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

PRESENTATION TO THE NUCLEAR WASTE TECHNICAL REVIEW BOARD

SUBJECT: MODELING OF GLASS DISSOLUTION

PRESENTER: WILLIAM L. BOURCIER

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

PRESENTER'S TELEPHONE NUMBER: (415) 423-3745

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

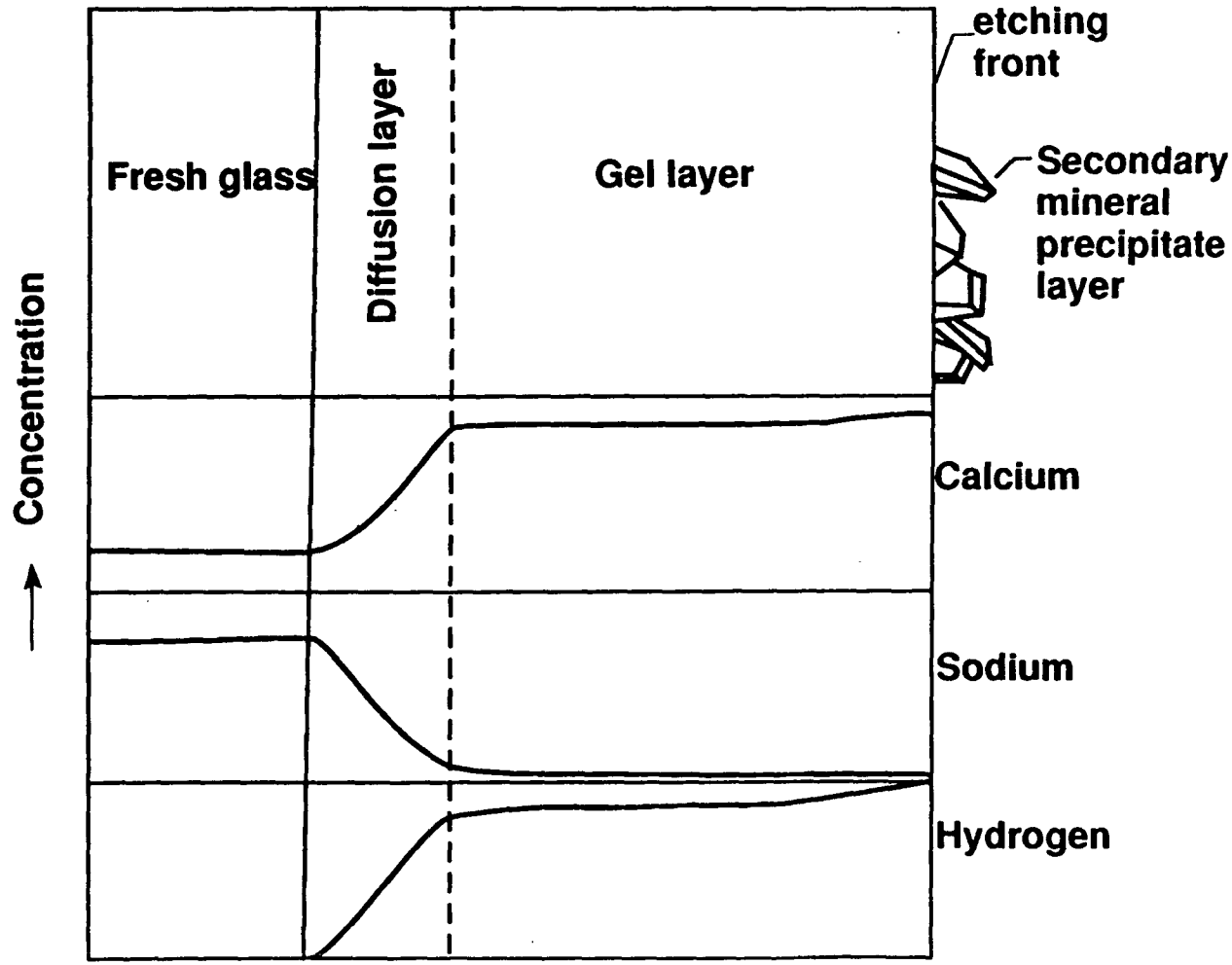
- DATA TO SUPPORT THE MODEL FROM SIMPLE EXPERIMENTS DESIGNED TO ISOLATE INDIVIDUAL GLASS DISSOLUTION MECHANISMS

