUM
CHLORIDE

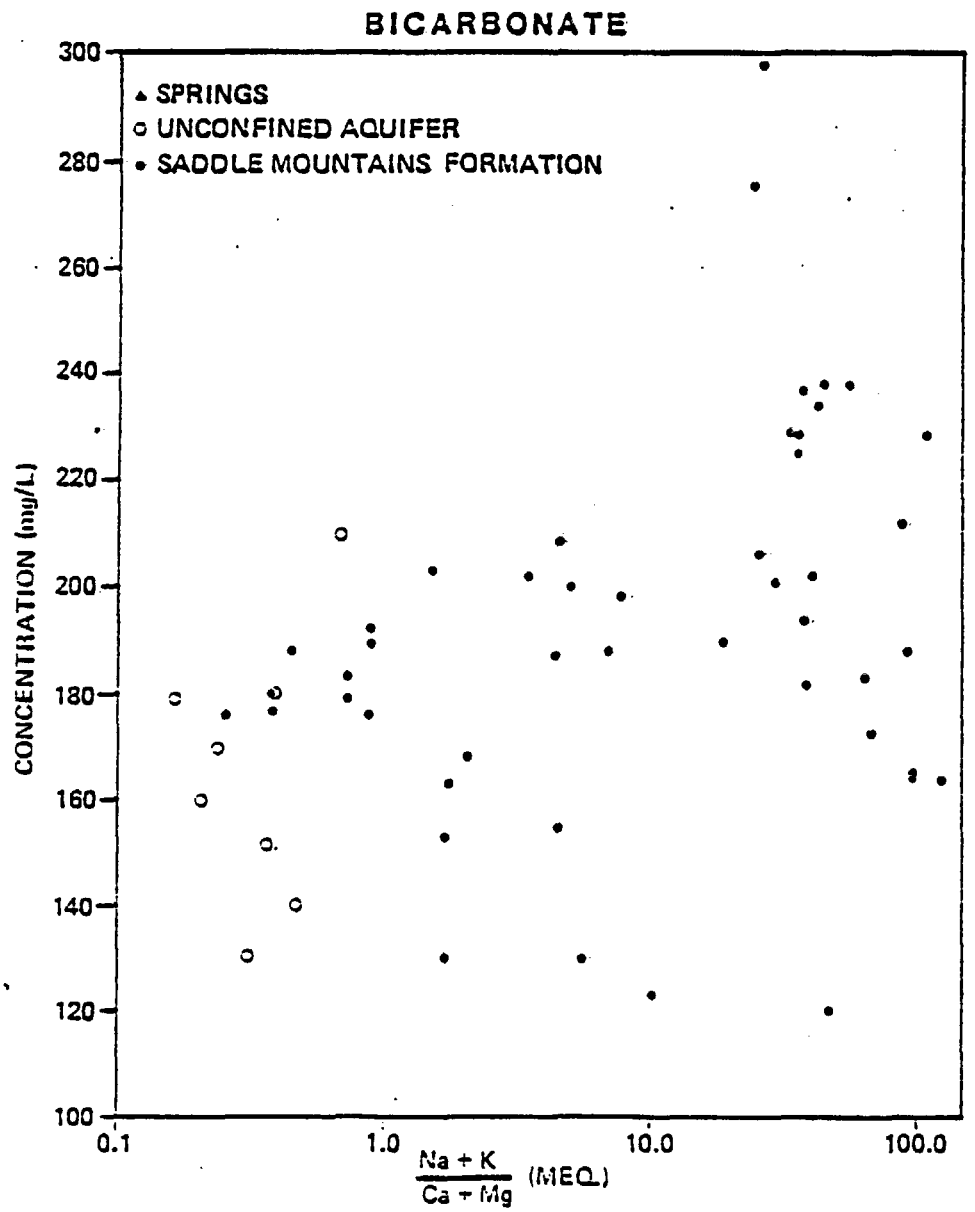

SODIUM
COLD CREEK INTERBED
HUNTZINGER FLOW
CALCIUM
CHLORIDE


SODIUM
UMATILLA MEMBER
MABTON INTERBED
CALCIUM
CHLORIDE



SADDLE MOUNTAINS FORMATION GROUNDWATERS


▲ SPRINGS
○ UNCONFINED AQUIFER
• SADDLE MOUNTAINS FORMATION
Na + K (MEQ.)
Ca + Mg (MEQ.)
0
1
2
3
4
5
suggests cation exchange
clays & zeolites
calcite ppt.

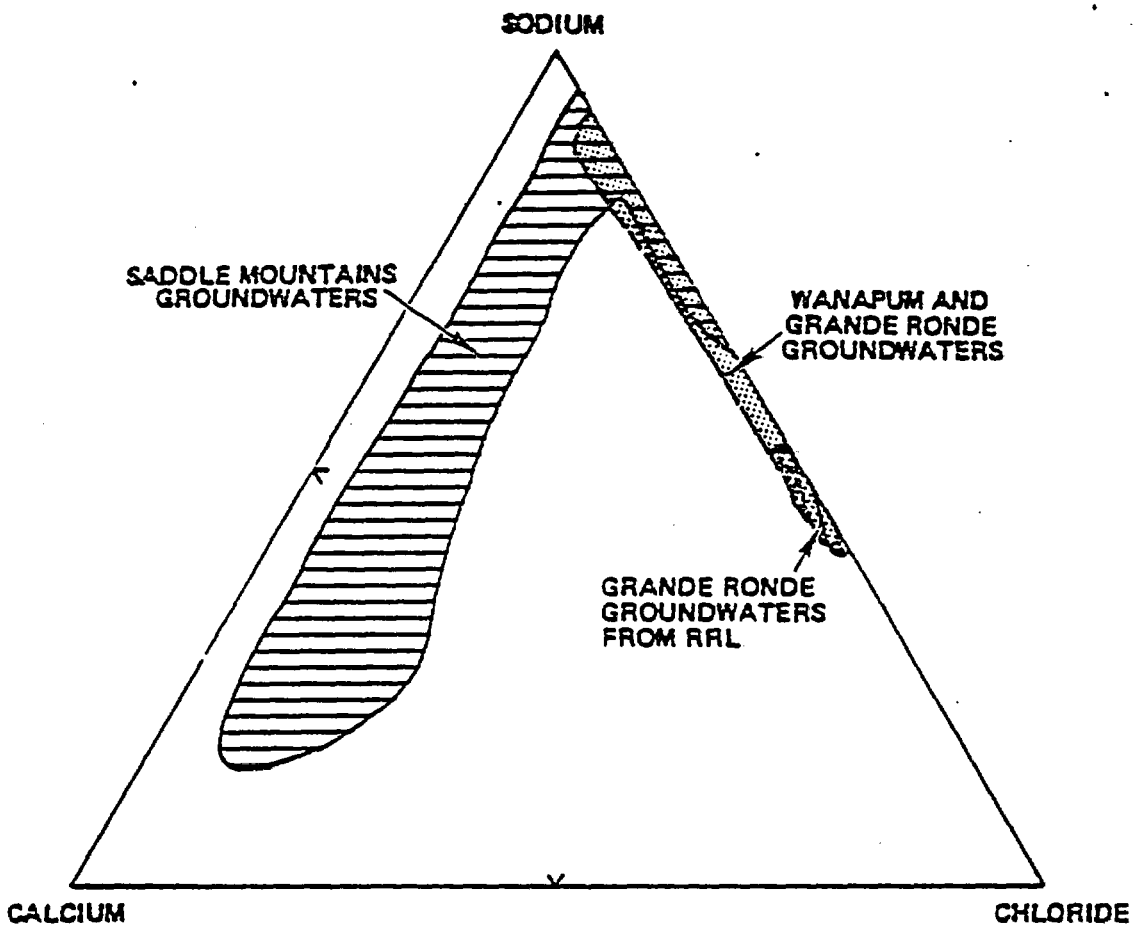

BICARBONATE
▲ SPRINGS
o UNCONFINED AQUIFER
• SADDLE MOUNTAINS FORMATION
CONCENTRATION (mg/L)
300
280
260
240
220
200
180
160
140
120
100
0.1
1.0
10.0
100.0
Na + K / Ca + Mg (MEQ.)

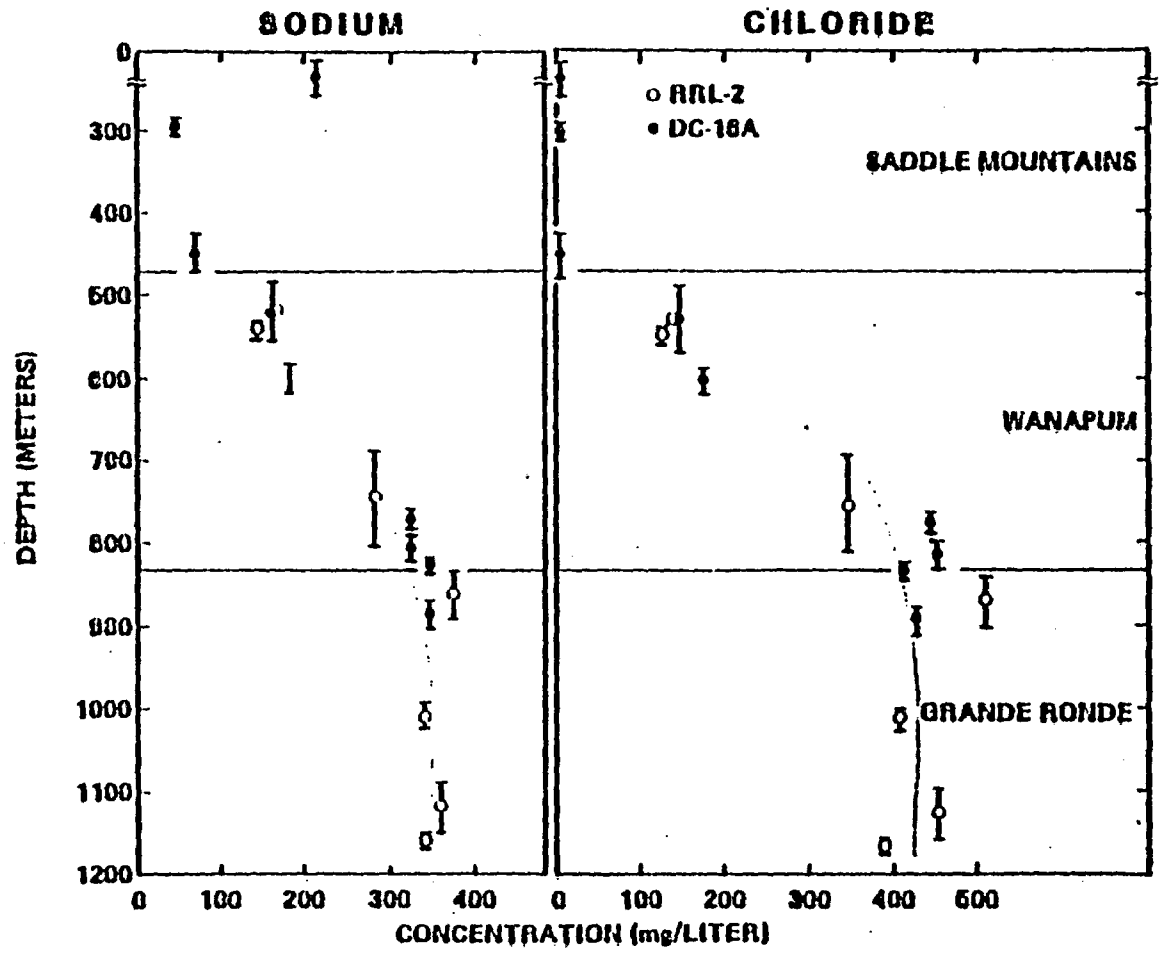
SUMMARY - ROCK/WATER INTERACTION

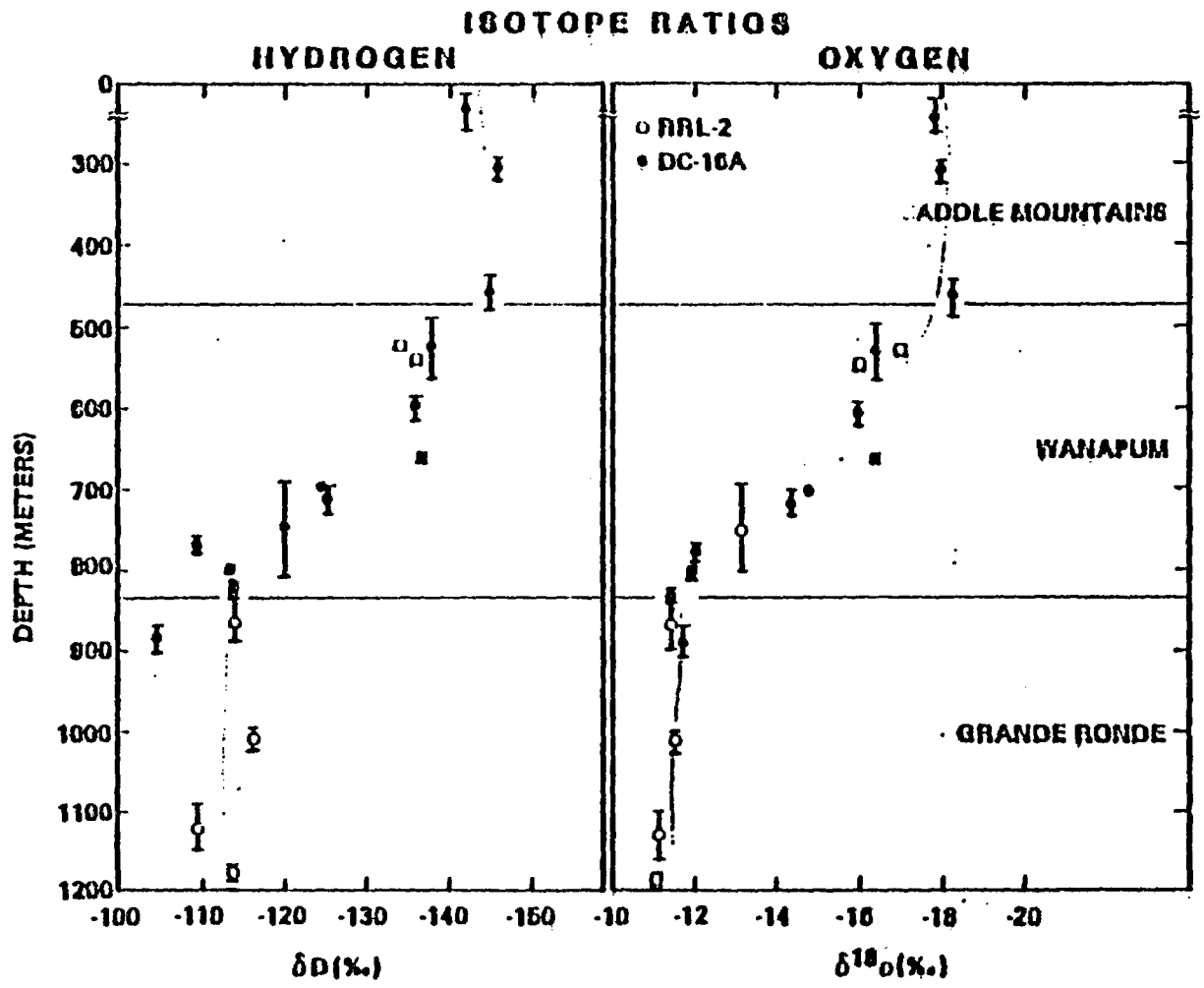
- A GEOCHEMICAL TREND HAS BEEN IDENTIFIED FOR SHALLOW GROUNDWATERS

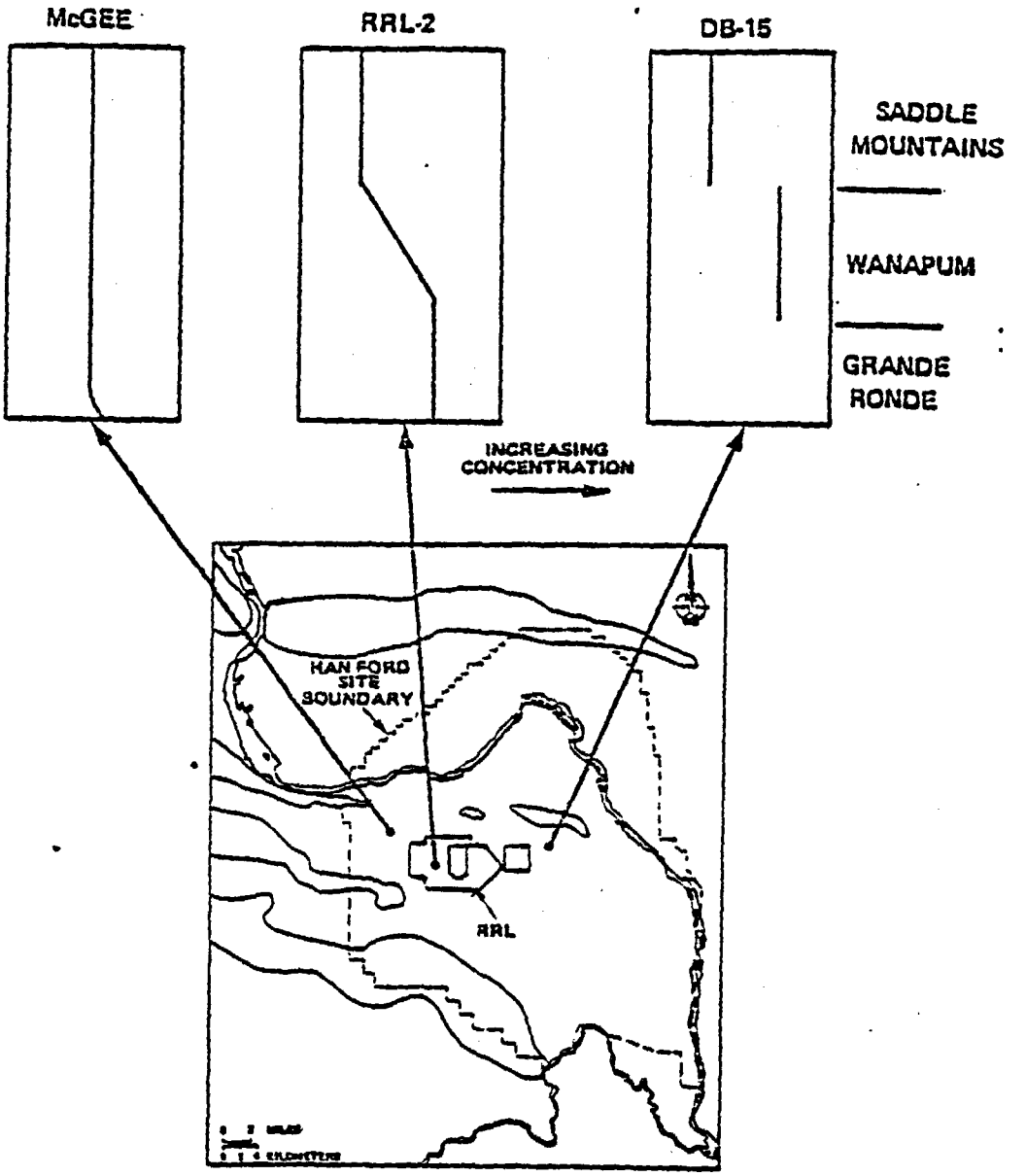
- MAJOR REACTIONS SEEM TO INCLUDE:
  - GLASS DISSOLUTION
  - ION EXCHANGE BETWEEN GROUNDWATER AND PHASES SUCH AS CLAYS AND/OR ZEOLITES

- IT IS UNCLEAR IF HIGH CHLORIDE GROUNDWATERS RESULT FROM ROCK/WATER INTERACTION


SODIUM
SADDLE MOUNTAINS GROUNDWATERS
WANAPUM AND GRANDE RONDE GROUNDWATERS
GRANDE RONDE GROUNDWATERS FROM RRL
CALCIUM
CHLORIDE

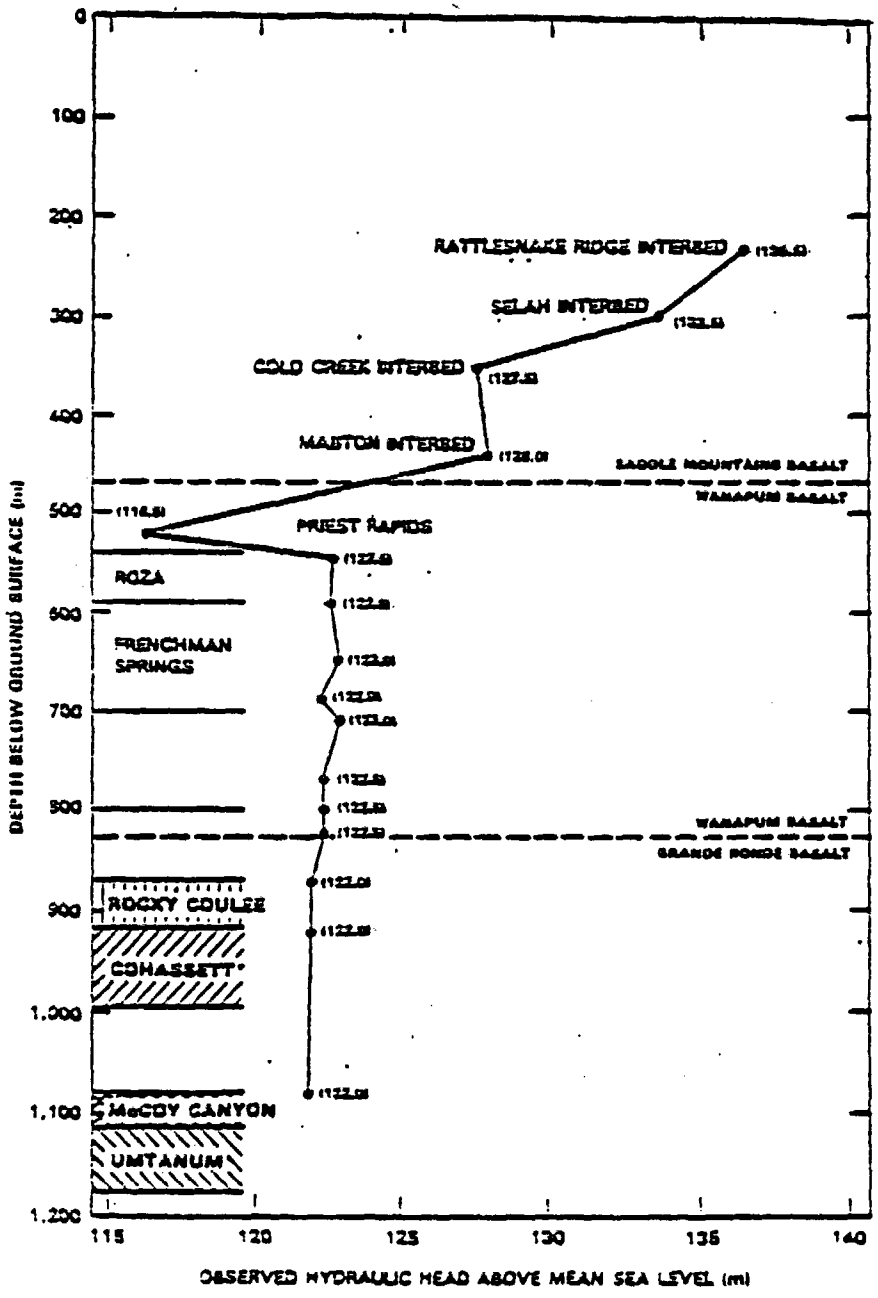

SODIUM
CHLORIDE
o RRL-2
• DC-18A
SADDLE MOUNTAINS
WANAPUM
GRANDE RONDE
DEPTH (METERS)
0
300
400
500
600
700
800
900
1000
1100
1200
0
100
200
300
400
0
100
200
300
400
500
CONCENTRATION (mg/LITER)


ISOTOPE RATIOS
HYDROGEN
OXYGEN
DEPTH (METERS)
0
300
400
500
600
700
800
900
1000
1100
1200
-100
-110
-120
-130
-140
-150
δD(‰)
-10
-12
-14
-16
-18
-20
δ18O(‰)
RRL-2
DC-16A
ADDLE MOUNTAINS
WANAPUM
GRANDE RONDE

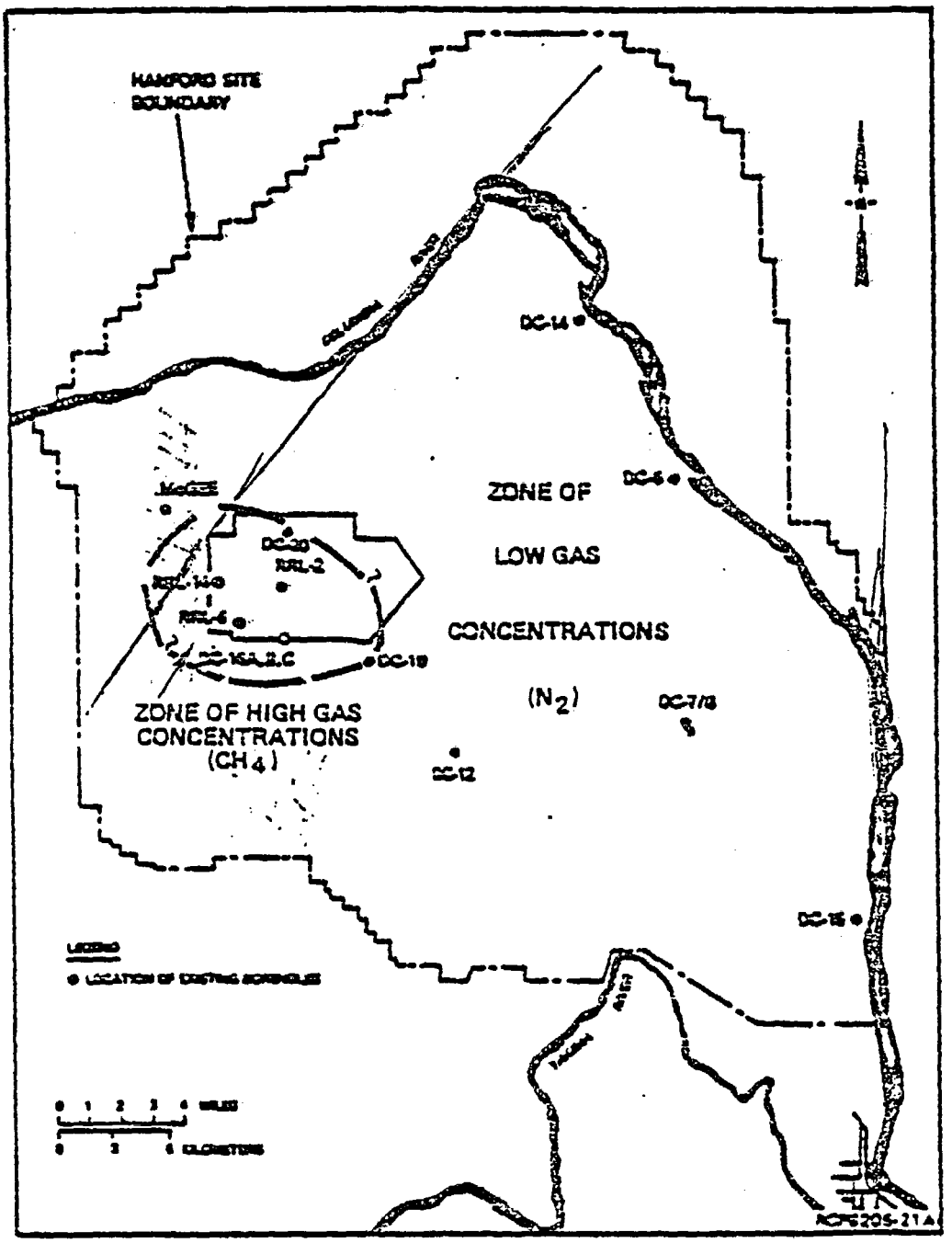


VERTICAL PROFILES OF CHLORIDE FROM THREE BOREHOLES AT HANFORD

HYDRAULIC HEADS DC-16A



DISSOLVED GASES IN THE GRANDE RONDE FORMATION

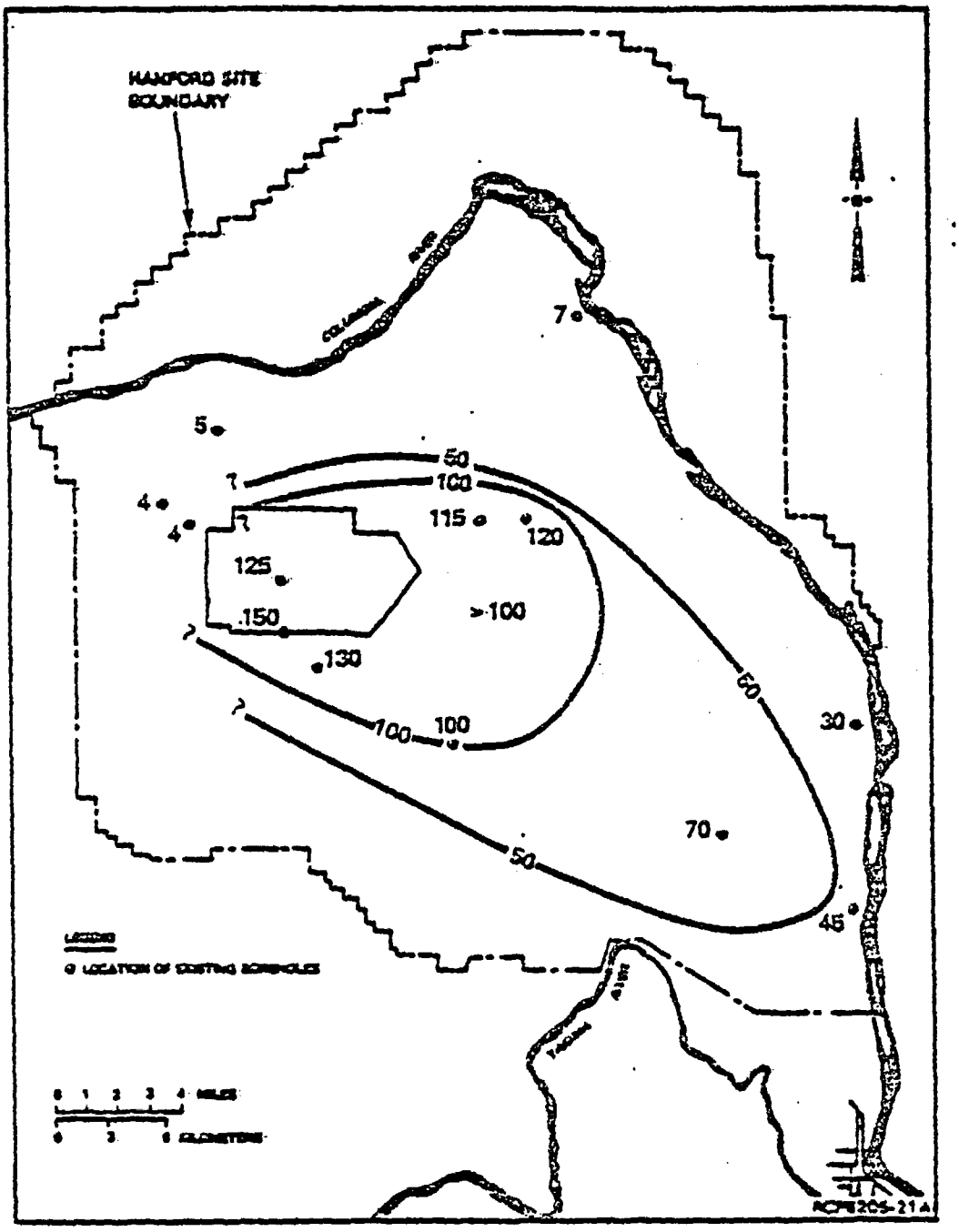


SIGNIFICANT

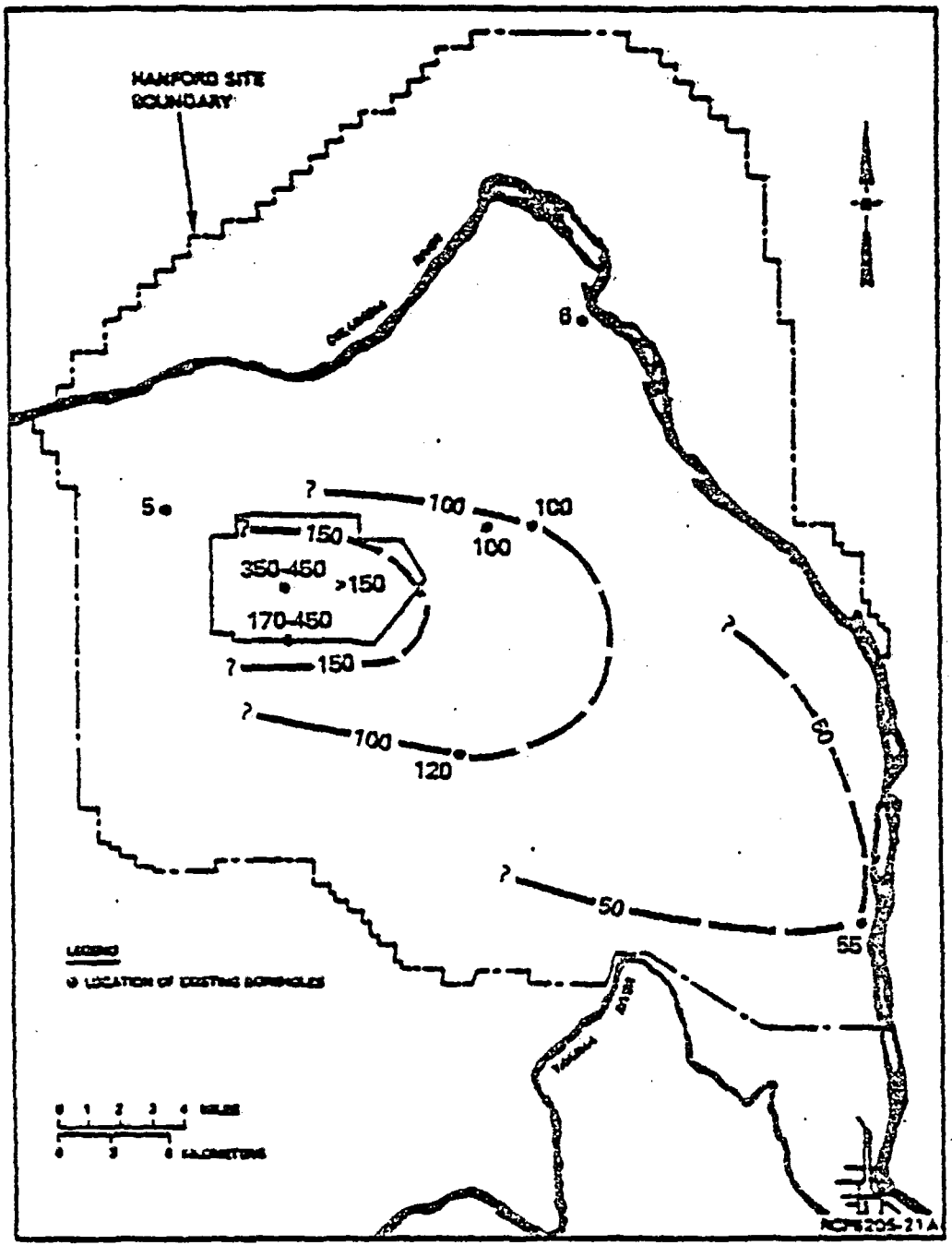
FACTS ABOUT GASES IN THE RRL

- HIGHER CONCENTRATIONS WITHIN THE WANAPUM AND GRANDE RONDE FORMATIONS THAN ELSEWHERE AT HANFORD
- METHANE DOMINATED WITHIN THE WANAPUM AND GRANDE RONDE FORMATIONS
- NITROGEN DOMINATED WITHIN THE SADDLE MOUNTAINS FORMATION (LOW CONCENTRATION)
- TEMPORARY GAS BUBBLING OBSERVED FROM SEVERAL FRENCHMAN SPRINGS FLOW TOPS IN DC-19 FOLLOWING DRILLING
- SIMILAR GAS BUBBLING OBSERVED IN ONE FRENCHMAN SPRINGS ZONE IN DC-20 (DURATION UNKNOWN)
- MEASURED GAS CONCENTRATIONS IN GRANDE RONDE FORMATION OF DC-19 SIGNIFICANTLY LOWER THAN IN RRL-2 AND DC-16

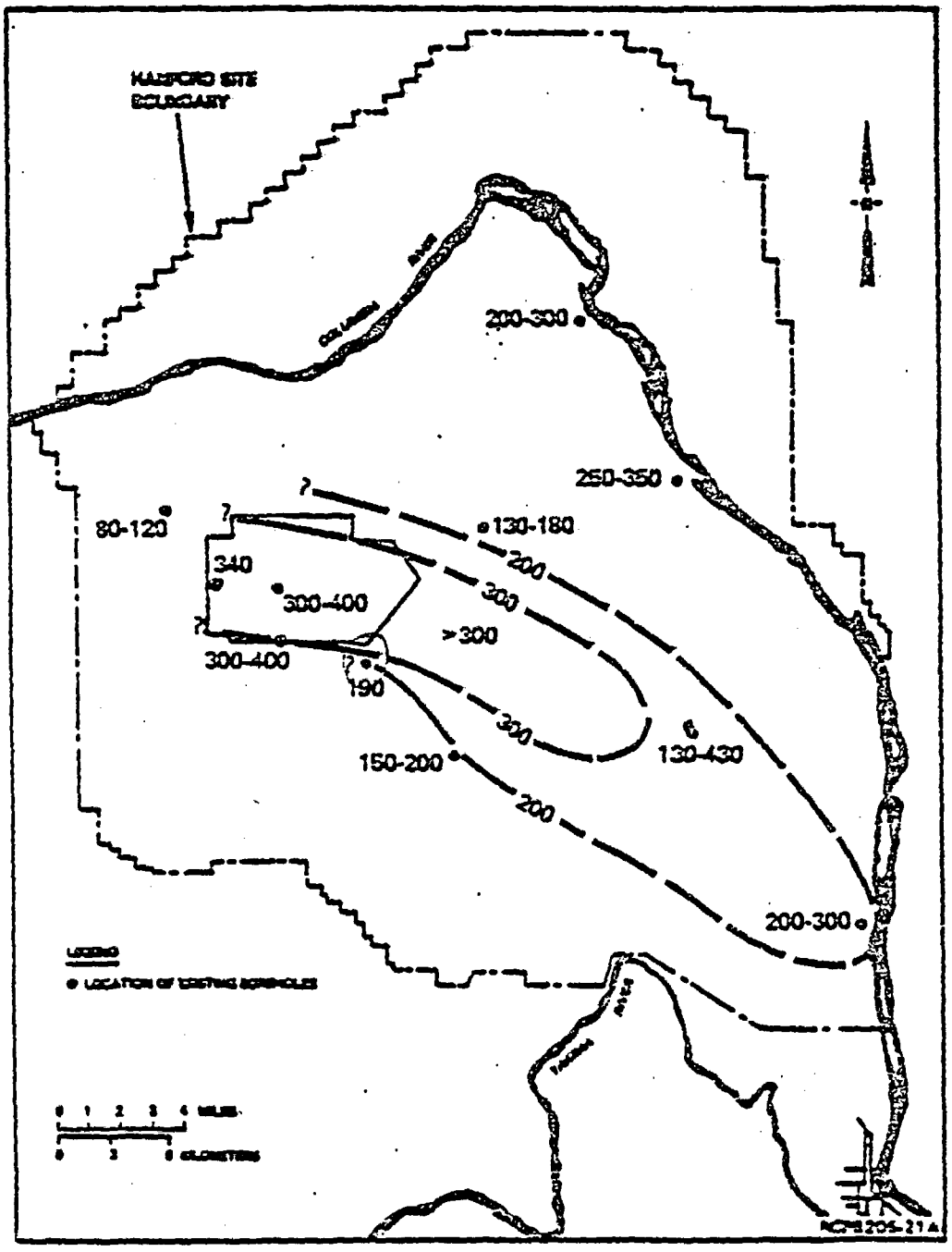
CHLORIDE CONTOURS (Mg/L) - U. WANAPUM GROUNDWATERS



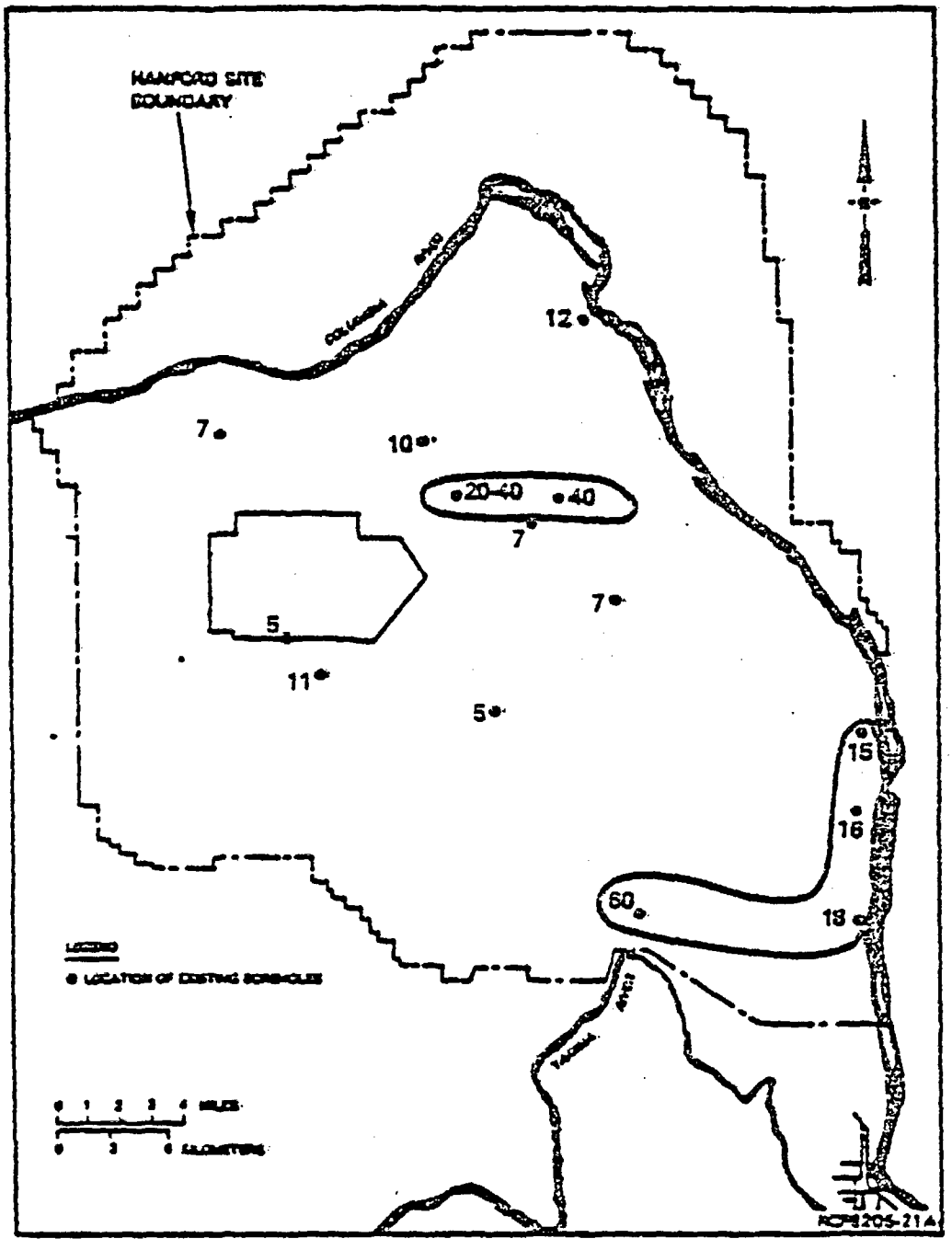
CHLORIDE CONTOURS (Mg/L) - L. WANAPUM GROUNDWATERS

