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

PRESENTATION TO
THE NUCLEAR WASTE TECHNICAL REVIEW BOARD

SUBJECT: **EXPERIMENTAL BASES FOR GLASS MODELING**

PRESENTER: KEVIN G. KNAUSS

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

PRESENTER'S
TELEPHONE NUMBER: (415) 422-1372

AUGUST 28-29, 1990

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WHAT DOES A VALIDATED RELEASE MODEL REQUIRE?

→● A CONCEPTUAL MODEL BASED UPON A FUNDAMENTAL UNDERSTANDING OF THE GLASS DISSOLUTION MECHANISMS

→● DATA TO SUPPORT THE MODEL FROM SIMPLE EXPERIMENTS DESIGNED TO ISOLATE INDIVIDUAL GLASS DISSOLUTION MECHANISMS

● A DATABASE OF SITE-SPECIFIC AND NATURAL ANALOGUE DATA TO TEST THE MODEL

OUTLINE OF PRESENTATION

- **EXPERIMENTAL DESIGN**

- **JUSTIFICATION - WHY NOT USE MATERIALS CHARACTERIZATION CENTER (MCC) OR SITE - SPECIFIC LEACH TESTS?**

- **DISSOLUTION RATE CONSTANT AND ACTIVATION ENERGY EXPERIMENTS**
  - **FLUID CHEMISTRY RESULTS**
  - **SOLID ANALYSES**

- **COMPARISON OF RATE CONSTANTS AND ACTIVATION ENERGIES**

- **CURRENT WORK TO VALIDATE MODEL**

EXPERIMENTAL WORK SUPPORTING MODELING: EXPERIMENTAL DESIGN

- **DISSOLUTION RATE CONSTANT AND FUNCTIONAL DEPENDENCE OF RATE ON pH**

$$r = s \, k_r \, (a_{H}+)^{-\eta} \; (1 - \frac{Q}{K})^{1} \quad \text{then} \quad \log r = \log (sk_r) + \eta \, pH$$

  - DISSOLUTION EXPERIMENTS DESIGNED USING EQ3/6 ALLOW APPLICATION OF REDUCED FORM OF RATE EQUATION
  - DILUTE BUFFERS DESIGNED USING EQ3/6 FIX pH

- **CHEMICAL "AFFINITY" EFFECTS AND ACTIVATION ENERGY**
  - REACT CRUSHED GLASS AT MODERATE TEMPERATURE IN FLOWING CELLS WHILE MAINTAINING LOW CONCENTRATIONS OF ELEMENTS IN SOLUTION ☞ <u>ACTIVATION ENERGY</u>
  - REACT GLASS MONOLITHS AT HIGH TEMPERATURE IN DICKSON BOMBS TO ELEVATE SOLUTION CONCENTRATIONS AND RUN ELEMENT-SPIKED FLUIDS THROUGH FLOW-THROUGH CELLS AT MODERATE TEMPERATURE ☞ <u>CHEMICAL "AFFINITY" EFFECTS</u>

- **CHEMISTRY OF REACTED GLASS SURFACE**
  - REACT GLASS MONOLITHS UNDER A VARIETY OF CONDITIONS AND DO DETAILED SURFACE ANALYSIS AND CHARACTERIZATION

WHY ONE CANNOT DEVELOP A MODEL FROM SITE-SPECIFIC LEACH TESTS

- MCC-TYPE TESTS ARE SIMPLE QUALITY CONTROL (QC) VEHICLES TO MONITOR A PRODUCTION PROCESS

- CANNOT ISOLATE FORWARD (DISSOLUTION) REACTIONS FROM BACKWARD (PRECIPITATION) REACTIONS (MEANS AND SPINOSA [1986] *AM. CERAM. SOC. BULL.*, 65, 780)

- CANNOT ISOLATE RATE CONSTANT, pH AND CHEMICAL AFFINITY EFFECTS IN DESCRIBING THE FORWARD RATE EXPRESSION

- CANNOT ISOLATE EFFECTS OF INTERACTIONS BETWEEN WATER AND CANISTER OR OTHER REPOSITORY MATERIALS FROM THOSE BETWEEN GLASS AND WATER

WHY ONE CANNOT DEVELOP A MODEL FROM SITE-SPECIFIC LEACH TESTS

(CONTINUED)

- SOLUTION COMPOSITIONS ARE CONTROLLED BY A CONVOLUTION OF COMPETING PROCESSES, AND SO IS THE NATURE OF THE GLASS ALTERATION LAYER