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

GLASS COMPOSITIONS (CATION MOLE %)

Component	SRL–165	Simple Glass (nominal)
Si	43.4	42.3
Fe	6.2	–
Al	4.7	10.5
B	9.7	12.1
Na	14.5	30.0
Li	16.0	–
Ca	1.2	5.1
Mg	0.8	–
U	0.5	–
Mn	1.4	–
Ni	1.2	–
Ba	.03	–
Ti	.07	–
Zn	.02	–
Zr	.03	–
Cs	.06	–
Sr	.05	–
P	2.0	–

SCHEMATIC OF GLASS ALTERATION LAYERS AND ELEMENT PROFILES

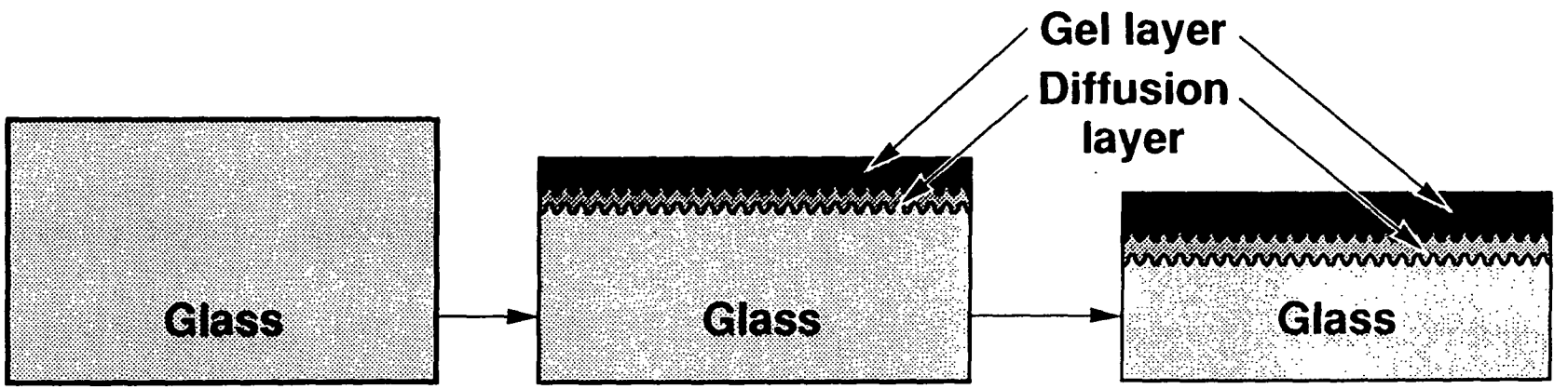


GLASS DISSOLUTION MODEL

Hydration of the surface and ion exchange of alkalis

Diffusion layer thickens until rate of diffusion of alkalis equals rate of dissolution of network structure of gel

Diffusion and gel layers migrate into the glass maintaining a nearly constant thickness (steady state)