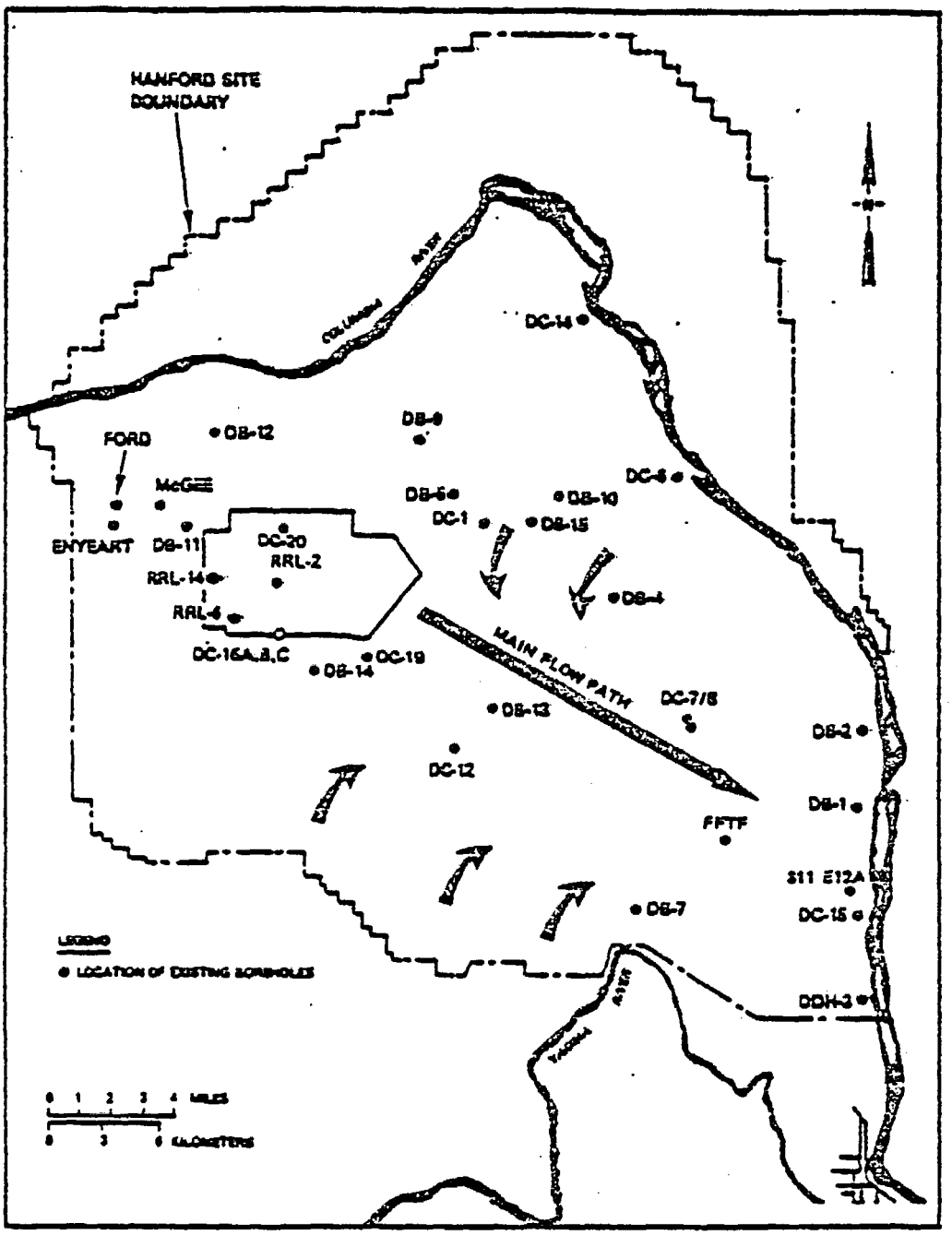


SODIUM CONTOURS (Mg/L) - U. GRANDE RONDE



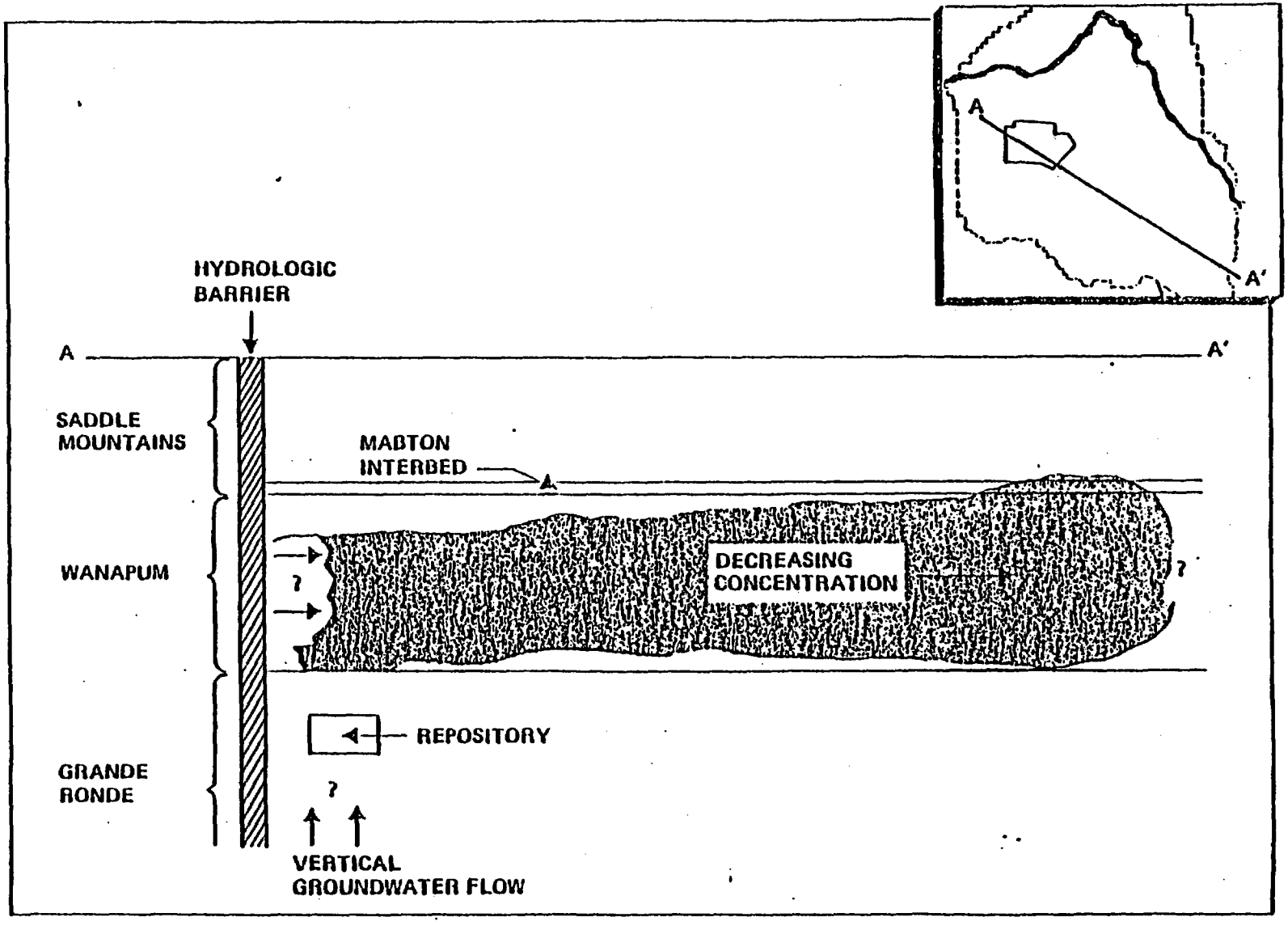
CHLORIDE CONCENTRATIONS (Mg/L) - MABTON INTERBED





TENTATIVE FLOW MODEL BASED ON HYDROCHEMISTRY

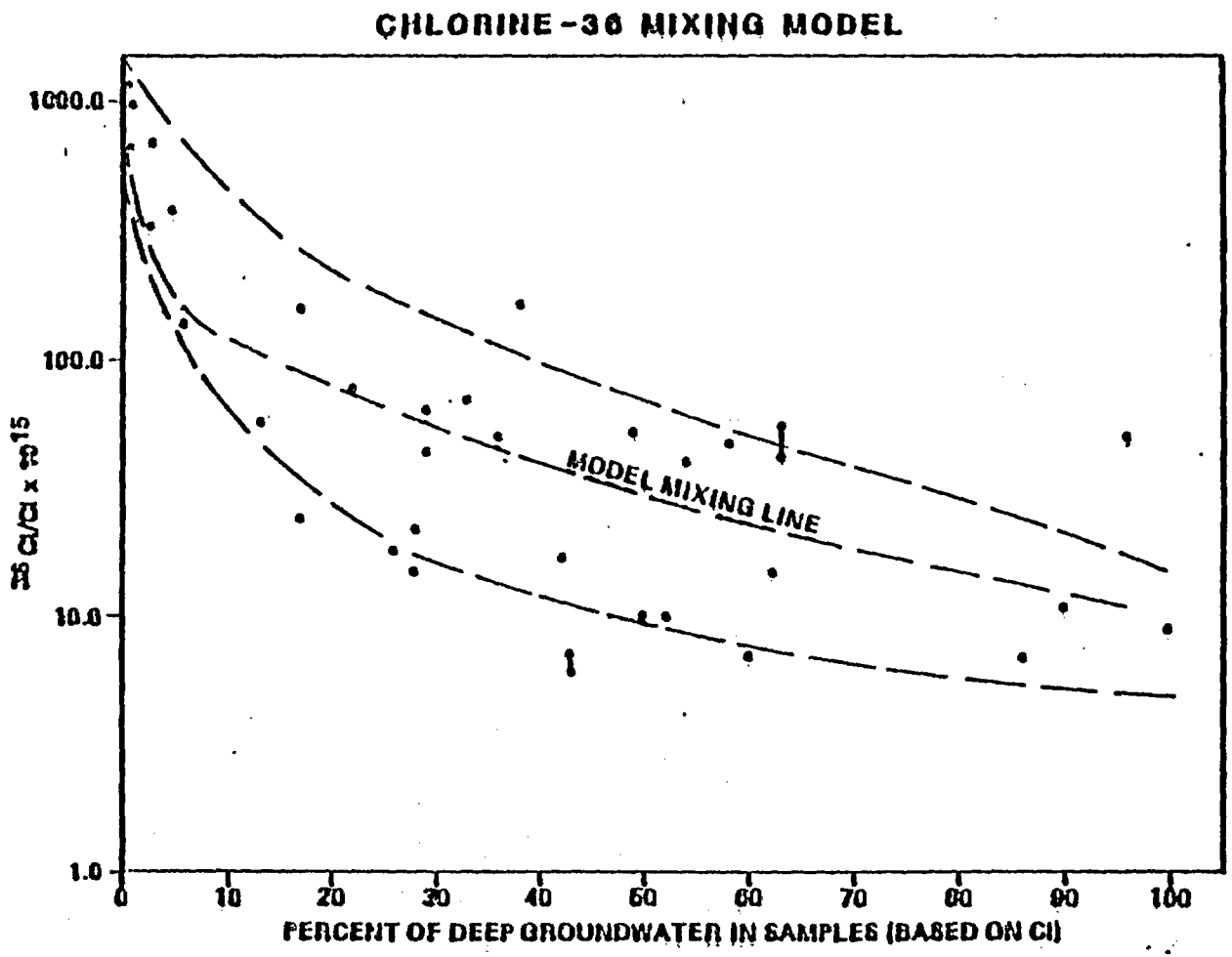
SCHEMATIC CROSS SECTION AA'
SHOWING LOCATION OF HYPOTHESIZED MIXING PLUME



SIGNIFICANT UNCERTAINTIES OF HYPOTHESIZED CONCEPTUAL FLOW MODEL

- POSSIBLE LOCATIONS OF VERTICAL MOVEMENT OF GROUNDWATER
  - HYDROLOGIC BARRIER?
  - WITHIN THE RRL ZONE?
  - ACROSS THE HANFORD SITE BUT ENHANCED IN THE RRL DUE TO HIGH VERTICAL PERMEABILITY?
  - ALONG MAJOR STRUCTURAL FEATURES?

- POSSIBLE MECHANISMS OF VERTICAL MOVEMENT OF GROUNDWATER
  - DIFFUSION?
  - RESPONSE TO VERTICAL HEAD GRADIENTS?


CHLORINE-36 MIXING MODEL
1000.0
100.0
10.0
1.0
36Cl/Cl x 10^15
MODEL MIXING LINE
0
10
20
30
40
50
60
70
80
90
100
PERCENT OF DEEP GROUNDWATER IN SAMPLES (BASED ON Cl)

SUMMARY - CONCEPTUAL FLOW MODEL INTERPRETATIONS

- MIXING OF GROUNDWATERS IS OBSERVED IN RRL BOREHOLES
- APPARENT UPWARD MOVEMENT OF DEEP GROUNDWATERS IS OCCURRING
- NO INFORMATION REGARDING THE RATE OF MIXING IS AVAILABLE
- THE HYDROLOGIC BARRIER MAY BE RELATED TO THE MIXING PROCESS IN THE RRL
- OTHER STRUCTURES SUCH AS THE GABLE MOUNTAIN - GABLE BUTTE AND RATTLESNAKE HILLS ANTICLINES MAY ALSO PERMIT VERTICAL GROUNDWATER FLOW
- GROUNDWATER FLOW WITHIN THE WANAPUM BASALTS APPEARS TO BE TO THE SOUTHEAST

FUTURE PLANS- CONCEPTUAL FLOW MODEL

- ATTEMPT TO CONFIRM MIXING AND REFINE MIXING ZONE
  - RESAMPLE SELECTED BOREHOLES
  - CONSIDER DRILLING ADDITIONAL BOREHOLES
  - INTEGRATE HYDROCHEMISTRY WITH RESULTS OF THE PIEZOMETRIC NETWORK AND HYDROLOGIC MODELS
- EVALUATE THE POTENTIAL SIGNIFICANCE OF METHANE IN THE RRL
  - IMPROVE SAMPLING AND ANALYSES OF GASES
  - EXPAND THE NETWORK OF GAS SAMPLE SITES
  - CONSIDER THE ADVISABILITY OF A DEEP BOREHOLE
- EVALUATE THE ROLE OF THE HYDROLOGIC BARRIER IN GROUNDWATER MIXING

Basalt Crystallization
Interactions

EXPERIMENTAL CONDITIONS
BASALT/WATER TESTS

- STARTING MATERIALS:
  - BASALT (UMTANUM AND COHASSETT FLOW ENTABLATURE)
  - SYNTHETIC GROUNDWATER
- MESH FRACTIONS: -120+230, -16+60
- T = 100° C, 150 °C, 200° C, 300° C
- P = 30 MEGAPASCALS (300 BARS)
- WATER/ROCK MASS RATIO = 2-50
- TEST DURATIONS = 26-318 DAYS

WP-8312-79

SYNTHETIC GRANDE RONDE GROUNDWATER COMPOSITION

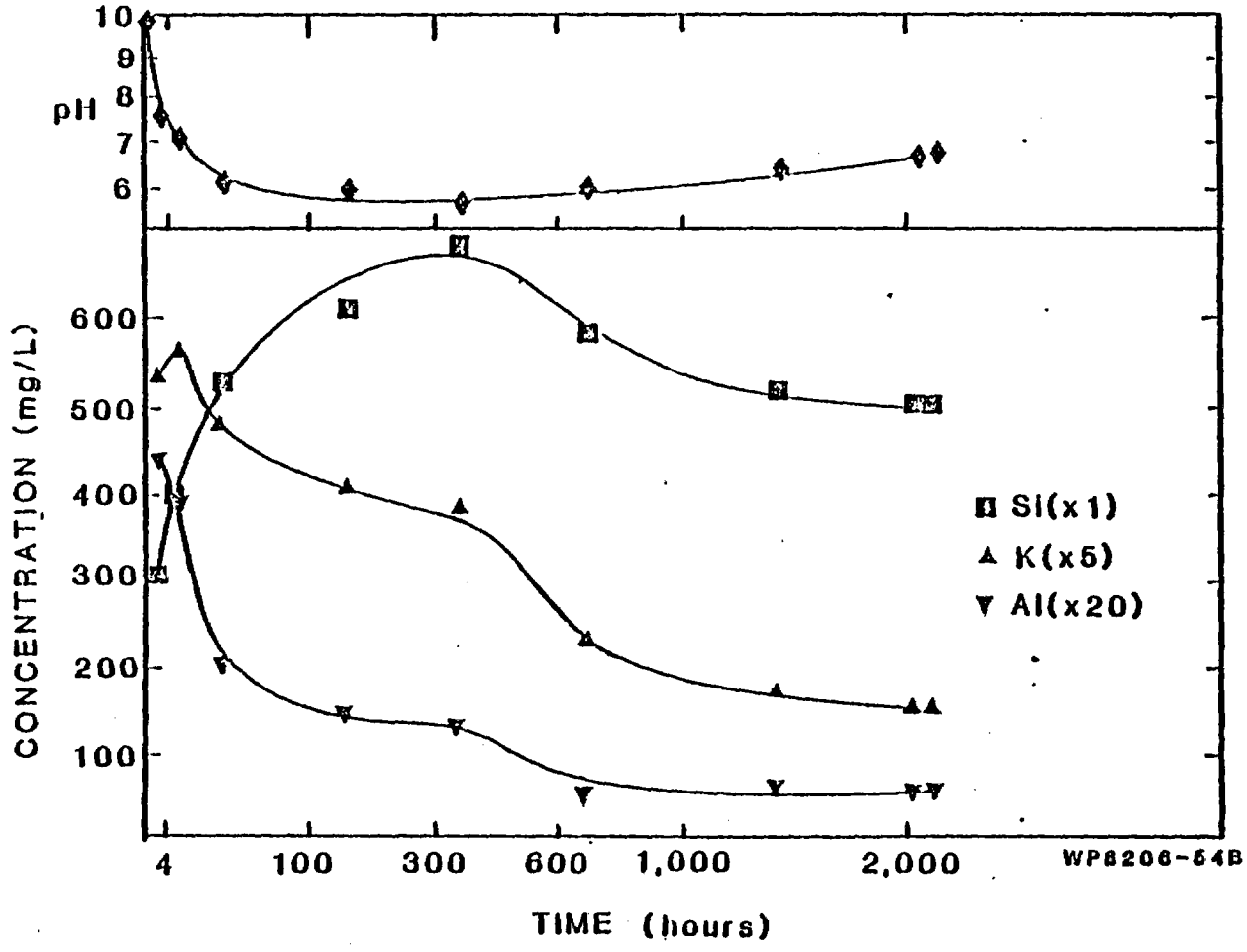
GR-3

COMPONENT	CONCENTRATION (mg/L)	COMPONENT	CONCENTRATION (mg/L)
Si	32	Fe	<0.01
Na	340	F^-	33
Al	<0.08	Cl^-	280
K	3.8	SO_4^{2-}	170
Ca	2.8	$(CO_3)_T$	70
Mg	0.3	pH(R.T.)	9.7

WP-8312-88

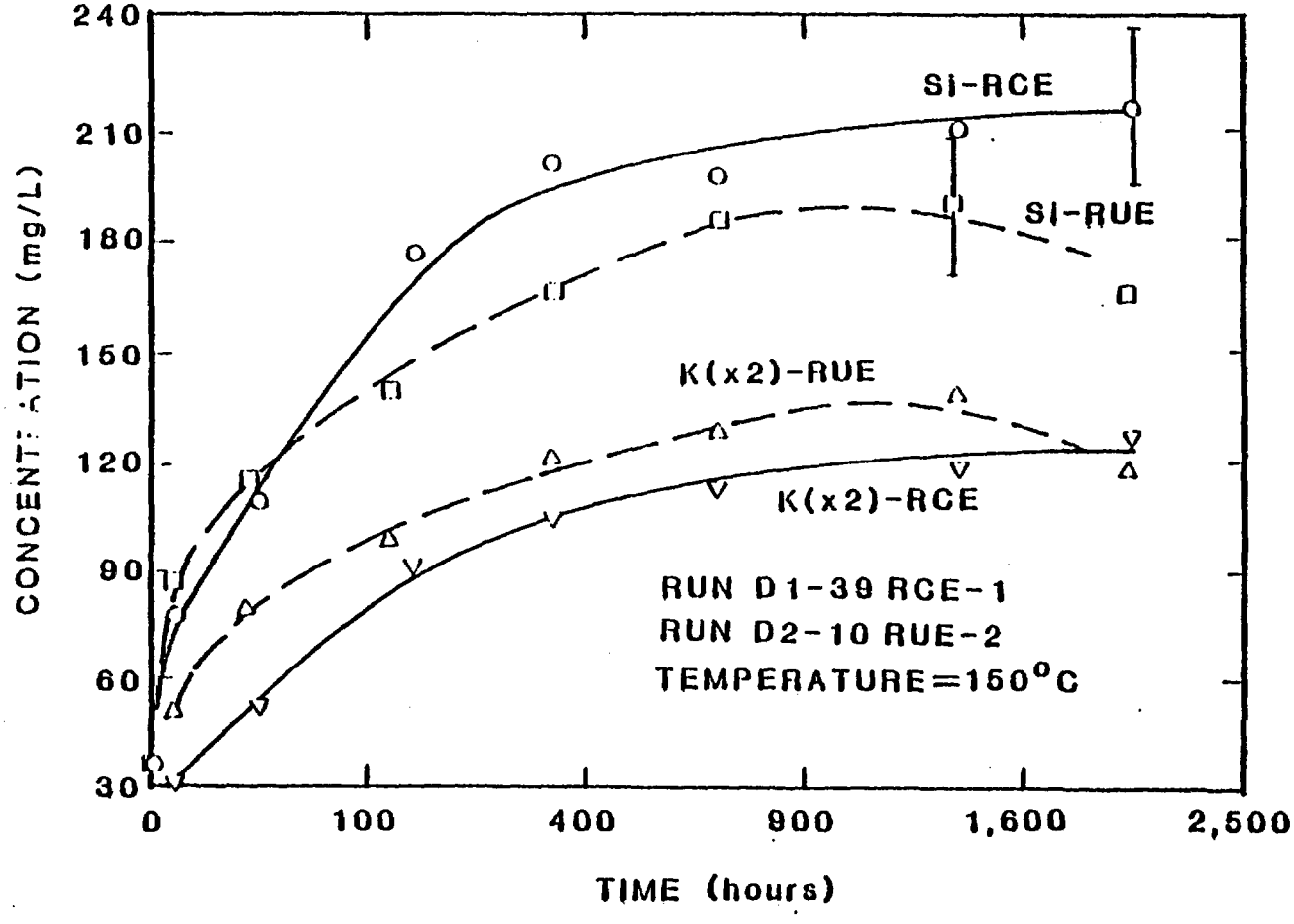
SOLUTION CATIONS AND pH vs TIME

BASALT-SYNTHETIC GROUNDWATER, 300°C



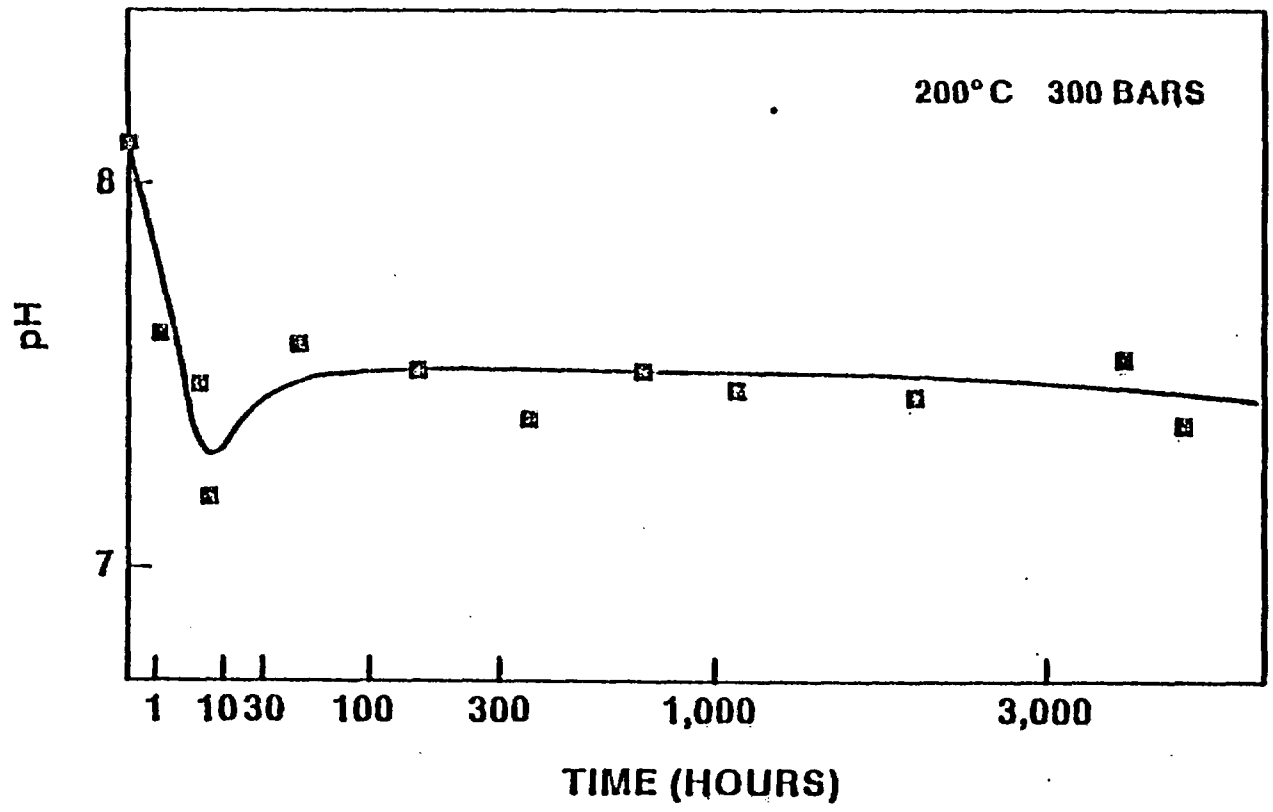
K-rich zeolite

COMPARISON OF SOLUTION COMPOSITION DATA IN TESTS WITH UMTANUM AND COHASSETT BASALT, 150°C



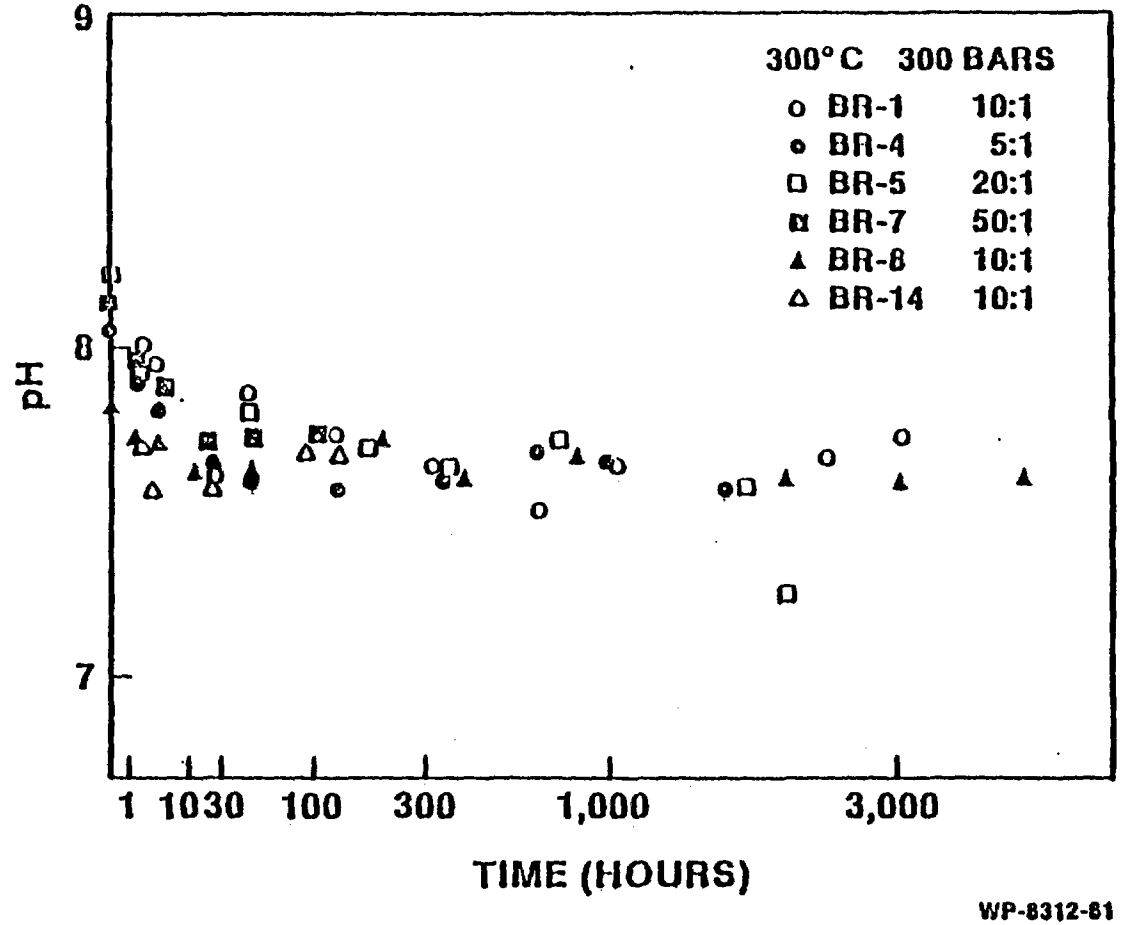
WP8608-39B

CALCULATED HIGH-TEMPERATURE pH BASALT/WATER TESTS



WP-8312-82

CALCULATED HIGH-TEMPERATURE pH BASALT/WATER TESTS



water/rock ratio

WP-8312-61

RESULTS OF SOLUTION ANALYSIS
BASALT/WATER TESTS

(pH—ANIONS)

- STEADY-STATE pH (25° C MEASUREMENTS)
  - 300° C TESTS, pH=6.5-7.0
  - 100° C-150° C TESTS, pH=8.0-8.5
- F^-, Cl^-, SO_4^{2-}, TOTAL INORGANIC CARBON
  - STEADY-STATE CONCENTRATIONS ≤ INITIAL VALUES

WP8401-53

RESULTS OF SOLID REACTION PRODUCT CHARACTERIZATION

BASALT/WATER SYSTEM

- OBSERVED ALTERATION ASSEMBLAGES AT 300° C
  - IRON SMECTITE
  - ZEOLITES: MORDENITE, FERRIERITE
  - POTASSIUM FELDSPAR
  - SILICA (PREDOMINANTLY CRISTOBALITE)
  - MINOR ILLITE
- MINOR ALTERATION OBSERVED AT 100° C-150° C FOR TEST DURATIONS UP TO 318 DAYS
  - IRON SMECTITE IS ONLY POSITIVELY IDENTIFIED PRODUCT

WP8401-54

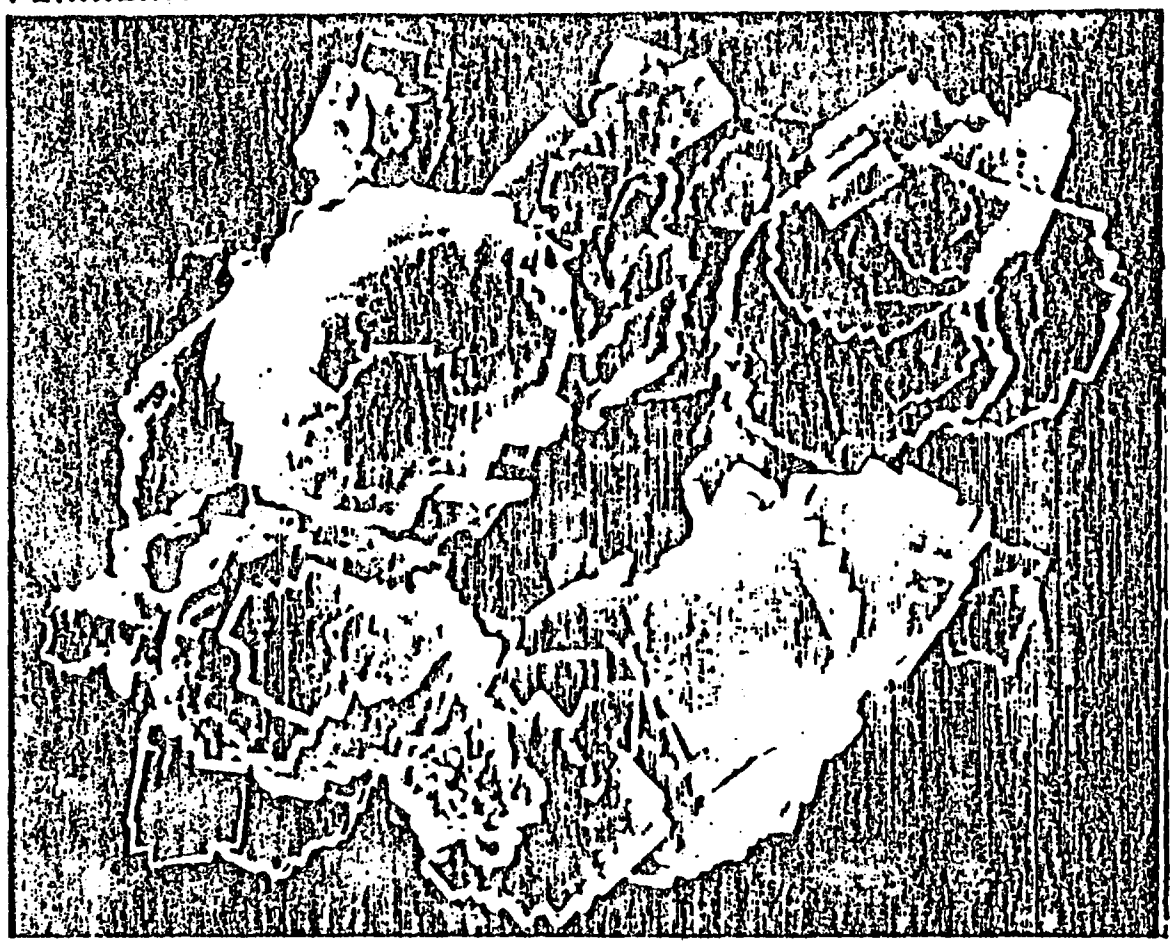
ALTERATION MINERALS IN GRANDE RONDE BASALT

- OCCURRENCE: FRACTURE FILLINGS, VUGS, VESICLES
- IRON SMECTITE
- ZEOLITES
  - CLINOPTILOLITE
  - MORDENITE
- SILICA PHASES (OPAL, QUARTZ, CRISTOBALITE, TRIDYMITE)

WP6401-56

FERRIERITE

BASALT/WATER
D3-9 300°C

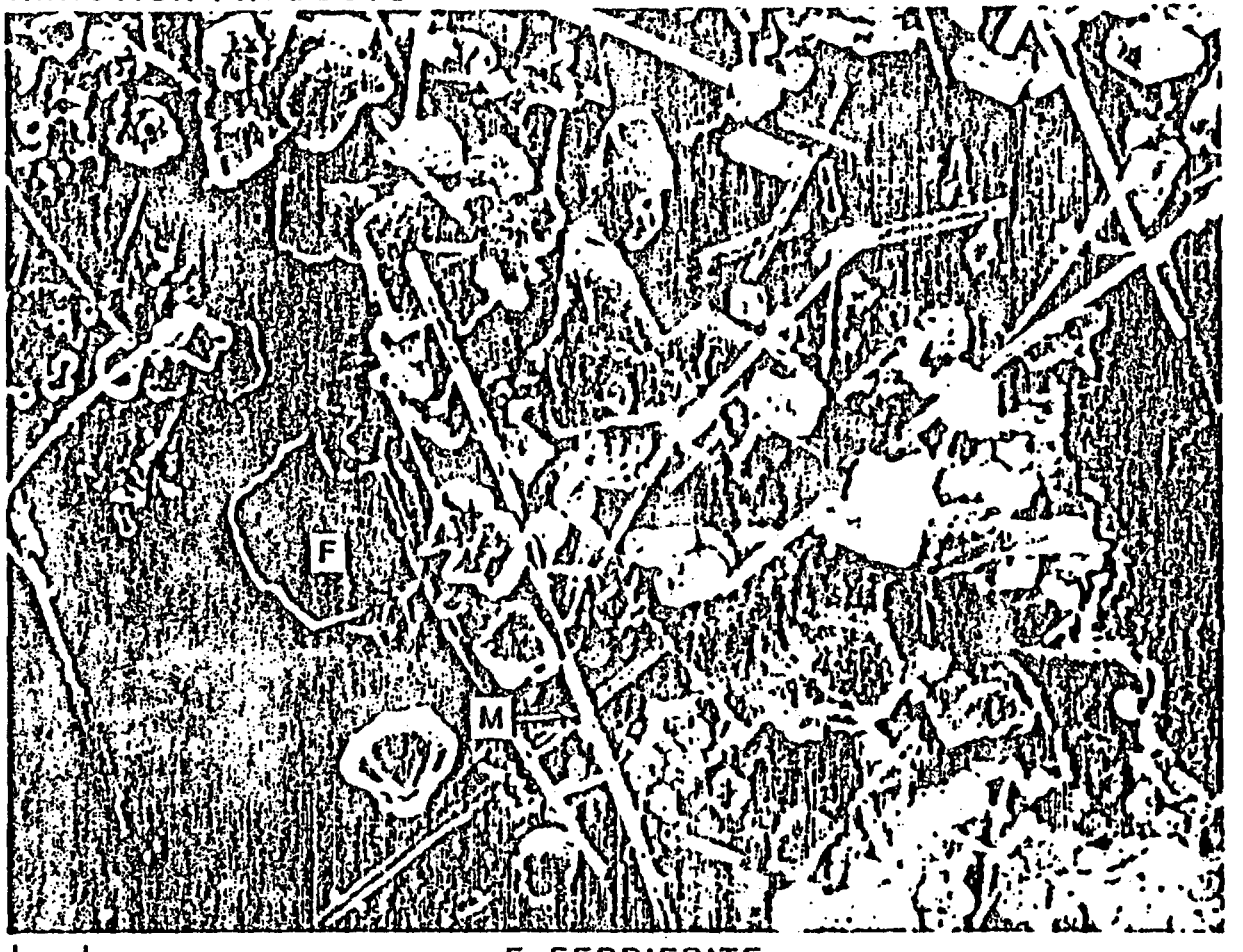


1.0 μm

WP6309-14A

BASALT/WATER
D3-9 300°C

REACTION PRODUCTS

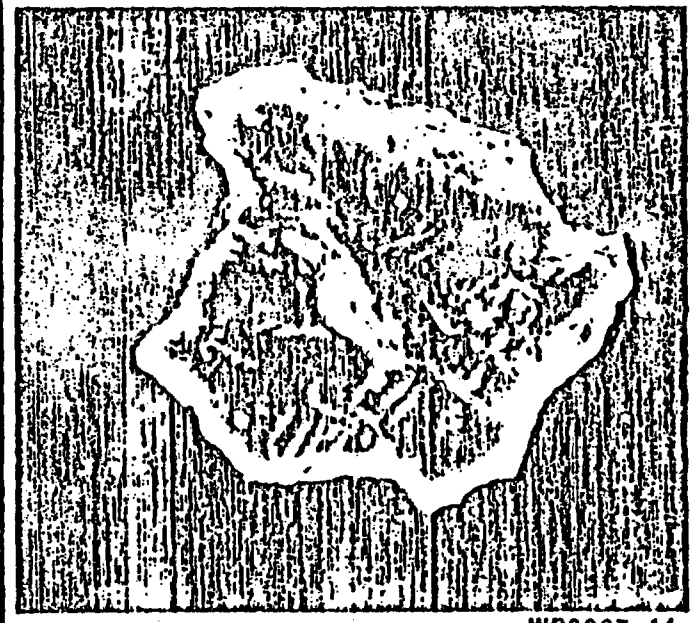


1.0 μm

F-FERRIERITE
M-MORDENITE

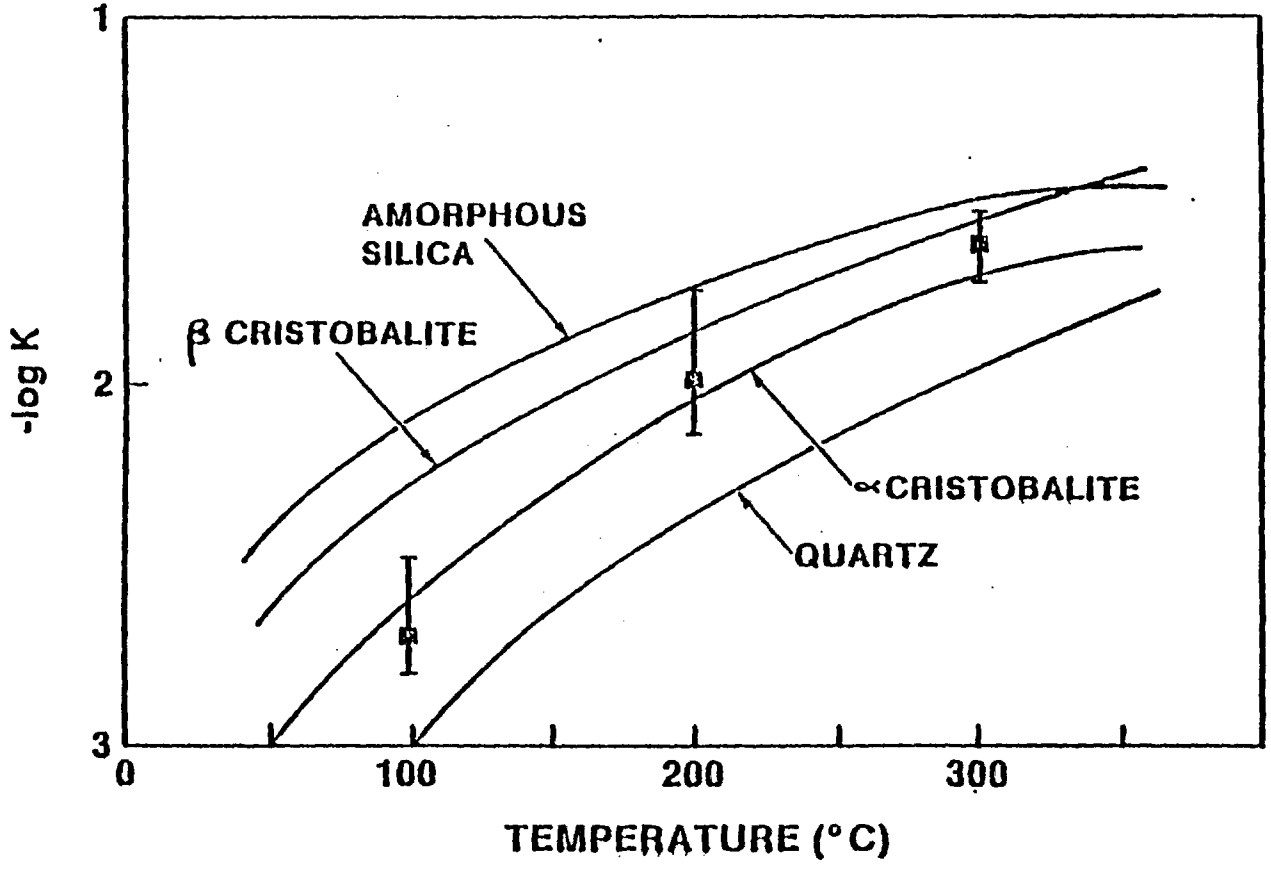
WP6309-13A

BASALT GRAIN FOLLOWING HYDROTHERMAL TEST



WP8307-14

SOLUBILITIES OF SILICA POLYMORPHS vs. TEMPERATURE: COMPARISON WITH EXPERIMENTAL SILICA CONCENTRATIONS



WP-8312-65

APPLICATIONS

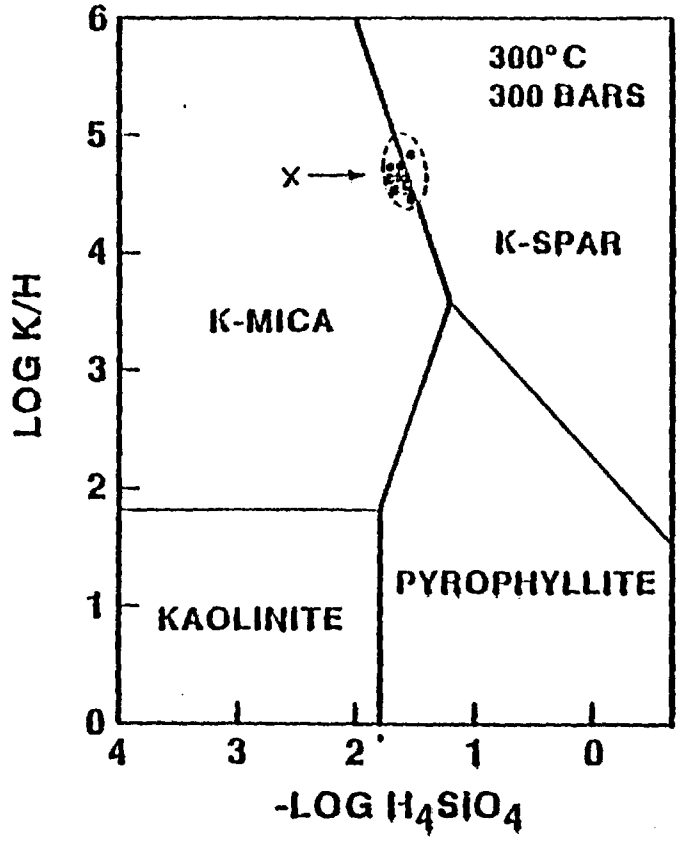
- ALTERATION ASSEMBLAGE STABILITY
  - AT 300° C, EXPERIMENTAL ASSEMBLAGES ARE METASTABLE BUT SIMILAR TO THOSE EXPECTED IN LONG-TERM LOW-T (100°-150° C) TESTS

    PARAGENESIS OF SMECTITE + ZEOLITES IN GEOTHERMAL AREAS IN ICELANDIC BASALTS

    ZEOLITE STABILITY STUDIES
- PREDICTION OF ALTERATION IN NWRB
  - TEMPERATURE - TIME HISTORY
  - METASTABLE PERSISTENCE OF PHASES IN NATURAL SYSTEMS
  - EFFECT OF FLOW RATE-FLUID FLUX

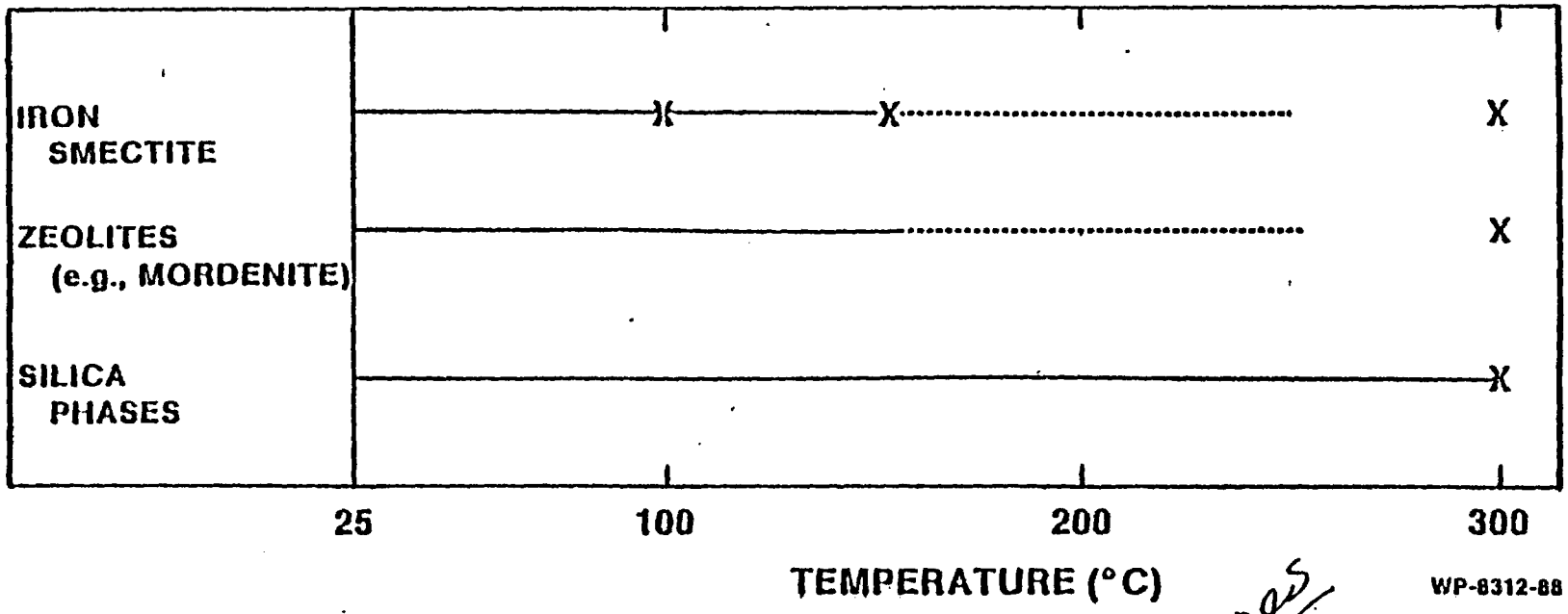
WP6401-56

ACTIVITY DIAGRAM OF SOLUTION COMPOSITIONS AND MINERAL STABILITY FIELDS



WP-8312-86

COMPARISON OF EXPERIMENTAL vs. NATURAL ALTERATION ASSEMBLAGES



WP-8312-88

references

PRELIMINARY FLOW-THROUGH TESTS

CONDITIONS

- T-300°C, P=30 MPa, DURATION=76 DAYS

  FLOW RATE= 7 mL/day

- MAJOR FINDINGS
  - ALTERATION ASSEMBLAGE CONSISTS OF Fe-RICH CHLORITE, AMPHIBOLE, ALBITE, MINOR ILLITE (?) BASED ON PRELIMINARY STEM WORK
  - COLUMNS PLUGGED DUE TO BASALT ALTERATION
- INTERPRETATION
  - FORMATION OF ALTERATION ASSEMBLAGE RESULTED IN DECREASE IN PERMEABILITY
- • Increased flow rates increase reaction on can be used to study reactions that won't occur in Dickson type experiments