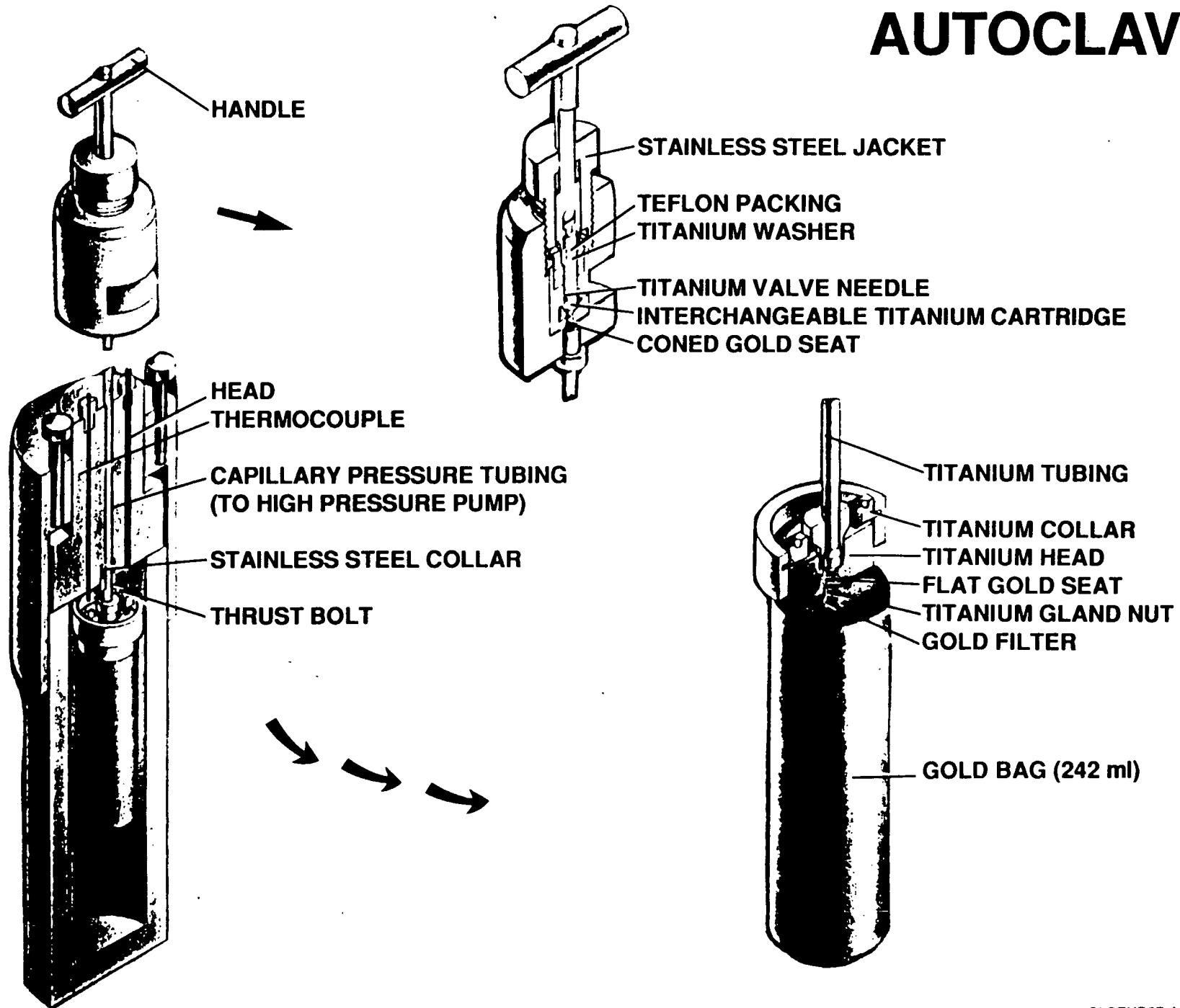- TOO MANY UNKNOWNS, NOT ENOUGH EQUATIONS

