Rates and Mechanisms of Microbially-Mediated Metal Reduction

Breakout Session

Session Introduction

Objectives:

- Share most recent research results obtained with FRC and other field sediments.
- Encourage collaboration amongst NABIR investigators to establish more direct links to field-scale projects.
- Provide support and specific information for reactive transport modeling of the FRC site.

Agenda

- Session introduction; Bill Burgos, PSU
- Microbial U(VI) reduction in FRC sediment columns; Baohua Gu, ORNL
- Limitations on microbial activity and mechanisms of U(IV) oxidation at the FRC; Lee Krumholz, OSU
- Coupled Fe(III) and U(VI) bioreduction in iron-rich sediments; Eric Roden, UA
- Rates of direct and indirect bioreduction of U(VI) and Tc(VII); Chongxuan Liu, PNNL
- Mechanisms, Rates, and Rate Formulations: Goals of breakout session; Bill Burgos, PSU
- Group participation/discussion/input

Rates and Mechanisms of Microbially-Mediated Metal Reduction

Deliverable from Breakout Session:

Report to summarize and synthesize state of knowledge

Draft Report Format:

1 – mechanisms of metal reduction;
2 – rates of metal reduction;
3 – comprehensive reaction network operative at the FRC site;
4 – emerging research needs/knowledge gaps.

Mechanisms, Rates, and Rate Formulations

Mechanism:
Series of elementary reactions that describes the formation of final reaction products from initial reactants

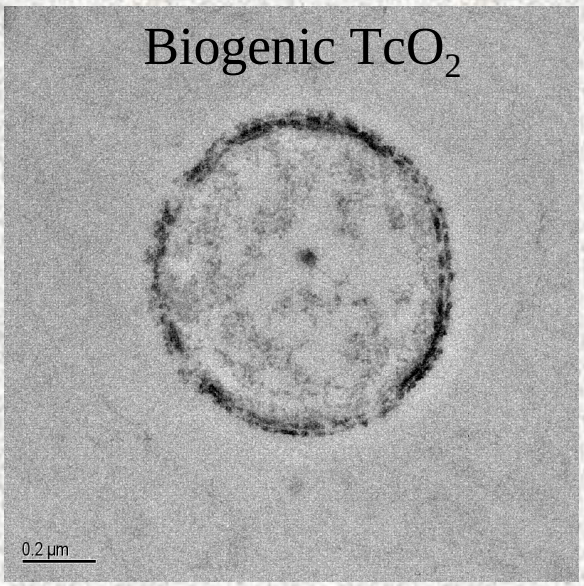
Rate:
Reaction velocity (e.g., consumption of reactant versus time)

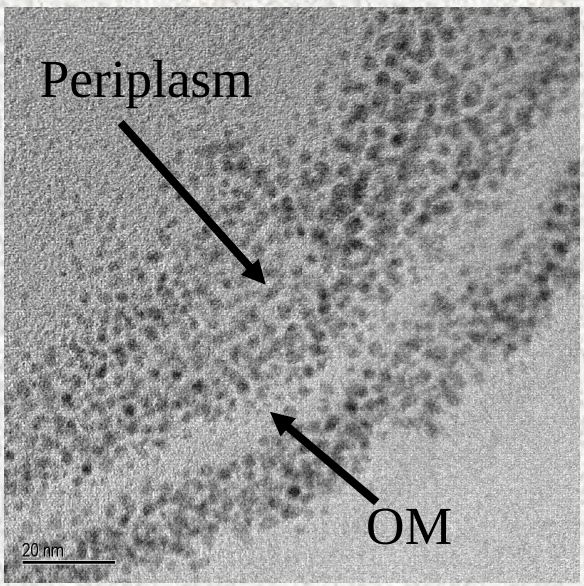
Rate Formulation:
Mathematical equation used to represent the measured rate

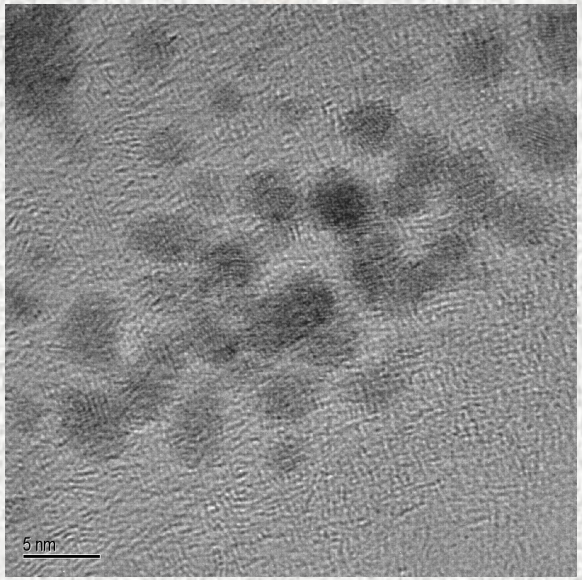
Qualitative Assessment of Reaction Mechanism

where does reduction occur?
what enzymes are involved?