CONCLUSIONS
(BASALT/WATER SYSTEM)

- SOLUTION COMPOSITION
  - STEADY-STATE IN SITU pH IS ALKALINE FROM 100°-300° C
  - STEADY-STATE CONCENTRATIONS OF COMPLEXING AGENTS (F^-, Cl^-, SO_4^{2-}, TC) ≤ VALUES IN SYNTHETIC GROUNDWATER
- AT 300° C: IN 'STATIC' TESTS BASALT ALTERS TO METASTABLE ASSEMBLAGE OF ZEOLITES, KSPAR, FE-SMECTITE, SILICA, ± ILLITE
- AT 100°-150° C: MINOR ALTERATION OF BASALT TO FE-SMECTITE OCCURS
- TESTS PERFORMED UNDER ELEVATED CONDITIONS (300° C) ARE REQUIRED TO 'ACCELERATE' REACTION RATES FOR PREDICTIVE MODELS

WP8491-58

PACKING MATERIAL STUDIES

WP6401-59

FUNCTIONAL REQUIREMENTS OF THE PACKING MATERIAL COMPONENT

- MINIMIZE CANISTER CORROSION DURING THE CONTAINMENT PERIOD (UP TO 1,000 YEARS)
  - DELAY WATER CONTACT WITH THE CANISTER
  - MINIMIZE GROUNDWATER FLUX PAST THE CANISTER
  - BUFFER OXYGEN CONTENT NEAR THE CANISTER
  - LOCALIZE CORROSION PRODUCTS AT THE PACKING MATERIAL/CANISTER INTERFACE

WP8401-80

FUNCTIONAL REQUIREMENTS OF THE PACKING MATERIAL COMPONENT (CONTINUED)

- PREVENT RADIONUCLIDE TRANSPORT INTO THE HOST ROCK DURING THE CONTAINMENT PERIOD IN THE EVENT OF PREMATURE CANISTER BREAKTHROUGH AND WASTE FORM DISSOLUTION
- REDUCE THE RADIONUCLIDE RELEASE RATE TO THE HOST ROCK AFTER THE CONTAINMENT PERIOD

these require sorption

WP-8312-103

PACKING MATERIAL TEST OBJECTIVES

- DETERMINE THE THERMAL STABILITY LIMITS OF BENTONITE IN A DRY ENVIRONMENT
- DETERMINE THE EFFECTS OF HYDROTHERMAL CONDITIONS AND THE PRESENCE OF BASALT AND GROUNDWATER ON BENTONITE STABILITY

WP-8312-93

STARTING MATERIALS

BENTONITE:	Na-MONTMORILLONITE	85%
	QUARTZ	5%
(-400 MESH)	FELDSPAR	5%
	OTHERS	5%
BASALT:	MESOSTASIS	48%
	PLAGIOCLASE	29%
(-120+230 MESH)	PYROXENE	17%
	OPAQUES	5%
	CLAY	1%

WP-8312-105

EXPERIMENTS

BENTONITE DEHYDRATION STUDIES

- BENTONITE ONLY
- ATMOSPHERIC PRESSURE
- 250° C-550° C

HYDROTHERMAL EXPERIMENTS

- BENTONITE + GROUNDWATER
- BASALT + BENTONITE +GROUNDWATER
- 30 MPa PRESSURE
- 150° C-300° C

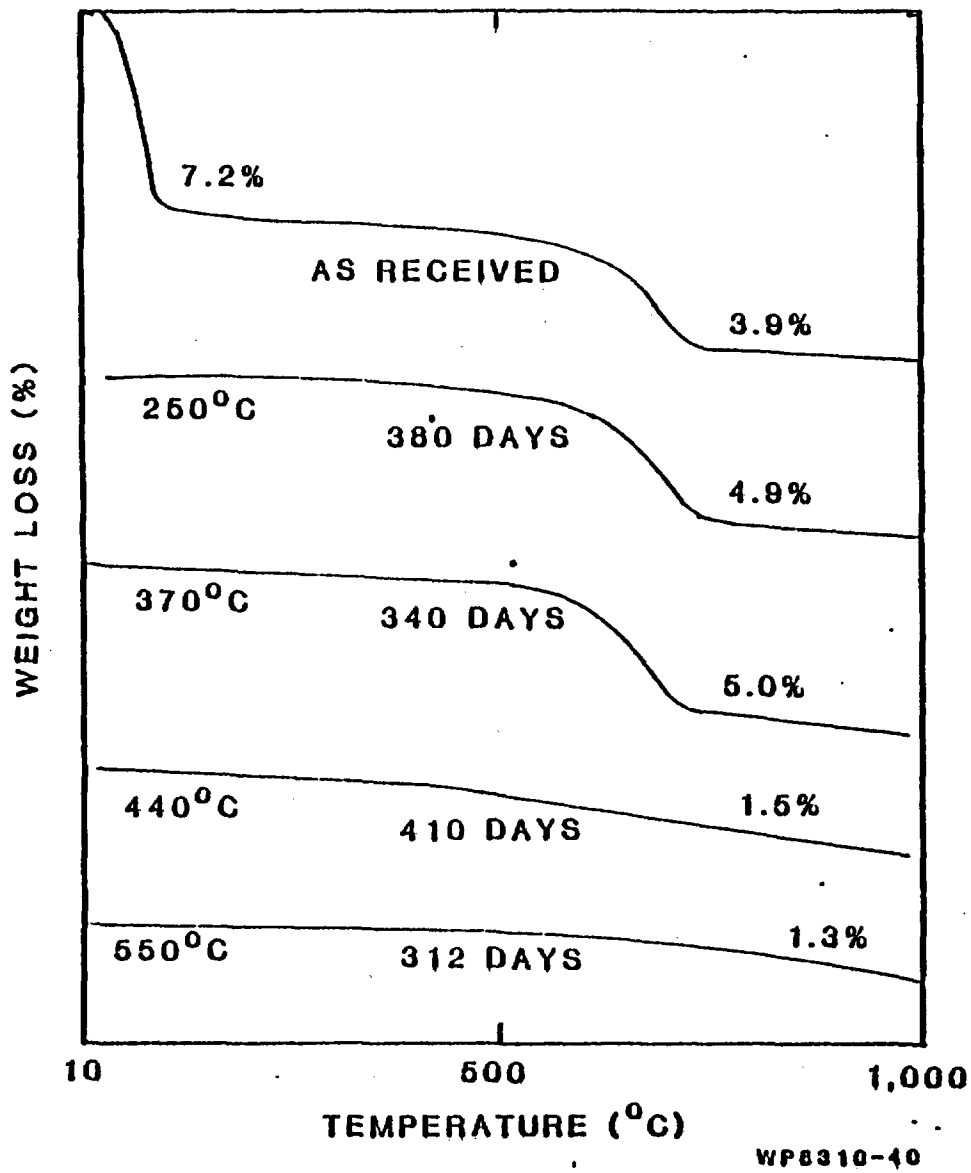
WP-8312-106

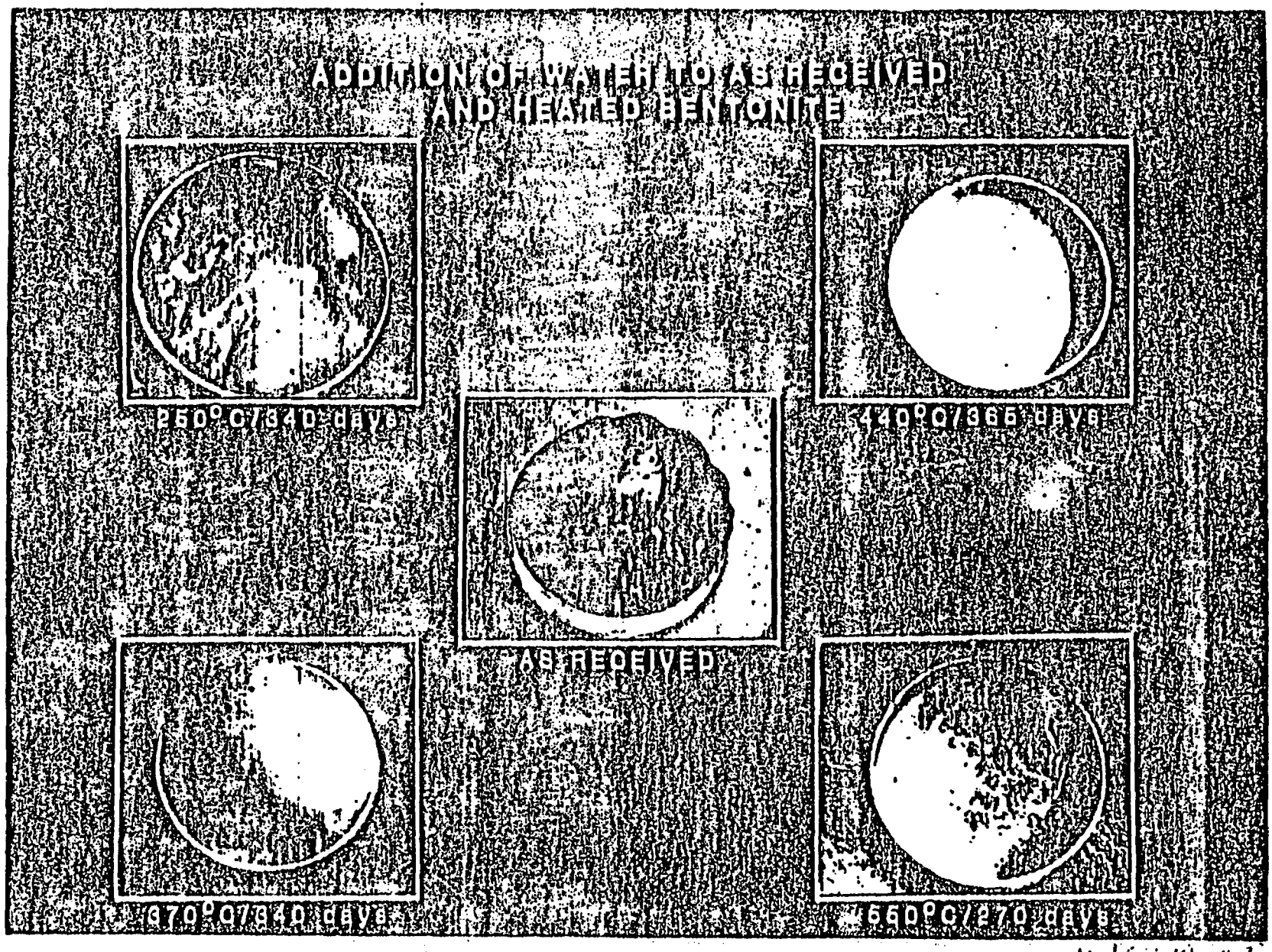
BENTONITE DEHYDRATION

TEMPERATURE (°C)	EXPERIMENT DURATION (DAYS)
250	340
370	1, 4, 8, 13, 21, 28, 340
440	1, 4, 8, 13, 21, 28, 365
550	1, 4, 8, 13, 21, 28, 270

WP-8312-107

BENTONITE DEHYDRATION (TGA)




ADDITION OF WATER TO AS RECEIVED
AND HEATED BENTONITE
250°C/340 days
440°C/365 days
AS RECEIVED
370°C/340 days
660°C/270 days

BENTONITE + GROUNDWATER HYDROTHERMAL EXPERIMENT D3-15

300° C, 217 DAYS, W/S = 10, DICKSON

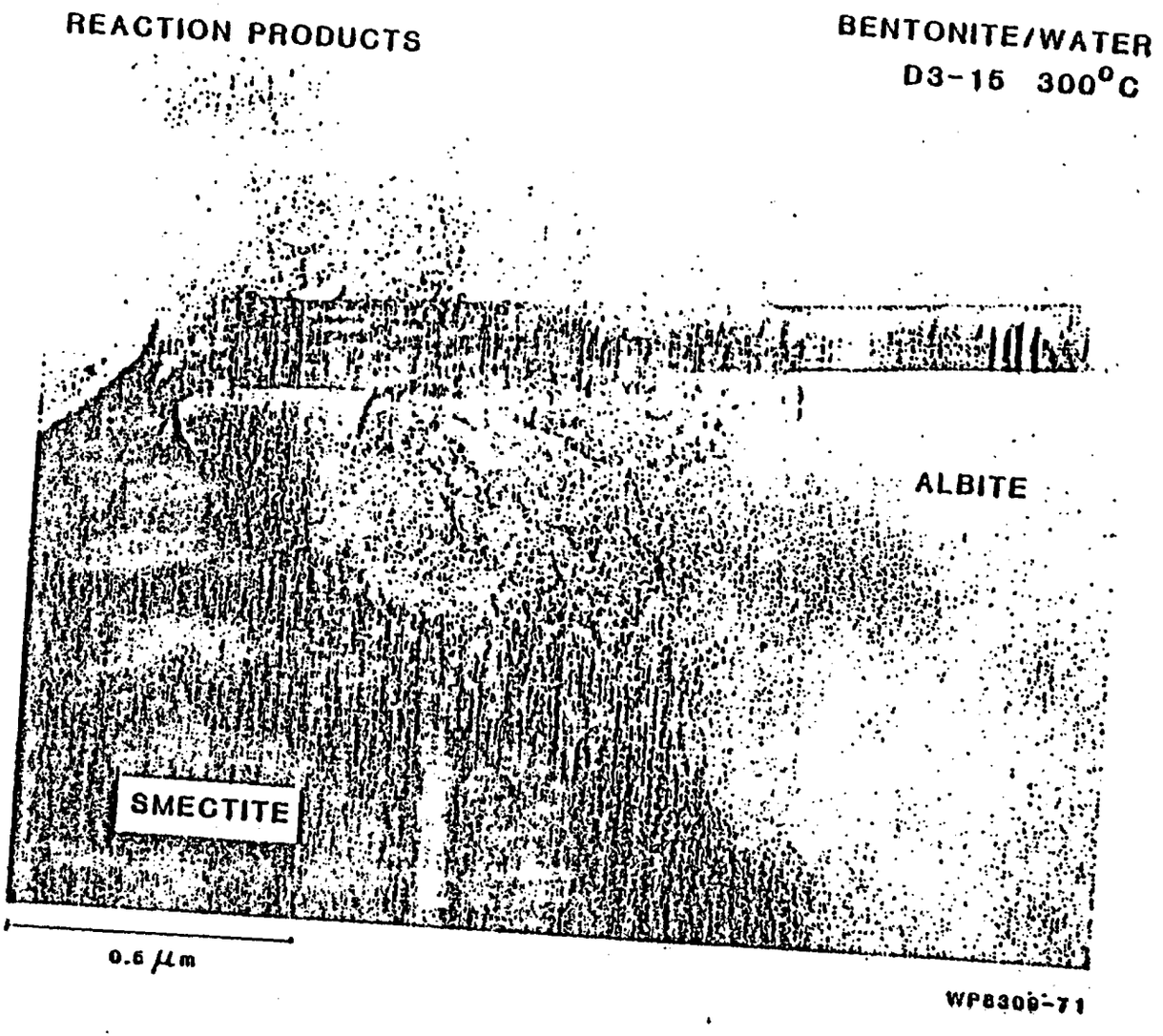
ALTERATION OBSERVED

- PARTIAL DISSOLUTION OF CLAY
- STEADY STATE AFTER 25 DAYS
- SUBSTITUTION OF Ca, Fe
- SMECTITE STRUCTURE PRESERVED

SOLID REACTION PRODUCTS OBSERVED

- QUARTZ, ALBITE, (HALITE)

WP-8312-108


REACTION PRODUCTS
BENTONITE/WATER
D3-15 300°C
ALBITE
SMECTITE
0.5 μm
WP8309-71

BASALT + BENTONITE + GROUNDWATER HYDROTHERMAL EXPERIMENT D4-1

150° C, 120 DAYS, W/S = 10, B/B = 1, DICKSON

ALTERATION OBSERVED

- PARTIAL DISSOLUTION OF CLAY AND BASALT MESOSTASIS
- SMECTITE STRUCTURE PRESERVED
- SUBSTITUTION OF Fe, K

SOLID REACTION PRODUCT OBSERVED

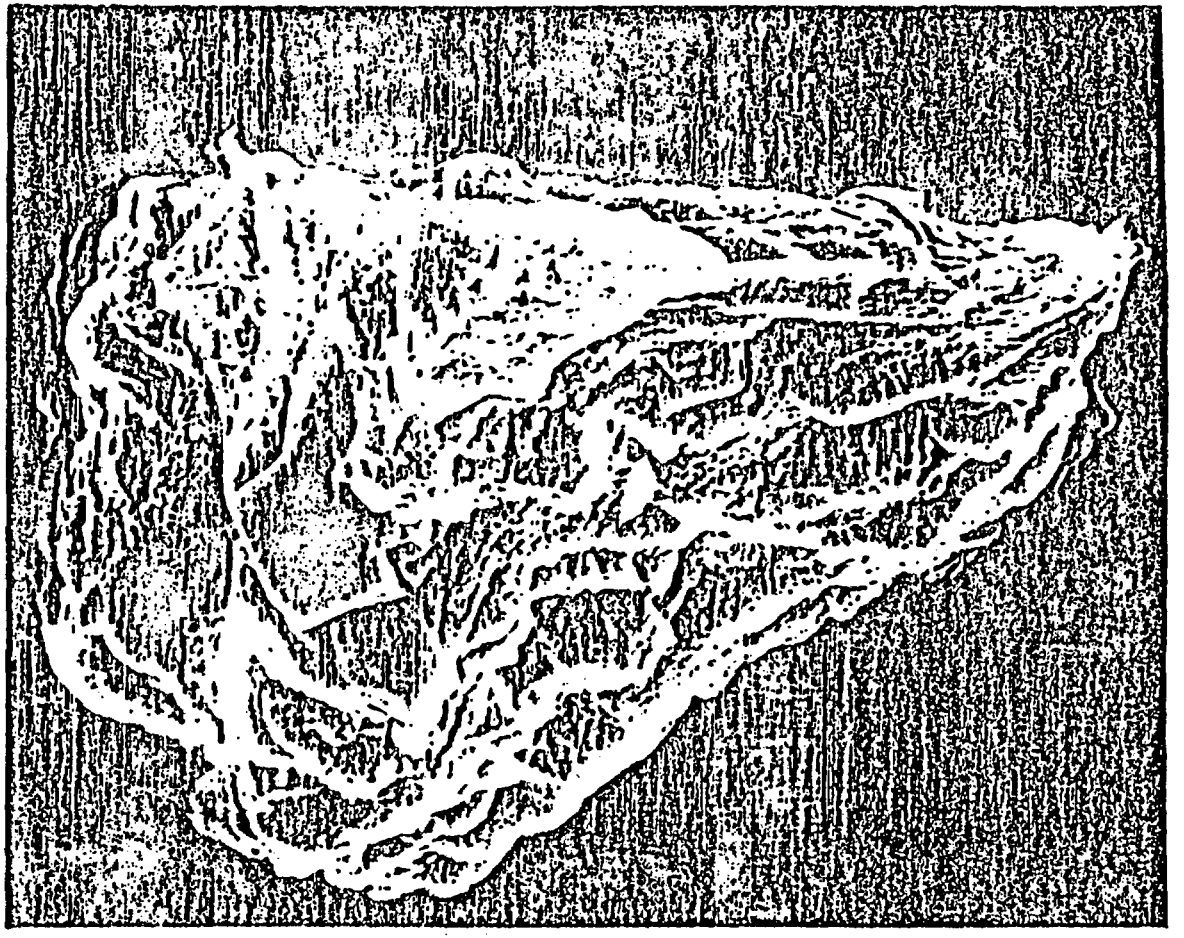
- Fe-SMECTITE

WP-8312-109

BASALT/BENTONITE/WATER

ETCHED BASALT

D4-1 150°C



10 μm

WP8309-68

BASALT + BENTONITE + GROUNDWATER HYDROTHERMAL EXPERIMENT D1-13

300°C, 60 DAYS, W/S = 10, B/B = 1, DICKSON

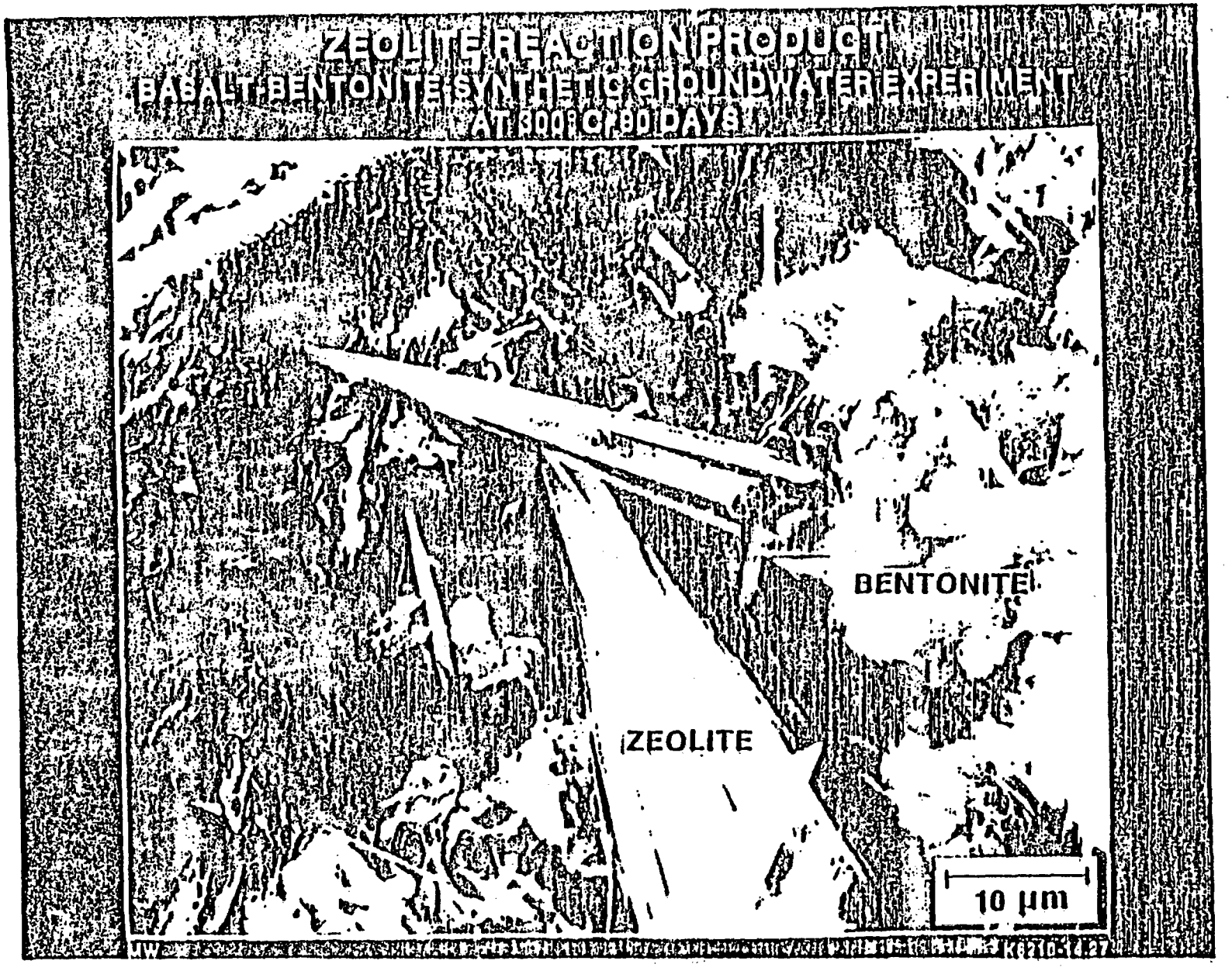
ALTERATION OBSERVED

- PARTIAL DISSOLUTION OF CLAY AND BASALT MESOSTASIS
- STEADY STATE AFTER 60 DAYS

SOLID REACTION PRODUCTS OBSERVED

- Fe-SMECTITE, QUARTZ, CRISTOBALITE, K-FELDSPAR, MORDENITE, FERRIERITE

WP-8312-110


ZEOLITE REACTION PRODUCT
BASALT-BENTONITE-SYNTHETIC GROUNDWATER EXPERIMENT
AT 300°C/90 DAYS
BENTONITE
ZEOLITE
10 µm

BASALT + BENTONITE + GROUNDWATER HYDROTHERMAL EXPERIMENT 143-13

300° C, 379 DAYS, W/S = 1, B/B = 1, COLD-SEAL

ALTERATION OBSERVED

- EXTENSIVE DISSOLUTION OF CLAY AND BASALT

SOLID REACTION PRODUCTS OBSERVED

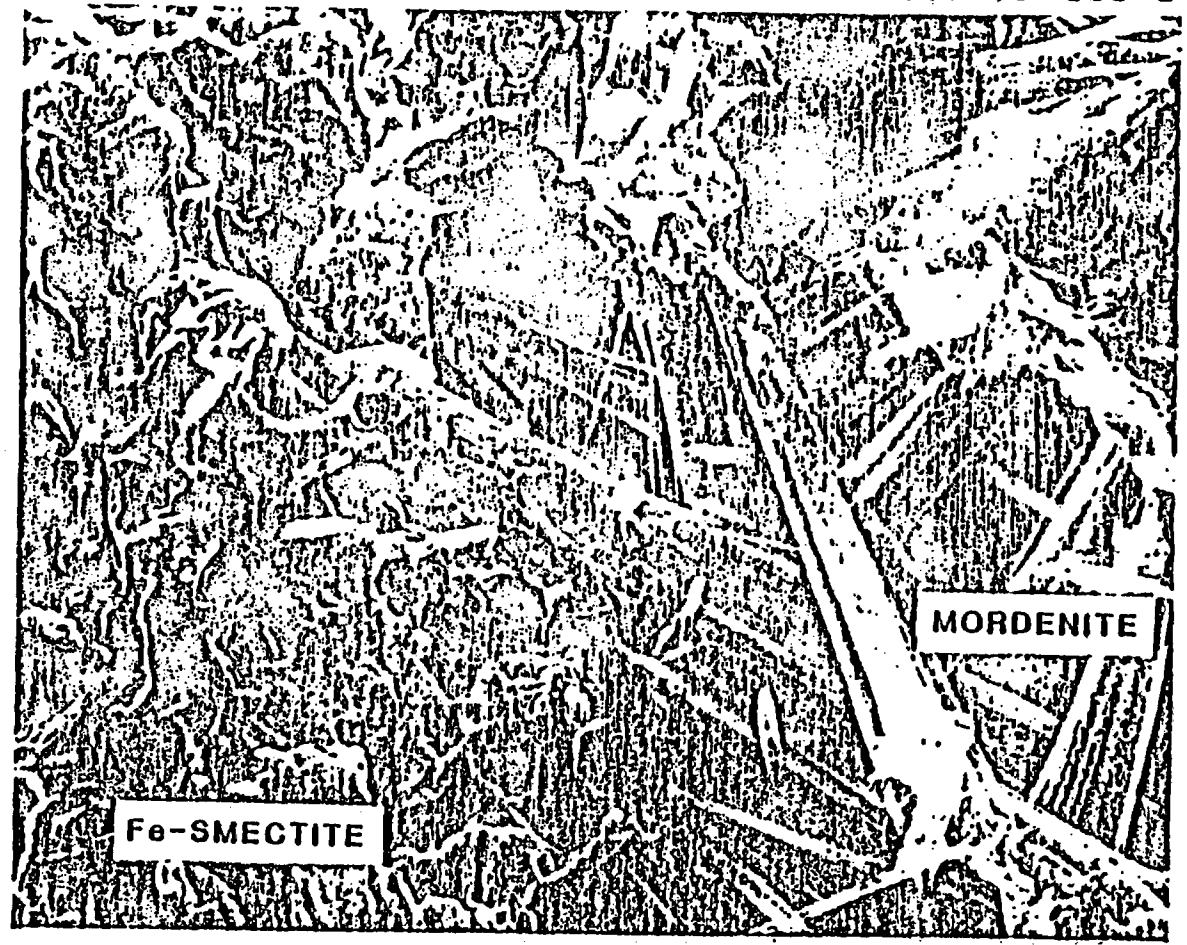
- Fe-SMECTITE, MORDENITE, CRISTOBALITE, ALBITE

WP-8312-111

BASALT/BENTONITE/WATER

REACTION PRODUCTS

143-13 300°C



10 μm

WP8309-70

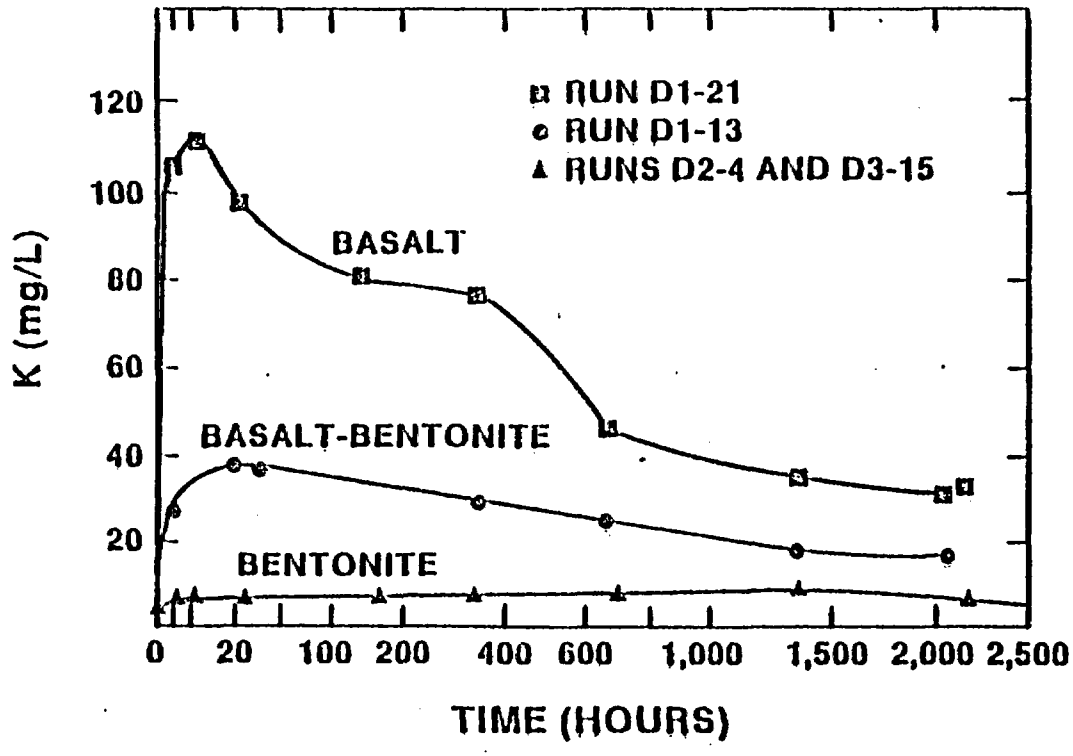
RESULTS OF SOLUTION ANALYSIS BASALT/BENTONITE/WATER TESTS

(pH-ANIONS)

- STEADY-STATE pH (25° C MEASUREMENTS)
  - 300° C TESTS, pH = 5.5 ± 0.2
  - 150° C TESTS, pH = 7.0-7.5
- F^-, Cl^-, SO_4^{2-}, TOTAL CARBON
  - F- DECREASES SIGNIFICANTLY
  - Cl^- ≤ INITIAL VALUE
  - SO_4^{2-} DECREASES AT 300° C
    INCREASES AT 150° C
  - TC > INITIAL VALUE

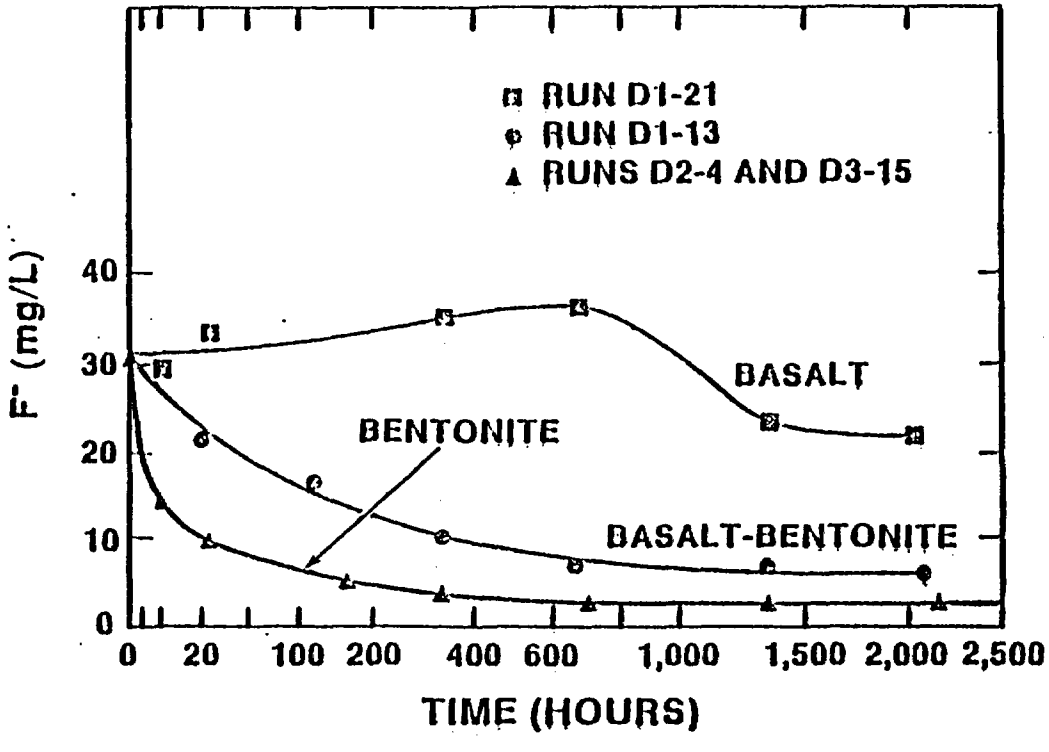
WP-8312-94

COMPARISON OF POTASSIUM vs. TIME IN TESTS AT 300° C



WP-8312-86

COMPARISON OF FLUORIDE vs. TIME IN TESTS AT 300° C



WP-8312-85

CONCLUSIONS

- IN A DRY ENVIRONMENT, Na-MONTMORILLONITE RETAINS ITS STRUCTURAL AND SWELLING PROPERTIES IN A YEAR-LONG EXPERIMENT AT 370° C
- IN A HYDROTHERMAL ENVIRONMENT, WITH OR WITHOUT BASALT, Na-MONTMORILLONITE IS CONVERTED TO AN Fe-SMECTITE, WITH SOME SUBSTITUTION OF K. POTASSIUM IS ALSO PARTITIONED INTO FELDSPAR AND ZEOLITES

no smectite/illite clays observed

WP-8312-112

CONCLUSIONS (CONTINUED)

- IN A 300° C HYDROTHERMAL ENVIRONMENT, STEADY STATE CONDITIONS ARE ATTAINED IN A FEW MONTHS, BUT THE MINERAL ASSEMBLAGE IS METASTABLE
- KINETICS MAY BE AS IMPORTANT AS THERMODYNAMIC STABILITY IN MODELING MINERALOGICAL CHANGES IN A REPOSITORY

WP-8312-113

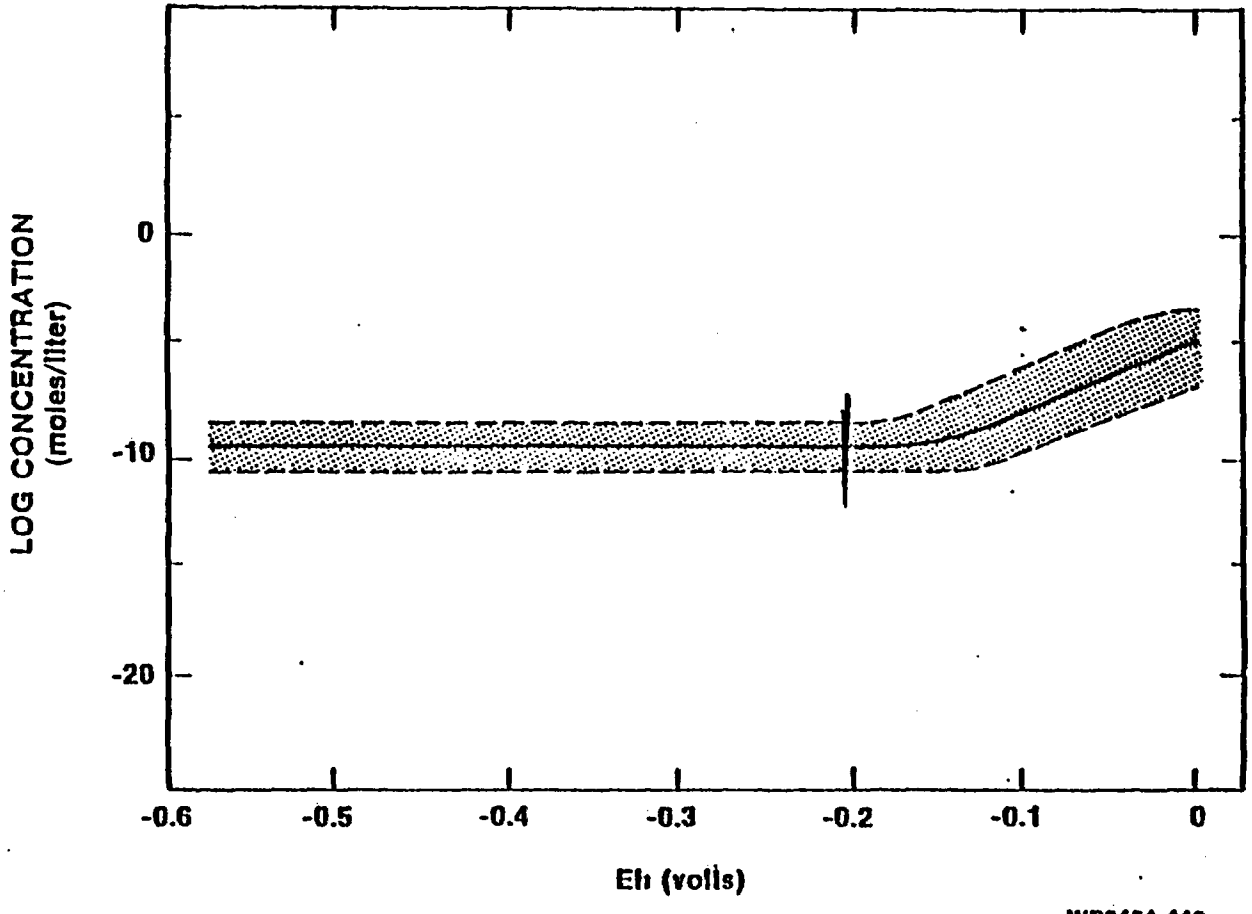
Eh - pH Analysis

Eh

- INDICATES THE GENERAL OXIDATION STATE OF THE SYSTEM
- ? CAN BE USED TO PREDICT THE STABILITY OF SOLID PHASES AND AGUEOUS SPECIES IN THE SYSTEM