☞ <u>ENORMOUS BODY OF GLASS "LEACH" DATA IN NUCLEAR WASTE LITERATURE IS FROM EXPERIMENTS DESIGNED TO RESEMBLE REPOSITORY. THIS GREATLY COMPLICATES RETRIEVAL OF RATE DATA OR DATA RELEVANT TO ANY FUNDAMENTAL PROPERTIES OF GLASS DISSOLUTION MECHANISM</u>
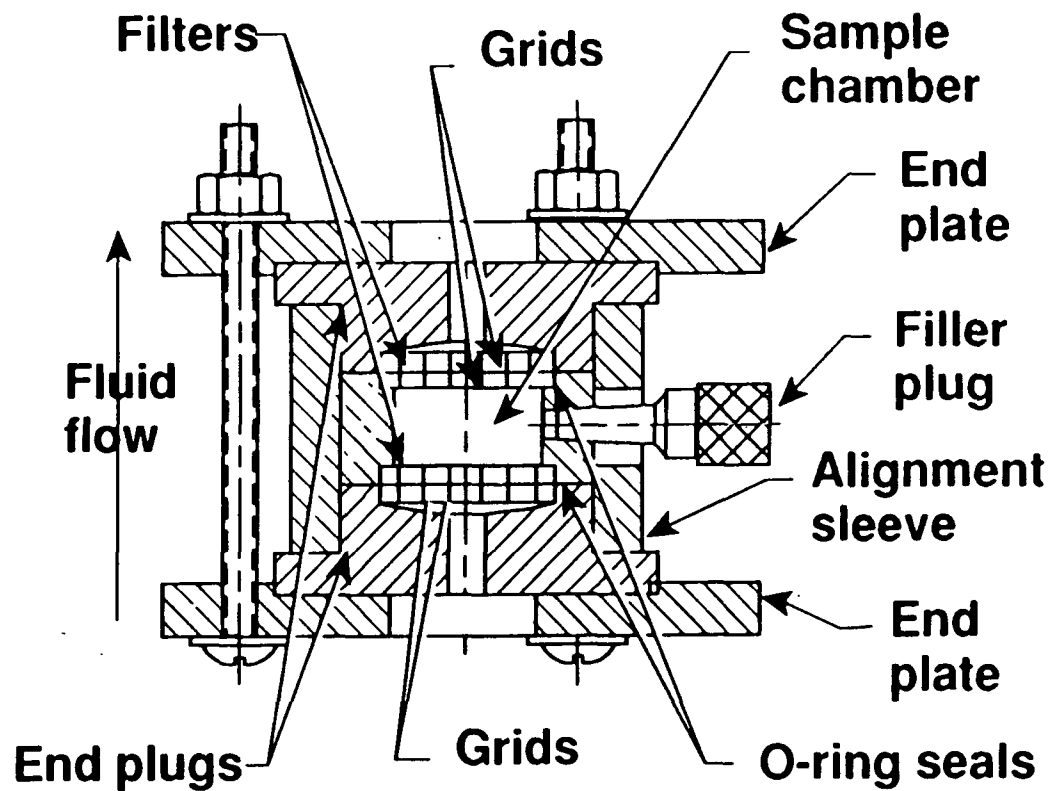
BUFFER COMPOSITIONS CALCULATED
USING EQ3/6

COMPOSITION	pH		
0.005 m KCl & HCl	1.0		
0.005 m KHPhth & HCl	2.0	→	4.0
0.005 m KHPhth & KOH	5.0	→	6.0
0.005 m B(OH)$_3$ & KOH	8.0	→	10.0
0.005 m KCl & KOH	12.0	→	13.0

DICKSON TYPE AUTOCLAVE

HANDLE

STAINLESS STEEL JACKET

TEFLON PACKING
TITANIUM WASHER

TITANIUM VALVE NEEDLE
INTERCHANGEABLE TITANIUM CARTRIDGE
CONED GOLD SEAT

HEAD
THERMOCOUPLE

CAPILLARY PRESSURE TUBING
(TO HIGH PRESSURE PUMP)