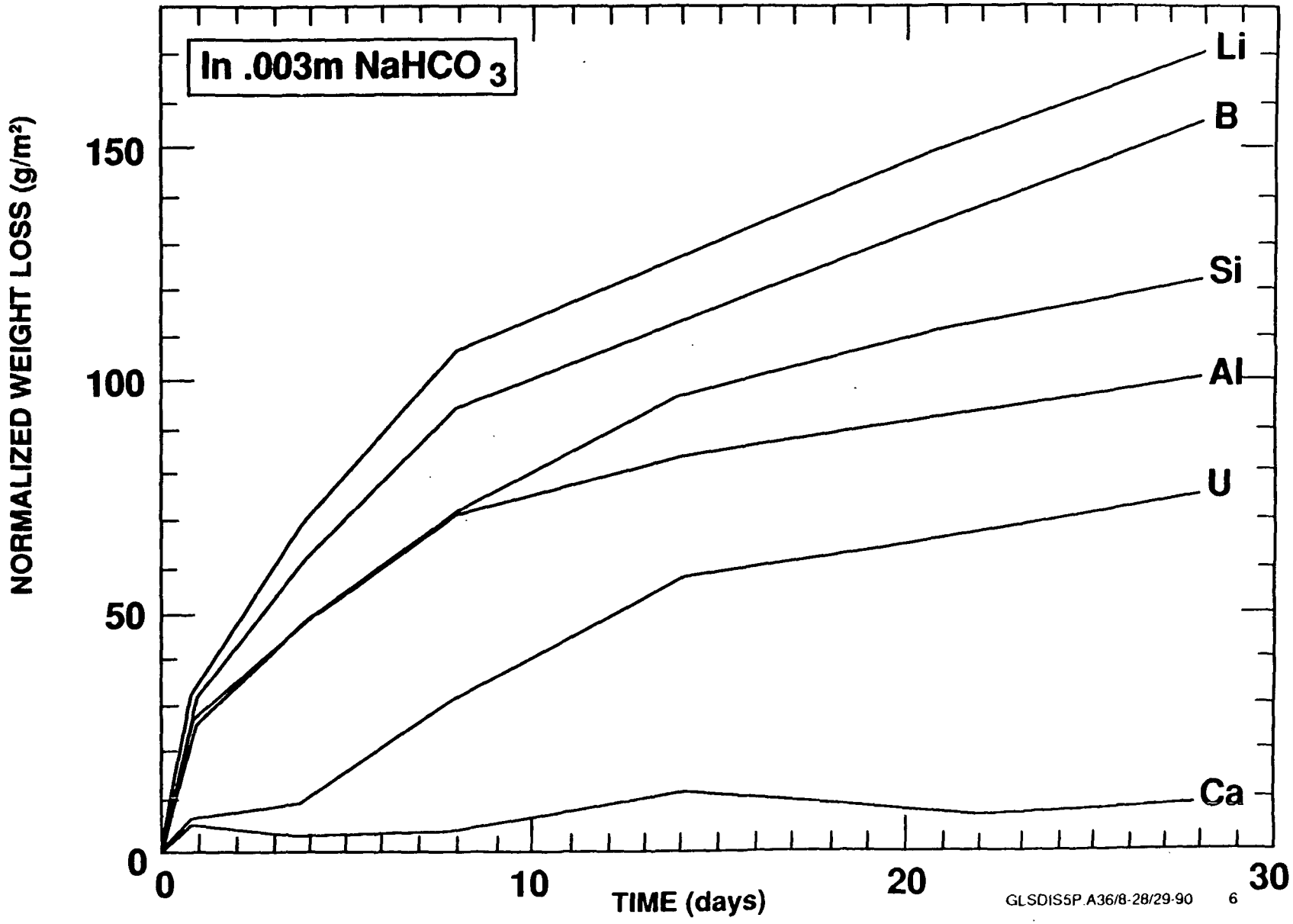


Dissolution of gel layer controls glass dissolution rates

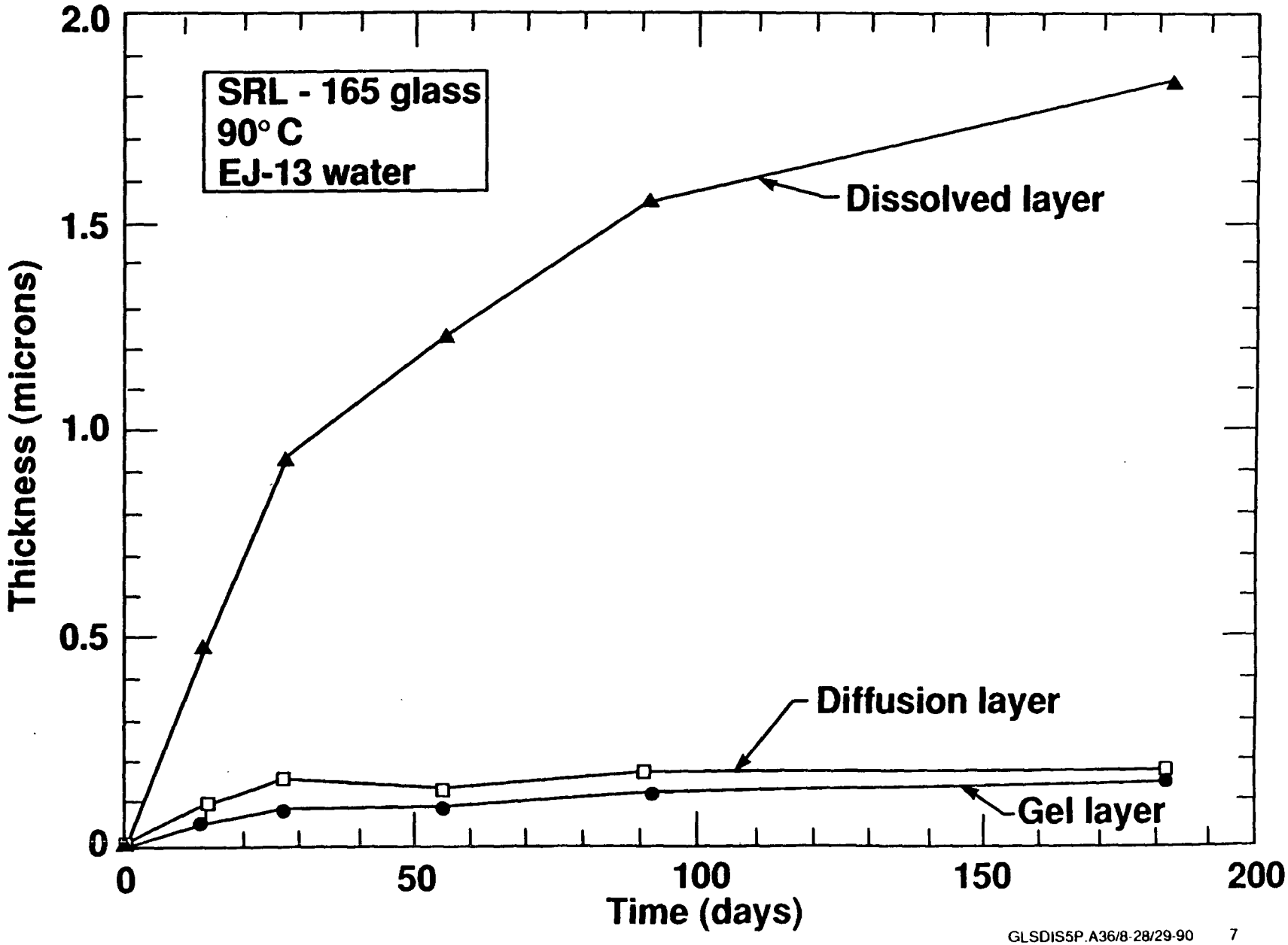
- **short-term — dissolution affinity of gel**
- **long-term — precipitation of secondary phases**

AEM MICROGRAPH OF REACTED GLASS SURFACE

NORMALIZED RELEASE FROM SRL-165 GLASS AT 150°C



THICKNESS OF SURFACE LAYERS AS A FUNCTION OF TIME



MODELING APPROACHES AND LIMITATIONS

- SOLUBILITY LIMITS
  - ASSUME PURE CRYSTALLINE PHASES PRECIPITATE AND CONTROL RADIONUCLIDE SOLUBILITIES

- HYDRATION THEORY
  - PROVIDES RELATIVE DURABILITIES OF GLASSES FROM SIMPLE THERMODYNAMIC MODEL BUT CAN NOT BE USED TO PREDICT LONG-TERM GLASS DISSOLUTION RATES

- MECHANISTIC MODELS
  - COMBINE SOLUBILITY LIMITS AND MODIFIED HYDRATION THEORY TO MAKE LONG-TERM DISSOLUTION RATE PREDICTIONS POSSIBLE BUT NEED RESULTS FROM EXPERIMENTS THAT QUANTIFY MODEL PARAMETERS (SUCH AS RATE, CONSTANT, AFFINITY TERM, ETC.)