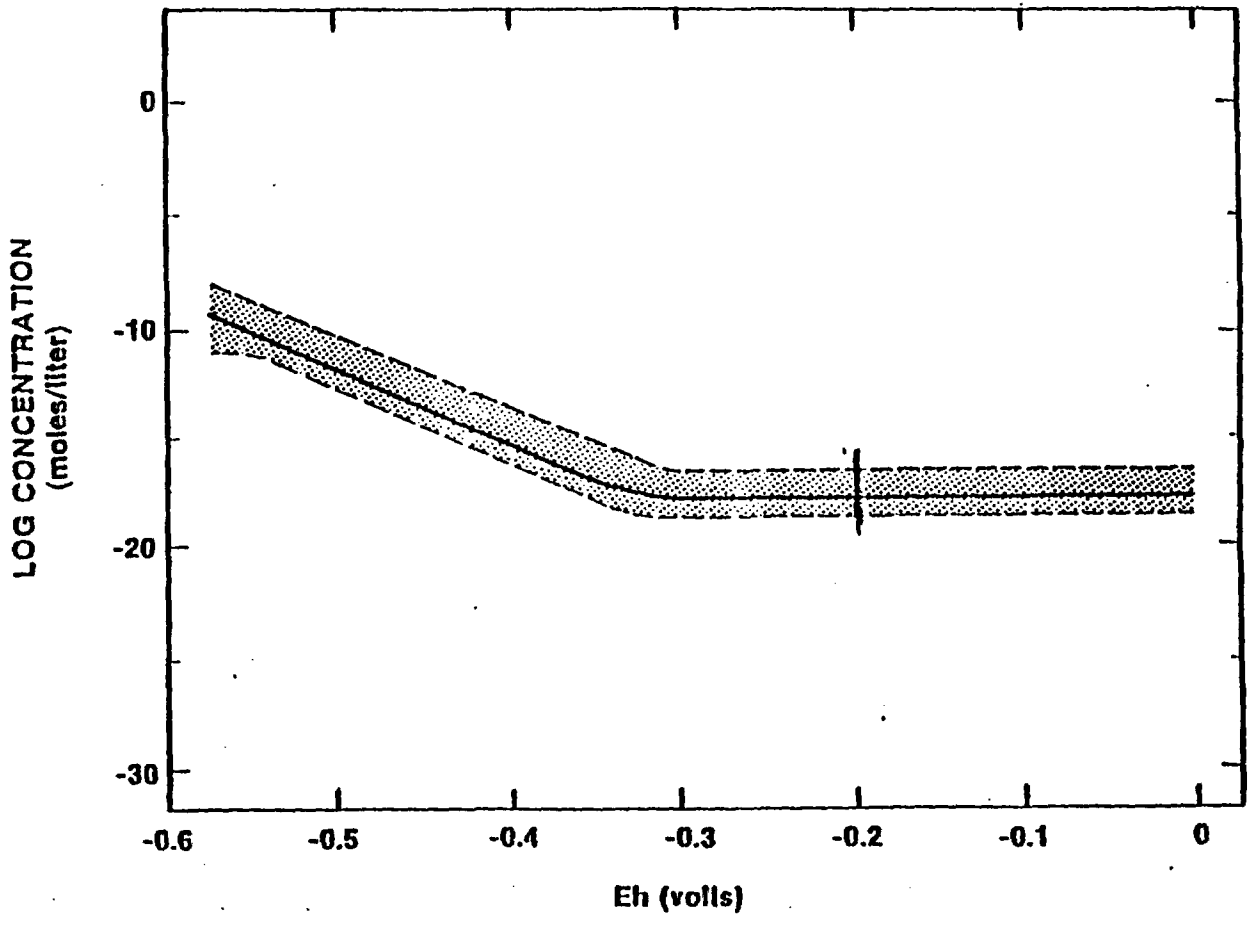
canister
corrosion
sorption

SOLUBILITY OF URANIUM AS A FUNCTION OF Eh AT 25°C



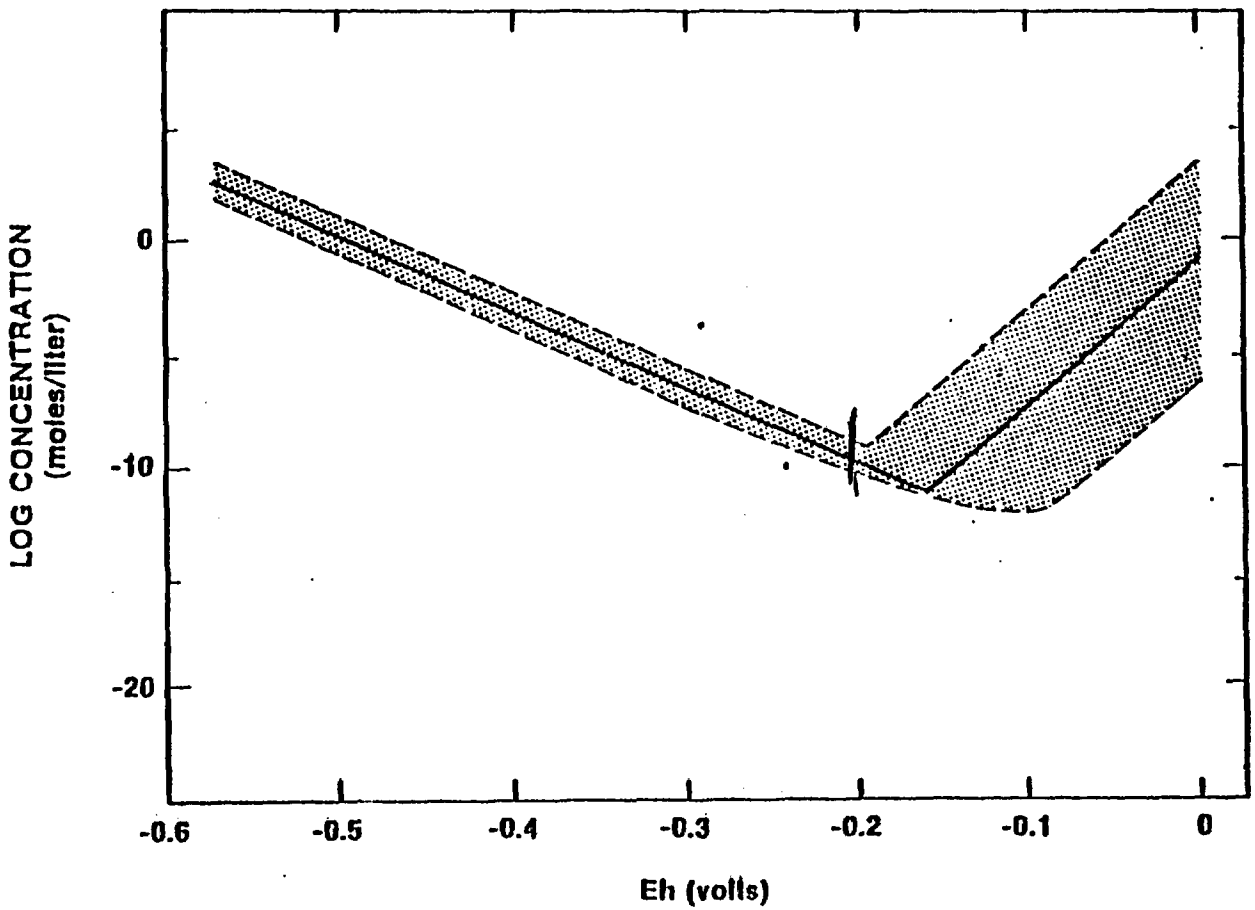
WP8401-118

SOLUBILITY OF TIN
AS A FUNCTION OF Eh at 25° C



WP0401-119

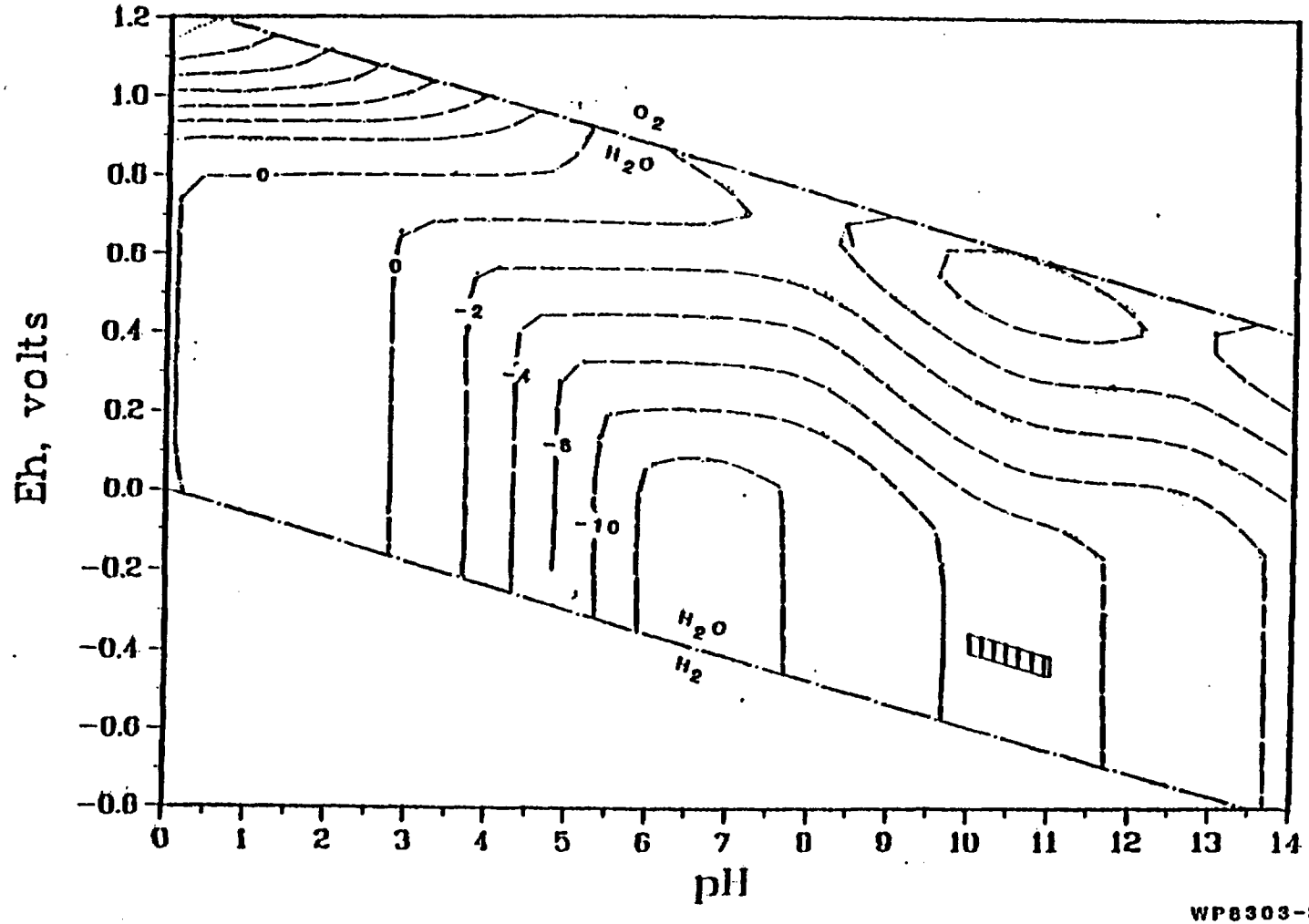
SOLUBILITY OF SELENIUM AS A FUNCTION OF Eh AT 25°C



WP8401-120

Eh–pH DIAGRAM FOR NEPTUNIUM

LOG AQUEOUS CONCENTRATION CONTOURS

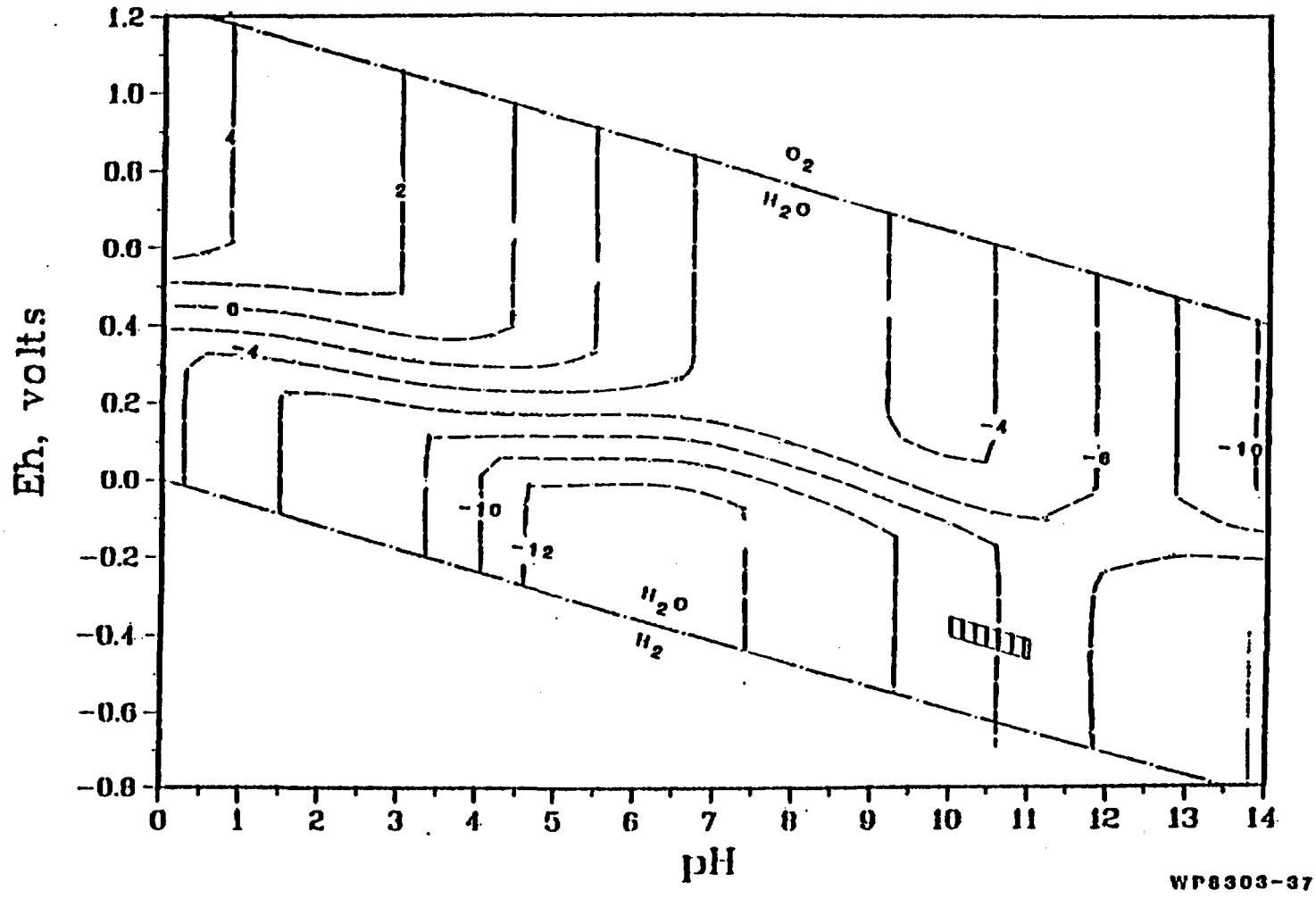


WP8303-36

GR-3

Eh–pH DIAGRAM FOR URANIUM

LOG AQUEOUS CONCENTRATION CONTOURS

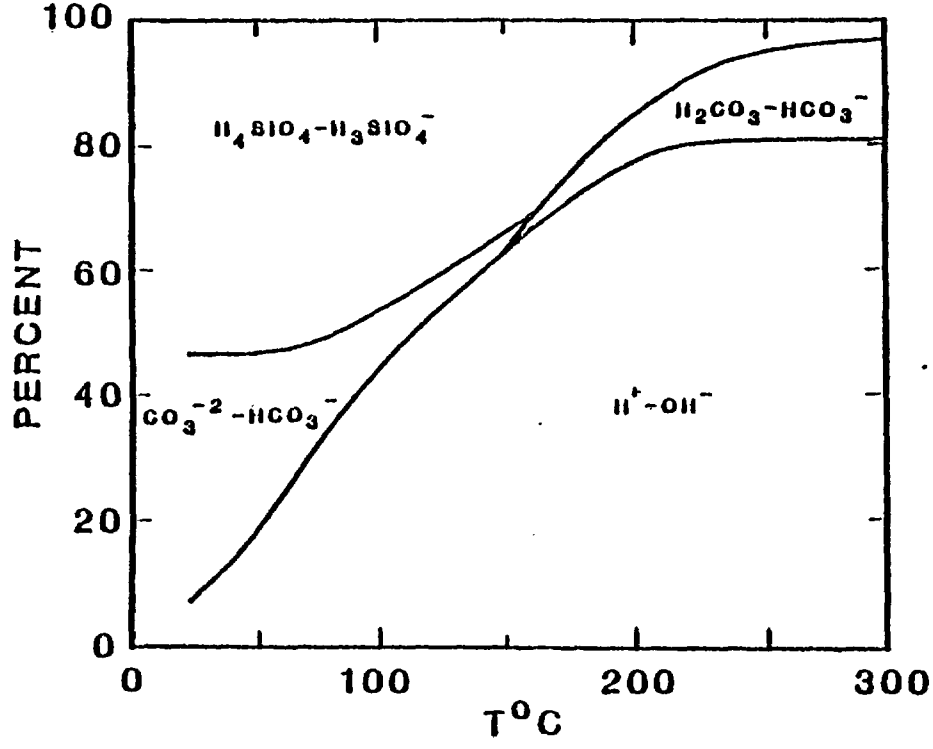


WP6303-37

pH BUFFER INTENSITY

PERCENTAGE CONTRIBUTION

OF VARIOUS SPECIES AND ACID-BASE PAIRS



using GR-3 dissociation constants then which will decate

WP8312-51

Eh CONTROL IN THE SYSTEM BASALT + GROUNDWATER

$$Fe^{+2}_{(glass)} \rightarrow Fe^{+2}_{(aq)} \quad (1)$$

$$Fe^{+2}_{(aq)} \rightarrow Fe^{+3}_{(aq)} + e^{-} \quad (2)$$

$$Fe^{+3}_{(aq)} + O_2 \rightarrow \text{OXIDES+OXYHYDROXIDES} \quad (3)$$

WP8401-121

SOURCES OF Eh DATA

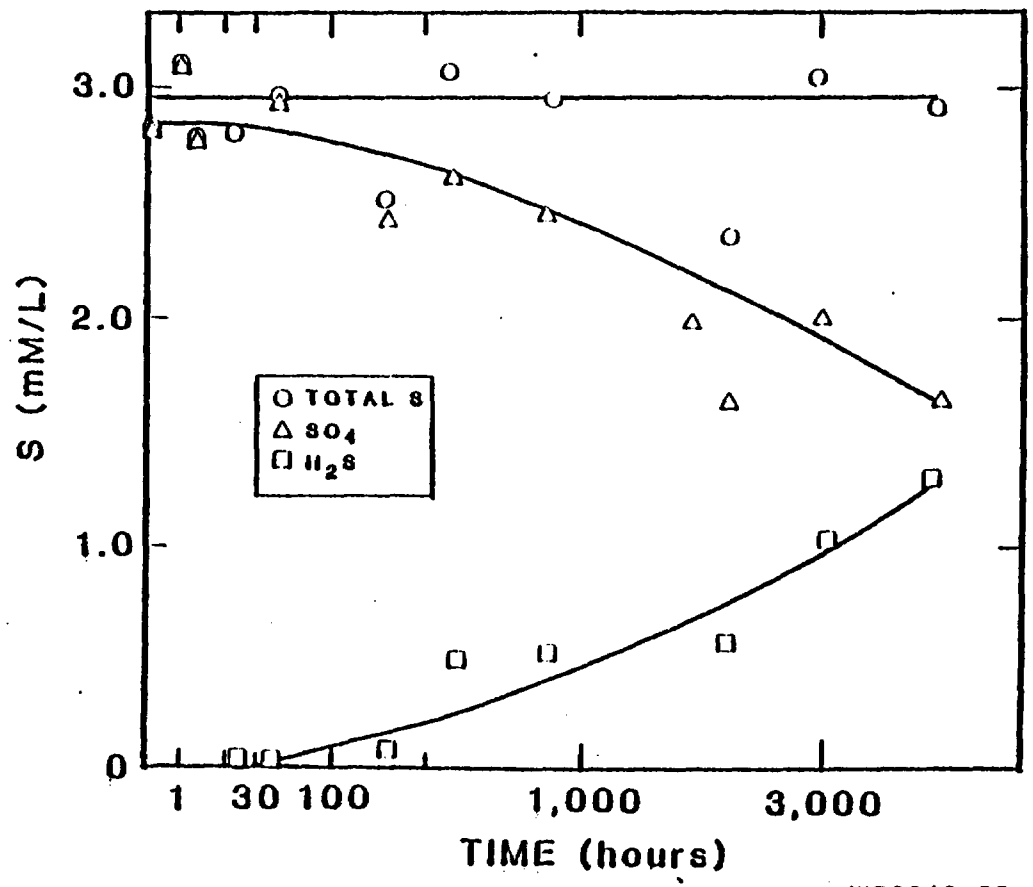
- SO_4^{-2}/HS^- CONCENTRATIONS IN BASALT + GROUND WATER EXPERIMENTS AT 300° C
- As^{+3}/As^{+5} CONCENTRATIONS IN BASALT + GROUND WATER EXPERIMENTS AT 300° C
- DISSOLVED O_2 CONCENTRATIONS IN BASALT + GROUND WATER EXPERIMENTS AT 100° and 150° C
- ELECTROCHEMICAL Eh MEASUREMENTS IN BASALT + GROUND WATER EXPERIMENTS AT 60° C

WP8401-122

SULFATE-SULFIDE CONCENTRATIONS

FOR BASALT PLUS GROUNDWATER

AT 300°C, 300 bars

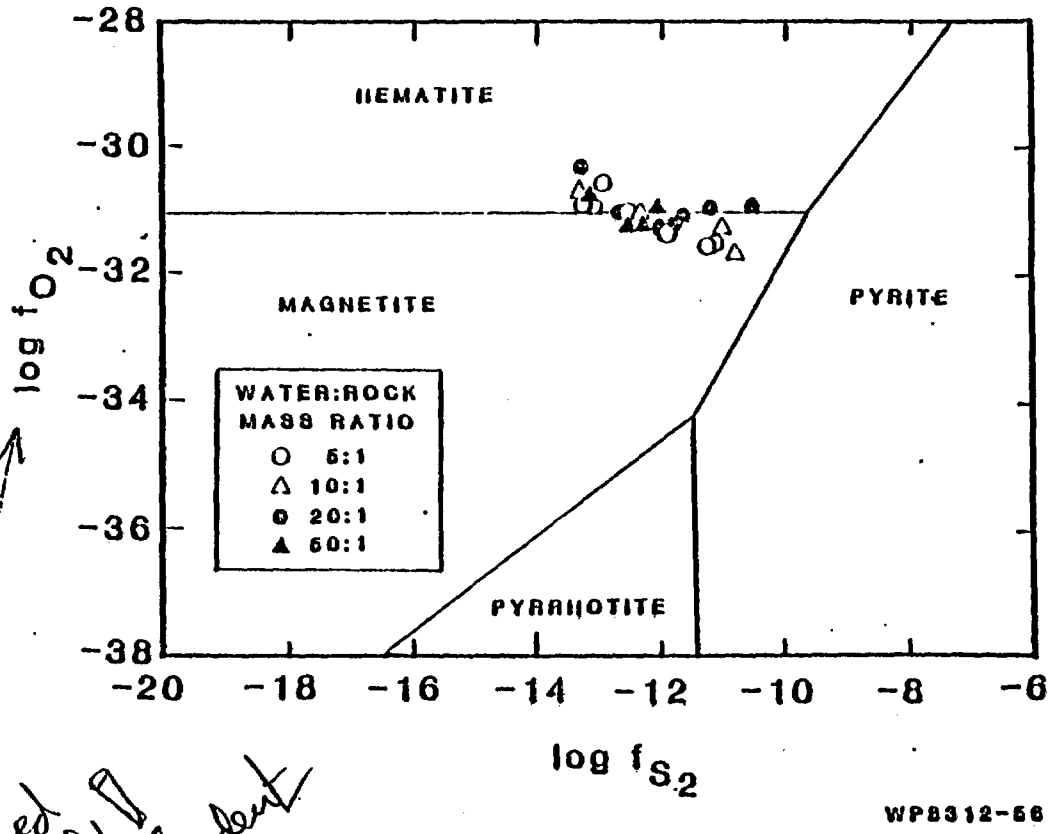


WP8312-55

SYSTEM Fe-O-S

PHASE EQUILIBRIA

AT 300°C, 300 bars



stated

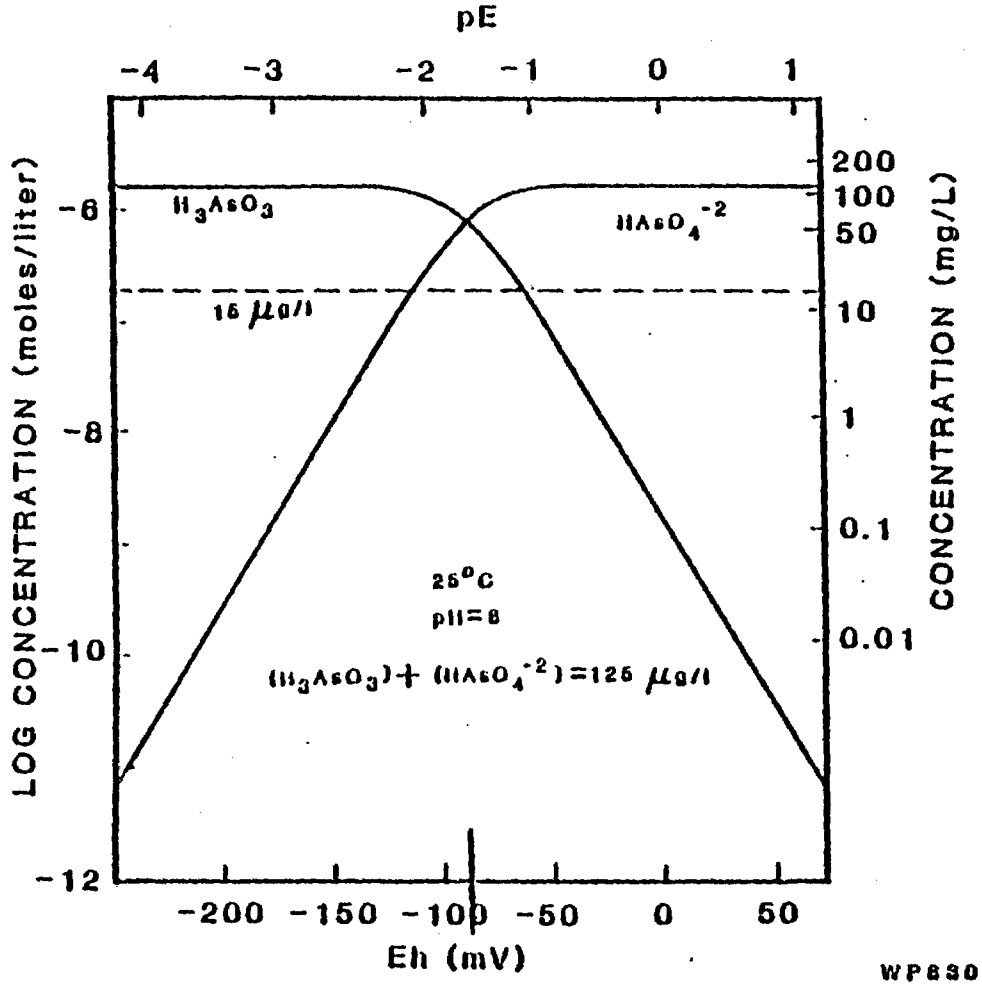
derived from SO_4 & not independent

METHODS

- ARSENIC OXIDATION STATE ANALYSIS
  - As (III)/As(V) CHERRY, et.al., 1979
  - HYDRIDE GENERATION - FLAME AAS
  - HYDRIDE GENERATION - GRAPHITE FURNACE AAS
- DISSOLVED OXYGEN (D.O.) MEASUREMENTS
  - MEMBRANE ELECTRODE
  - COLORIMETRIC

WP8302-48B

CONCENTRATIONS OF As(V)-As(III) SPECIES AS A FUNCTION OF Eh



WP8302-37

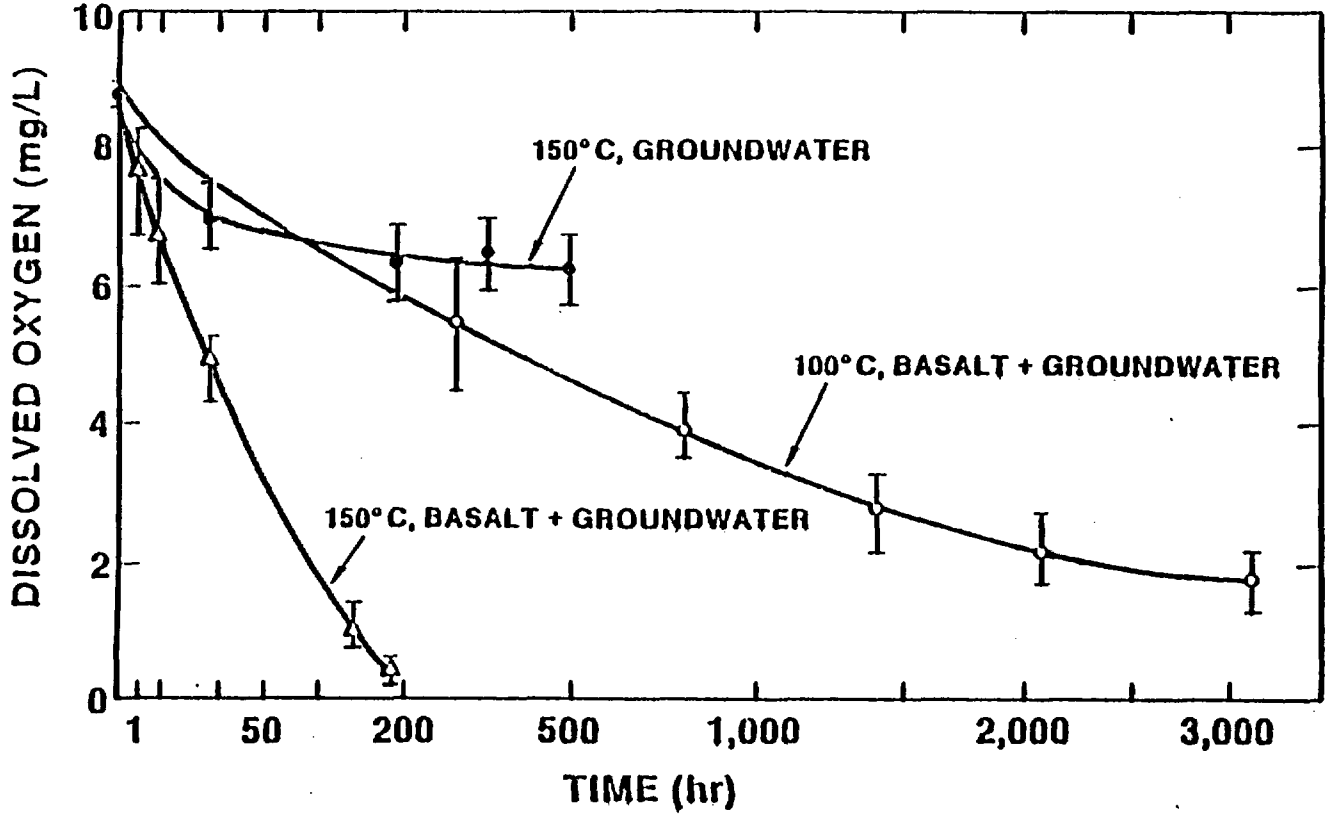
EXPERIMENTAL CONDITIONS

- As OXIDATION STATES
  - BASALT+DEIONIZED WATER WITH 125 μg/l As(V), 300°C, 300 bars, W/R=10

- D.O.
  1) BASALT+SYNTHETIC GRANDE RONDE GROUNDWATER 100°C and 150°C, 300 bars, W/R=10
  2) SYNTHETIC GRANDE RONDE GROUNDWATER 150°C, 300 bars

WP8302-49A

DISSOLVED OXYGEN CONSUMPTION DATA
FROM SYNTHETIC GRANDE RONDE BASALT GROUNDWATER EXPERIMENTS



K6311-3.102
WP6302-39D

REDOX CONDITIONS

BASALT/WATER TESTS

- As(III)/As(V) DETERMINATIONS BY ATOMIC ABSORPTION
  - RESULTS: AT 300°C AFTER 11 DAYS, CALCULATED UPPER LIMIT FOR Eh=-400 ± 100 mV
- DISSOLVED OXYGEN (D.O.) CONSUMPTION BY BASALT
  - RESULTS: AT 150°C, D.O. CONTENT DECREASED FROM 8.5-9 mg/L TO 0.4 mg/L IN 8 DAYS
- FUTURE STUDIES
  - RATE DATA, FURTHER Eh CALCULATIONS
  - REDOX BUFFERING CAPACITY OF BASALT

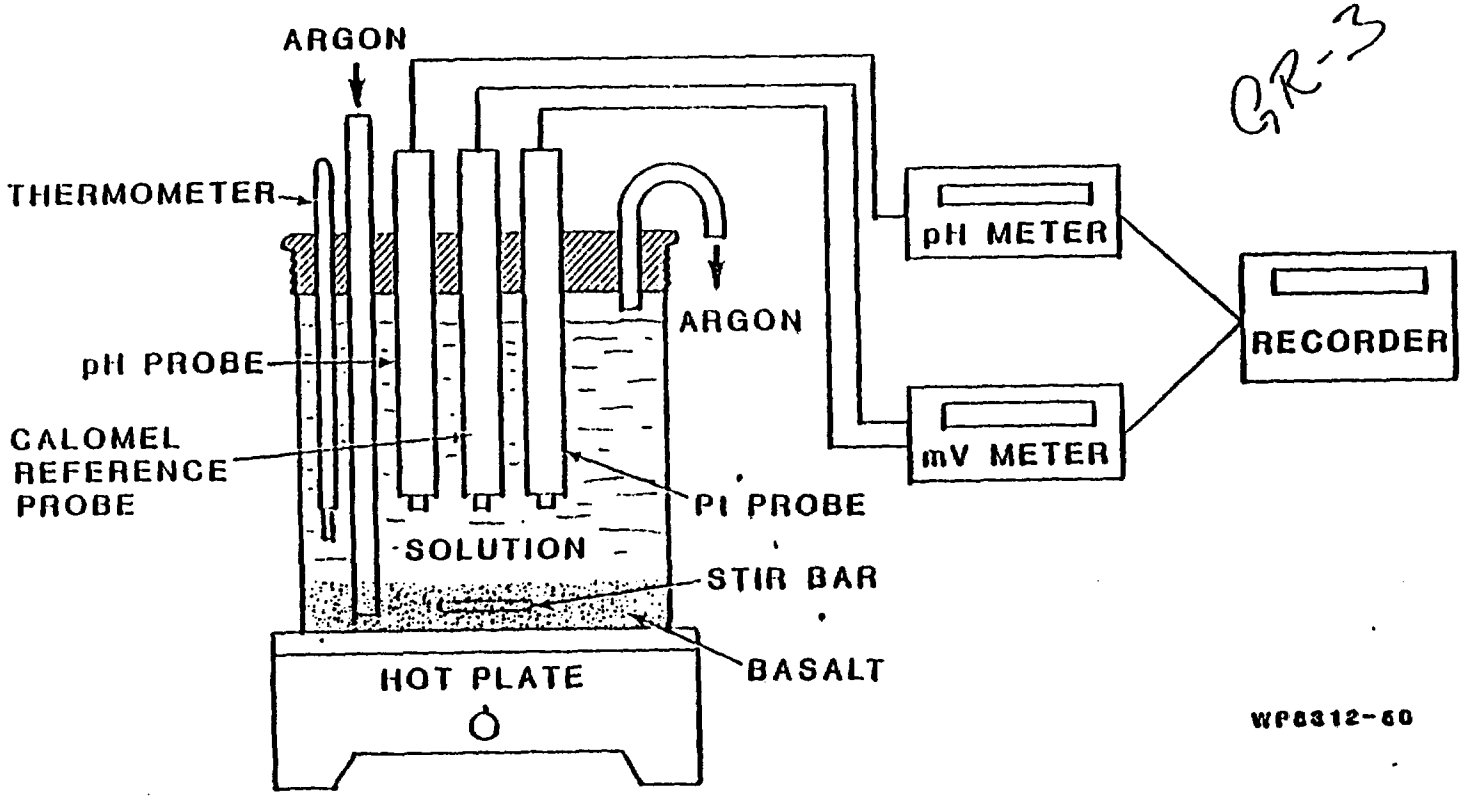
Se(IV)/Se VI
flow through
teflon diffusion membrane

WP8311-55B

EXPERIMENTAL APPARATUS

USED AT SAVANNAH RIVER LABORATORIES
BY C. JANTZEN

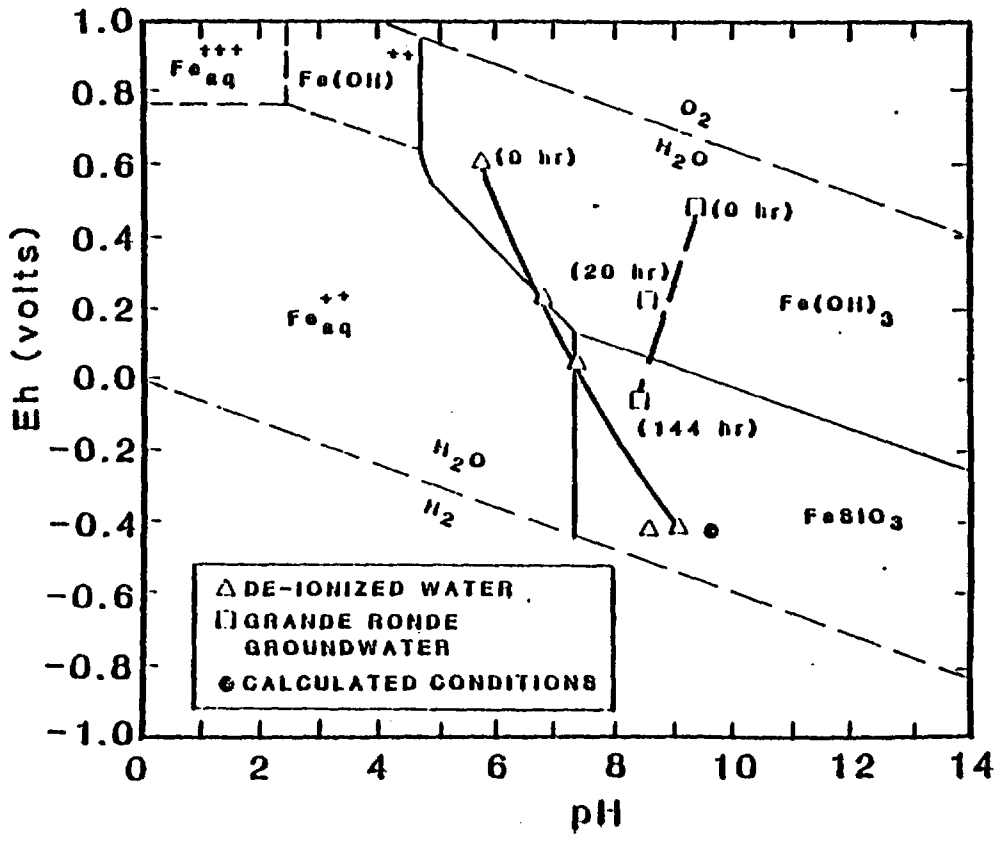
GR-3



WP6312-60

GRANDE RONDE GROUNDWATER EXPERIMENT

BWIP BASALT PLUS SIMULATED GROUNDWATER AT 60°C



WP8312-40

CONCLUSIONS

- Eh MEASUREMENTS ARE DIFFICULT BUT CAN BE MADE WITH PT ELECTRODES WHEN REDOX SPECIES PRESENT IN SUFFICIENT CONCENTRATIONS
- CAN REACH LOW Eh AT LOW TEMPERATURE AND SHORT TIMES
- SA/V AND RESIDENCE TIME OF THE SOLID EFFECTS Eh
- Eh VALUES OF -0.4 VOLT AT pH OF 8.5 CAN BE ACHIEVED WHEN CRUSHED BASALT IS USED AS A SOLID REDUCTANT IN DEIONIZED WATER

WP8401-123

CONCLUSION

SULFER SPECIATION, ARSENIC SPECIATION, DISSOLVED OXYGEN AND ELECTROCHEMICAL MEASUREMENTS ALL INDICATE THAT THE BASALT/GROUND WATER SYSTEM WILL ESTABLISH REDUCING CONDITIONS ON A LABORATORY TIME-SCALE.

WP8401-124

Radiology's Effects

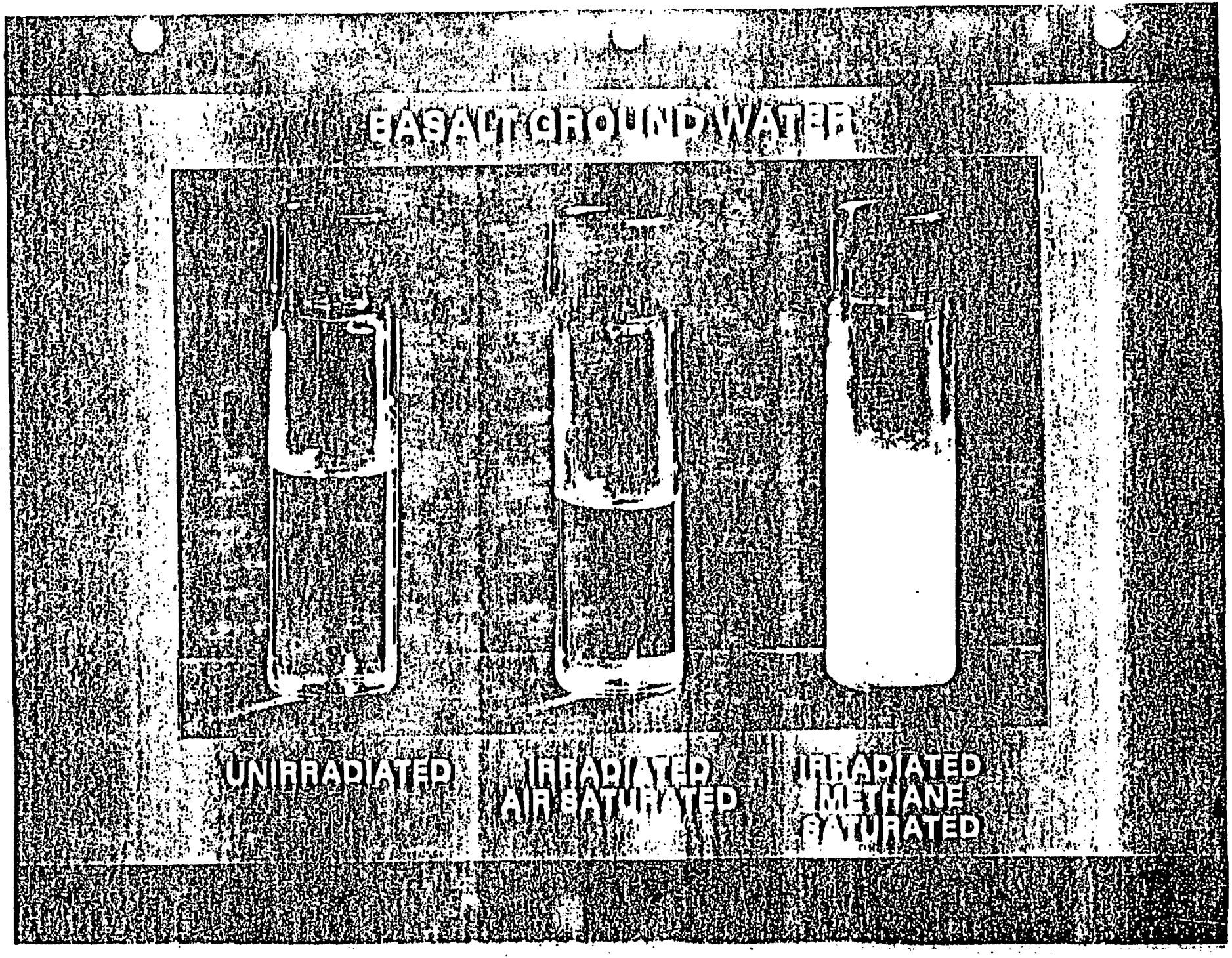
COMPOSITION OF SYNTHETIC GRANDE RONDE BASALT GROUNDWATER

COMPONENT	CONCENTRATION mg/liter
Si	35.5
Na	358
Ca	2.8
K	3.4
F	33.4
Cl	312
$SO_4^{=}$	173
$CO_3^{=}$(AS HCO_3^-)	100
CH_4	700
N_2	25
Ar	10
pH	9.8

GR-3

G-VALUES (YIELDS) OF PRIMARY RADIOLYSIS PRODUCTS IN WATER AND DILUTE AQUEOUS SOLUTIONS

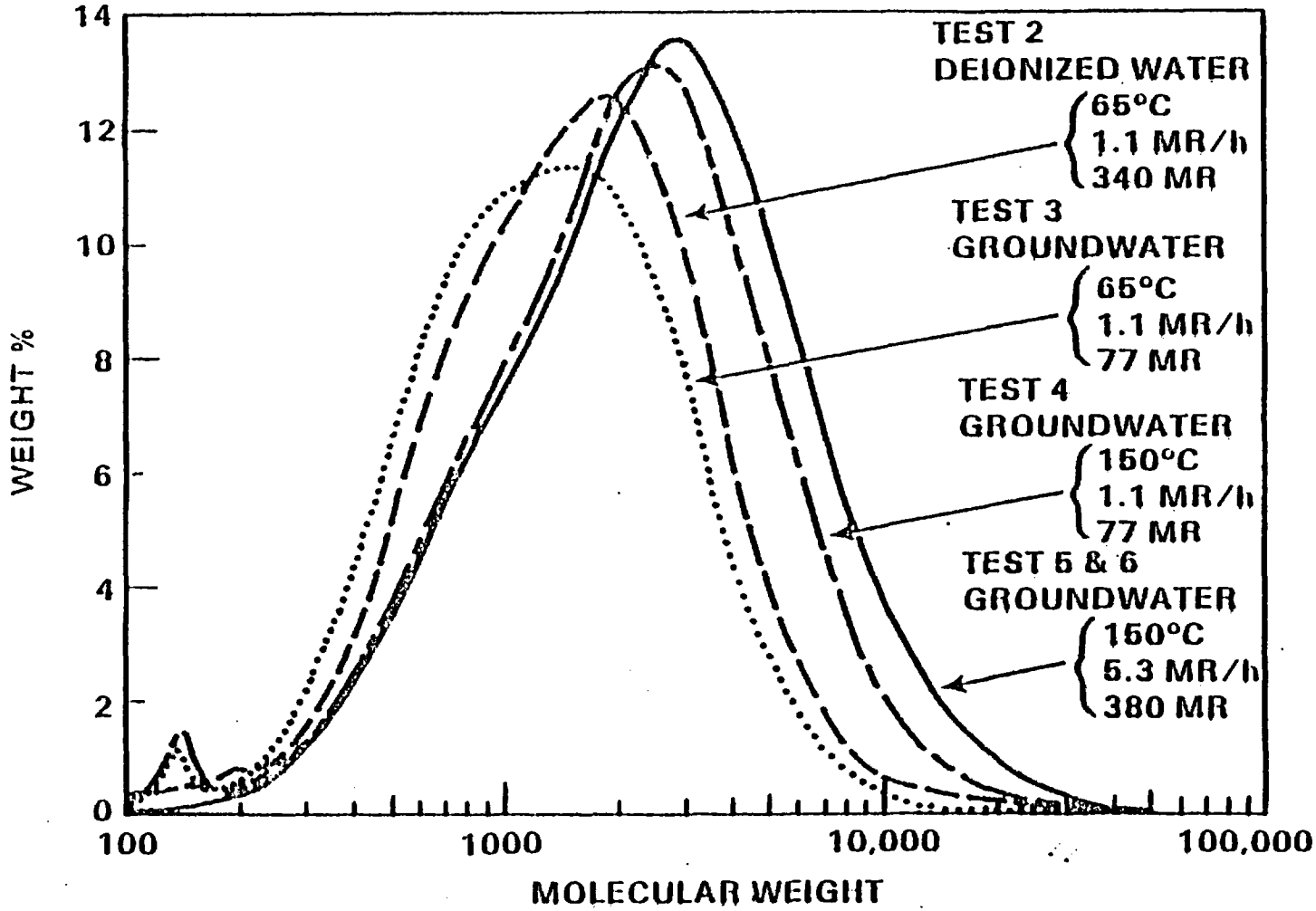
	H_2	H	e^-_{aq}	H^+	H_2O_2	OH	HO_2
GAMMA	0.45	0.44	2.8	2.8	0.72	2.7	0.0
ALPHA	1.3	0.21	0.06	0.06	0.99	0.24	0.22


BASALT GROUNDWATER
UNIRRADIATED
IRRADIATED
AIR SATURATED
IRRADIATED
METHANE
SATURATED

IRRADIATION CONDITIONS AND PROPERTIES OF IRRADIATED SOLUTIONS

	1	2	3	4	5	6
SOLUTION	BGW	DIW	BGW	BGW	BGW	BGW/Fe
IRRADIATION TEMP. (°C)	65	65	65	150	150	150
DOSE RATE (MR/h)	1.1	1.1	1.1	1.1	5.3	5.3
TOTAL DOSE (MR)	340	340	77	77	380	380
GAS COMPOSITION (VOL. %)						
HYDROGEN	26	46	6.1	9.9	24	22
METHANE	66	45	86	85	70	70
2,2-DIMETHYLPROPANE	0.054	0.14	0.034	0.52	0.30	0.62
SOLIDS ANALYSIS:						
MASS (g/ℓ)	4.4	3.0	2.0	2.4	2.1	2.2
CARBON (WT%)		84			86	86
HYDROGEN (WT%)		13			12	12
OXYGEN (WT%)		2.9			1.0	1.2
SOLUTION pH	9.6	6.8	9.6	9.6	9.5	9.3

MOLECULAR WEIGHT DISTRIBUTION OF POLYMERS GENERATED BY GAMMA RADIOLYSIS OF WATER CONTAINING METHANE



IRRADIATION CONDITIONS AND PROPERTIES OF IRRADIATED SOLUTIONS

	7	8	9
IRRADIATION TEMP. (°C)	150	150	150
DOSE RATE (Mrad/h)	0.52	0.52	0.023
TOTAL DOSE (Mrad)	38	38	38
GAS COMPOSITION (VOL. %):			
HYDROGEN	4.6	5.8	6.4
METHANE	88	87	85
NITROGEN	4.5	4.9	4.9
ARGON	2.3	2.3	2.7
MASS 44	0.19	0.22	0.28
2, 2-DIMETHYLPROPANE	0.13	0.18	0.22
2, 2-DIMETHYLBUTANE	0.055	0.074	0.088