STAINLESS STEEL COLLAR

THRUST BOLT

TITANIUM TUBING

TITANIUM COLLAR
TITANIUM HEAD
FLAT GOLD SEAT
TITANIUM GLAND NUT
GOLD FILTER

GOLD BAG (242 ml)
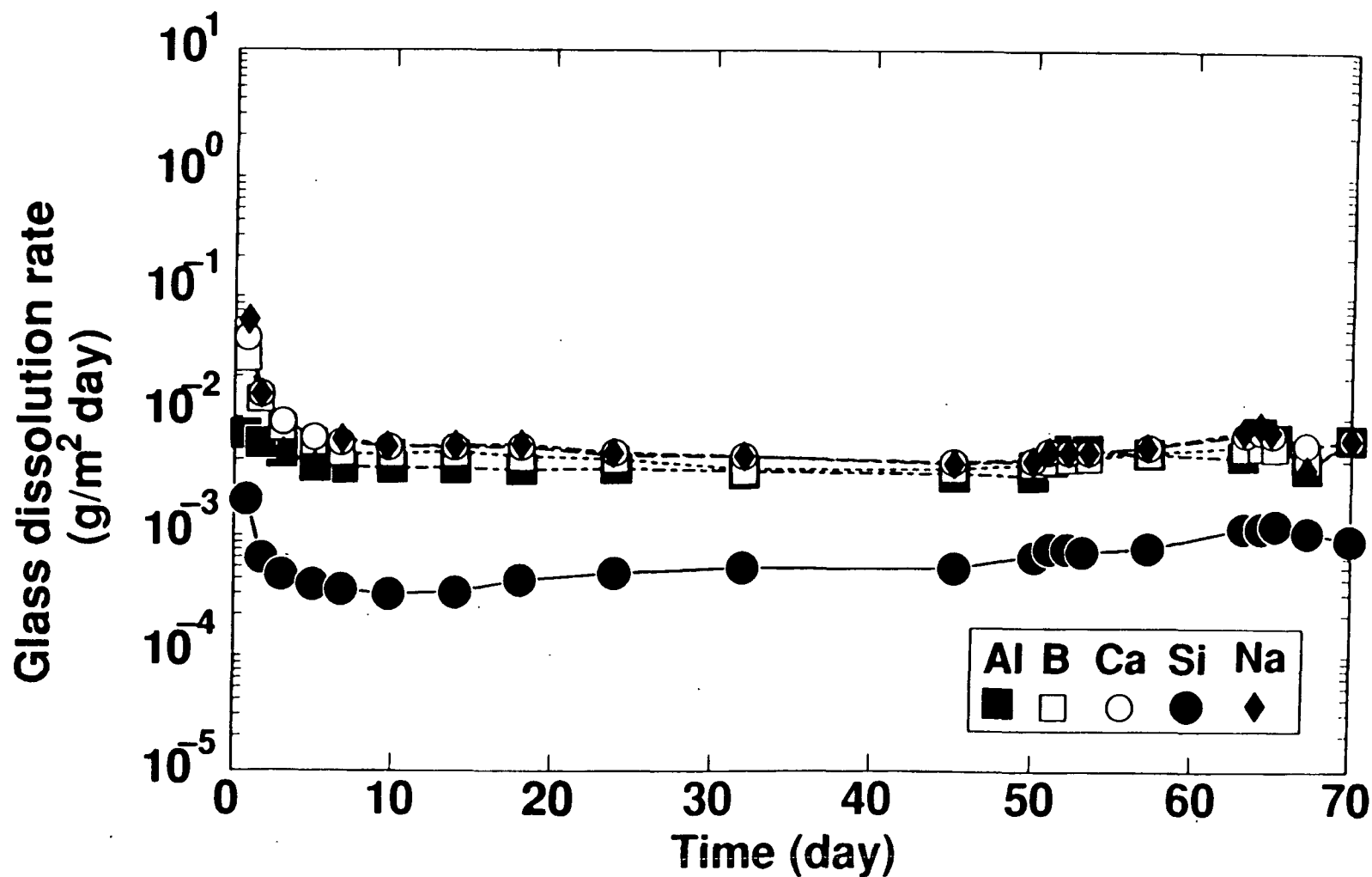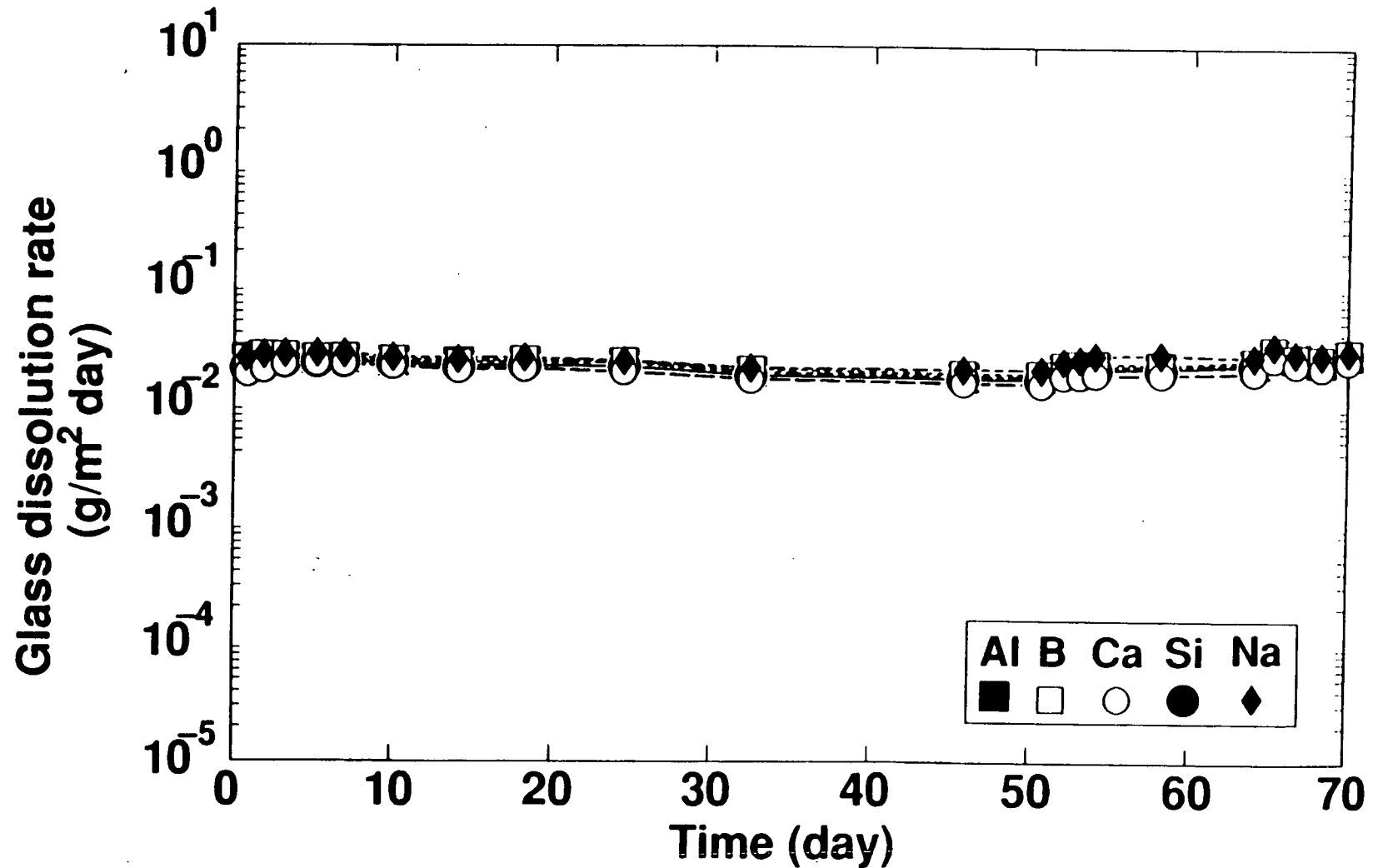
SINGLE-PASS, FLOW-THROUGH CELL