MECHANISTIC MODELING APPROACH

- IDENTIFY CHEMICAL PROCESSES OF GLASS DISSOLUTION
- PERFORM EXPERIMENTS THAT ISOLATE AND QUANTIFY THESE PROCESSES
- GENERATE MODEL OF GLASS DISSOLUTION
- VALIDATE MODEL WITH SITE-SPECIFIC EXPERIMENTS AND NATURAL ANALOGUES

POTENTIAL RATE-LIMITING PROCESSES

- ION EXCHANGE
- ➤ NETWORK HYDROLYSIS (BREAKING OF Si-O BONDS)
- DIFFUSION OF IONS OR WATER THROUGH GLASS OR ALTERATION LAYERS
- CHEMICAL TRANSPORT THROUGH FLUIDS IN ALTERATION LAYERS

RATE LAW USED TO MODEL DISSOLUTION KINETICS

- **RATE LAW**

$$\frac{dc_i}{dt} = \frac{S}{V} \nu k_r (a_{H^+})^{\eta} \left(1 - \frac{Q}{K}\right)$$

S/V	SURFACE AREA OVER VOLUME
Q	ACTIVITY PRODUCT FOR DISSOLUTION REACTION
ν	STOICHIOMETRIC FACTOR
k_r	RATE CONSTANT
K	EQUILIBRIUM CONSTANT FOR DISSOLUTION REACTION
η	ORDER OF pH DEPENDENCE

- **EXPERIMENTS MUST PROVIDE k_r, K, AND η**

WHAT IS EQ3/6?

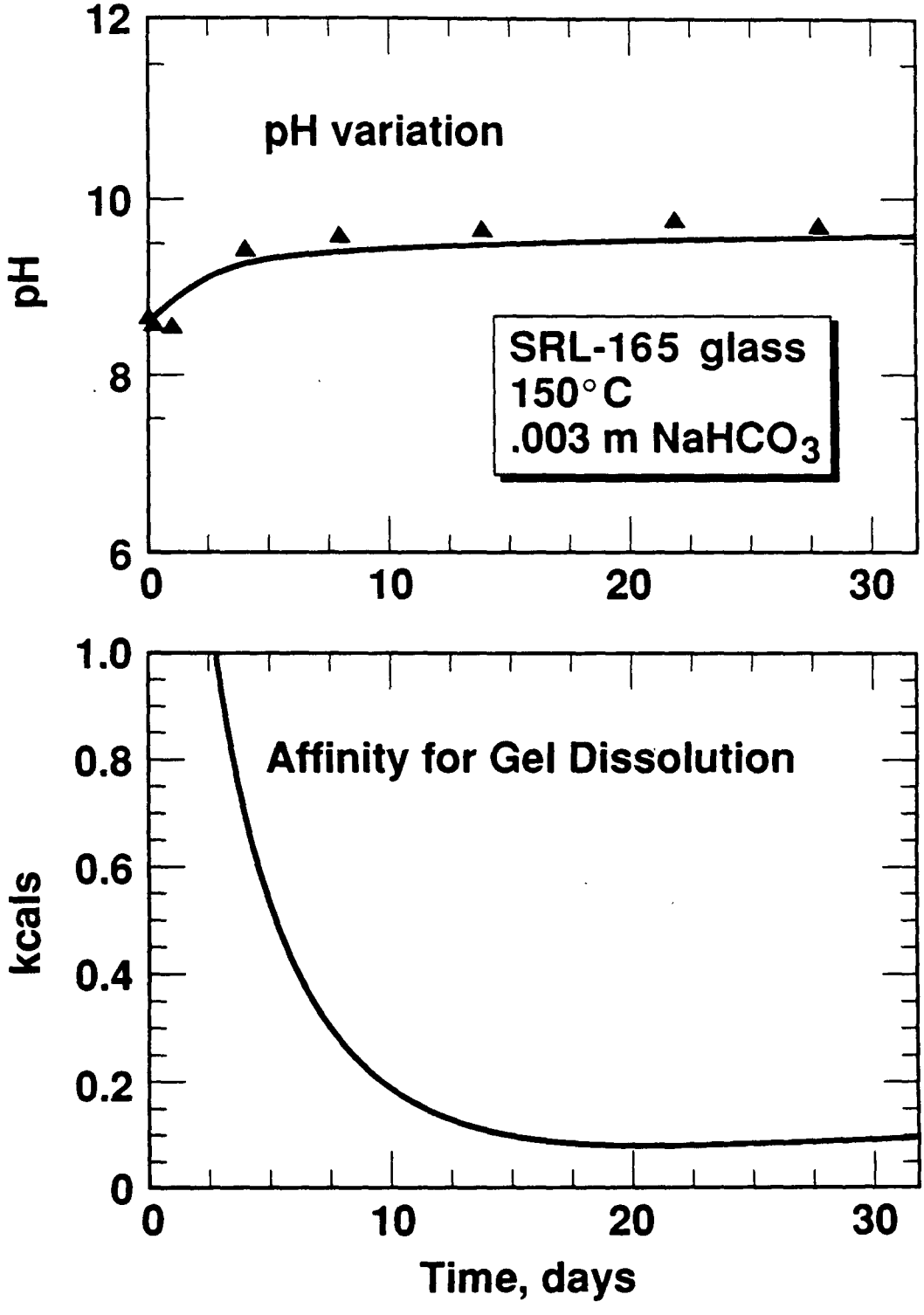
- SET OF COMPUTER PROGRAMS AND THERMODYNAMIC DATABASE TO SIMULATE FLUID-SOLID INTERACTIONS
- EQ3nr COMPUTES AQUEOUS SPECIATION AND MINERAL/SOLID SATURATION STATES
- EQ6 COMPUTES THE REACTION PATH OF A FLUID-SOLID SYSTEM