PROPOSED PRINCIPAL RADIOLYTIC REACTION OF WATER CONTAINING METHANE

$$mH_2O(\ell) + nCH_4(g) \rightarrow C_nH_{2n}O_m(s) + (n+m)\ H_2(g)$$

POSSIBLE REACTIONS INVOLVING METHANE

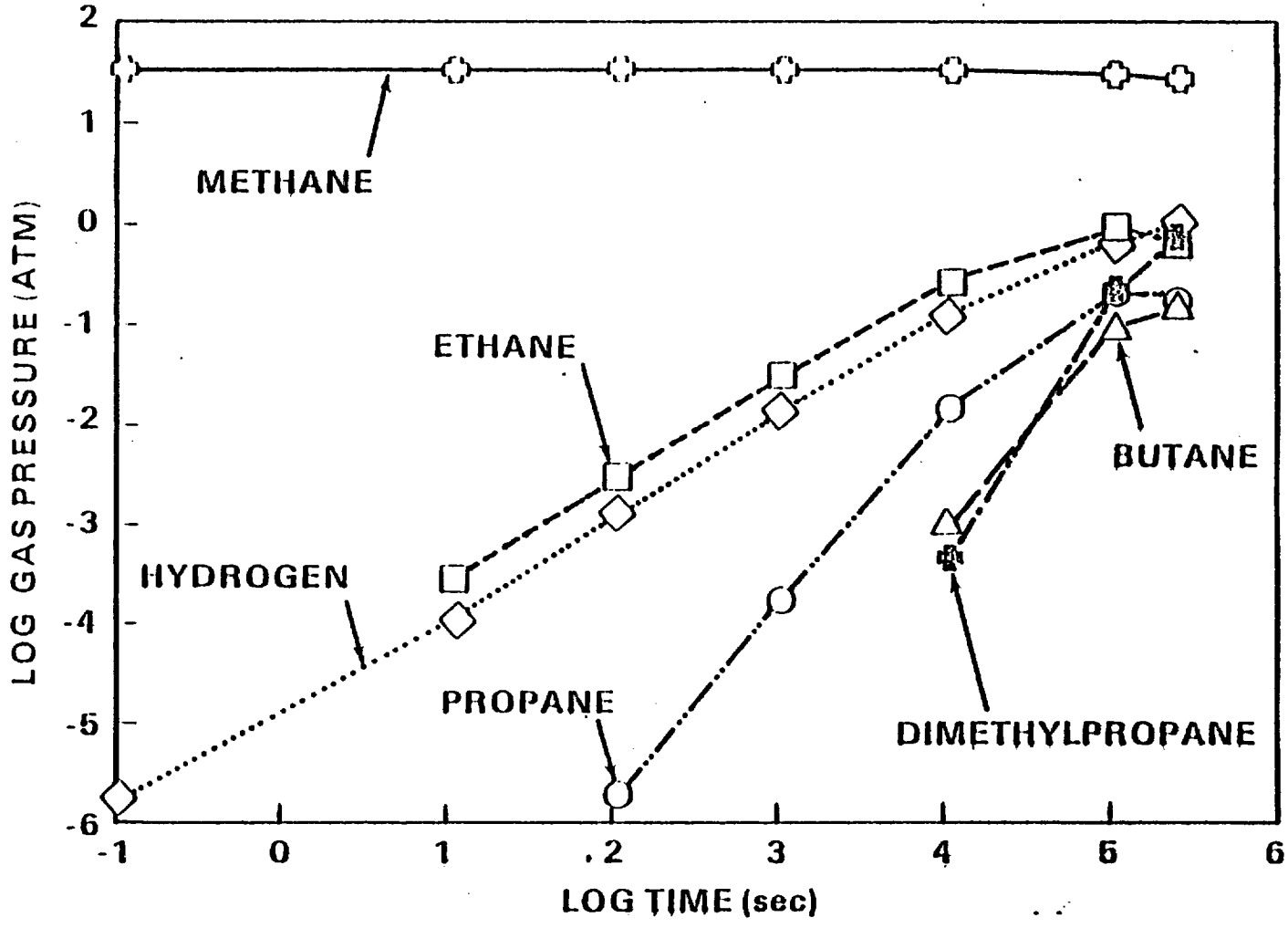
- $OH + CH_4 = CH_3 + H_2O$
- $OH + C_nH_{2n+2} = C_n H_{2n+1} + H_2O$
- $CH_3 + C_nH_{2n+1} = C_{n+1} H_{2n+4}$

IRRADIATION CONDITIONS AND PROPERTIES OF IRRADIATED SAMPLES

SAMPLE	WATER/GAS	DRY GAS	WET GAS
IRRADIATION TEMP. (°C)	150	150	150
DOSE RATE (Mrad/h)	1.1	1.2	1.2
TOTAL DOSE (Mrad)	77	88	88
GAS COMPOSITION (VOL. %)			
HYDROGEN	9.9	1.7	2.2
METHANE	84	91	90
NITROGEN	5.0	4.6	4.9
ARGON	0.38	2.5	2.4
MASS 44	0.45	0.18	0.23
2, 2-DIMETHYLPROPANE	0.52	0.0014	0.028
2, 2-DIMETHYLBUTANE	0.21	0.00038	0.012

RADIOLYTIC DECOMPOSITION OF METHANE

DOSE RATE = 1.1 Mrad/h



GAS COMPOSITION AND TOTAL PRESSURE AT 1.1 Mrad/h FOR 70h

	MAKSIM	RADIOL	STUDSVIK*	EXPERIMENT
	COMPOSITION (%)			
METHANE	86.5	86.4	83	86
HYDROGEN	3.3	3.3	14.2	6.1
DIMETHYLPROPANE	2.3	2.3	1.7	0.034
NITROGEN	5.0	5.0	---	5.5
	TOTAL PRESSURE (ATM)			
	29.1	28.7	32.6	32.7

*1.5 Mrad/h FOR 60h

CONCLUSIONS

- γ-RADIOLYSIS OF WATER CONTAINING METHANE GENERATES ORGANIC POLYMERS SIMILAR TO POLYETHYLENE
- POLYMERS CONTAIN A SMALL AMOUNT (1-3%) OF OXYGEN
- PARTICULATES ARE $> 0.1\ \mu m$ UNDER CONDITIONS TESTED
- AMOUNT AND NATURE OF POLYMERS DO NOT VARY WIDELY OVER RANGE OF CONDITIONS TESTED

Natural Histories

URANIUM ORE DEPOSITS AS A NATURAL ANALOG FOR THE BEHAVIOR OF URANIUM IN A NUCLEAR WASTE REPOSITORY LOCATED IN BASALT

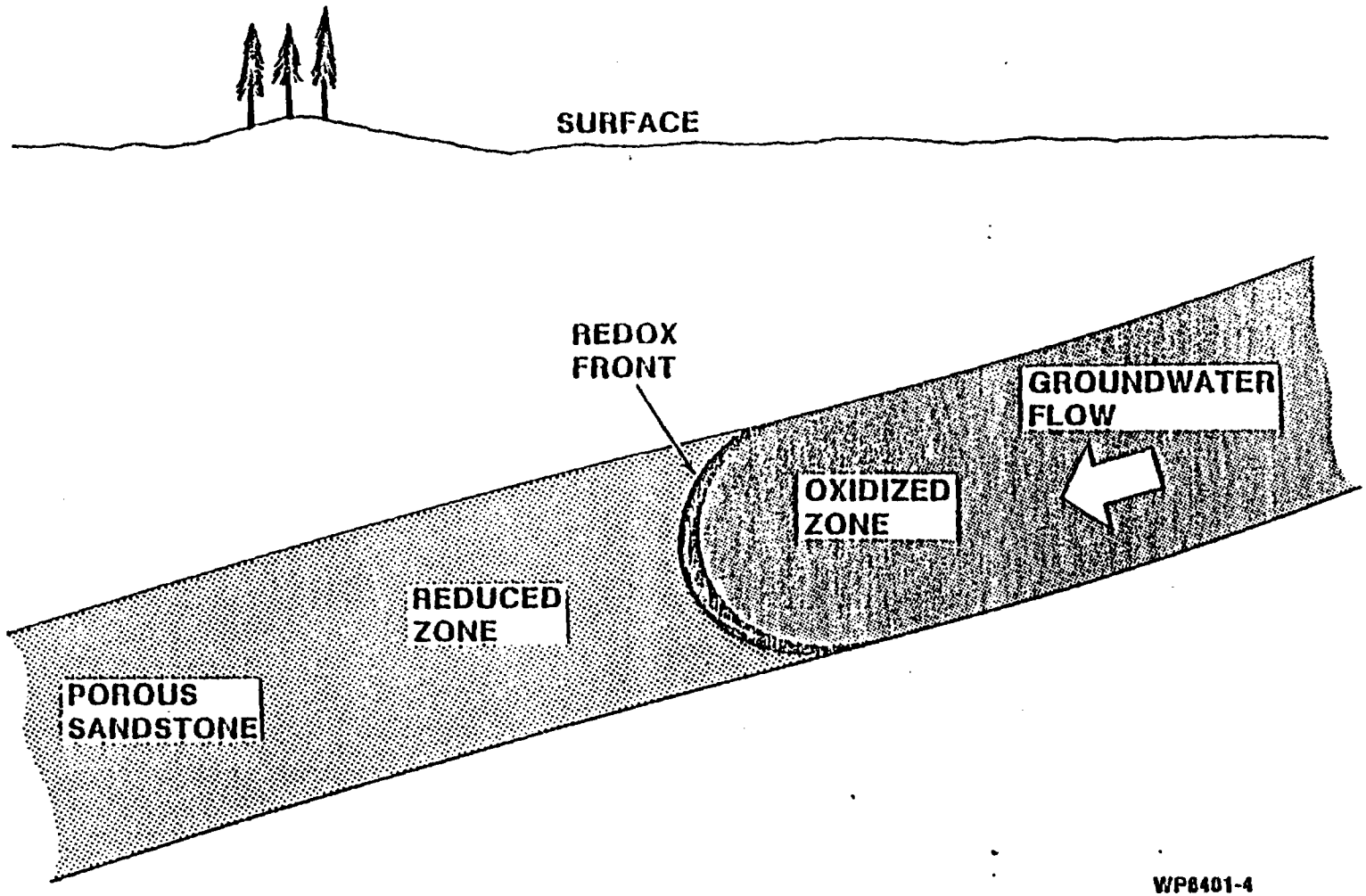
WP8401-2

U^{+4} / U^{+6} EQUILIBRIA

- $UO_2^{+2} + 4H^+ + 2e^- = U^{+4} + 2H_2O$
- E° = -0.33 VOLT
- U^{+6} STABLE IN OXIDIZING ENVIRONMENT
  FORMS AQUEOUS COMPLEXES WITH OH^-, CO_3^{-2} AND F^-
- U^{+4} STABLE IN REDUCING ENVIRONMENT
  PRECIPITATES AS OXIDE OR SILICATE MINERALS

WP6401-3

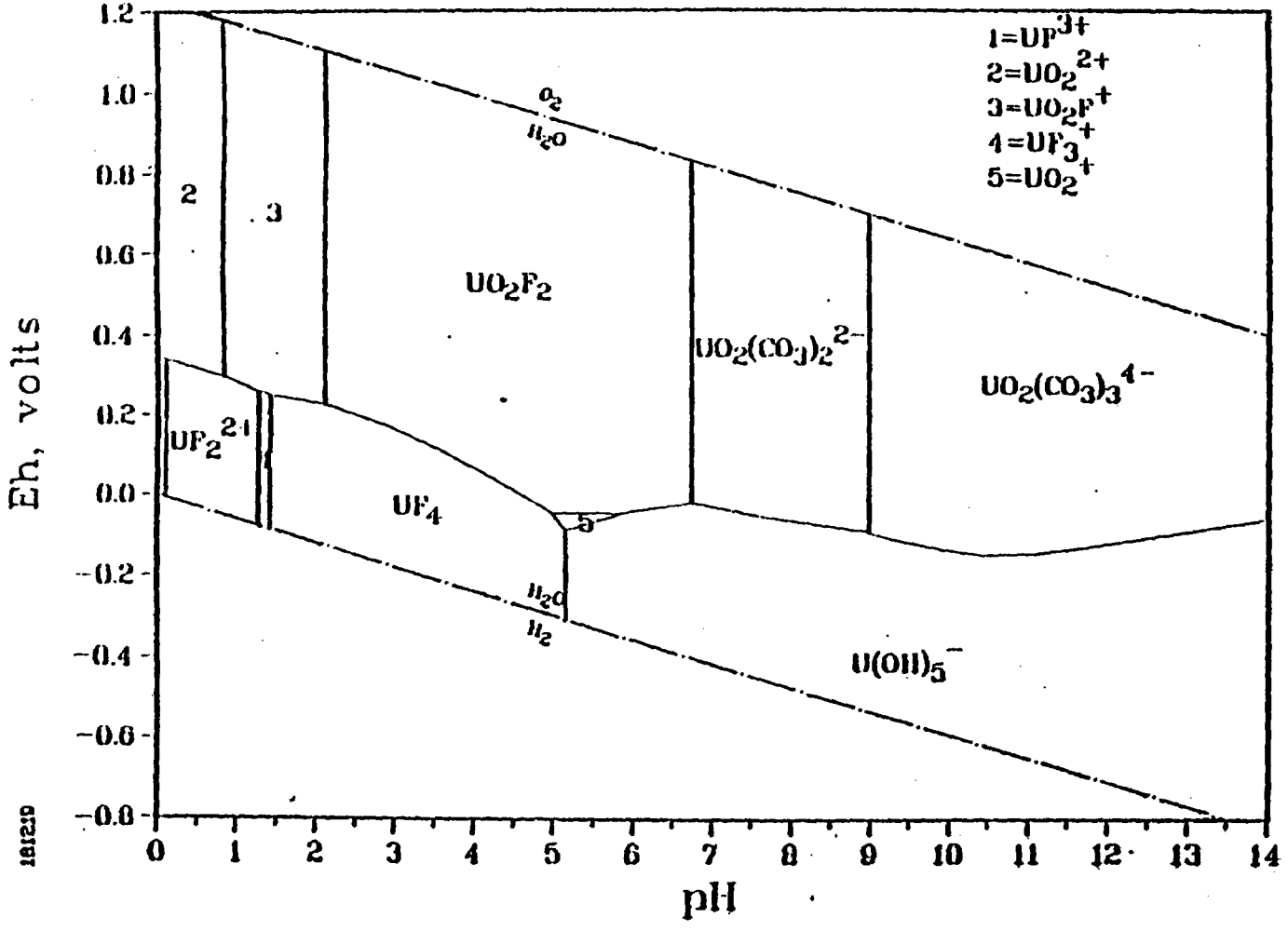
ROLL-FRONT URANIUM DEPOSIT



WP8401-4

Eh–pH DIAGRAM FOR URANIUM

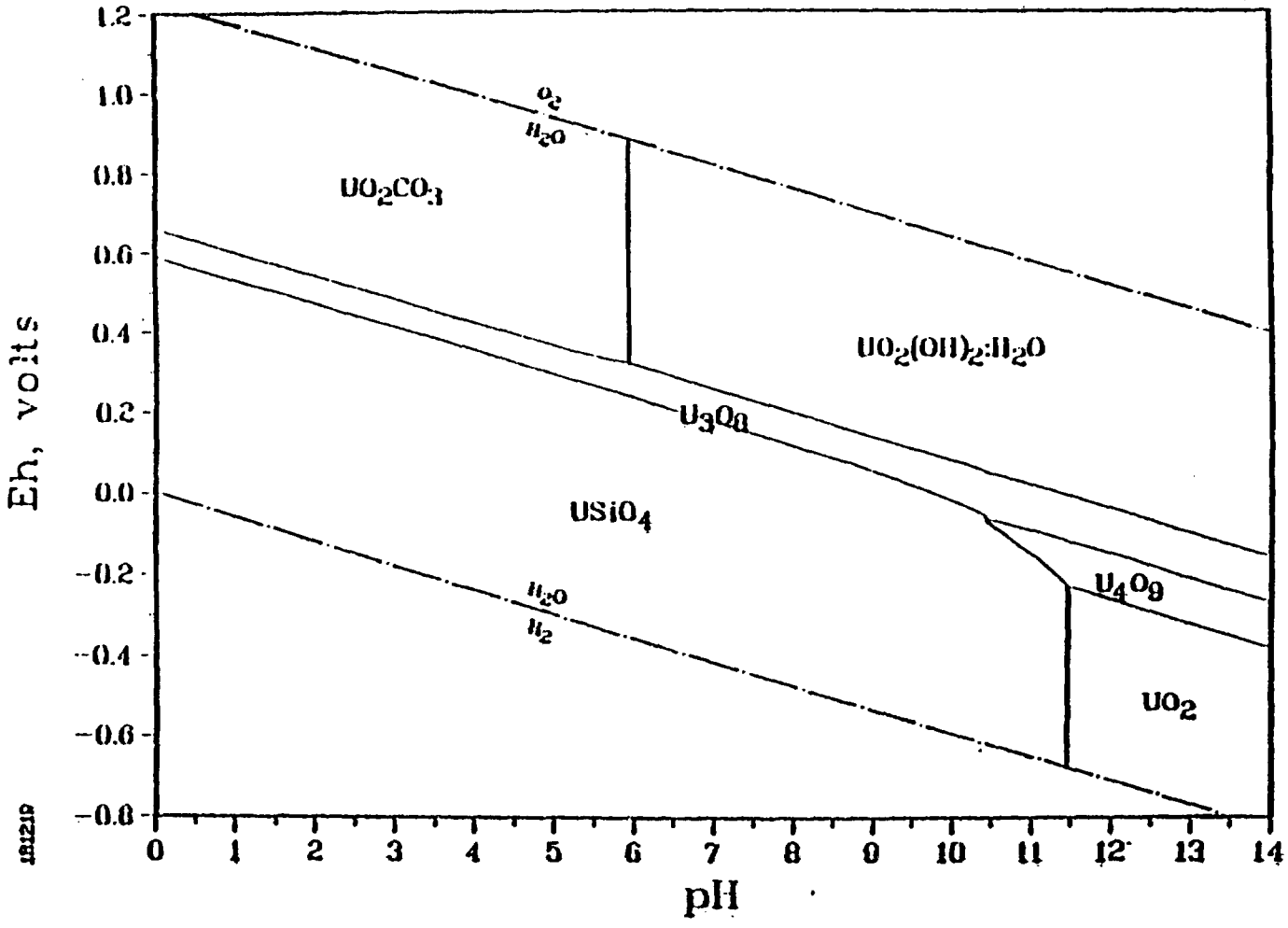
DOMINANT AQUEOUS SPECIES AT 298K



WP8401-13

Eh–pH DIAGRAM FOR URANIUM

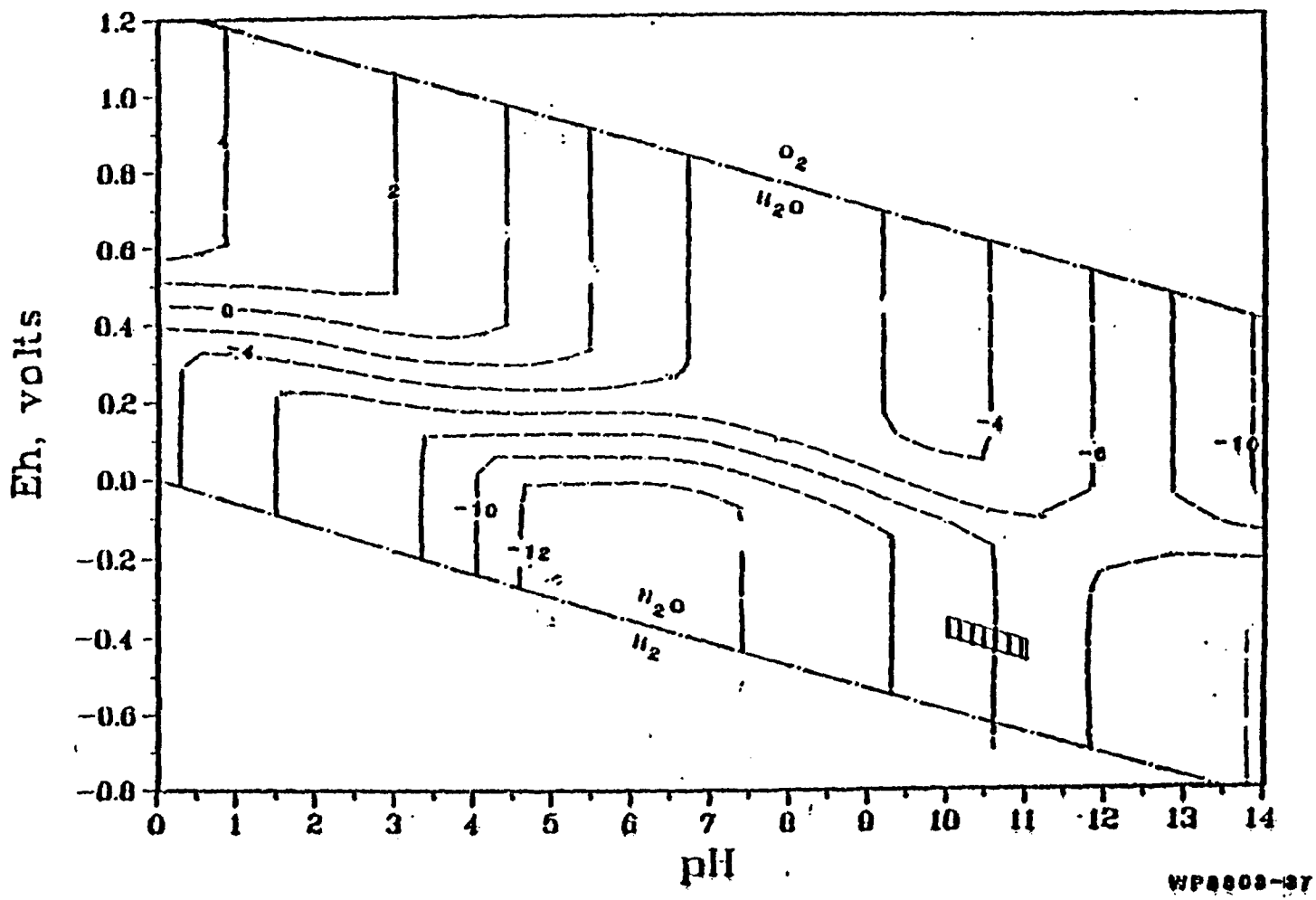
STABLE SOLIDS AT 298K



WP6401-14

Eh–pH DIAGRAM FOR URANIUM

LOG AQUEOUS CONCENTRATION CONTOURS



WP8803-37

SOLID PHASES CONTROLLING URANIUM SOLIBILITY

ORE DEPOSITS	SPENT FUEL	BOROSILICATE GLASS
UO_2 $U\ SiO_4$	UO_2 K-U SILICATES	UO_2 $U\ SiO_4$ K-U SILICATES

WP0401-5

CONCLUSION

URANIUM WILL HAVE VERY LOW MOBILITY IN AN ENVIRONMENT WHERE TETRAVALENT URANIUM IS THE STABLE FORM

FIELD STUDIES OF EXISTING NATURAL ALTERATION MINERALS AT HANFORD AS AN ANALOG FOR EVALUATION OF THE LONG-TERM STABILITY OF ALTERATION MINERALS WHICH FORM DURING WASTE/BARRIER/ROCK HYDROTHERMAL INTER-ACTION EXPERIMENTS

OBSERVED ALTERATION MINERALS

FIELD	EXPERIMENTAL
Fe - SMECTITE	Fe - SMECTITE
SILICA { QUARTZ, CHRISTOBALITE, TRIDYMITE }	SILICA { QUARTZ, CHRISTOBALITE, TRIDYMITE }
IRON OXYHYDROXIDE	IRON OXYHYDROXIDE
PYRITE	PYRITE
ZEOLITES { MORDENITE, CLINOPTILOLITE, PHILLIPSITE, ERIONITE, CHABAZITE }	ZEOLITES { MORDENITE, HEULANDITE, WAIRAKITE, FERRIERITE }
CELADONITE	ILLITE
APATITE	CHLORITE
GYPSUM	SCAPOLITE
	K - FELDSPAR

WP8401-10

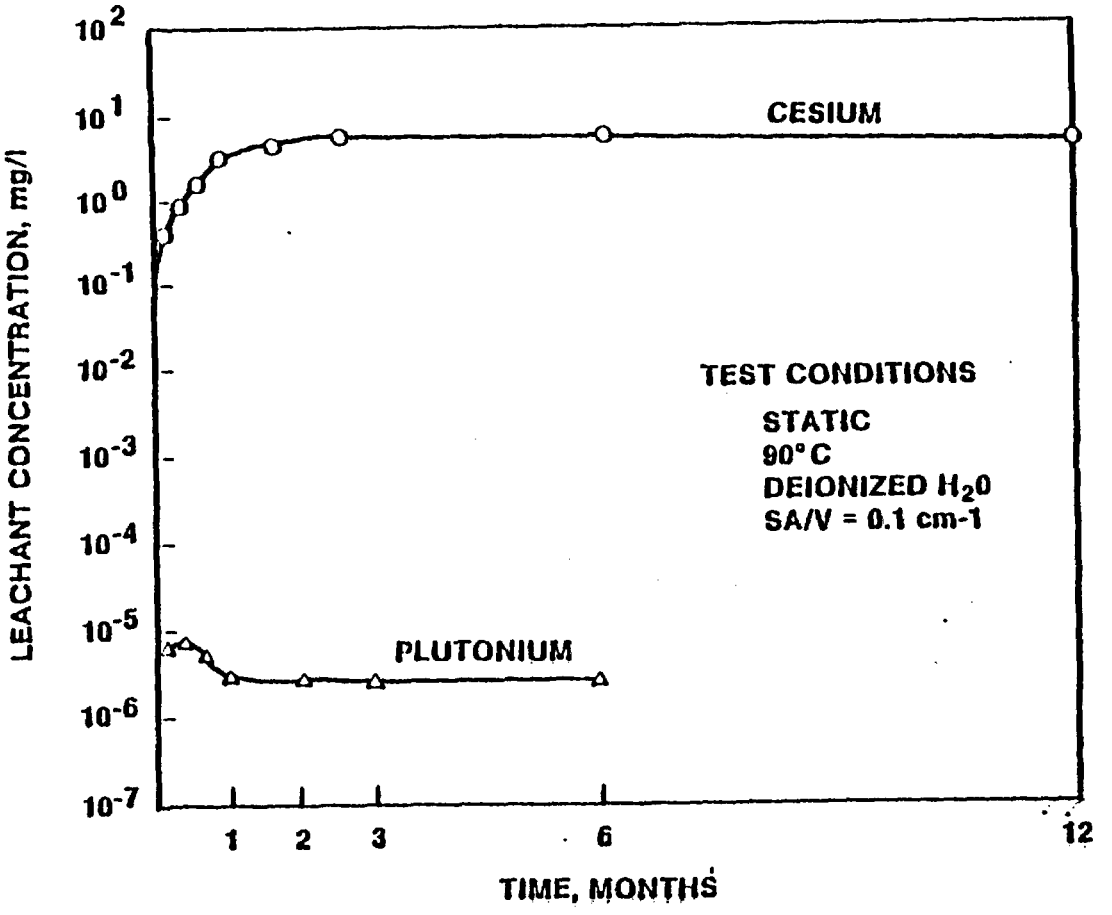
CONCLUSION

THE ALTERATION MINERALS WHICH FORM WITHIN THE THERMAL ZONE SURROUNDING A WASTE PACKAGE ARE STABLE MINERALS WHICH WILL PROBABLY PERSIST ON A REPOSITORY TIME SCALE

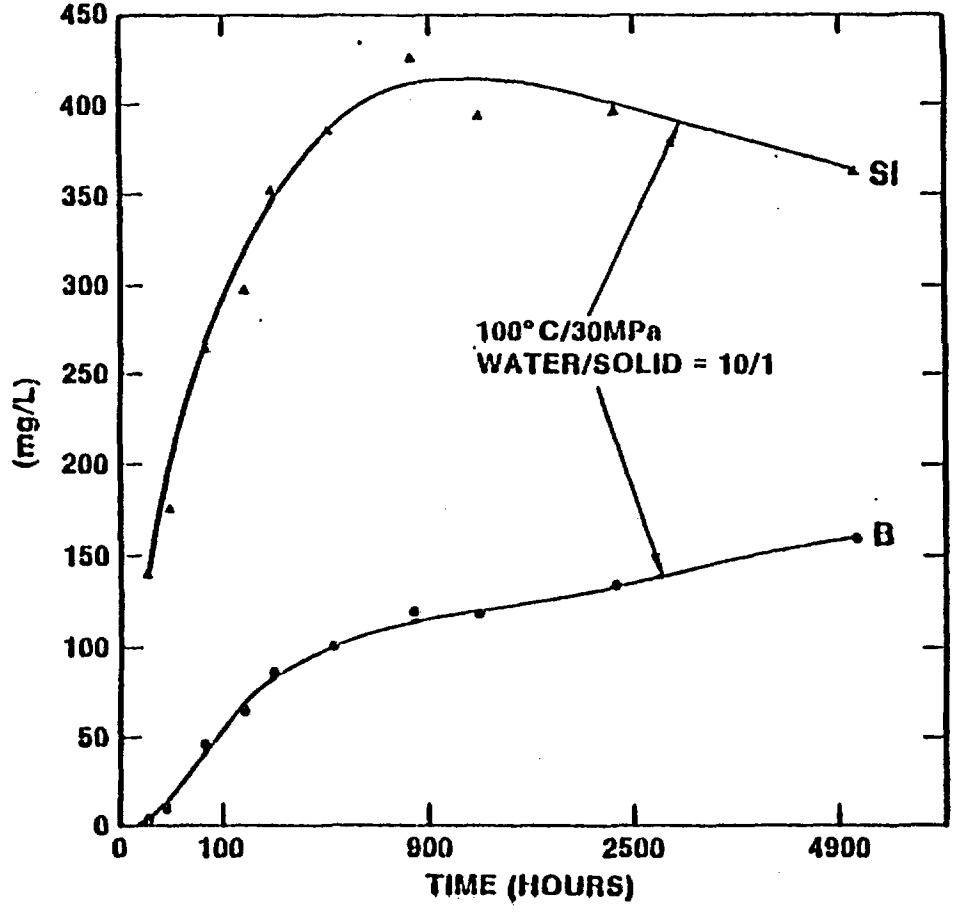
WP8401-11

Solubility

MCC-1 RESULTS FOR BOROSILICATE WASTE GLASS

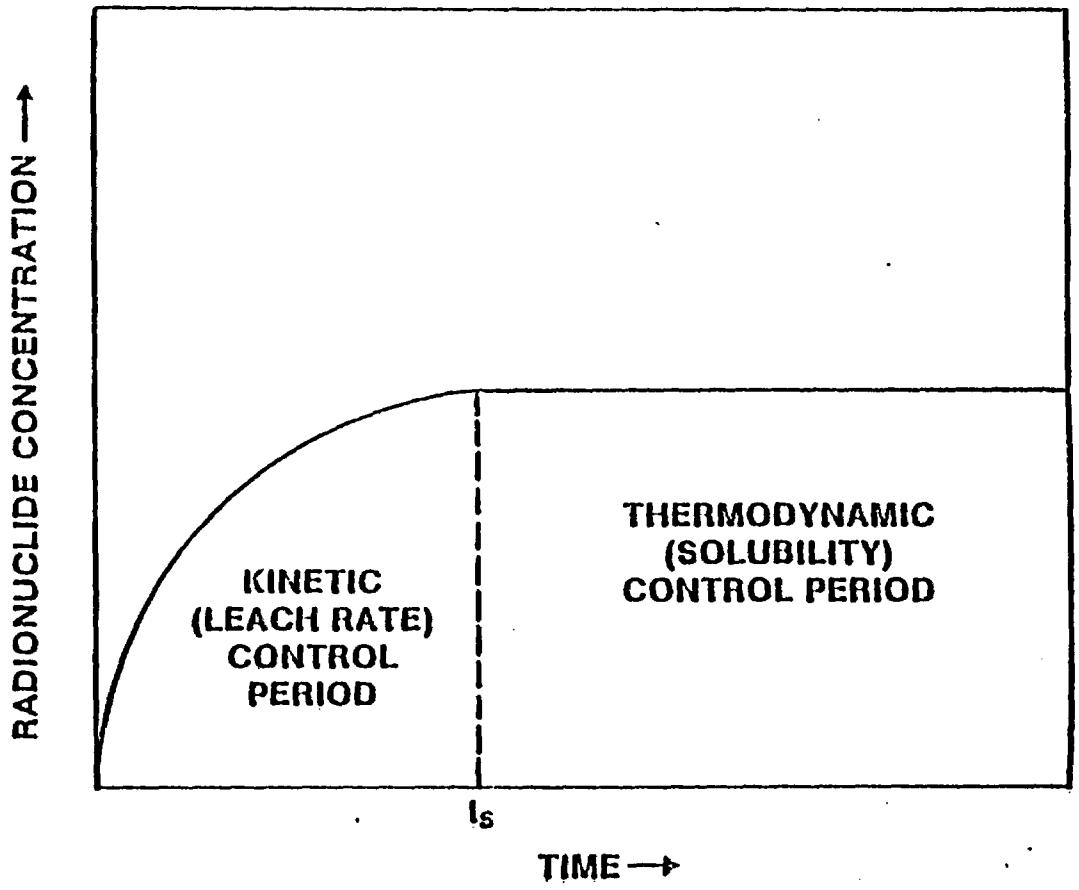


B AND Si SOLUTION CONCENTRATION VS TIME (BASALT/BOROSILICATE GLASS/GROUNDWATER)



WP8401-51

SCHEMATIC DIAGRAM OF DISSOLUTION/PRECIPITATION FOR WASTE FORM/WATER SYSTEM



WP8401-128

UTILITY OF SOLUBILITY AND LEACH RATE DATA IN WASTE PACKAGE DESIGN

SOLUBILITY ("STEADY STATE") DATA	LEACH RATE DATA
• DEFINES MAXIMUM POSSIBLE CONCENTRATION IN SOLUTION +	• DEFINES RATE WHICH SOLUTIONS ARE APPROACHING SOLUBILITY ("STEADY STATE") CONSTRAINTS
• WITH WATER FLOW RATES, DEFINES MAXIMUM POSSIBLE RELEASE RATES +	• REQUIRES KNOWN SURFACE AREA AND WATER FLOW RATE TO DEFINE RELEASE RATES
• TIME INDEPENDENT	• TIME DEPENDENT
• REQUIRED FOR LONG-TERM PERFORMANCE ASSESSMENT OF WASTE FORMS IN THE WASTE PACKAGE/REPOSITORY ENVIRONMENT	• SUITABLE FOR CHEMICAL DURABILITY SCREENING TESTS BETWEEN WASTE FORMS

• provide (more) source term for for field - must consider other processes to obtain (more) realistic estimates

11a

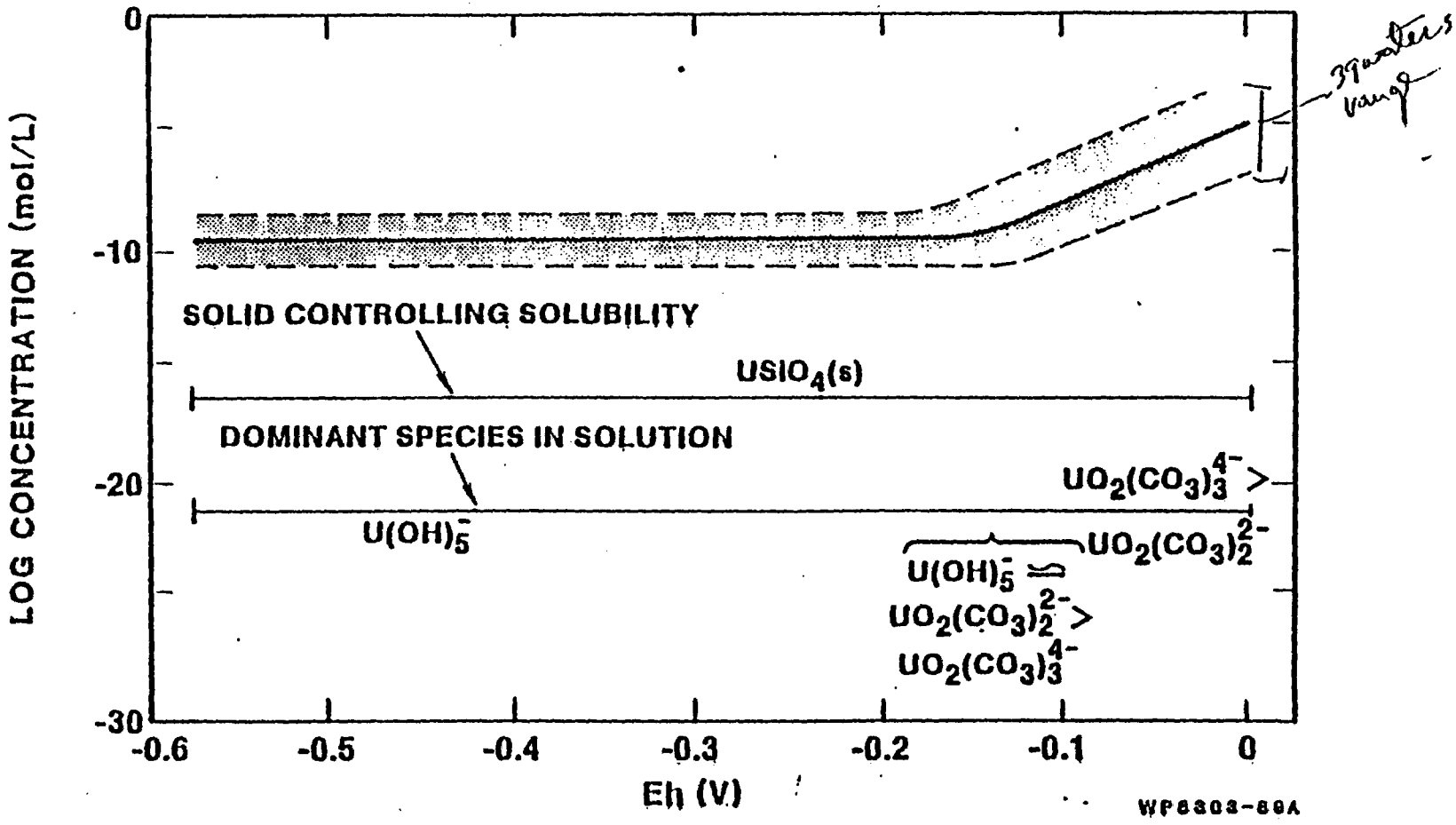
APPROACHES TO RADIONUCLIDE-SOLUBILITY DETERMINATIONS

- EXISTING LITERATURE DATA/CALCULATIONS

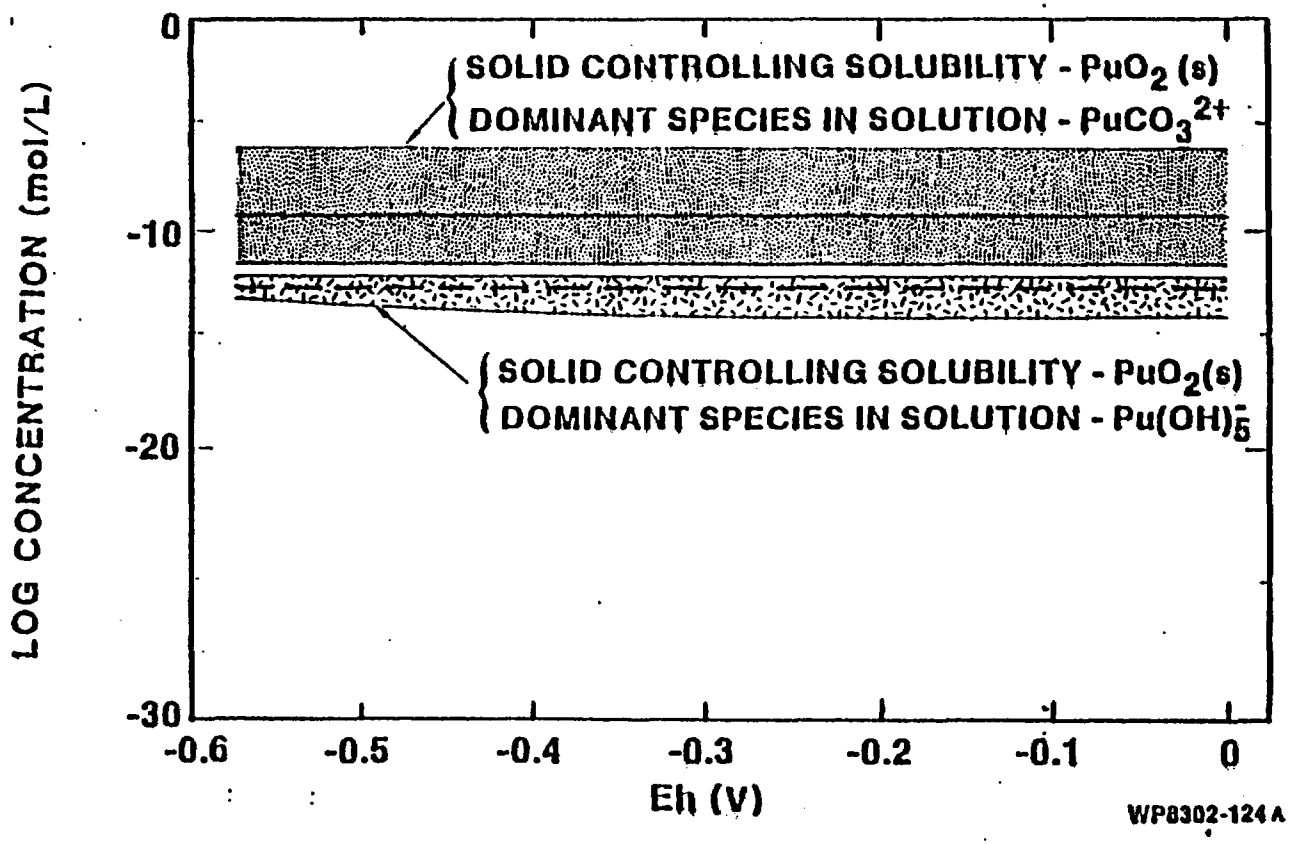
- EXPERIMENTAL DETERMINATION OF SOLUBILITY/ STEADY STATE CONCENTRATIONS
  - WASTE/BARRIER/BASALT INTERACTIONS
  - BASALT/BARRIER MATERIAL/RADIONUCLIDE INTERACTIONS

WP8401-129

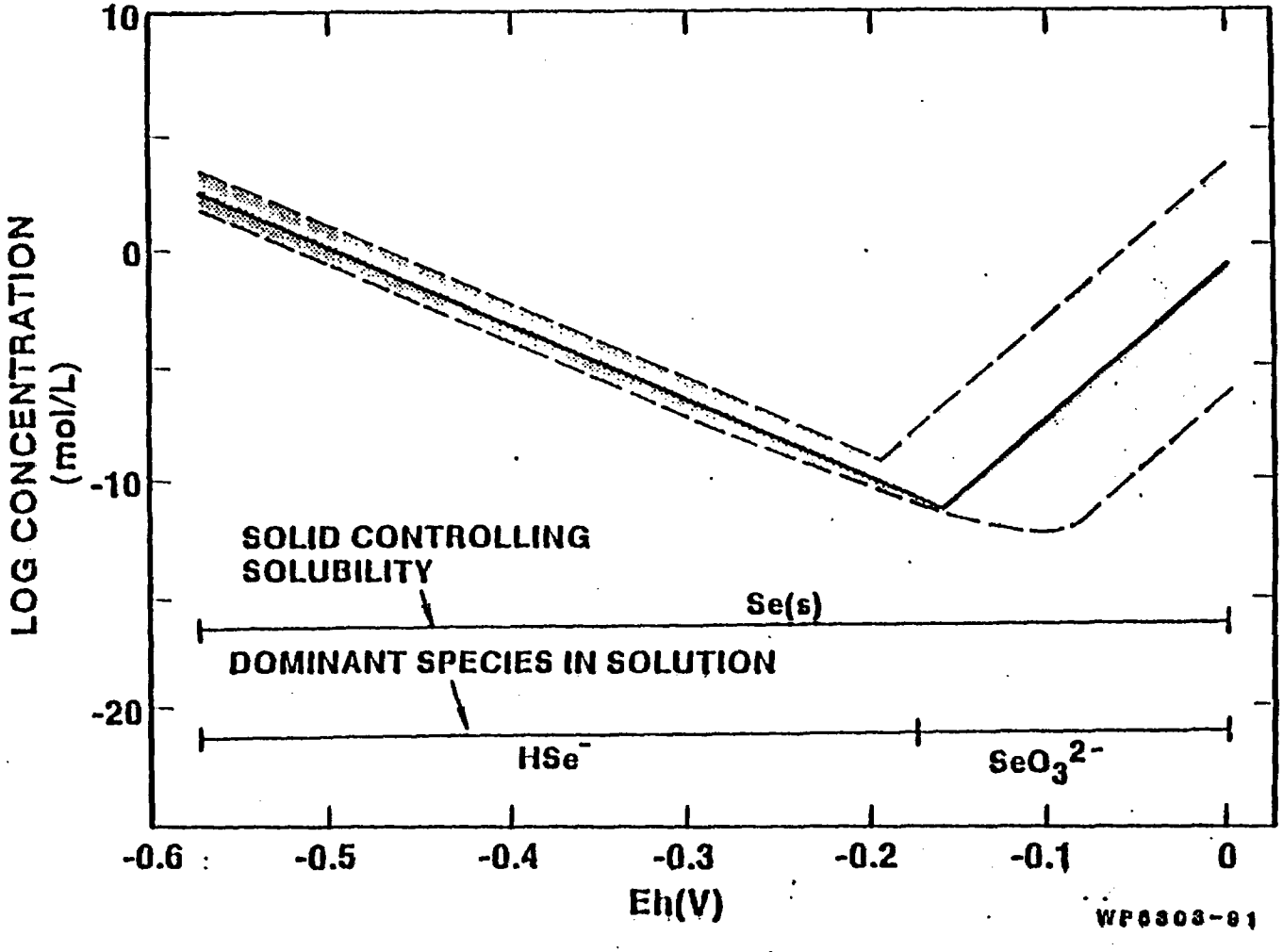
SOLUBILITY OF URANIUM AS A FUNCTION OF Eh AT 25° C