NORMALIZED GLASS DISSOLUTION RATE VS. TIME, pH 4.0, 25°C

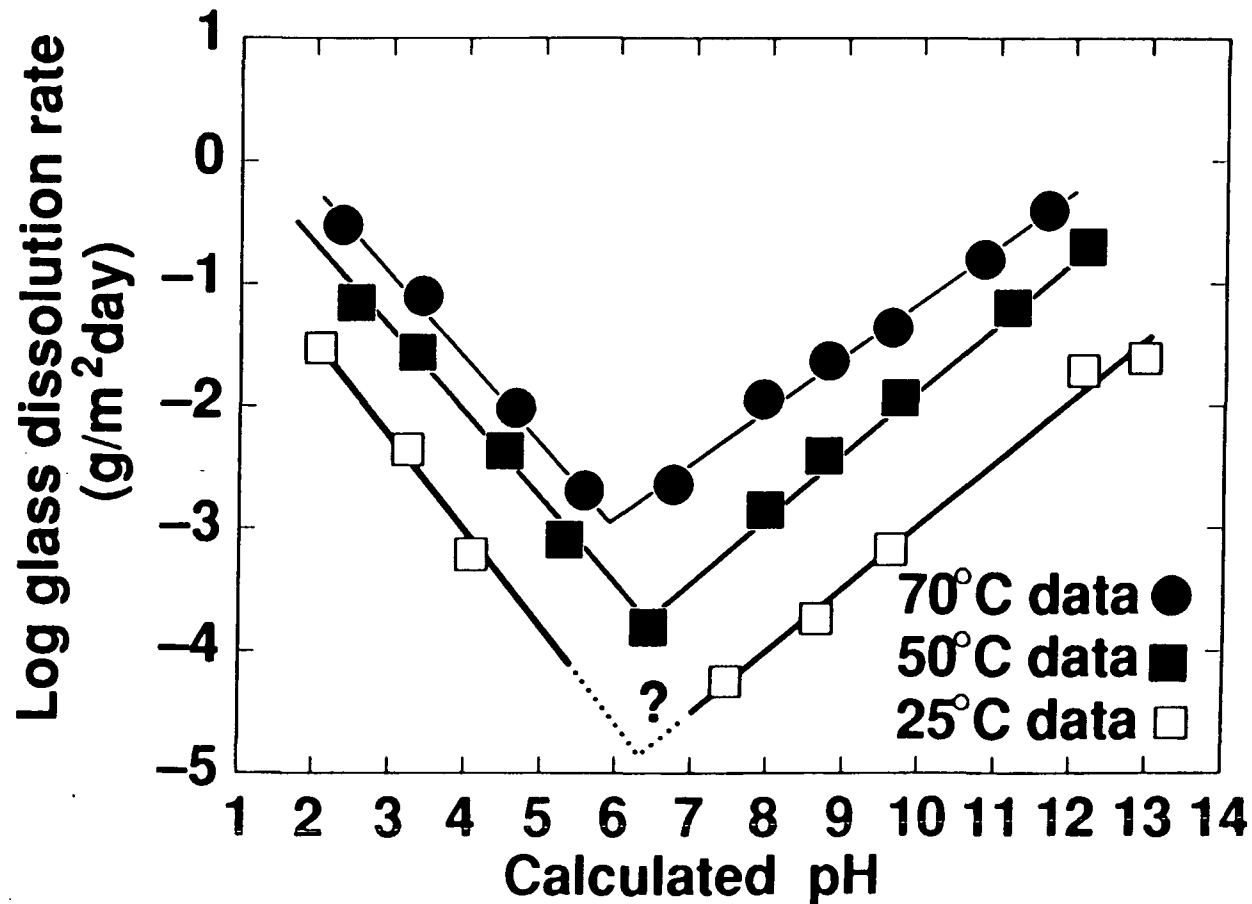# NORMALIZED GLASS DISSOLUTION RATE
VS. TIME, pH 12.1, 25°C