<u>APPLIED TO GLASS DISSOLUTION:</u>

USER INPUT →GLASS AND FLUID COMPOSITIONS AND RATE CONSTANT

CODE OUTPUT →GLASS DISSOLUTION RATE
→TYPES AND AMOUNTS OF SECONDARY PHASES
→SOLUTION COMPOSITION AS A FUNCTION OF TIME

COMPARISON OF EXPERIMENTAL RESULTS WITH MODEL SIMULATION



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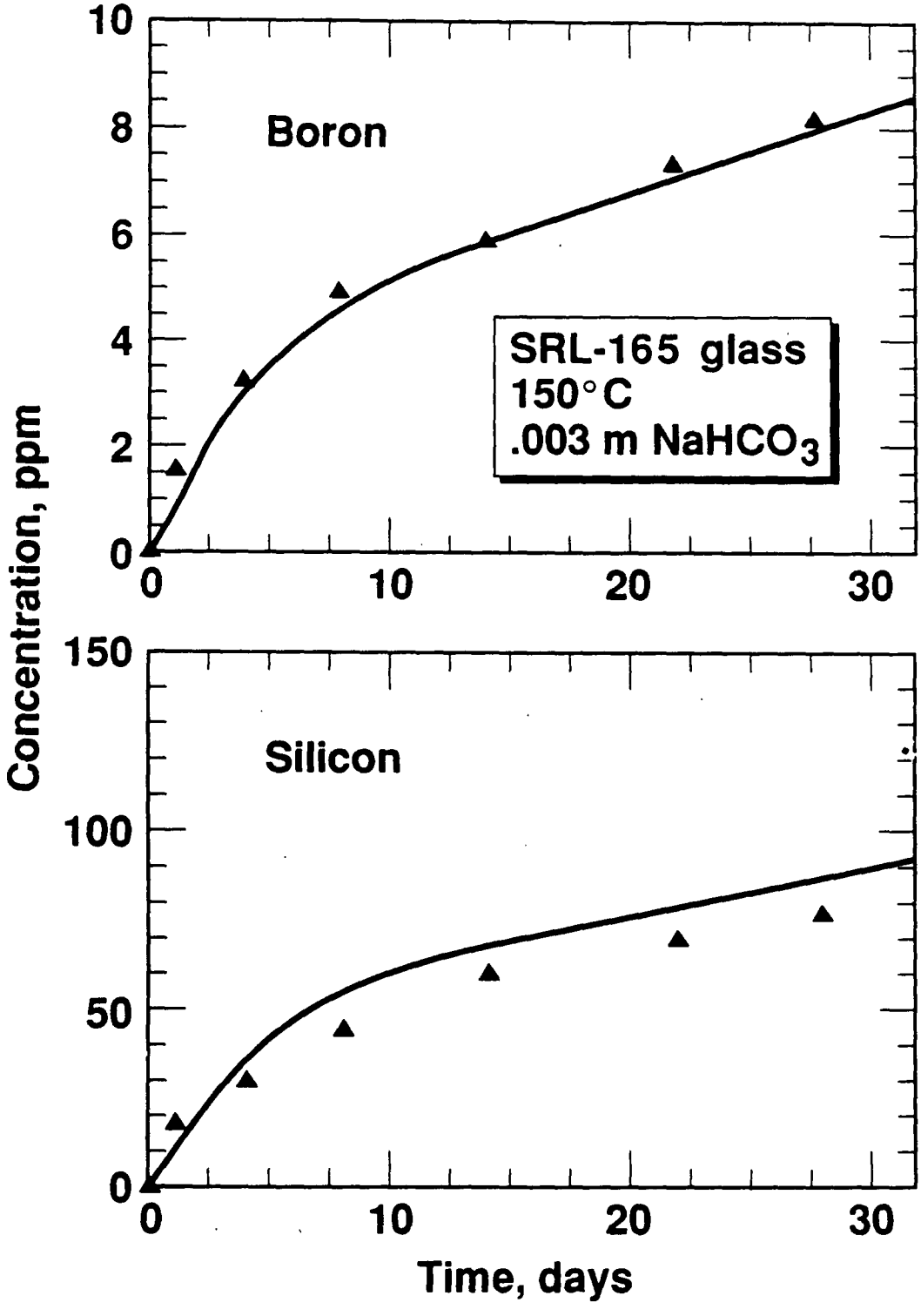