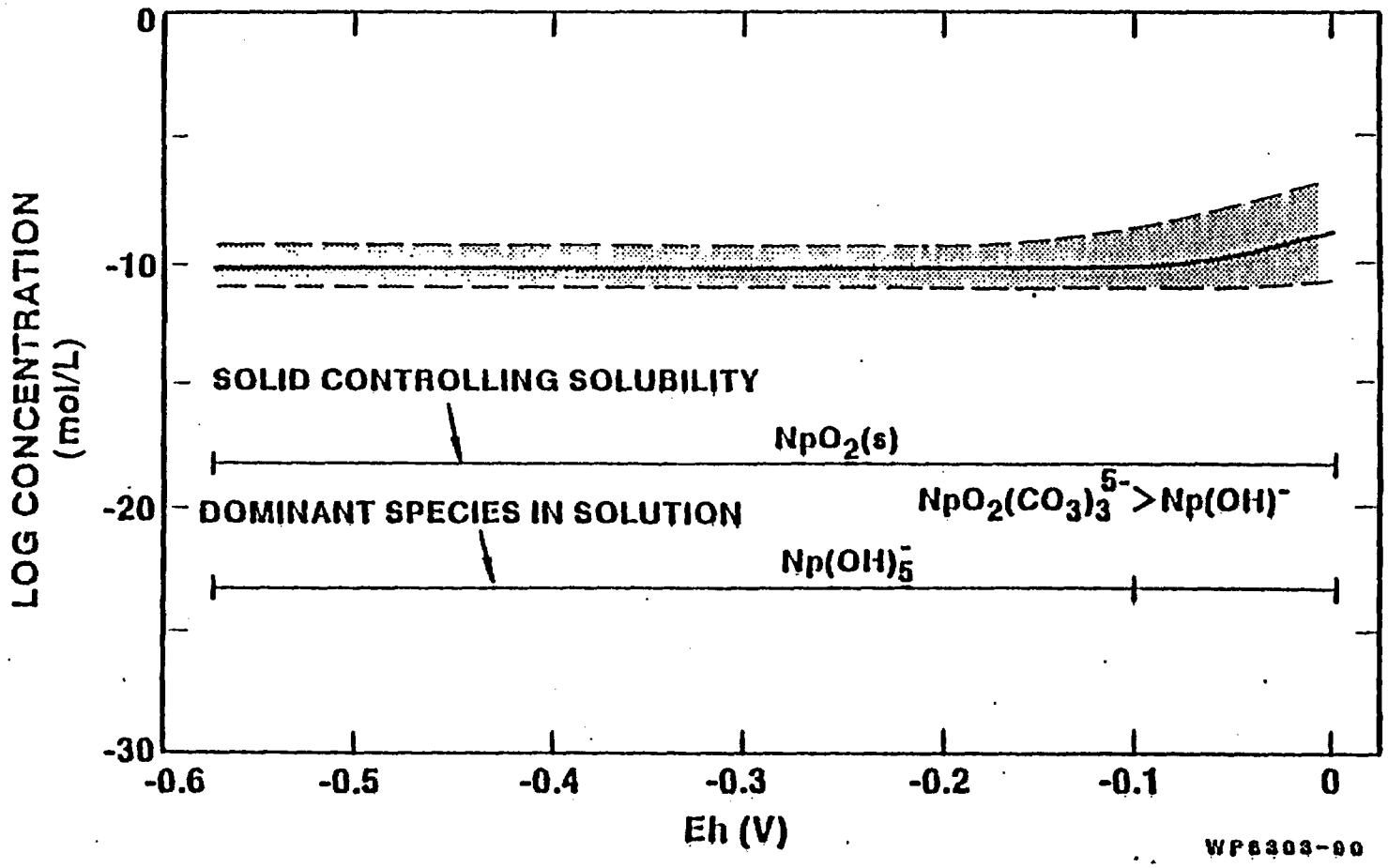
SOLUBILITY OF PLUTONIUM AS A FUNCTION OF Eh AT 25° C



SOLUBILITY OF SELENIUM AS A FUNCTION OF Eh AT 25° C



SOLUBILITY OF NEPTUNIUM AS A FUNCTION OF Eh AT 25° C



SUMMARY OF SOLUBILITY ESTIMATES FROM THERMODYNAMIC DATA

- IN GENERAL, OXIDE AND HYDROUS OXIDE SOLID PHASES PROVIDE SOLUBILITY CONTROL FOR MOST OF THE RADIONUCLIDES CONSIDERED
- THE PREDOMINANT SOLUBLE SPECIES FOR THE RADIONUCLIDES CONSIDERED ARE PREDICTED TO BE NEUTRAL OR ANIONIC HYDROXIDE AND CARBONATE COMPLEXES
- SELENIUM, PALLADIUM AND TIN SOLUBILITIES APPEAR TO BE A STRONG FUNCTION OF Eh UNDER REDUCING CONDITIONS

WP8401-139

LIMITATIONS TO THE EXCLUSIVE USE OF THERMODYNAMIC DATA

- ASSUMES PRIOR KNOWLEDGE OF SOLUBILITY LIMITING SOLID PHASE
- DETERMINATION OF RADIONUCLIDE SPECIATION AT EXPECTED CONCENTRATIONS IN CHEMICALLY COMPLEX SOLUTIONS RELEVANT TO REPOSITORY CONDITIONS IS NOT FEASIBLE NOR NECESSARY FOR ESTABLISHING DEFENSIBLE RADIONUCLIDE RELEASE RATES ?
- EXISTING SOLUBILITY DATA BASE IS LIMITED AND NON-SITE SPECIFIC
- EXTRAPOLATION OF 25°C SOLUBILITIES TO BEYOND 100°C IS QUESTIONABLE WITH ENTROPY/HEAT CAPACITY DATA to ~60°.
- MANY (MOST?) RADIONUCLIDES ENTER INTO SOLIDS IN TRACE AMOUNTS (SOLID SOLUTION) RATHER THAN FORMING THE MAJOR COMPONENT OF A SEPARATE PHASE evidence

WP8401-131

LIMITATIONS TO THE EXCLUSIVE USE OF THERMODYNAMIC DATA (Continued)

- SYNTHESIS OF RELEVANT RADIONUCLIDE-BEARING SOLIDS ARE DIFFICULT, OFTEN IMPOSSIBLE, WITH EXISTING TECHNOLOGY

Dale Perry's work

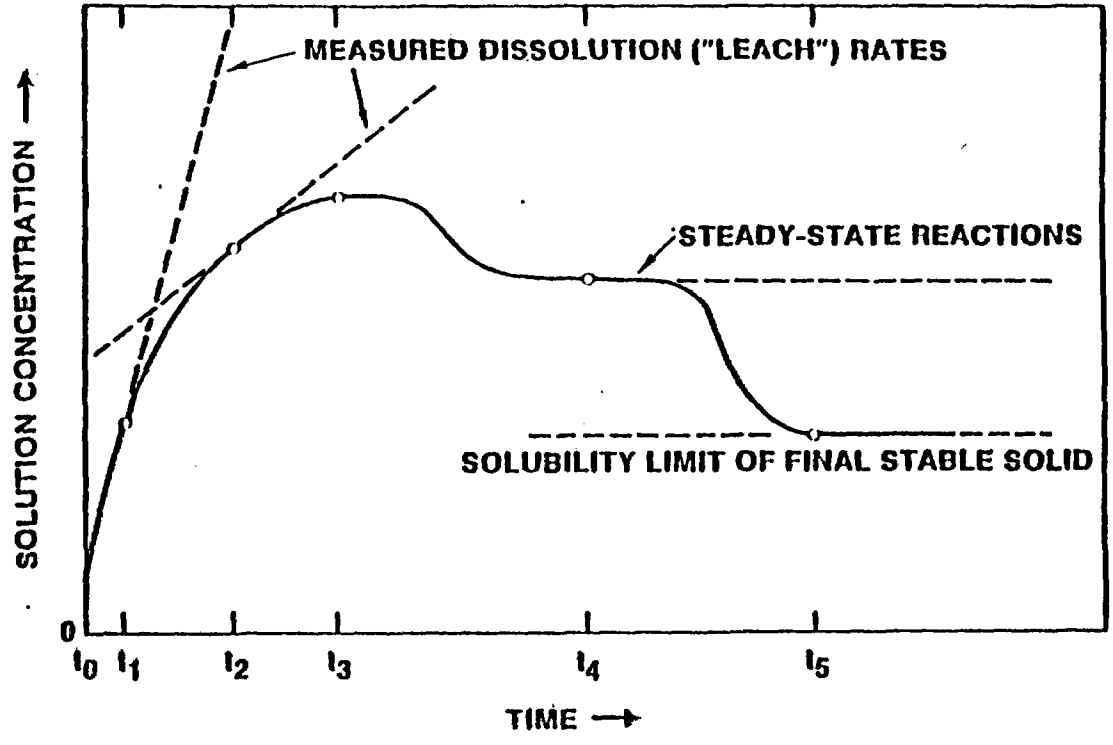
- RELIABLE SOLUBILITY MEASUREMENTS ABOVE 100°C ARE MEAGER FOR COMMON SOLIDS, REFLECTING DIFFICULTY OF OBTAINING HIGH TEMPERATURE DATA

- THERMODYNAMIC STABILITY OF A RADIONUCLIDE-BEARING SOLID WILL BE RELATED TO OVERALL CHEMICAL COMPOSITION OF THE SYSTEM BEING TESTED. INTERACTIONS WITH OTHER SOLIDS/BARRIER MATERIALS MAY BE IMPORTANT

- METASTABLE/NONEQUILIBRIUM REACTIONS ARE COMMON IN LABORATORY HYDROTHERMAL TESTS BELOW 300°C, AND ARE COMMON IN NATURE BELOW 100°C

WP8401-132

SOLID DISSOLUTION BEHAVIOR AS A FUNCTION OF TIME

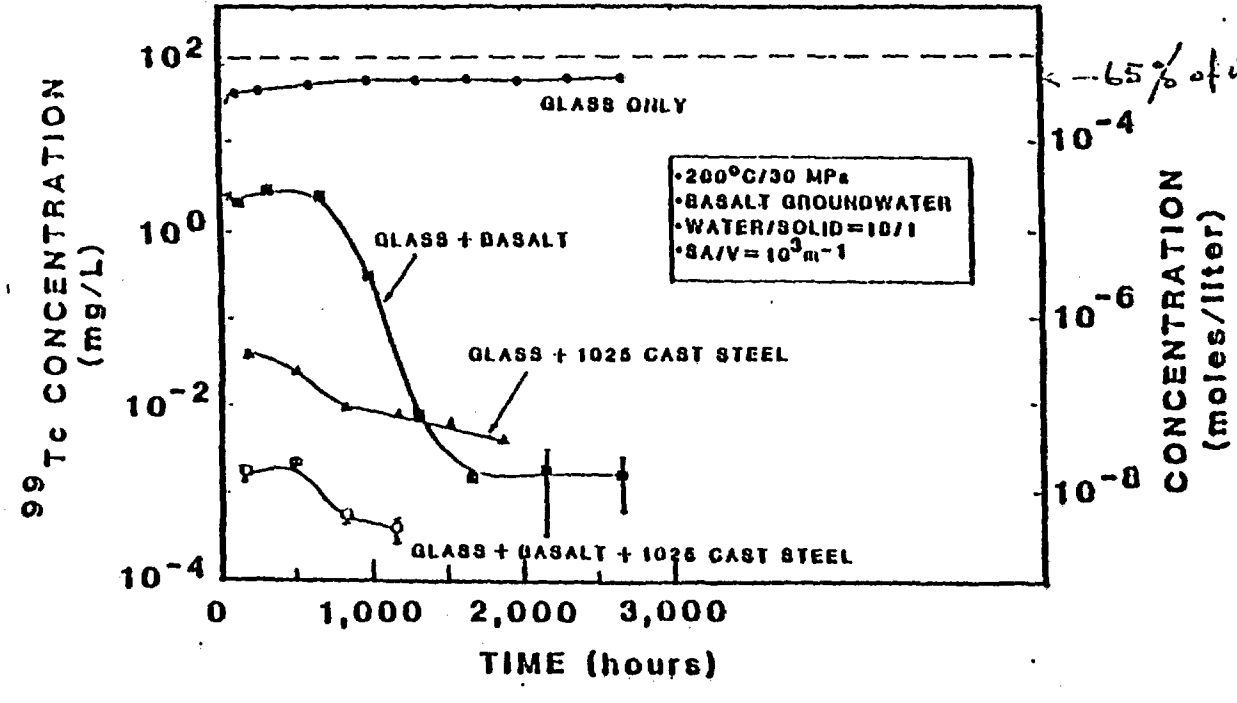


2K8312-5.9

STEADY-STATE CONCENTRATIONS
OF KEY RADIONUCLIDES FOR CHLW (76-68) GLASS

GR-4

(DASHED LINE IS CONCENTRATION REQUIRED
TO MEET 0.1 EPA LIMIT UNDER EXPECTED CONDITIONS)



← 65% of inventory. Tc in experiment

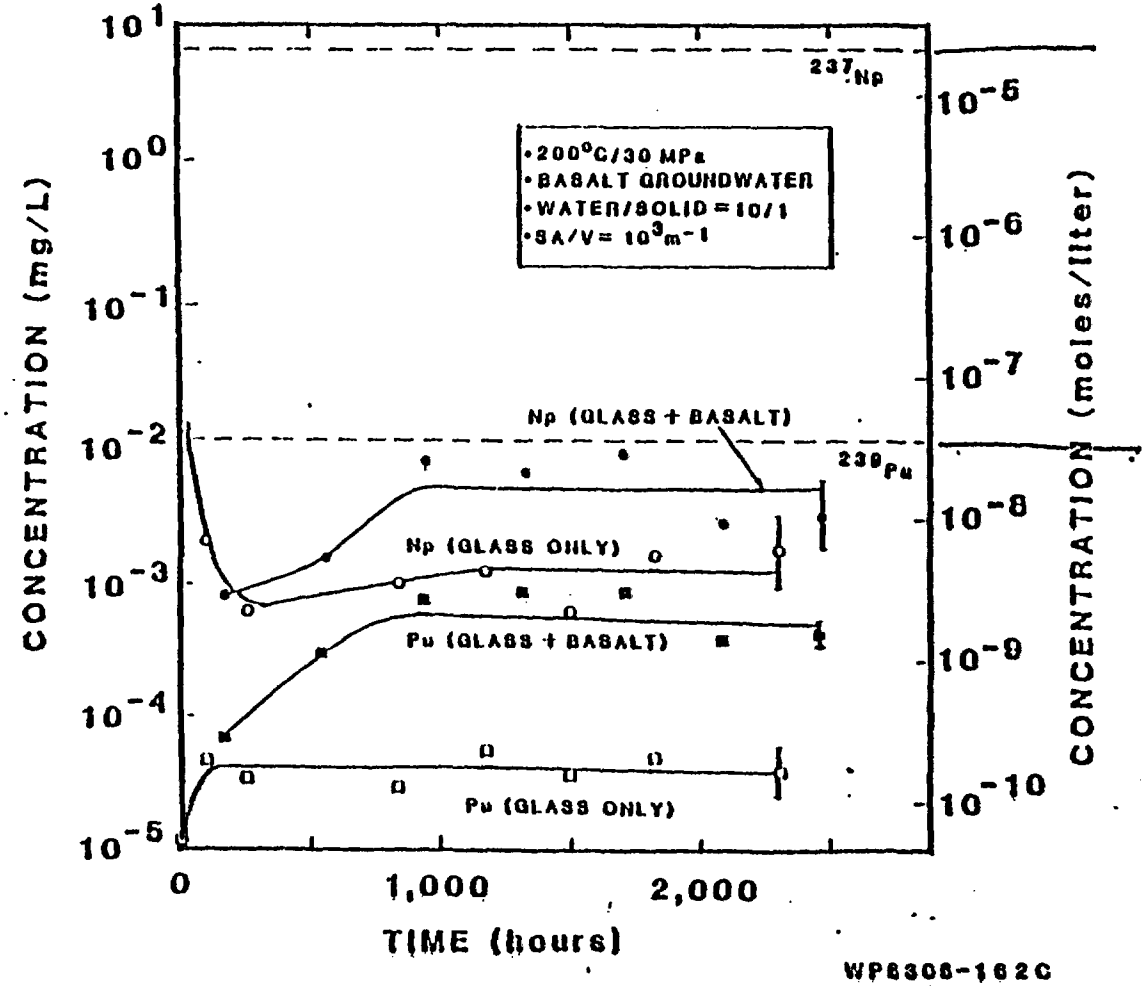
WP8306-163C

STEADY-STATE CONCENTRATIONS

OF KEY RADIONUCLIDES FOR CHLW (76-68) GLASS

GR-4

(DASHED LINES ARE CONCENTRATIONS REQUIRED TO MEET 0.1 EPA LIMIT UNDER EXPECTED CONDITIONS)

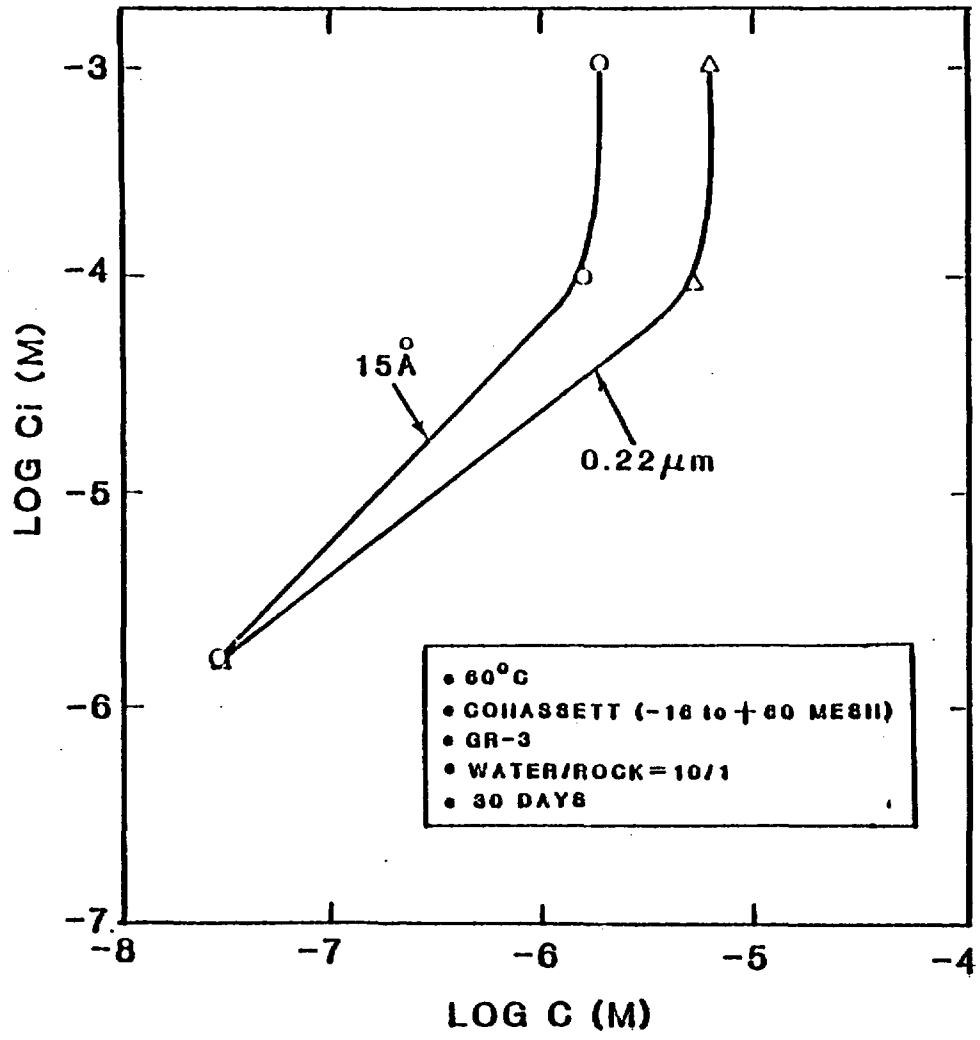


solubilities BWIP thinks it needs

WP8306-162C

STEADY STATE VS INITIAL U CONCENTRATIONS

UNDER REDUCING CONDITIONS



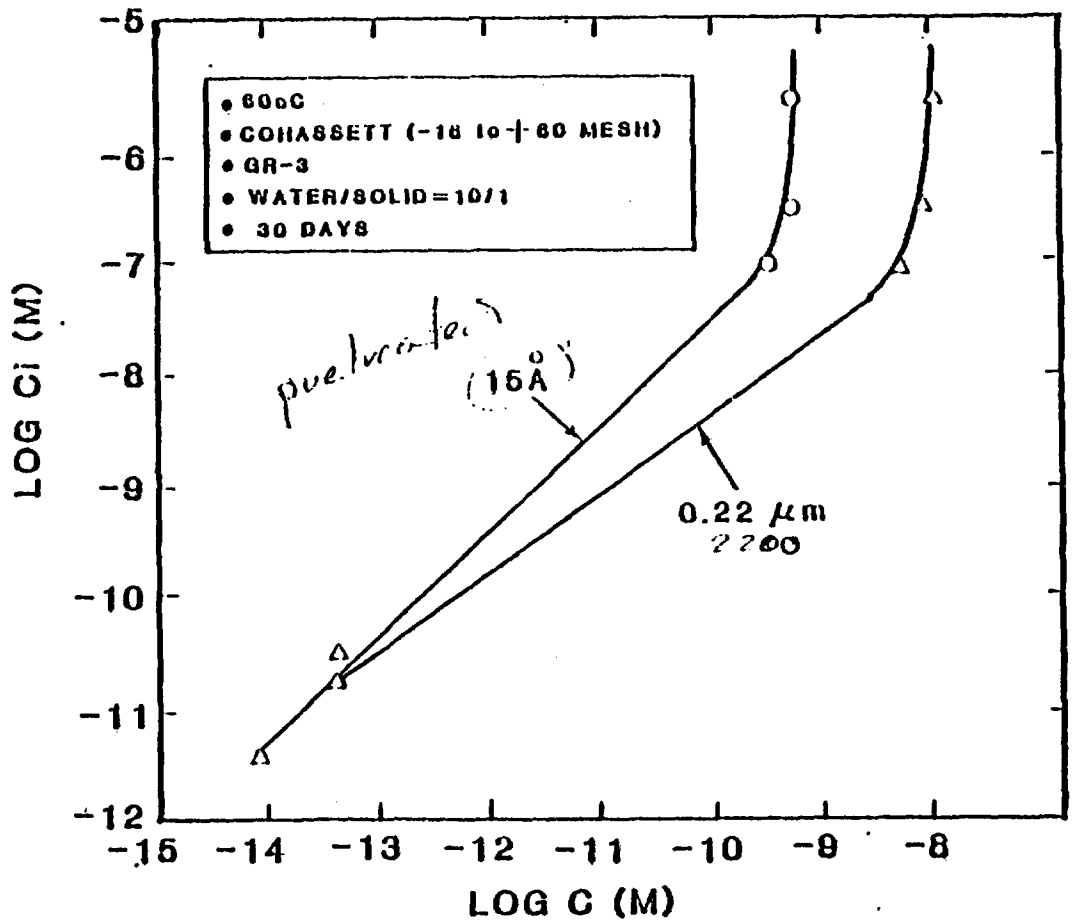
WP8401-114

hydrazine

calculated
10^{-10} (25°C.)

STEADY STATE VS INITIAL Pu SOLUTION CONCENTRATION

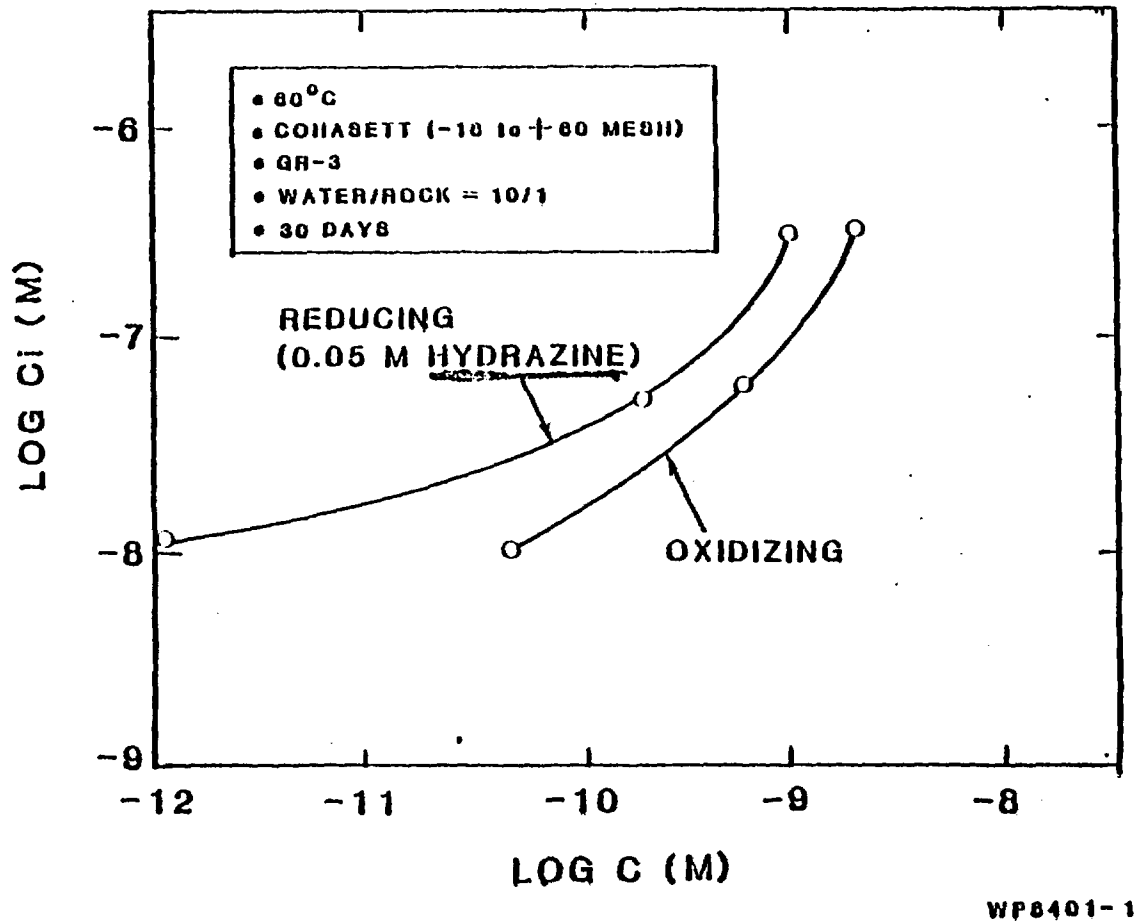
UNDER REDUCING CONDITIONS



calculated
10^{-9} to 10^{-12}

WP6401-116

STEADY STATE VS INITIAL Ra SOLUTION CONCENTRATIONS



WP8401-113

FUTURE EXPERIMENTAL WORK

- WASTE/BARRIER/ROCK INTERACTIONS

  CONTINUATION OF TRACER-LOADED BOROSILICATE GLASS/GROUNDWATER EXPERIMENTS AS A FUNCTION OF TEMPERATURE AND GAS CONCENTRATIONS (e.g., METHANE) WITH AND WITHOUT BASALT

  CONTINUATION OF FULLY LOADED BOROSILICATE GLASS AND SPENT FUEL HYDROTHERMAL TESTS WITH AND WITHOUT BASALT AND BARRIER ELEMENTS

  INITIATION OF OVER SATURATION HYDROTHERMAL TESTS WITH COLD WASTE FORMS, BASALT AND BARRIER MATERIALS

- BASALT/BARRIER MATERIAL/RADIONUCLIDE INTERACTIONS

  USE OF LOW OXYGEN ENVIRONMENT AND BASALT/GROUNDWATER INTERACTIONS INSTEAD OF HYDRAZINE TO ACHIEVE REDUCING CONDITIONS

  USE OF AS III/V TO ESTIMATE Eh OF EXPERIMENTAL SYSTEM

WP8401-136

FUTURE EXPERIMENTAL WORK (Continued)

LONG-TERM BATCH EXPERIMENTS TO MORE ACCURATELY DETERMINE STEADY STATE SOLUTION CONCENTRATION AND RADIONUCLIDE DISTRIBUTION BETWEEN SOLID AND LIQUID

USE OF CHEMICAL SPECIATION TECHNIQUES TO DETERMINE OXIDATION STATES OF MULTIVALENT RADIONUCLIDES IN SOLUTION AND SOLID (IF POSSIBLE)

EMPHASIS ON SOLIDS CHARACTERIZATION TO IDENTIFY RADIONUCLIDE-BEARING PRECIPITATES

we are doing
would like
to follow

WP8401-137

SUMMARY

- LEACH RATE DATA CANNOT BE USED TO EVALUATE LONG-TERM WASTE FORM PERFORMANCE BECAUSE IT IS AN INITIAL, TRANSITORY PHENOMENON.

- SOLUBILITY/STEADY-STATE CONCENTRATION LIMITS, IMPOSED BY RADIONUCLIDE-BEARING SOLIDS, REPRESENTS A TESTABLE AND DEFENSIBLE APPROACH TO EVALUATING LONG-TERM WASTE FORM PERFORMANCE.

- INITIAL ESTIMATES OF SOLUBILITY-LIMITED CONCENTRATIONS FOR RADIONUCLIDES HAVE BEEN BASED ON EXISTING THERMODYNAMIC AND LABORATORY DATA. THIS DATA WILL BE SUPERCEDED BY SITE-SPECIFIC LABORATORY TEST RESULTS.

WP0401-133

SUMMARY (Continued)

- THE PRIMARY APPROACH OF THE BWIP IS ON DETERMINATION STEADY-STATE RADIONUCLIDE CONCENTRATIONS, OBTAINED ON ACTUAL REFERENCE WASTE FORMS AND BARRIER MATERIALS, OVER THE RANGE OF TEST CONDITIONS REVELANT TO A REPOSITORY LOCATED IN BASALT

- STEADY-STATE/SOLUBILITY MEASUREMENT WILL BE GATHERED PRIMARILY FROM UNDERSATURATED (REALISTIC) CONDITIONS, SUPPORTED AND BRACKETED BY MEASUREMENTS OBTAINED FROM OVERSATURATED CONDITIONS

- RADIONUCLIDE RELEASE RATES WILL BE PROPORTIONAL TO THE PRODUCT OF STEADY-STATE CONCENTRATION AND GROUNDWATER FLOW RATE (PROPORTIONAL TO ONLY STEADY-STATE CONCENTRATION FOR DIFFUSIONAL FLOW CASE)

WP8401-134

Collocals

STATUS OF SITE CHARACTERIZATION

- EMPHASIS ON NATURAL COLLOIDS
  - MINERALOGICAL IDENTIFICATION
  - DEMONSTRATION OF STABILITY
  - DETERMINATION OF SIZE DISTRIBUTION
- LIMITATIONS TO CURRENT RESEARCH
  - CONTAMINATION BY DRILLING MUDS/PIPES
  - RESUSPENSION OF FILTERED COLLOIDS
  - MECHANICAL GENERATION OF COLLOIDS
- PREVIOUS STUDIES OF NATURAL (BUT NON-BASALTIC) SYSTEMS
  - NERETNIEKS (1978)

    COLLOIDS $\leq$ 0.6 ppb
  - BARNES (1976)

    Al_2O_3 COLLOIDS $\leq$ 3.0 ppb

WP8401-67

FACTORS CONTROLLING THE RADIONUCLIDE CARRYING CAPACITY OF REPOSITORY GROUNDWATER

SOLUBILITY - LIMITED CONCENTRATION

\- SORPTION OF RADIONUCLIDES

\+ COLLOIDS - CONTAINING RADIONUCLIDES

= TOTAL 'CONCENTRATION' OF RADIONUCLIDES IN GROUNDWATER

WP8401-63

VARIOUS CLASSIFICATIONS OF COLLOIDS

THERMODYNAMIC

- LYOPHILIC (STABLE) COLLOIDS
- LYOPHOBIC (METASTABLE) COLLOIDS
  (TYPICAL OF COLLOIDS IN GEOLOGIC SYSTEMS)

FORMATION PROCESS

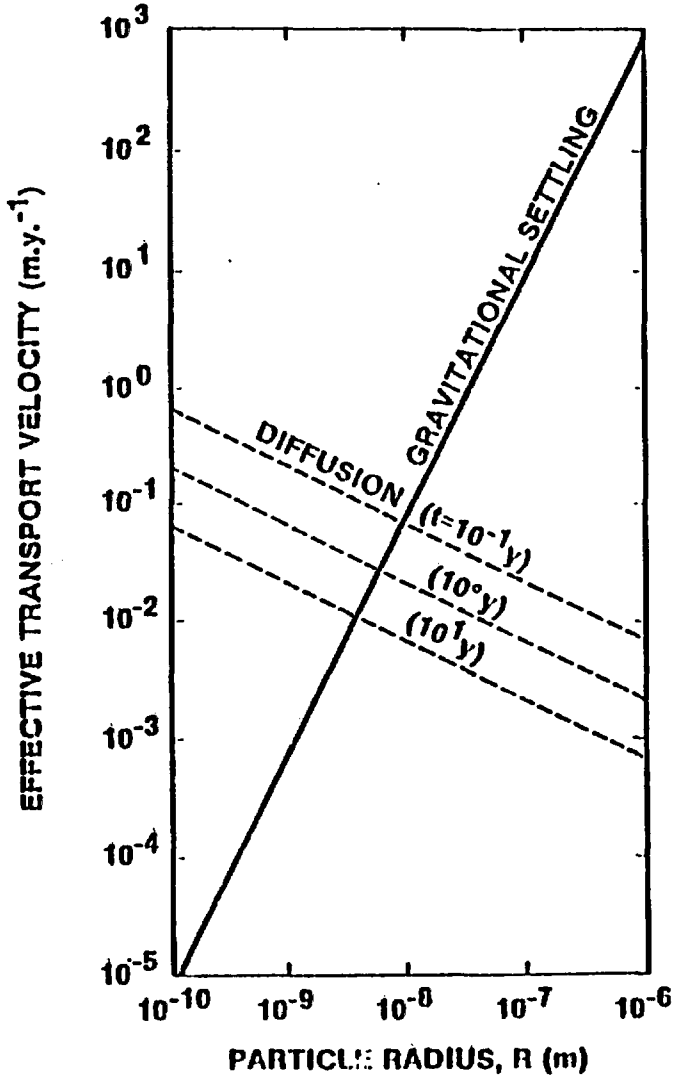
- PHYSICAL DISAGGREGATION/WEATHERING
  (e.g. CLAYS, 'RUST')
- PRECIPITATION
  (e.g., OXIDES OF Si, Al, Fe)

COMPOSITION

- TRUE COLLOIDS - PARTICLES IN WHICH A RADIONUCLIDE IS A STRUCTURAL COMPONENT (e.g. Pu HYDROXIDE POLYMERS)
- PSEUDO-COLLOIDS - PARTICLES ONTO WHICH A RADIONUCLIDE IS SORBED (e.g. CLAYS, SILICA, IRON OXIDES)

WP8401-64

EFFECTIVE TRANSPORT VELOCITIES VERSUS PARTICLE RADIUS (FROM APPS, et al., 1982)



WP8401-05

COLLOID RESEARCH AT THE BWIP

- CHARACTERIZATION OF POSSIBLE EXISTING COLLOIDS IN SITE GROUNDWATER
- IDENTIFICATION OF RADIONUCLIDE-BEARING COLLOIDS FORMED IN WASTE/BARRIER/ROCK TESTS
- ~~EVALUATION OF POTENTIAL TRANSPORT OF RADIONUCLIDE-BEARING COLLOIDS BY LABORATORY AND FIELD TESTS~~
- EVALUATION OF POTENTIAL TRANSPORT OF RADIONUCLIDE-BEARING COLLOIDS BY LABORATORY AND FIELD TESTS
- DETERMINATION OF RADIONUCLIDE DISTRIBUTION/ BETWEEN GROUNDWATER, COLLOIDS, AND GEOLOGIC SOLIDS

WP8401-66

STATUS OF SITE CHARACTERIZATION

- EMPHASIS ON NATURAL COLLOIDS
  - MINERALOGICAL IDENTIFICATION
  - DEMONSTRATION OF STABILITY
  - DETERMINATION OF SIZE DISTRIBUTION
- LIMITATIONS TO CURRENT RESEARCH
  - CONTAMINATION BY DRILLING MUDS/PIPES
  - RESUSPENSION OF FILTERED COLLOIDS
  - MECHANICAL GENERATION OF COLLOIDS
- PREVIOUS STUDIES OF NATURAL (BUT NON-BASALTIC) SYSTEMS
  - NERETNIEKS (1978)

    COLLOIDS $\leq$ 0.6 ppb
  - BARNES (1976)

    Al_2O_3 COLLOIDS $\leq$ 3.0 ppb

STATUS OF WASTE/BARRIER/ROCK TEST RESULTS

- DETERMINE TENDANCY FOR COLLOID FORMATION

  Pu~ Np > Tc > U.

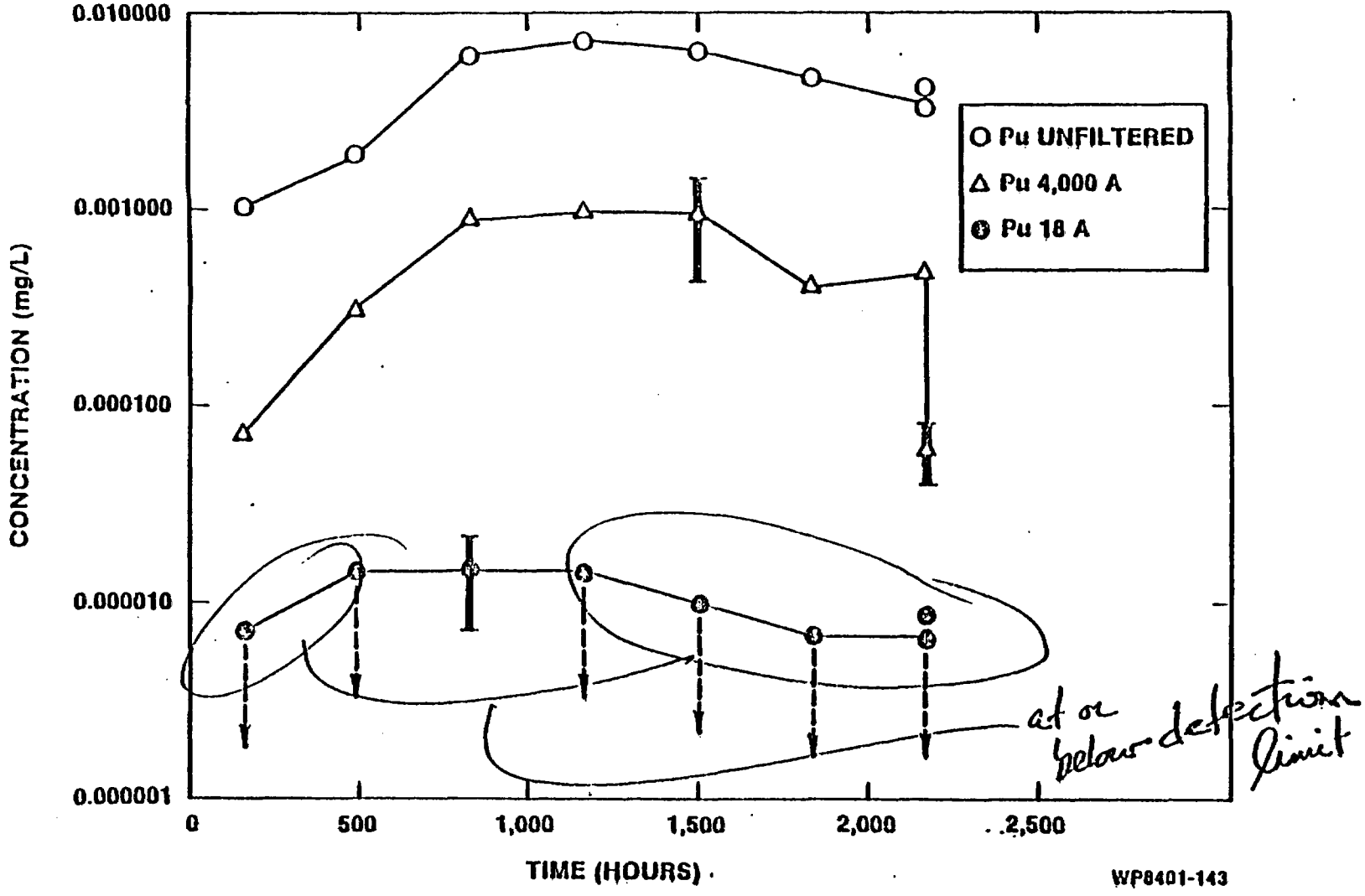
- EVALUATE THE EFFECT OF BARRIER MATERIALS ON FORMATION OF RADIONUCLIDE-BEARING COLLOIDS

- ESTABLISH COLLOID SIZE DISTRIBUTION FROM SOLUTION DATA
  - UNFILTERED
  - 400 nm FILTERED
  - 1.8 nm FILTERED

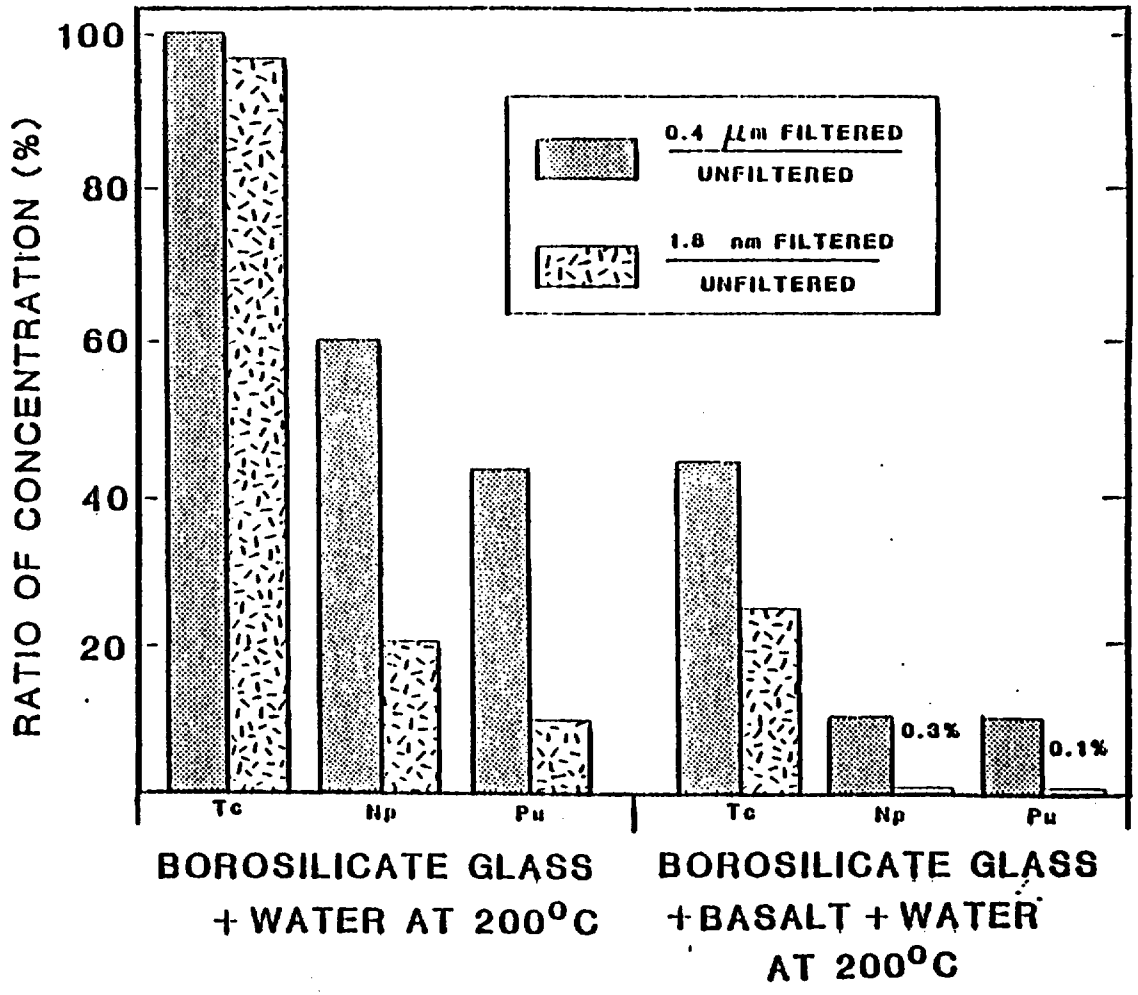
- CHARACTERIZE COMPOSITION AND MINERALOGY OF FILTERED COLLOIDS

WP8401-68

CONCENTRATIONS OF Pu IN HYDROTHERMAL TEST SOLUTION WITH GLASS + BASALT + GROUNDWATER AT 200° C (EFFECT OF FILTRATION)



FILTRATION EFFECT ON RADIONUCLIDE CONCENTRATIONS



WP6312-104

STATUS OF COLLOID SORPTION STUDIES

STATIC TESTS

- MEASUREMENT OF SORPTION FOR Se, Tc, ~~Tb~~ Pa, U, and Np ON SILICA AND BENTONITE COLLOIDS — L. Amos (PNL)
- DETERMINATION OF REDISTRIBUTION OF SORBED RADIONUCLIDES BETWEEN COLLOIDS AND BASALT
- EVALUATE EFFECT OF TEMPERATURE AND RADIONUCLIDE CONCENTRATION ON COLLOID FORMATION

DYNAMIC TESTS

- EVALUATE EFFECT OF FLOW RATE ON SORPTION BEHAVIOR AND COLLOID STABILITY
- DETERMINATION OF RADIONUCLIDE REDISTRIBUTION AND SILICA COLLOID SORPTION IN THE PRESENCE OF BASALT