LIMITING GLASS DISSOLUTION RATE
(g/m²·d, NORMALIZED TO EACH ELEMENT)
VS. *IN SITU* pH AT 25°C, 50°C AND 70°C

Limiting normalized glass dissolution rate vs. pH
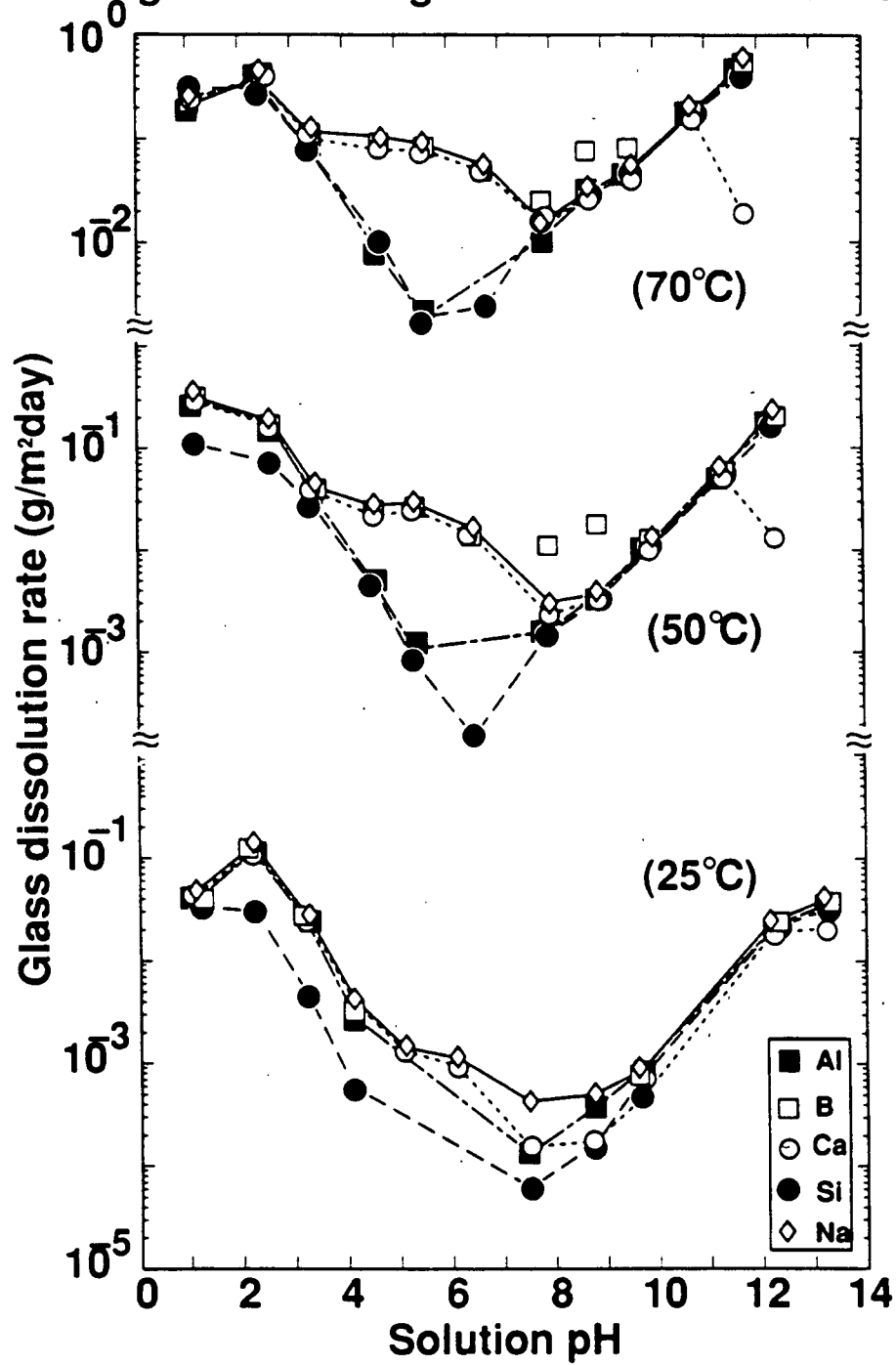
REGRESSION OF THE Si-NORMALIZED GLASS DISSOLUTION RATES (g/m²·d) VS. *IN SITU* pH AT 25°C, 50°C AND 70°C