MODEL DEVELOPMENT: CURRENT NEEDS

- **EXPERIMENTS THAT ISOLATE THE PROCESSES TAKING PLACE DURING GLASS DISSOLUTION, THE RESULTS OF WHICH CAN BE USED TO QUANTIFY THE MODEL**
  - FLOW-THROUGH TESTS WHICH PROVIDE pH DEPENDENCE OF RATE CONSTANT
  - FLOW-THROUGH TESTS WITH DOPED BUFFER SOLUTIONS THAT PROVIDE FORM OF AFFINITY TERM
  - CLOSED-SYSTEM TESTS DOPED WITH SECONDARY PHASES THAT WILL TEST MODEL-PREDICTED DEPENDENCE OF DISSOLUTION RATE ON SOLUTION COMPOSITION
  - CLOSED-SYSTEM AND FLOW-THROUGH TESTS IN D_2O THAT PROVIDE KEY INFORMATION ON RATE-LIMITING STEP

MODEL DEVELOPMENT: CURRENT NEEDS

(CONTINUED)

- EXPERIMENTS IN SIMPLE SYSTEMS THAT CAN BE USED TO VALIDATE MODEL
  - CLOSED-SYSTEM TESTS ON SIMPLE ANALOGUE GLASSES IN SIMPLE SOLUTIONS WITH COMPLETE CHARACTERIZATION OF RESULTS (SOLUTION COMPOSITION, SECONDARY PHASES, AND COMPOSITIONS OF ALTERATION LAYERS THROUGH TIME)
- EXPERIMENTS ON A RANGE OF GLASS COMPOSITIONS TO ESTABLISH COMPOSITIONAL EFFECTS ON GLASS DISSOLUTION RATE

MODEL DEVELOPMENT: FUTURE NEEDS

- **WHAT HAPPENS TO THE ACTINIDES**
  - INCORPORATED INTO SECONDARY PHASES
  - PRECIPITATE AS SEPARATE PHASES
  - ADSORBED ONTO SURFACES
  - REMAIN SOLUBLE AS DISSOLVED OR COLLOIDAL SPECIES
- **APPLY MODEL TO UNSATURATED CONDITIONS**
- **INCORPORATE SURFACE CHEMISTRY INTO MODEL**

SUMMARY

- AFFINITY (NETWORK HYDROLYSIS) MODEL HAS BEEN COUPLED TO EQ3/6
- MODEL HAS BEEN SHOWN TO PROVIDE GOOD AGREEMENT WITH CLOSED-SYSTEM TEST RESULTS
- EXPERIMENTS WHICH ISOLATE AND QUANTIFY GLASS DISSOLUTION PROCESSES ARE NEEDED FOR FURTHER MODEL DEVELOPMENT
- IMPROVEMENTS ARE NEEDED IN ORDER TO BETTER ACCOUNT FOR THE DEPENDENCE OF THE DISSOLUTION RATE ON GLASS COMPOSITION AND GLASS SURFACE CHEMISTRY