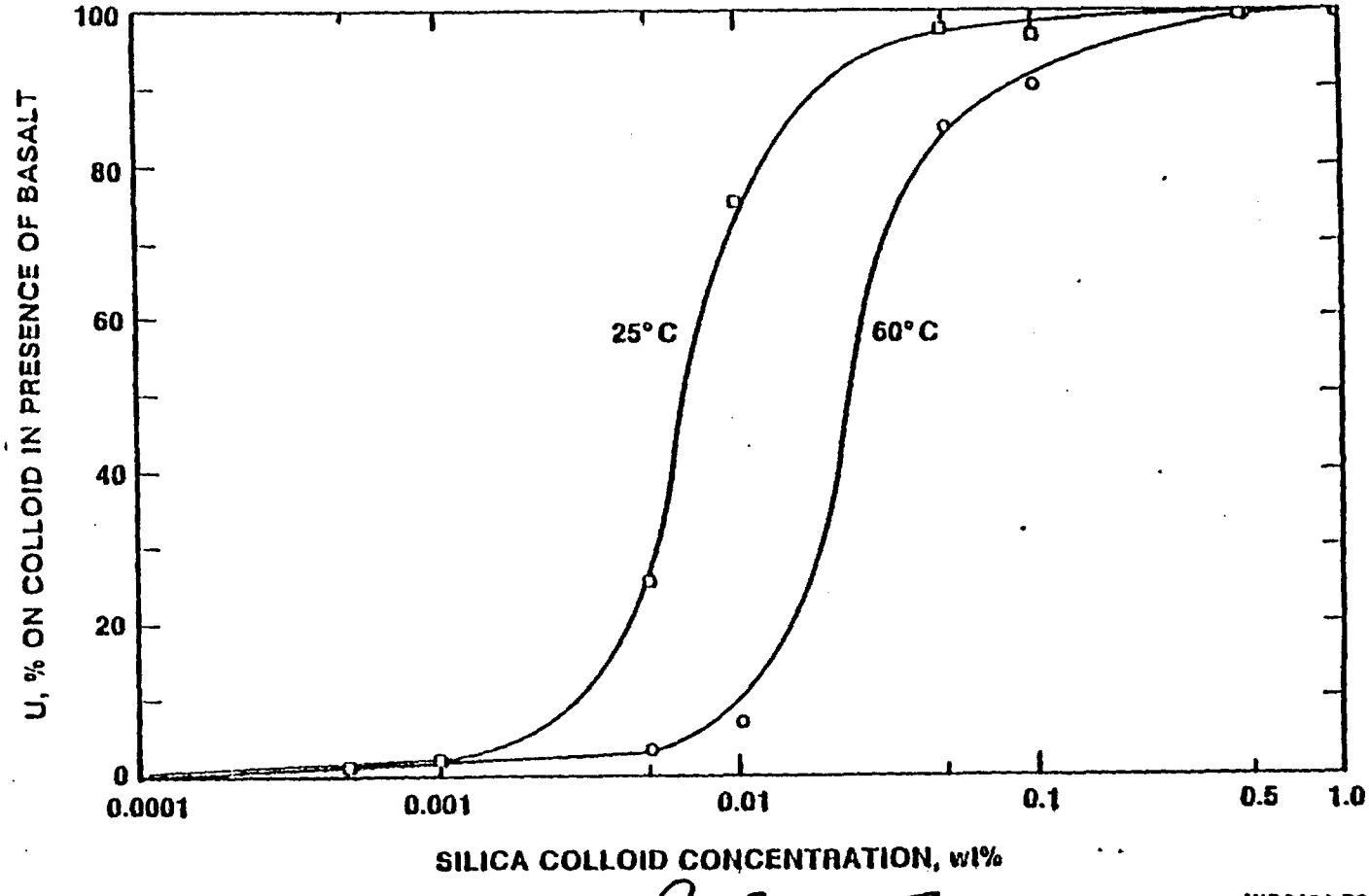
WP8401-70

RADIONUCLIDE DISTRIBUTION BETWEEN COLLOIDS + GROUNDWATER + BASALT

COLLOID SYSTEM	Se	Tc	Ra	U	Np
BENTONITE (OXIDIZING)	4%	1%	—	62%	47%
BENTONITE (REDUCING)	64%	36%	—	73%	94%
BENTONITE + BASALT (REDUCING)	BASALT	COLLOID	—	BASALT	COLLOID
SILICA (OXIDIZING)	0%	0%	99%	100%	99%
SILICA (REDUCING)	30%	86%	99%	98%	99%
SILICA + BASALT (REDUCING)	BASALT	BASALT	BASALT	COLLOID	COLLOID

WP8401-71

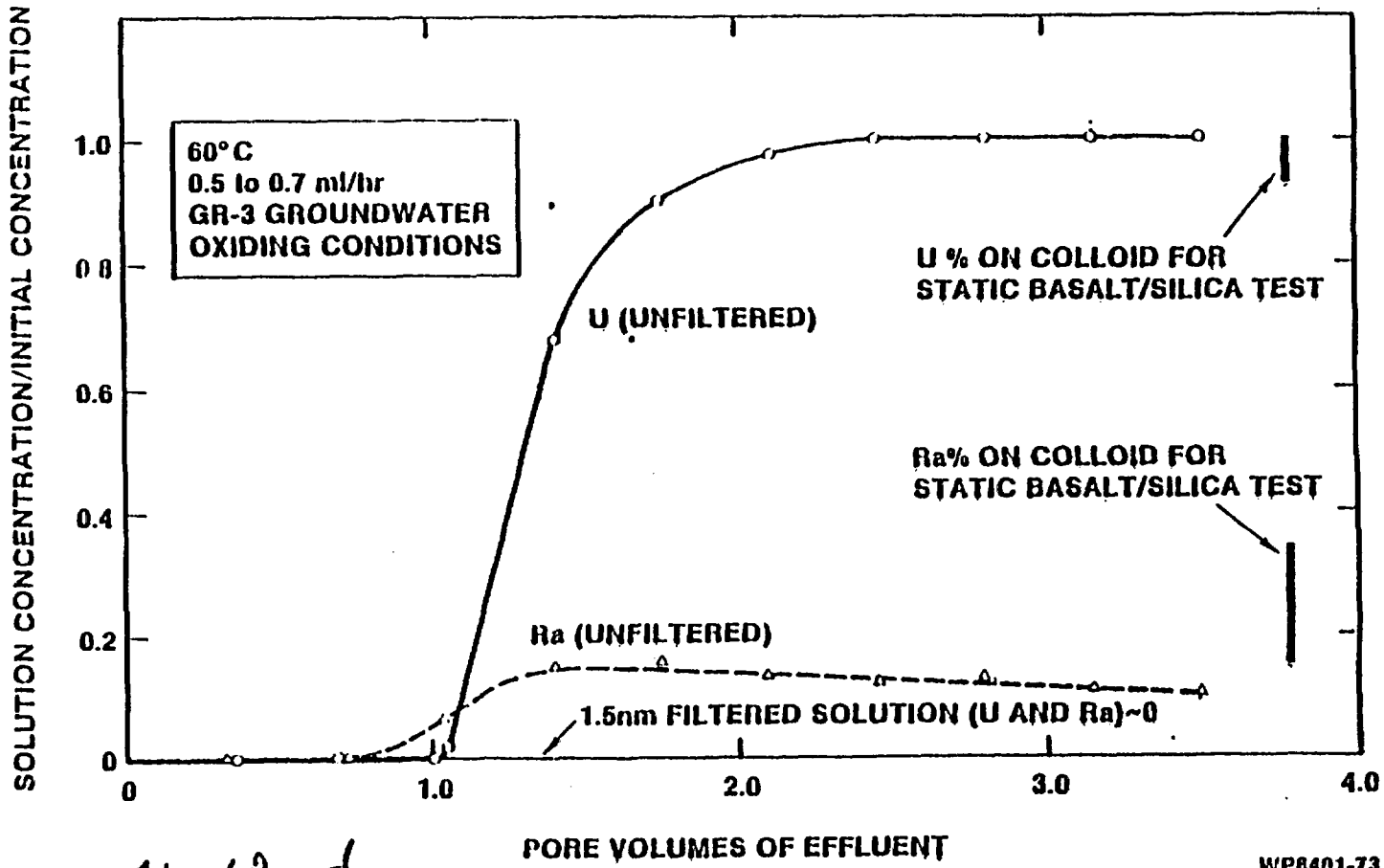
EFFECTS OF TEMPERATURE ON URANIUM SORPTION ON SILICA COLLOID IN THE PRESENCE OF COHASSETT BASALT



WP8401-72

sorption [illegible] at higher T

FLOW-THROUGH SORPTION BEHAVIOR OF 1 WT% SILICA COLLOID



WP8401-73

16-60 mesh

radium

FUTURE PLANS

- FIELD STUDIES ON POSSIBLE NATURAL COLLOIDS AWAIT DIRECT ACCESS WITHIN AN EXPLORATORY SHAFT
- IN SITU FIELD TESTS OF COLLOID TRANSPORT THROUGH REPOSITORY HORIZON
- CONTINUED CHARACTERIZATION OF COLLOIDS FORMED IN WASTE/BARRIER/ROCK TESTS
- LABORATORY STUDIES ON TRANSPORT OF RADIONUCLIDE-BEARING COLLOIDS WITHIN NATURAL (FRACTURES) AND ENGINEERED (POROUS) MATERIALS
  - PHYSICAL FILTRATION
  - COLLOID SORPTION
  - RADIONUCLIDE DISTRIBUTION
  - COLLOID STABILITY

WP8401-74

Sorption

USE OF SORPTION DATA RADIONUCLIDE RELEASE AND TRANSPORT MODELS

(1) Kd (DISTRIBUTION COEFFICIENT)

(2) $S = KC\hat{N}$ (FREUNDLICH ISOTHERM)

(3) $S = \dfrac{K_1 C}{1 + K_2 C}$ (LANGMUIR ISOTHERM)

(4) $\dfrac{d\,(S/S_\infty)}{dt} = K\,(S_\infty - S)$ (FIRST ORDER RATE EQUATION)

slow eg. column work (cf Mel Siegel)

(5) $Kd = K\$^{Nd/Ns} \times S_{max}^{(1 - Nd/Ns)}$ (FREUNDLICH ISOTHERM FOR HYSTERESIS)

van Geunahten

WP-8312-72

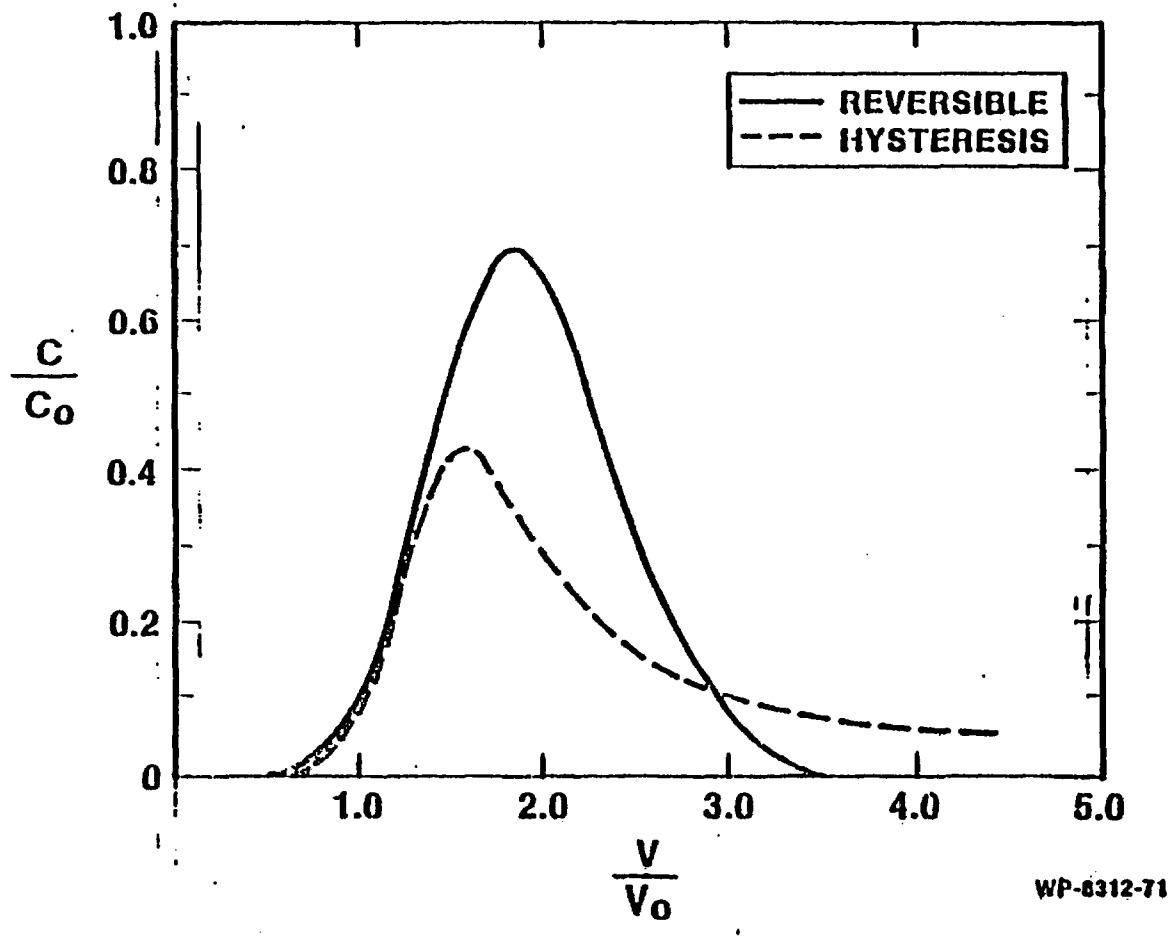
ASSUMPTIONS USING Kd FOR MODELING

- INSTANTANEOUS SORPTION AND DESORPTION
- LINEAR SORPTION ISOTHERMS
- SINGLE-VALUED ADSORPTION AND DESORPTION ISOTHERMS

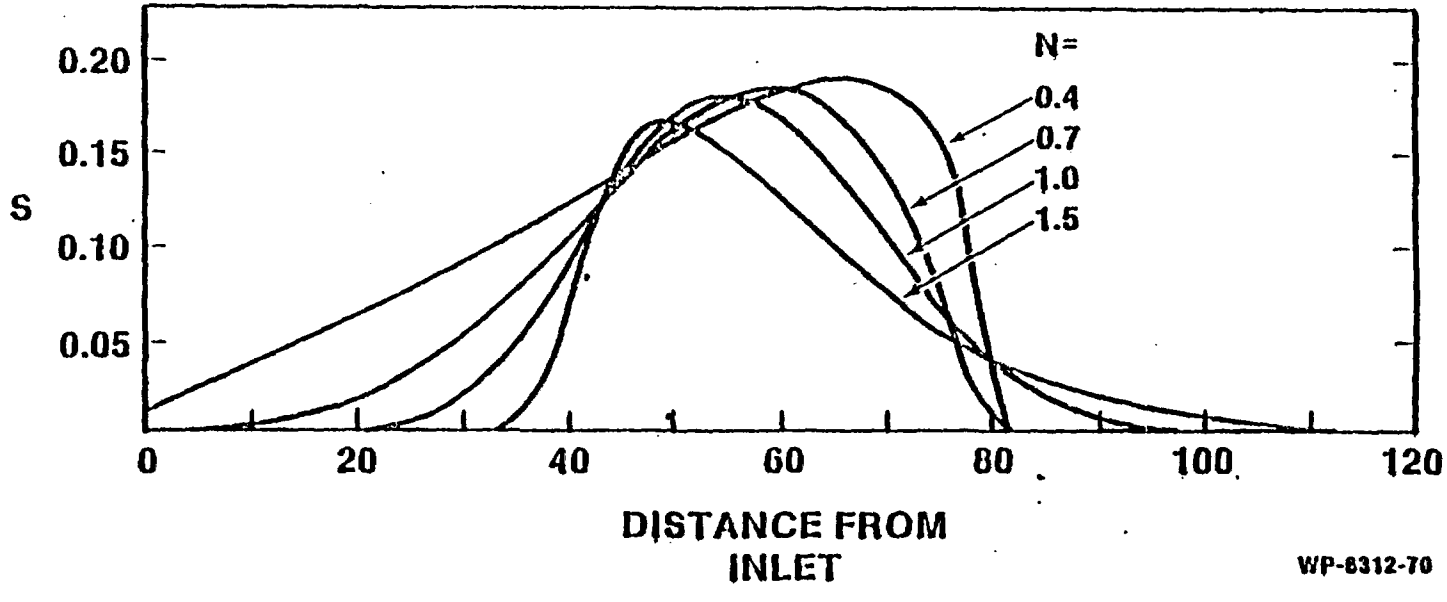
find that none of these conditions hold

WP8401-135

EFFECT OF SORPTION HYSTERESIS ON SOLUTE TRANSPORT (ELUTION CURVES)



EFFECT OF NON-LINEAR SORPTION ON SOLUTE TRANSPORT



ESTIMATED ENVIRONMENTAL PARAMETERS

1,000 YEARS AFTER REPOSITORY SEALING

PARAMETER	VALUES FOR		REFERENCES
	NEAR FIELD	FAR-FIELD	
TEMPERATURE (°C)	51 TO 150	AMBIENT TO 51	ALTENHOFEN (1981)
PRESSURE (MPa)	9.3 TO 11.1	< 11.1	SMITH ET AL., (1983)
GROUNDWATER FLOW VELOCITY (M/YR)	DIFFUSION CONTROLLED	10^{-4} TO 19	DOE (1982)
Eh (VOLTS)	~ -0.45	-0.2 TO -0.4	JACOBS AND APTED (1981)
pH	6 TO 10	9 TO 10	APTED AND MYERS (1982)
GROUNDWATER COMPOSITION	ALTERED GRANDE RONDE	GRANDE RONDE	DOE (1982)
GEOLOGIC OR ENGINEERED SOLIDS COMPOSITION	BASALT BACKFILL CANISTER SEAL	BASALT SECONDARY MINERALS FLOW TOPS INTERBEDS	DOE (1982)
RADIATION DOSE RATE	DEPENDS ON DISTANCE FROM SOURCE	NIL	

No

WP8401-77

KEY RADIONUCLIDES STUDIED

^{129}I	^{79}Se
^{99}Tc	^{239}Pu
^{237}Np	^{14}C
^{226}Ra	^{135}Cs
^{234}U	^{90}Sr
^{210}Pb	^{242}Am

Sr not considered

WP-8312-68

ADVANTAGES OF THE BATCH METHOD

- SIMPLER DESIGN AND OPERATION
- A LARGER NUMBER OF EXPERIMENTS CAN BE RUN SIMULTANEOUSLY
- ALLOWS LONGER EQUILIBRIUM TIMES FOR SLOW REACTIONS
- SOLUTION FLOW RATE, POROSITY, AND DISPERSION ARE NOT VARIABLES
- NO PROBLEMS WITH CHANNELING
- RESULTS ARE MUCH SIMPLER TO INTERPRET

WP8401-136

ADVANTAGES OF THE FLOW-THROUGH METHOD

- SIMULATES ACTUAL FIELD CONDITIONS MORE CLOSELY
- CAN DISTINGUISH BETWEEN MORE THAN ONE SORPTION REACTION OR RADIONUCLIDE SPECIES
- THE EFFECTS OF SORPTION/DESORPTION KINETICS, IRREVERSIBLE SORPTION REACTIONS, AND NON-LINEAR ISOTHERMS CAN BE EVALUATED UNDER REALISTIC FLOW CONDITIONS
- THE COMPOSITION OF THE INFLUENT SOLUTION CAN BE MORE CAREFULLY CONTROLLED SINCE THE SOLUTION IS CONTINUALLY REPLENISHED

WP8401-137

CONTROL OF Eh

- EXCLUDE OXYGEN, LET SYSTEM (SOLIDS AND GROUNDWATER) CONTROL THE Eh
- ADD REDOX COUPLE WITH APPROPRIATE Eh

WP-8312-60

REQUIREMENTS FOR REDOX COUPLE

- MUST BE SOLUBLE AND CHEMICALLY STABLE AT THE pH AND TEMPERATURE OF THE EXPERIMENT
- REACT RAPIDLY WITH THE RADIOELEMENT OF INTEREST AT THE REQUIRED Eh
- NOT FORM COMPLEXES WITH RADIOELEMENTS OR INTERFERE WITH THE SORPTION REACTION
- NOT PRODUCE REACTION PRODUCTS THAT WOULD INTERFERE WITH THE SORPTION REACTION

WP-8312-67

REDUCING AGENTS TESTED FOR Eh CONTROL

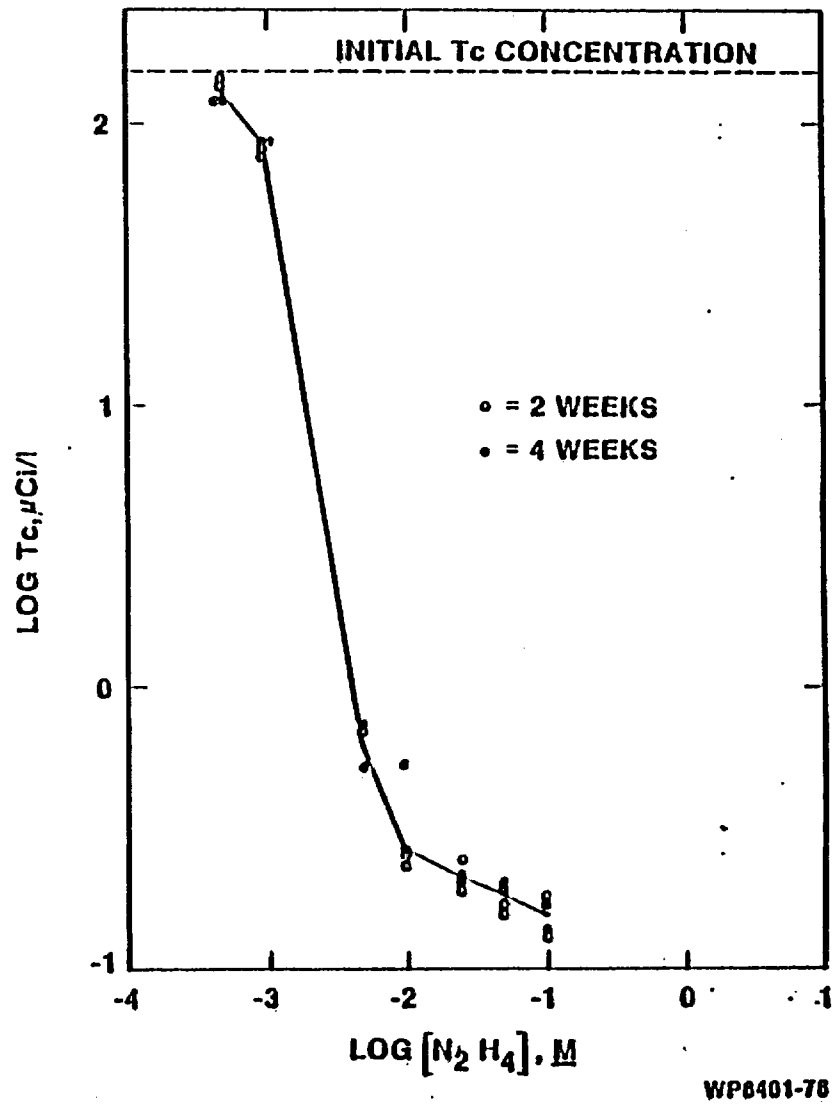
REDUCING AGENT	APPROXIMATE CALCULATED Eh RANGE (1) VOLTS	REQUIRED CRITERIA			
		SOLUBLE AND STABLE?	RAPID REACTION?	COMPLEX FORMATION?	INNOCUOUS REACTION PRODUCTS?
N_2H_4	-0.7 TO -0.8 (2)	YES	YES	NO	YES
SO_3^{2-}	-0.5 TO -0.6	YES	NO	POSSIBLE	YES
$S_2O_3^{2-}$	-0.1 TO -0.25	YES	FAIR	POSSIBLE	YES
HS^-	-0.3 TO -0.4	YES	NO	POSSIBLE	YES
QUINHYDRONE	+0.2 TO +0.1	YES	?	POSSIBLE	NO

(1) IN THE RANGE OF pH 8 TO 10, 25°C AND (OXIDIZED SPECIES) = (REDUCED SPECIES) (EXCEPT FOR N_2H_4).

(2) Eh VALUES FOR 0.05 M N_2H_4.

WP-8312-65

EFFECT OF HYDRAZINE CONCENTRATION ON Tc SORPTION ON ALTERED PACKING MATERIAL



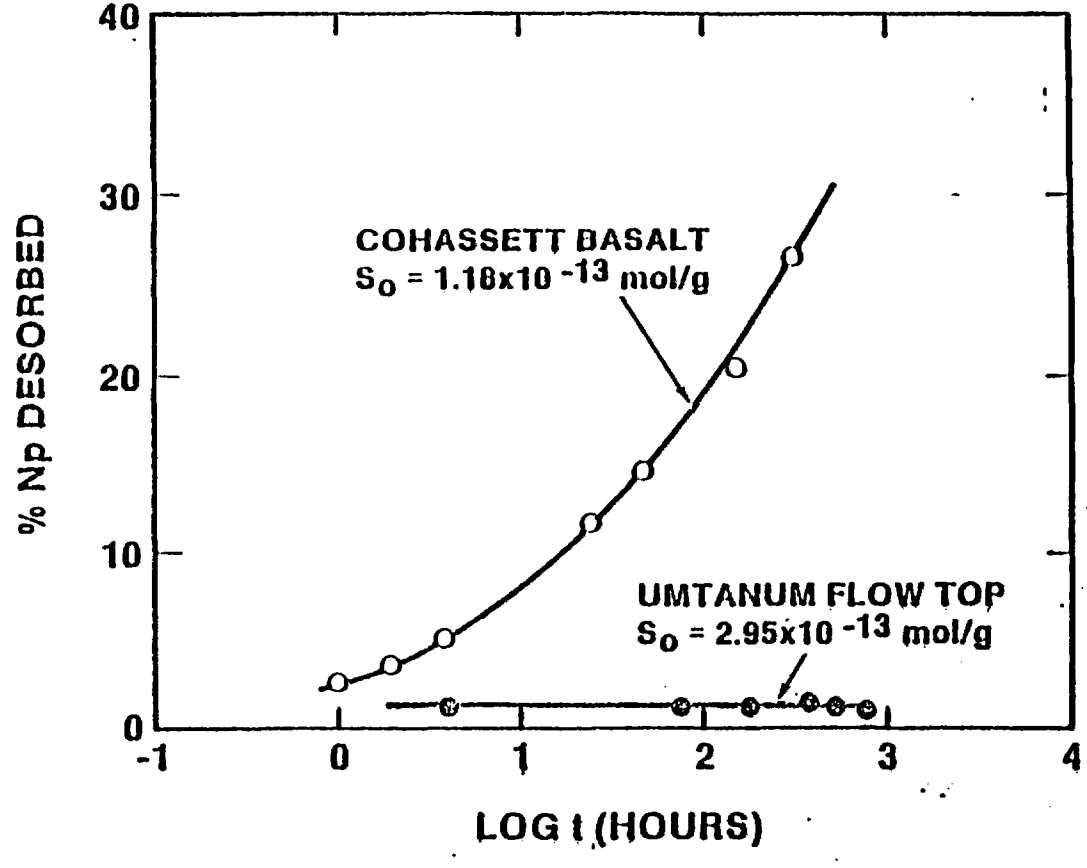
WP6401-76

RADIONUCLIDE SORPTION PARAMETERS EVALUATED

- KINETICS OF SORPTION AND DESORPTION
- STEADY-STATE SORPTION AND DESORPTION ISOTHERMS
- GROUNDWATER COMPOSITION
- Eh AND pH
- TEMPERATURE

WP-6312-64

NEPTUNIUM DESORPTION RATE CURVES
(TEMPERATURE = 60° C, OXIDIZING CONDITIONS)



WP8401-50

CONCLUSIONS

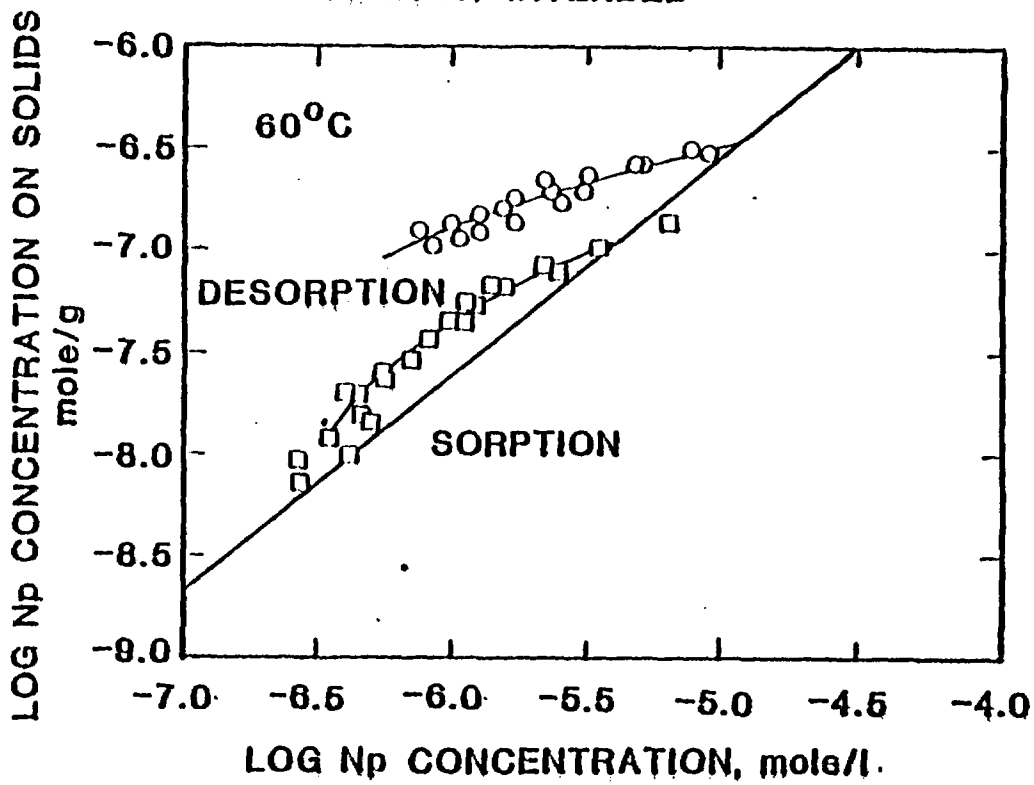
FROM RADIONUCLIDE SORPTION KINETICS STUDIES

- SORPTION ON FRESH (UNALTERED) BASALT IS MUCH SLOWER THAN ON FLOW TOP BASALT WHICH CONTAINS SECONDARY MINERALS
- DESORPTION RATES ARE MUCH LESS THAN SORPTION RATES (RADIONUCLIDES ARE IRREVERSIBLY SORBED)
- RADIONUCLIDE SORPTION ON UMTANUM AND COHASSETT BASALTS IS NOT MEASUREABLY DIFFERENT
- SORPTION RATES FOR U, Np, Pb, and Tc ARE GREATER UNDER REDUCING CONDITIONS
- SORPTION RATES FOR U, Np, AND Pu ARE SIMILAR FOR A GIVEN SORBENT AND OXIDATION STATE
- BECAUSE OF SLOW SORPTION RATES, LABORATORY FLOW-THROUGH (COLUMN) SORPTION MEASUREMENTS ON FRESH CRUSHED BASALT ARE NOT PRACTICAL AT LOW TEMPERATURES - FLOW TOP BASALT CAN BE USED, HOWEVER

WP8401-79

SORPTION/DESORPTION ISOTHERMS FOR Np (OXIDIZING)

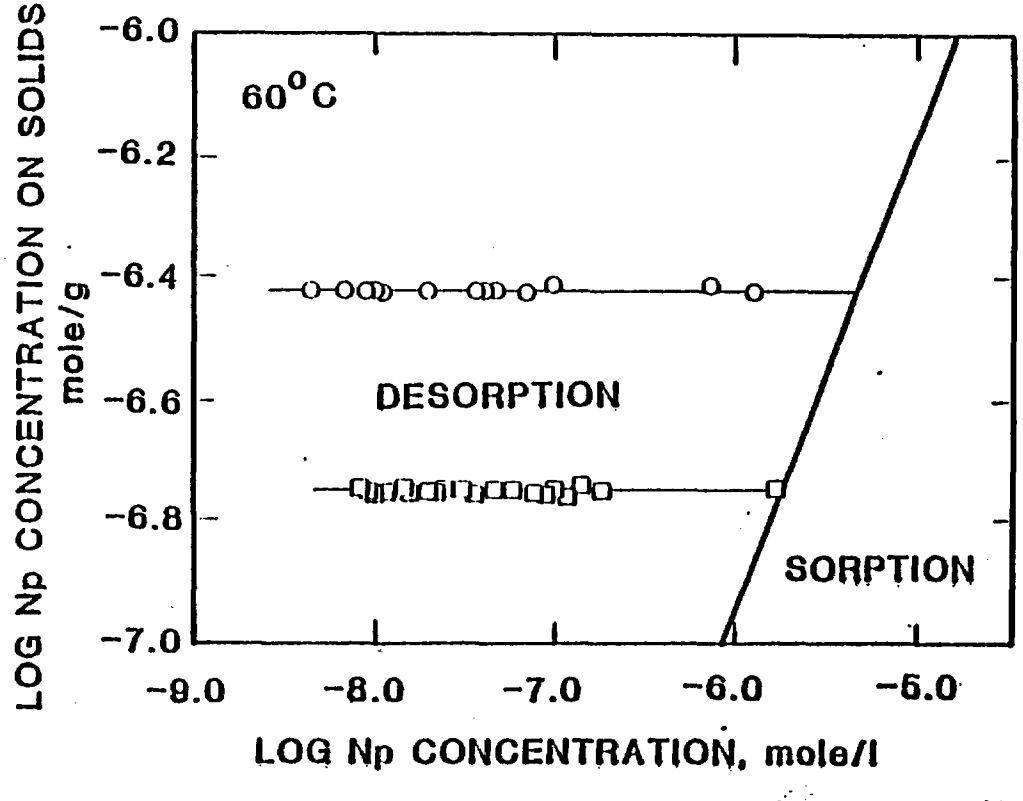
MABTON INTERBED



WP6302-26

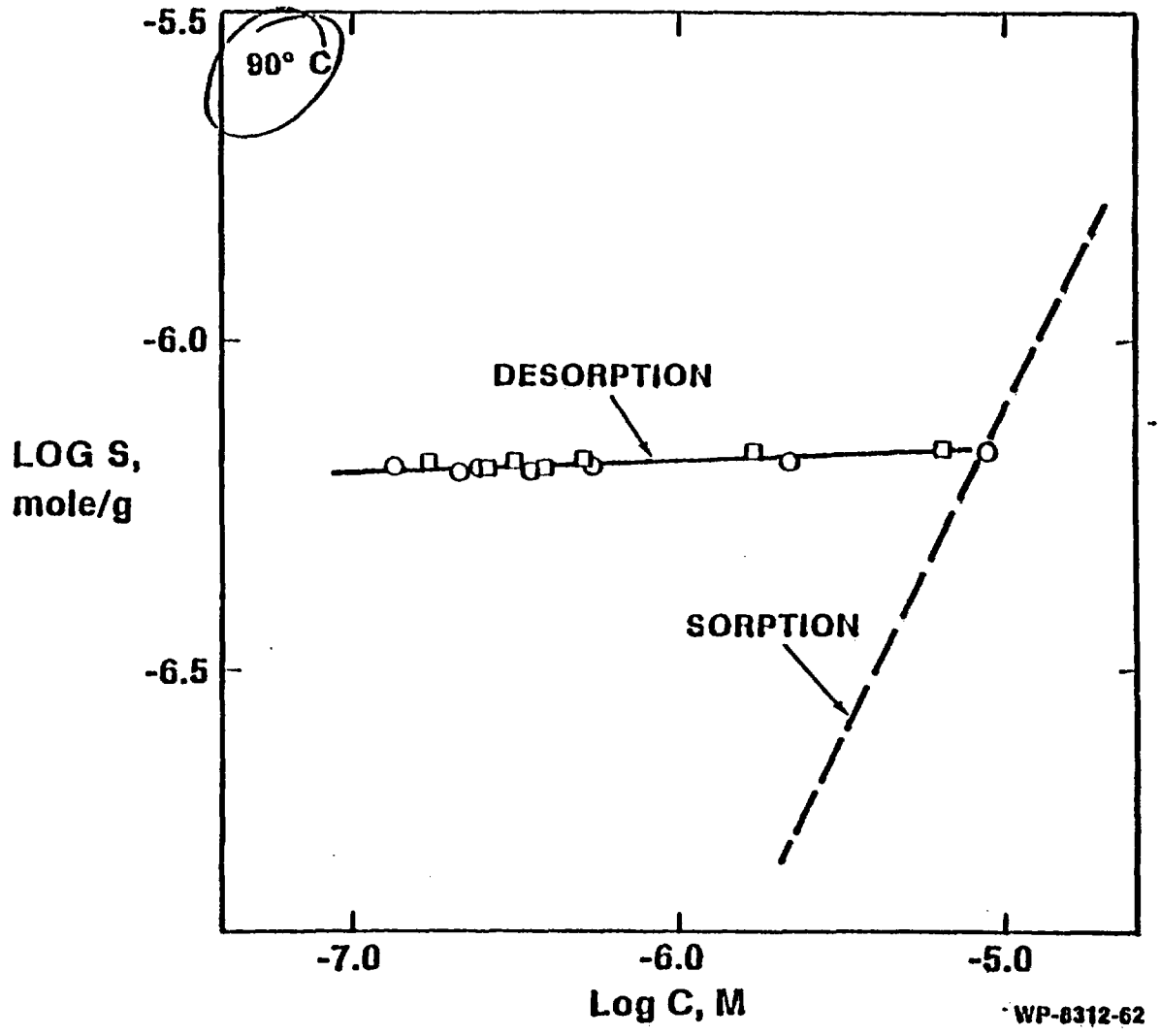
SORPTION/DESORPTION ISOTHERMS FOR Np (REDUCING)

MABTON INTERBED

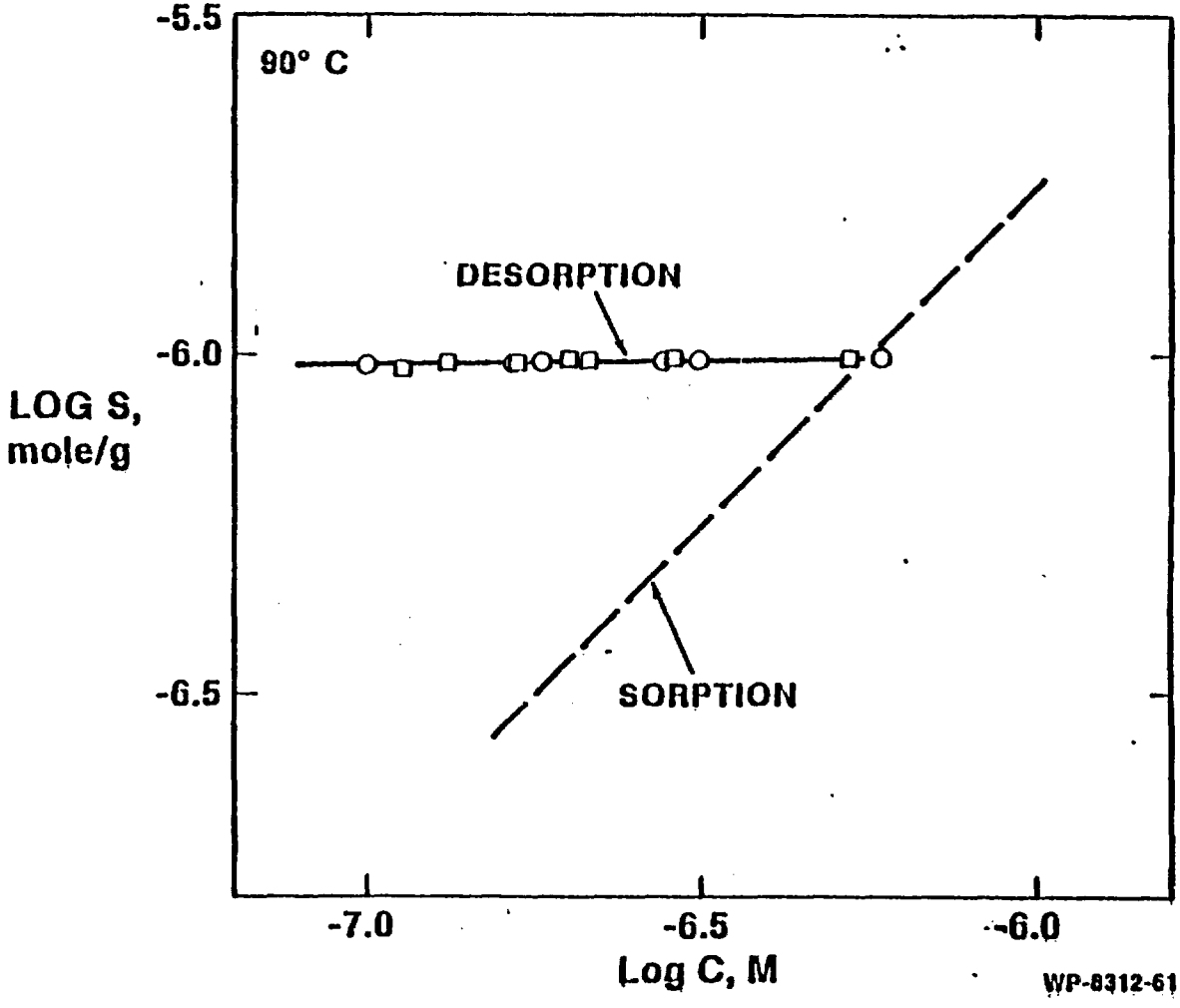


WP6302-27

SORPTION/DESORPTION ISOTHERMS FOR SE (REDUCING) ALTERED BACKFILL



SORPTION/DESORPTION ISOTHERMS FOR Tc (REDUCING) ALTERED BACKFILL



SORPTION/DESORPTION FREUNDLICH CONSTANTS

		MABTON INTERBED (60°)			ALTERED PACKING MATERIAL (90° C)		
ISOTOPE	REDOX	N_s	N_d	N_s/N_d	N_s	N_d	N_s/N_d
Se	REDUCING	1.0	0.023	47	0.99	0.011	90
Tc	REDUCING	0.58	0.011	113	1.03	0.015	69
Np	OXIDIZING	1.0	0.68	1.7	1.09	0.12	9.1
Np	REDUCING	0.87	0.002	435	0.96	0.014	69
U	OXIDIZING	0.96	0.084	12	0.70	0.17	4.1
U	REDUCING	0.79	0.006	182	0.94	0.012	78
Ra	REDUCING	0.98	0.052	36	-	-	-

WP-8312-60

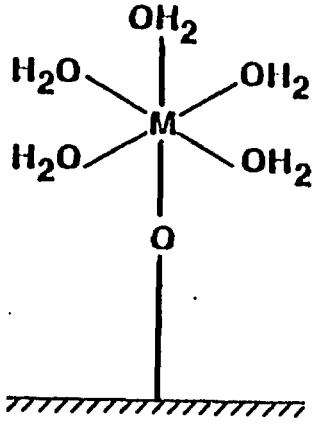
N_s/N_d - indication of hysteresis

SIGNIFICANT GROUNDWATER VARIABLES FOR SORPTION

RADIONUCLIDE	SIGNIFICANT VARIABLES
Cs	K^+, Na^+
Sr	Na^+, Ca^{2+}
Tc	Eh
Se	Eh, Ca^{2+}
Np	Eh, CO_3^{2-}, HCO_3^-
Pu	Eh, Ca^{2+}, SO_4^{2-}
Am	Na^+, pH
Ra	K^+, Na^+

WP6209-6

STRUCTURE AND BONDING IN SURFACE COMPLEXES



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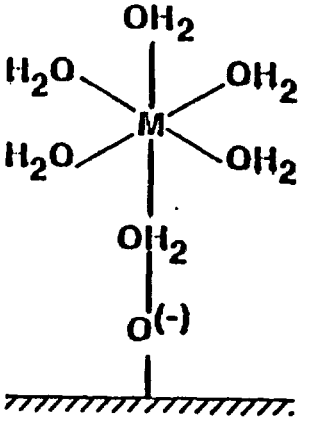

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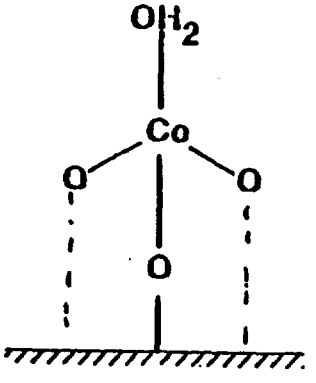

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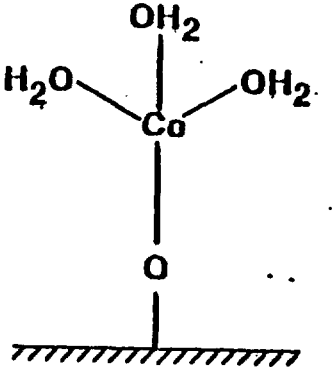


IV

WP8401-80

FUTURE NEAR-FIELD SORPTION STUDIES

- BATCH MEASUREMENTS OF SORPTION/DESORPTION ISOTHERMS AND SORPTION CAPACITY FOR PACKING MATERIAL, ALTERED BASALT, COLLOIDS AND CANISTER CORROSION PRODUCTS.
- FLOW-THROUGH MEASUREMENTS AND MODELING OF RADIONUCLIDE TRANSPORT IN LABORATORY COLUMNS USING THESE MATERIALS
- DEVELOPMENT OF METHODS FOR CONTROLLING AND MEASURING Eh AT LOW TEMPERATURE IN LABORATORY EXPERIMENTS

Will White

- LABORATORY MEASUREMENTS OF COLLOID TRANSPORT THROUGH ENGINEERS BARRIERS

WP6401-81

SUMMARY OF SITE SYSTEM SORPTION STUDIES

SOLID PHASE	SOLUTION	RADIONUCLIDES	EXPERIMENT TYPE	REDOX CONDITIONS	TEMPERATURE (°C)
1. MIXED SECONDARY MINERALS - POMONA FLOW (NSTF), BLENDED	GR-1 GR-2	Se, Sr, Tc, I, Cs, Ra, U, Np, Pu, Am	BATCH, <60 DAYS	OXIDIZING	23, 60
2. RATTLE-SNAKE RIDGE INTERBED, CRUSHED	GR-2	Se, Sr, Tc, Cs, Ra, U, Np, Am	BATCH, 14 DAYS	OXIDIZING, REDUCING (HYDRAZINE)	23, 60, 85
3. UMTANUM FLOW TOP, CRUSHED	GR-3	Se, Tc, Pb, Ra, Th, U, Np, Pu	BATCH, <1-56 DAYS COLUMN	OXIDIZING, REDUCING (HYDRAZINE)	60
4. MABTON INTERBED UNCONSOLI-DATED	GR-1A	Sr, Tc, Cs, Ra, U, Np, Pu, Am	BATCH, 14 DAYS	OXIDIZING, REDUCING (HYDRAZINE)	23, 60, 85

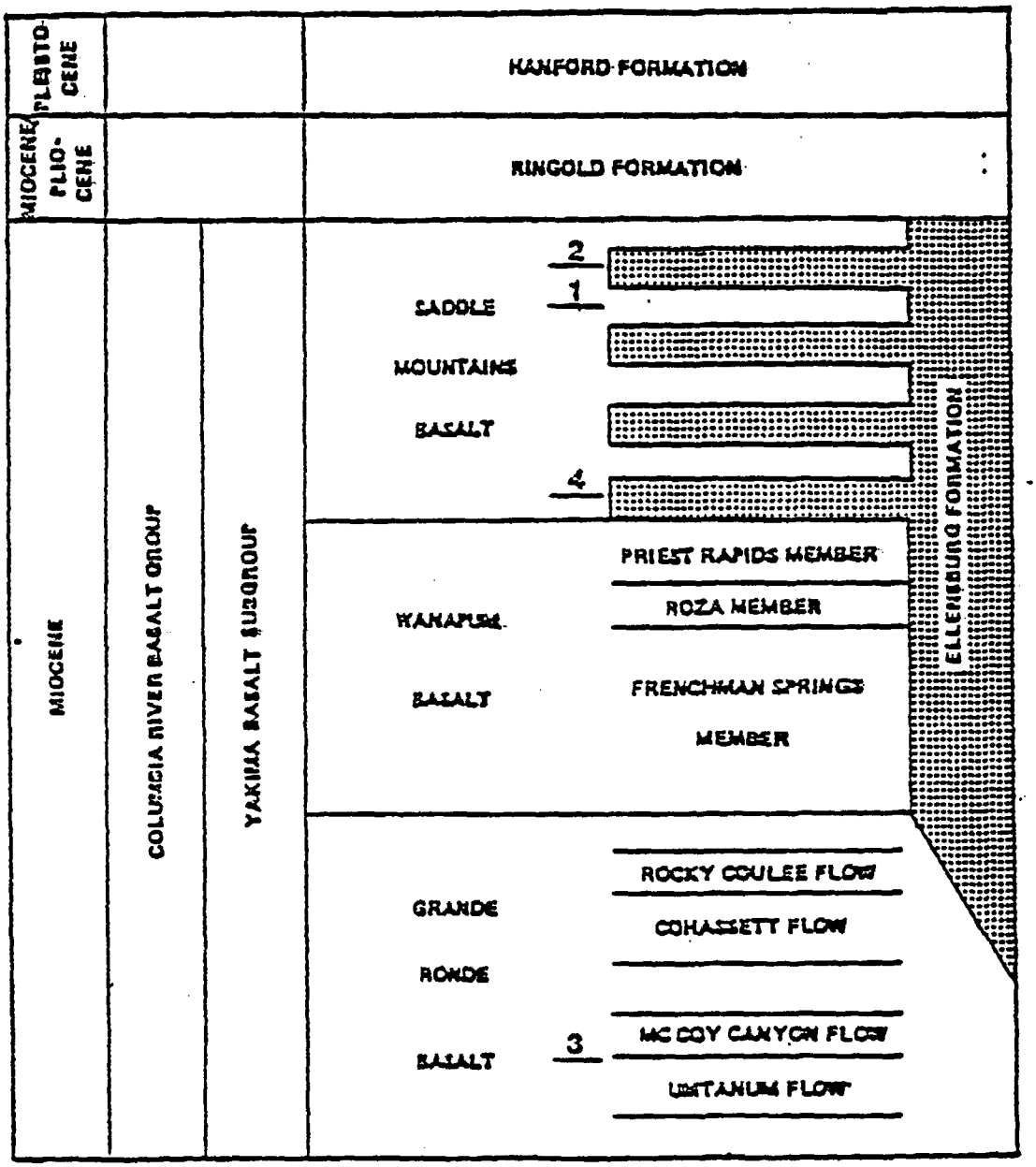
REFERENCES: (1) SALTER, ET AL., 1981 (RHO-BWI-LD-43); AMES, ET AL., 1980, 1980, 1981 (PNL-3145, PNL-3146, PNL-3902).