Simple glass dissolution rate vs. pH normalized to Si release

SUMMARY OF RATE CONSTANTS AND REACTION ORDER IN pH

- **WE USED THE SIMPLE RATE LAW TO CALCULATE DISSOLUTION RATE CONSTANTS AND REACTION ORDER WITH RESPECT TO pH AT EACH TEMPERATURE USING THE Si-NORMALIZED GLASS DISSOLUTION DATA OVER TWO pH INTERVALS (THE TWO SIDES OF THE U-SHAPED DISSOLUTION RATE VS. pH CURVES)**

$$\log r = \log (sk_r) + \eta\, pH$$

pH RANGE	log k (g glass/m²·d)			η (REACTION ORDER IN pH)		
	25°C	50°C	70°C	25°C	50°C	70°C
LOW	-0.77	+0.72	+1.20	-0.48	-0.70	-0.69
HIGH	-8.10	-7.00	-5.10	+0.51	+0.51	+0.40

SEM OBSERVATION AND EMP ANALYSES

25°C, 50°C AND 70°C EXPERIMENTS

- WELL-DEVELOPED GEL LAYER AT LOW TO NEUTRAL pH, DEPENDING ON TEMPERATURE, NONE OBSERVED AT HIGHER pHs

- GEL DEVOID OF Na, Ca AND Al (B NOT ANALYZED) AT LOW pH IN ACCORD WITH FLUID CHEMISTRY RESULTS

- GRAIN SURFACES IN RUNS WITH pH > 7.9 AT 70°C COVERED BY CIRCULAR ETCH PITS OFTEN ALIGNED WITH CURVED LEDGES PRODUCED BY CONCHOIDAL FRACTURE

- ABUNDANT Ca-RICH, FINE-GRAINED SECONDARY MINERALS PRESENT IN pH 13 RUN AT 70°C

ETCH PITS FORMED ON GLASS GRAINS
IN 70°C pH 12 EXPERIMENT

FOURIER TRANSFORM INFRARED (FTIR) AND MAGIC ANGLE SAMPLE SPINNING NUCLEAR MAGNETIC RESONANCE (MASS NMR) RESULTS

- FTIR SPECTRA CONFIRM FLUID CHEMISTRY RESULTS AND SHOW THAT IN ACID SOLUTIONS THE ALTERED GLASS SURFACE CONTAINS ABUNDANT H_2O AND OH^-, WHILE IN ALKALINE SOLUTIONS THE GLASS SURFACE RESEMBLES THE UNREACTED GLASS

- ^{27}AI AND ^{29}Si MASS NMR SPECTRA ALSO CONFIRM FLUID CHEMISTRY RESULTS AND SHOW THAT THE AI AND Si ENVIRONMENTS ON THE GLASS SURFACE IN THE ALKALINE EXPERIMENTS RESEMBLE THAT OF THE UNREACTED GLASS, WHILE THE ALTERED GLASS SURFACE IN THE ACID EXPERIMENTS IS VERY DIFFERENT

COMPARISON OF DISSOLUTION RATE CONSTANTS

- **USING A TRANSITION STATE THEORY-LIKE RATE EQUATION OF THE FORM**

$$r = s \, k_r \, (a_{H^+})^{-\eta} \left(1 - \frac{Q}{K}\right)$$

BOURCIER ET AL. (1989) MODELED THE DISSOLUTION OF SRL-165 GLASS IN 0.003 m NaHCO$_3$ (pH 8.5) AT 150°C OBTAINED FROM CLOSED-SYSTEM (DICKSON BOMB) EXPERIMENTS. AS A FIRST APPROXIMATION THEY ASSUMED NO pH DEPENDENCY. THEY USED THE RATE CONSTANT AS A FITTING PARAMETER AND ESTIMATED A RATE CONSTANT OF 6.1 x 10^{-9} g/cm^2 • sec FOR SRL-165

COMPARISON OF DISSOLUTION RATE CONSTANTS

(CONTINUED)

- USING THE pH 8.5 REGRESSED RATE FOR OUR SIMPLE GLASS AT 70°C AND OUR MEASURED ACTIVATION ENERGY (20 kcal/mol) WE CALCULATE A 150°C DISSOLUTION RATE OF 6.2 x 10^{-9} g/cm^2 • sec. THIS IS EQUIVALENT TO THE RATE CONSTANT MEASURED BY BOURCIER ET AL.

☞ FOR THESE TWO GLASSES THERE IS NO COMPOSITIONAL DEPENDENCY IN THE <u>RATE CONSTANT.</u> THE MEASURED <u>RATE</u> IN TWO INITIALLY SIMILAR EXPERIMENTS MAY DIFFER, HOWEVER, DUE TO CHEMICAL AFFINITY EFFECTS

COMPARISON OF DISSOLUTION ACTIVATION ENERGIES

Reaction	Activation Energy (kcal/mol)	Process Control	Reference
$I + I \rightarrow I_2$ in CCl_4 solvent	3	diffusion	Benson (1960)
SiO_2 (qtz) dissolution	16 – 18	surface reaction	Rimstidt and Barnes (1980)
$NaAlSi_3O_8$ (ab) dissolution	14 (neutral pH)	surface reaction	Knauss and Wolery (1986)
glass dissolution (range in composition)	14 – 22	surface reaction	White (1986)
basalt dissolution	16	surface reaction	Crovisier et al. (1987)
simple glass dissolution	20 ± 2 (6 < pH < 11)	surface reaction	Knauss et al. (1990)

☞ ACTIVATION ENERGIES LARGER THAN APPROXIMATELY 5 kcal/mol ARE INDICATIVE OF A SURFACE REACTION CONTROLLED DISSOLUTION PROCESS RATHER THAN A DIFFUSIONALLY CONTROLLED PROCESS

CONCLUSIONS

- **GLASS DISSOLUTION IS STRONGLY pH DEPENDENT AND DISSOLUTION MODELS MUST EXPLICITLY ACCOUNT FOR THIS DEPENDENCY**

- **THE FACT THAT THE DISSOLUTION ACTIVATION ENERGY IS 20 kcal/mol, ETCH PITS WERE OBSERVED ON THE REACTED GLASS GRAINS, AND RELEASE RATES WERE LINEAR WITH TIME SUGGESTS A SURFACE REACTION CONTROLLED DISSOLUTION PROCESS OVER THE INTERVAL pH 6 THROUGH pH 11**

CONCLUSIONS
(CONTINUED)

- RATE CONSTANTS, ACTIVATION ENERGY AND REACTION ORDER WITH RESPECT TO pH DETERMINED IN THESE WELL-CONSTRAINED EXPERIMENTS MAY BE USED TO DEVELOP GEOCHEMICAL MODELS USING A TST-LIKE RATE EQUATION THAT INCLUDES A TERM FOR THE CHEMICAL AFFINITY FOR DISSOLUTION OF THE DISSOLVING GLASS (GEL) SURFACE

☞ THE AFFINITY TERM CAN ACCOUNT FOR THE PARABOLIC SHAPE IN RELEASE TRENDS CHARACTERISTIC OF CLOSED SYSTEMS, WHICH HAS PREVIOUSLY BEEN ATTRIBUTED TO DIFFUSIONAL CONTROL OF THE DISSOLUTION PROCESS

EXPERIMENTAL WORK SUPPORTING MODELING: CURRENT EXPERIMENTS WITH SIMPLE GLASS

MODEL VALIDATION: THE FORM OF THE RATE EQUATION AND THE EFFECTS OF CHEMICAL AFFINITY

- **RUN ELEMENT-SPIKED FLUIDS THROUGH FLOW-THROUGH CELLS AT SEVERAL TEMPERATURES**

  <u>CHEMICAL "AFFINITY" EFFECTS</u>

  - USE SODIUM METASILICATE TO FIX DISSOLVED Si AT APPROX. 50% SATURATION w.r.t. AMORPHOUS SILICA SOLUBILITY
  - RUN EXPERIMENTS AT pH 2, 6 AND 12
  - RUN EXPERIMENTS AT 25° AND 70°C

- **RUN CLOSED SYSTEM (DICKSON BOMB) EXPERIMENTS AT SEVERAL TEMPERATURES**

  <u>CHEMICAL "AFFINITY" EFFECTS AND MODEL VALIDATION</u>

  - RUN EXPERIMENTS IN 0.003 m $NaHCO_3$ (pH 8.5)
  - RUN EXPERIMENTS AT 100°, 150°, 200°, AND 250°C