(2) BARNEY, 1982 (RHO-BW-ST-35P).

(3) BARNEY, ET AL., 1983 (RHO-BWI-TI-168).

(4) BARNEY, 1984 (ACS SYMPOSIUM SERIES, NO. 246).

STRATIGRAPHIC HORIZONS FOR WHICH SITE SORPTION STUDIES HAVE BEEN CONDUCTED



SUMMARY OF SITE SYSTEM SORPTION RESULTS

- IN GENERAL, TESTED RADIONUCLIDES SORB WELL UNDER REDUCING CONDITIONS; EXCEPTIONS ARE I AND C
- FACTORS AFFECTING SORPTION/DESORPTION

(1) REDOX POTENTIAL

Tc, U, Np, Pu ARE AFFECTED - MORE SORPTION AT LOWER OXIDATION STATE

(2) COMPLEXATION

Cl^-, F^-, CO_3^{-2}, HCO_3^-, AND SO_4^{-2} HAVE BEEN TESTED. POSSIBLE COMPLEXES ARE Np-CARBONATE, Pu-SULFATE

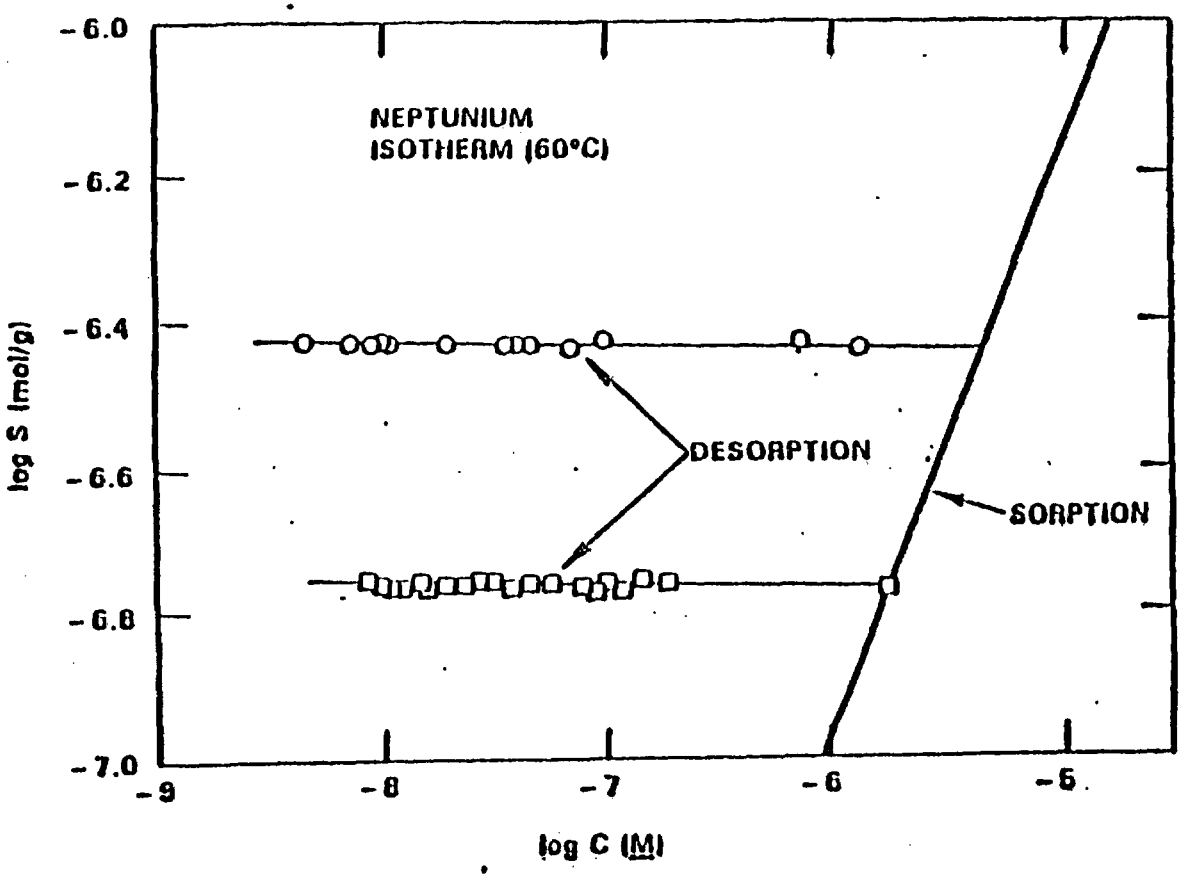
(3) IONIC STRENGTH

Sr, Cs, Ra AFFECTED

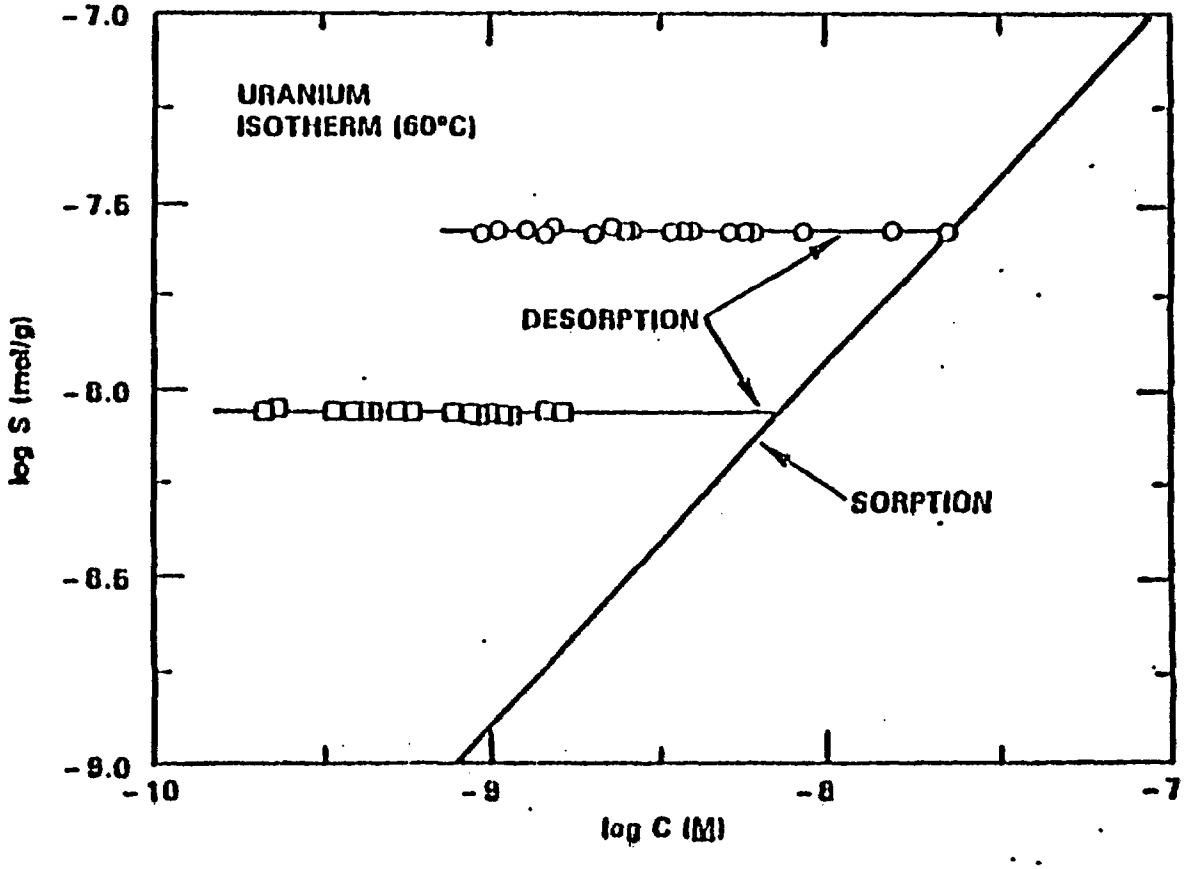
(4) REVERSIBILITY

MOST SORPTION/DESORPTION REACTIONS FOLLOW DIFFERENT PATHS (HYSTERESIS)

SORPTION/DESORPTION HYSTERESIS FOR NEPTUNIUM ON MABTON INTERBED (BARNEY, 1984, ACS SYMPOSIUM SERIES No. 246)



SORPTION/DESORPTION HYSTERESIS FOR URANIUM ON MABTON INTERBED (BARNEY, 1984, ACS SYMPOSIUM SERIES No. 246)

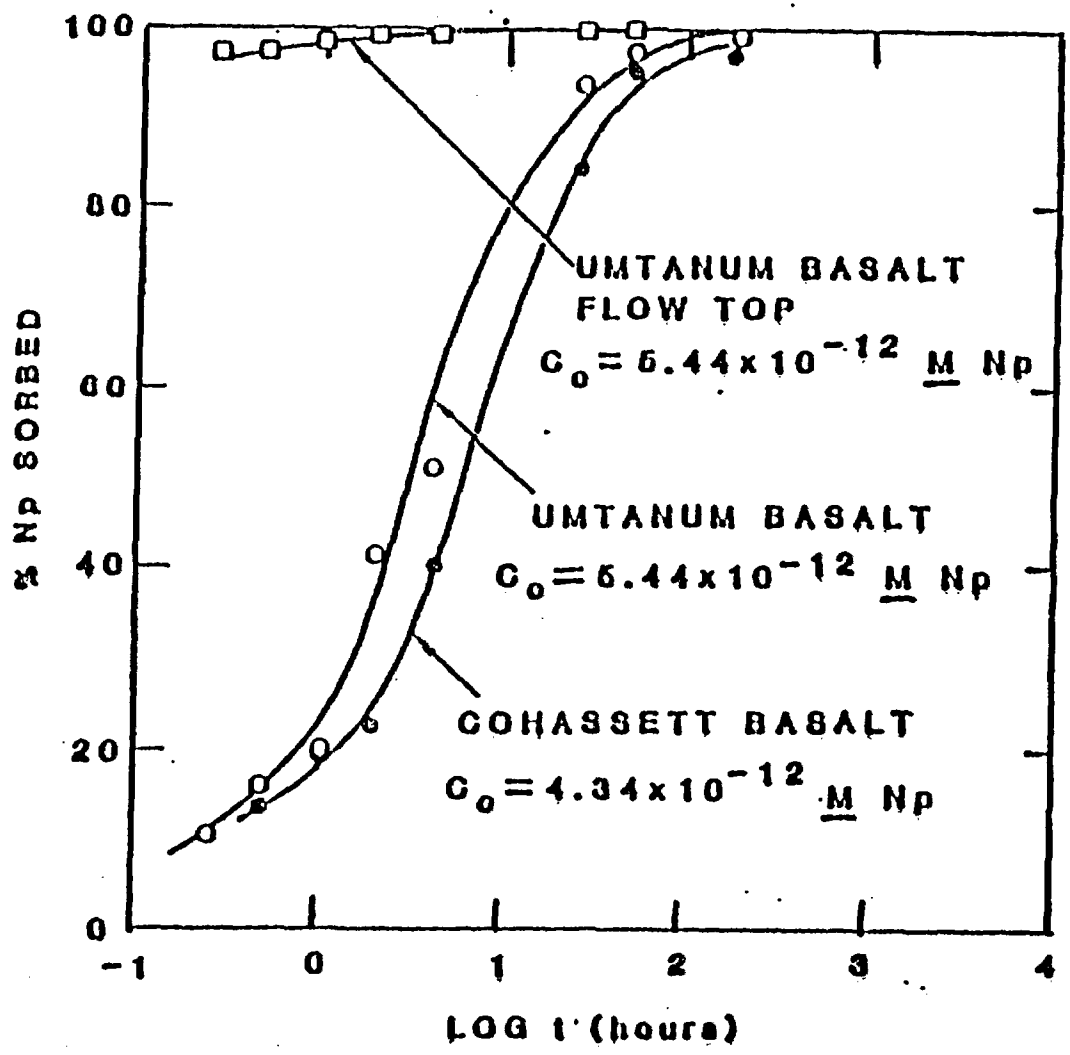


SUMMARY (CONTINUED)

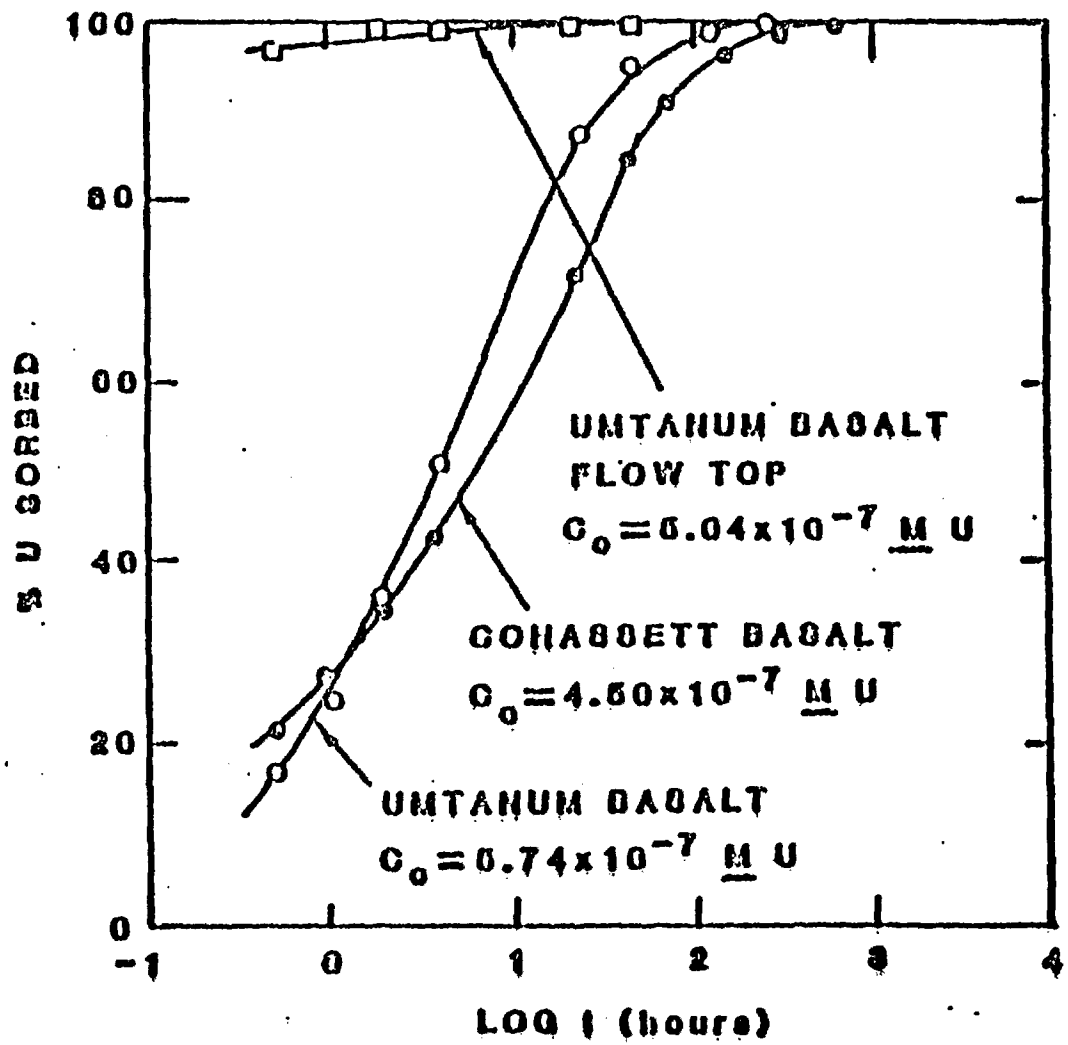
- COMPARISON OF FLOW TOP VERSUS BASALT SORPTION PROPERTIES
  - SORPTION IS GENERALLY GREATER ON FLOW TOP
  - REACTIONS ARE GENERALLY FASTER FOR FLOW TOP
  - DESORPTION IS LESS FOR FLOW TOP
- COMPARISON OF FLOW TOP VERSUS INTERBED SORPTION PROPERTIES - IN GENERAL, SORPTION IS GREATEST ON MABTON INTERBED AND APPROXIMATELY THE SAME FOR UMTANUM FLOW TOP AND RATTLESNAKE RIDGE SANDSTONE.

PROBLEM: EXPERIMENTS NOT CONDUCTED AT SAME RADIONUCLIDE CONCENTRATIONS SO ISOTHERMS WERE EXTRAPOLATED BEYOND THE CONCENTRATION RANGES FOR WHICH THEY WERE DERIVED.

SORPTION KINETICS FOR NEPTUNIUM
(BARNEY ET AL., 1983, SD-BWI-TI-168)

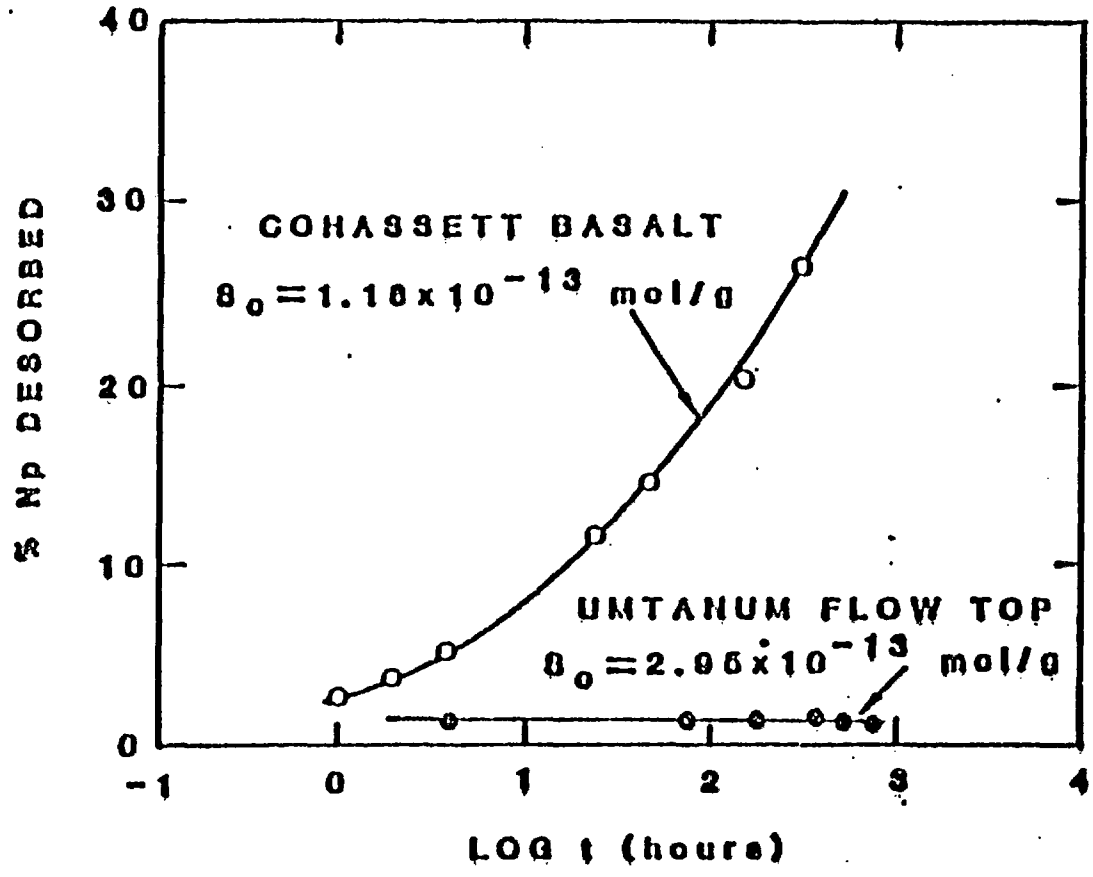


SORPTION KINETICS FOR URANIUM
(BARNEY ET AL., 1984, SD-BWI-TI-168)



COMPARISON OF NEPTUNIUM DESORPTION KINETICS
BETWEEN FLOW TOP AND BASALT

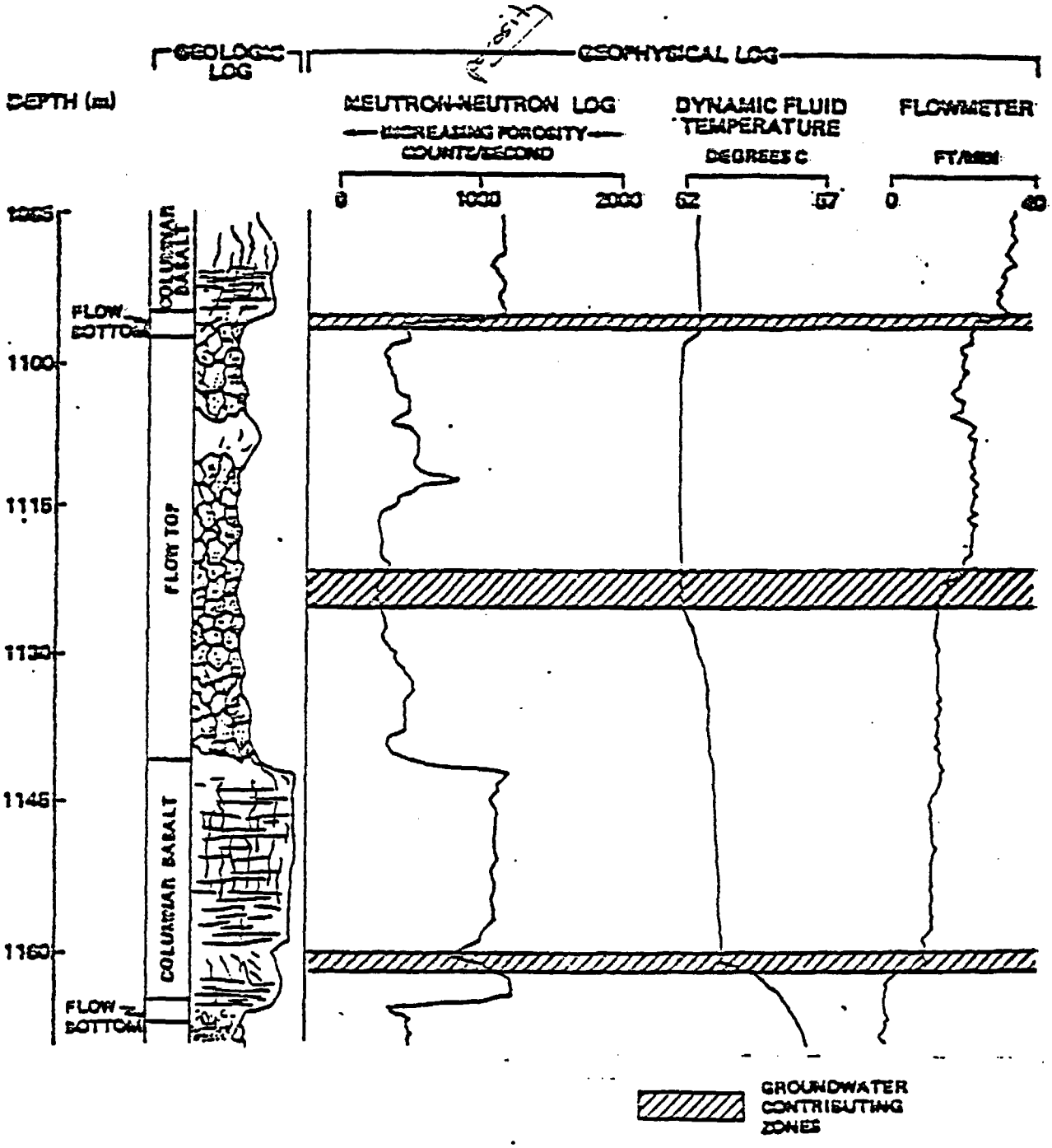
(BARNEY ET AL., 1984, SD-BWI-TI-168)



LAB SORPTION STUDIES

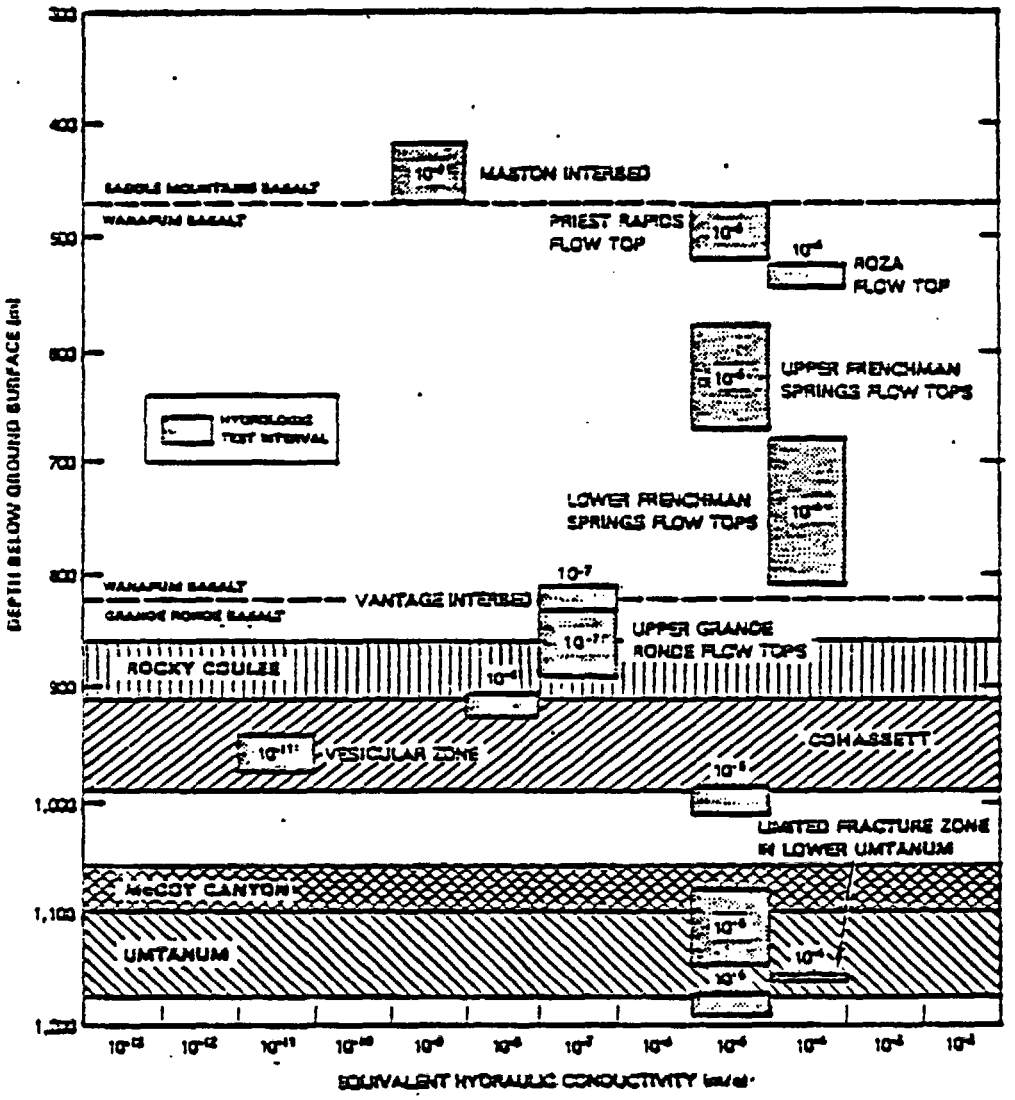
- GEOMEDIA SAMPLES
  - COLLECTION - ID LIKELY FLOW PATHS, CORE VS. OUTCROP, CORE PHOTOS, CORE EXAMINATION
  - PREPARATION - SAMPLE DISAGGREGATION, PARTICLE SIZE, COMPOSITE SAMPLES
  - CHARACTERIZATION - MINERALOGY, PHYSICAL AND CHEMICAL CHARACTERISTICS (CEC, SURFACE AREA, PARTICLE SIZE DISTRIBUTION)
- RADIONUCLIDE SORPTION/DESORPTION
  - KEY RADIONUCLIDES
  - BATCH AND COLUMN EXPERIMENTS YIELDING ISOTHERMS AND BREAKTHROUGH CURVES
  - EVALUATE SORPTION AS A FUNCTION OF TIME, GROUNDWATER CHEMISTRY, SOLID: SOLUTION RATIO, COMPLEXANTS

INFORMATION USED TO IDENTIFY GROUNDWATER FLOW ZONES

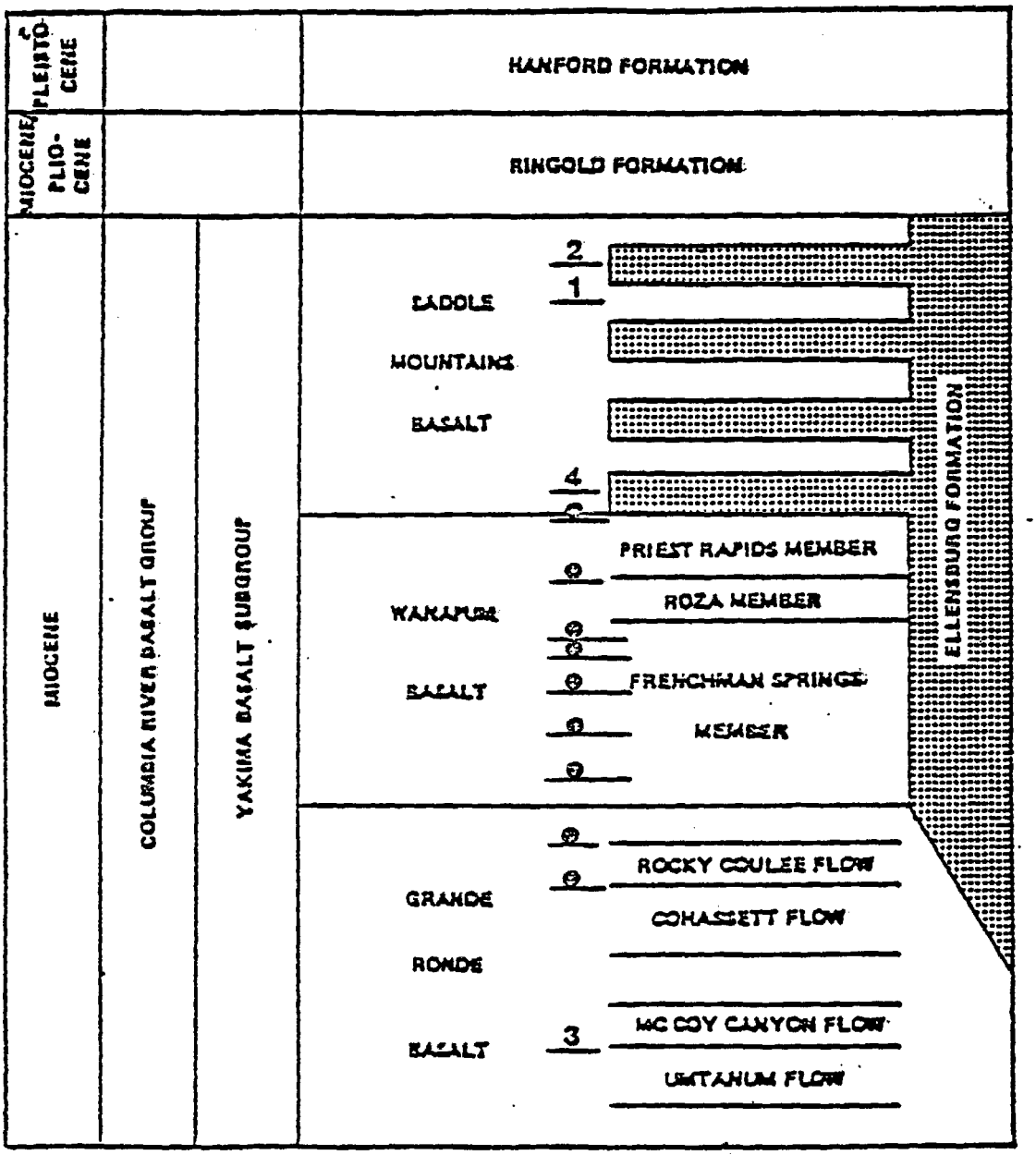


Source 2

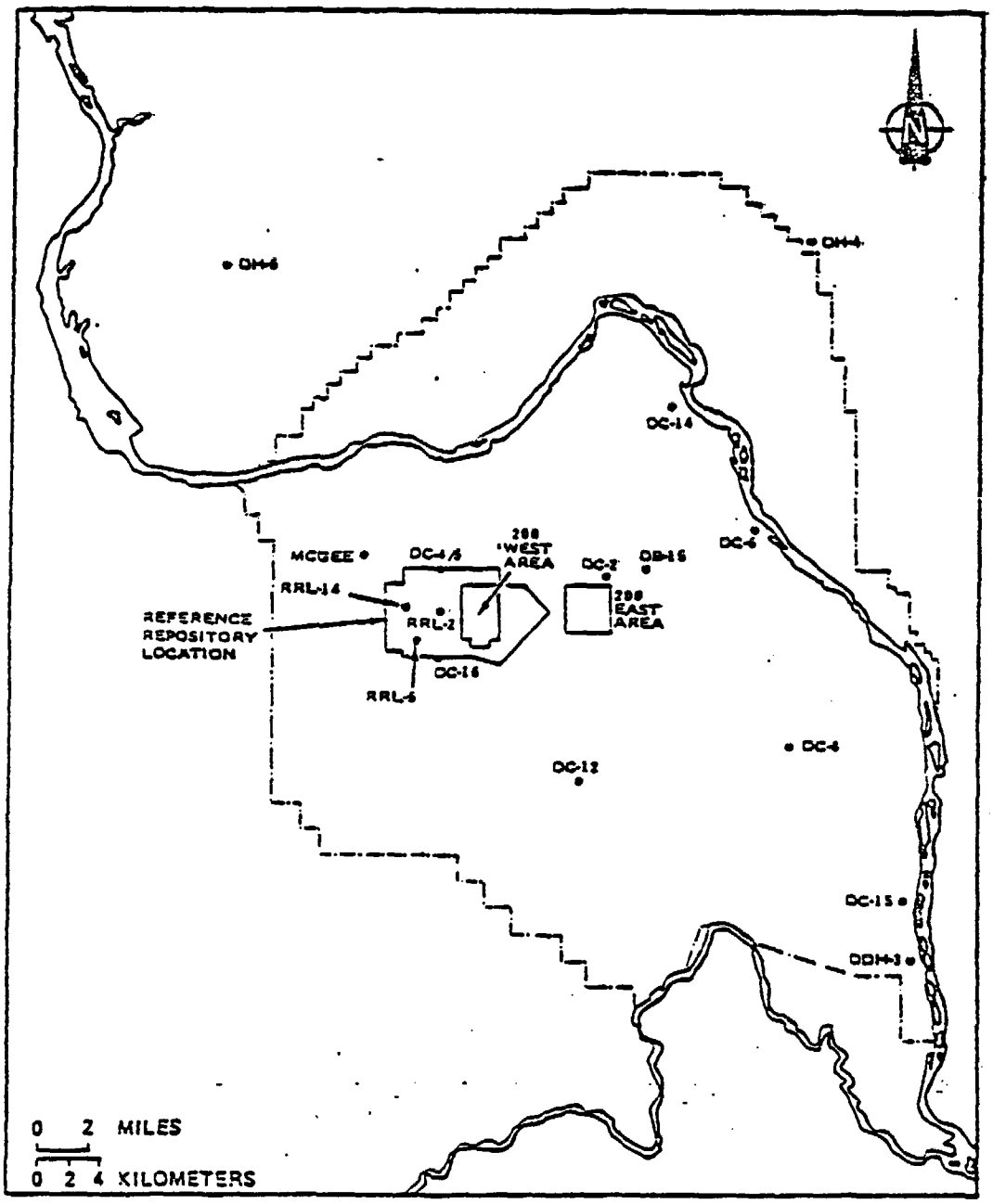
Example RRL-2



STRATIGRAPHIC HORIZONS FOR WHICH SITE SORPTION STUDIES HAVE BEEN CONDUCTED AND ARE PLANNED



BOREHOLES FOR WHICH CORE IS AVAILABLE



PRELIMINARY LIST OF KEY RADIONUCLIDES FOR A NWRB

(100 YEAR OLD CHLW OR SPENT FUEL)

ELEMENT	RADIONUCLIDE (PRIORITY 1)
CARBON	(^{14}C)*
IODINE	(^{129}I)*
SELENIUM	^{79}Se
TECHNETIUM	^{99}Tc
NEPTUNIUM	^{237}Np
PLUTONIUM	^{239}Pu, ^{242}Pu
TIN	^{126}Sn
*( )=SPENT FUEL ONLY	

ELEMENT	RADIONUCLIDE (PRIORITY 2)
STRONTIUM	(^{90}Sr)*
CESIUM	(^{135}Cs, ^{137}Cs)*
RADIUM	(^{226}Ra)*
CURIUM	^{243}Cm, ^{245}Cm, ^{246}Cm
PROTACTINIUM	^{231}Pa
NICKEL	^{59}Ni, ^{63}Ni
URANIUM	^{233}U, ^{234}U, ^{235}U
LEAD	^{210}Pb
ZIRCONIUM	^{93}Zr
PALLADIUM	^{107}Pd
THORIUM	^{229}Th, ^{230}Th, ^{232}Th
PLUTONIUM	^{238}Pu, ^{240}Pu, ^{241}Pu
AMERICIUM	^{241}Am, ^{243}Am
*( )=EXISTING DATA SUFFICIENT	

COLLOIDS IN THE SITE SYSTEM

- RATIONALE - THE RETARDATION MECHANISM FOR COLLOIDS IS FILTRATION. FILTRTATION IS GEOMETRY (PORE SIZE) DEPENDENT. THEREFORE, COLLOID MIGRATION CANNOT BE EVALUATED USING DISTURBED SYSTEMS (E.G., CORE SAMPLES) IN THE LAB BUT MUST BE EVALUATED UNDER FIELD CONDITIONS OVER LONG FLOW PATHS.
- NATURAL COLLOIDS
  - QUANTITY AND PARTICLE SIZE IN NATURAL GROUNDWATERS
  - MINERALOGICAL CHARACTERIZATION
  - REQUIREMENTS
    - (1) ACCESS TO GROUNDWATER - SURFACE BOREHOLE OR ES
    - (2) LONG BOREHOLE-CLEANUP TIME - REMOVE CUTTINGS, DRILLING FLUID, RESUSPENDED NATURAL COLLOIDS
- FIELD TRACER TESTS
  - USE PARTICULATE TRACERS OF VARYING SIZE

FIELD STUDIES - NATURAL RADIONUCLIDE DISEQUILIBRIUM

- RECENTLY PROPOSED TECHNIQUE TO EVALUATE NATURAL RADIONUCLIDE SORPTION - NEED TO EVALUATE APPLICABILITY IN BASALT SYSTEM.
- RATIONALE - IF THERE IS NO PARTITIONING OF ISOTOPES AND SECULAR EQUILIBRIUM HAS BEEN REACHED, ACTIVITY RATIOS OF ISOTOPES IN THE SAME DECAY CHAIN SHOULD BE UNITY. THE DEGREE OF DISEQUILIBRIUM REFLECTS PARTITIONING OF ISOTOPES.
- APPROACH
  - SAMPLE GROUNDWATER OF INTEREST
  - ANALYZE FOR RADIONUCLIDES IN THE ^{238}U AND ^{232}Th DECAY CHAINS

    $^{238}U \rightarrow {}^{234}U \rightarrow {}^{230}Th \rightarrow {}^{226}Ra \rightarrow {}^{222}Rn \rightarrow {}^{210}Pb \rightarrow {}^{210}Bi \rightarrow {}^{210}Po$

    $^{232}Th \rightarrow {}^{228}Ra \rightarrow {}^{228}Th \rightarrow {}^{224}Ra \rightarrow {}^{220}Rn$
  - EVALUATE ACTIVITY RATIOS, DETERMINE RETARDATION FACTORS (DISTRIBUTION COEFFICIENTS)
- ADVANTAGES
  - LARGE SCALE, NATURAL CONDITIONS
- PROBLEMS
  - PARTITIONING NOT DUE TO SORPTION, OPEN SYSTEM (MIXING)

FIELD STUDIES - TRACER TESTS

- APPROACH - MEASURE FIELD SORPTION CHARACTERISTICS OF SELECT LIST OF RADIONUCLIDES AND EXTRAPOLATE INFORMATION TO OTHER RADIONUCLIDES USING LAB SORPTION RESULTS.
- POSSIBLE BOREHOLES - DC-7/8, DC-4/5, DC-16A, B, C,
- BENEFITS
  - DETERMINE SORPTION AT FIELD SCALE UNDER NATURAL CONDITIONS
  - DEMONSTRATION THAT THE SYSTEM CAN RETARD RADIONUCLIDE MIGRATION
  - VALIDATION OF SORPTION VALUES USED IN PERFORMANCE ASSESSMENT MODELS
- PROBLEMS
  - LIMITED SET OF RADIONUCLIDES THAT CAN BE USED
  - COSTLY AND DIFFICULT TO CONDUCT

SUMMARY OF SITE SYSTEM RADIONUCLIDE TRANSPORT

SORPTION STUDIES HAVE BEEN CONDUCTED ON GEOMEDIA FROM FOUR GROUNDWATER FLOW ZONES

THE BWIP HAS IDENTIFIED THE NEED FOR COMPREHENSIVE STUDIES ON GEOMEDIA FROM ADDITIONAL LIKELY GROUND-WATER FLOW PATHS (FLOW TOPS)

RATIONALE FOR SELECTING GEOMEDIA SAMPLES CONSISTS OF IDENTIFYING ZONES OF HIGHEST GROUNDWATER FLOW

LABORATORY SORPTION/DESORPTION STUDIES WILL BE CONDUCTED UNDER APPROPRIATE CONDITIONS

COLLOID MIGRATION STUDIES INVOLVE CHARACTERIZATION OF NATURAL COLLOIDS

FIELD TESTS ARE UNDER CONSIDERATION