Tc Reduction by *Shewanella putrefaciens* CN32







Membrane Components of Gram-negative Bacterium

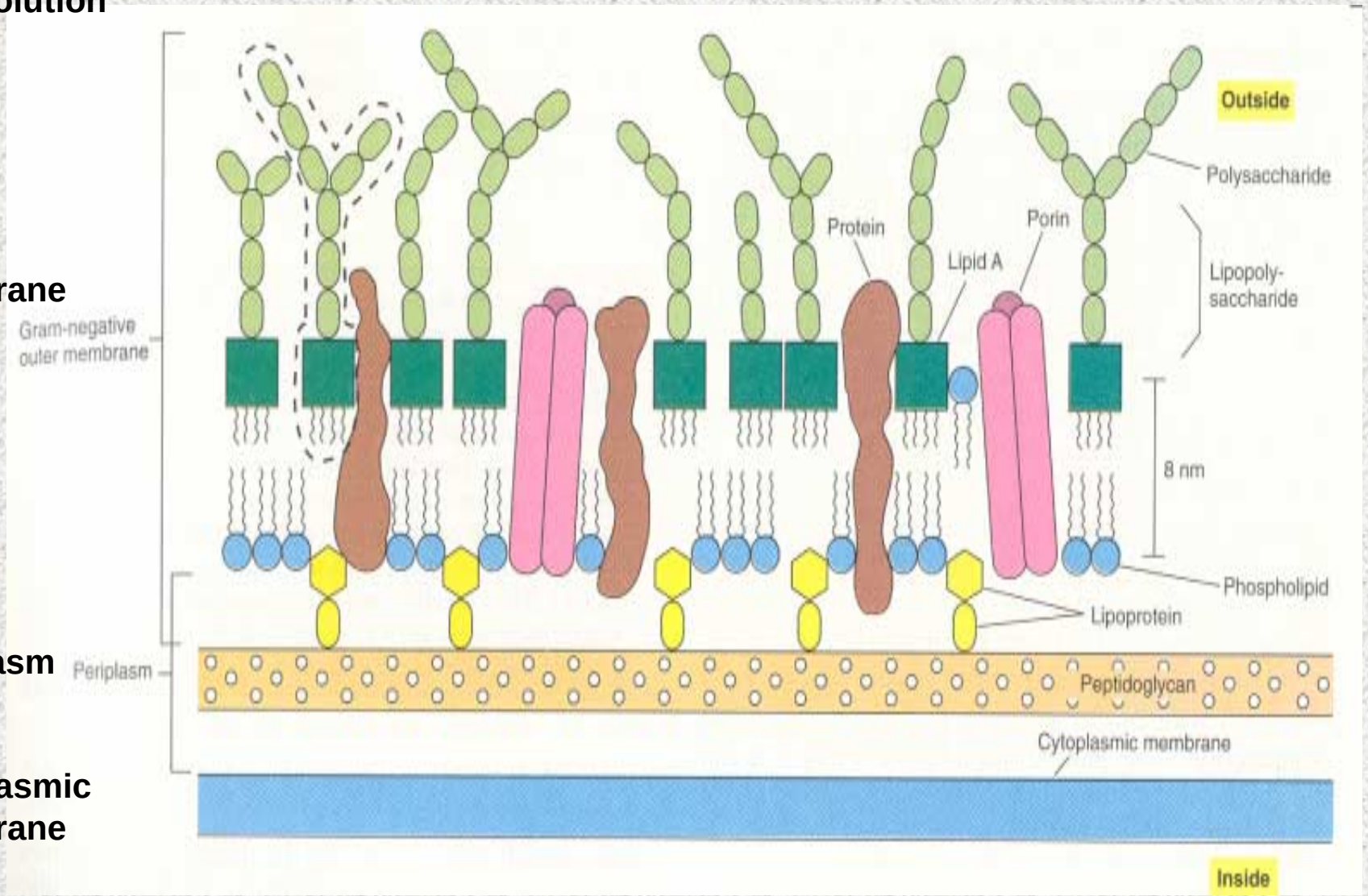
bulk solution

outer membrane

periplasm

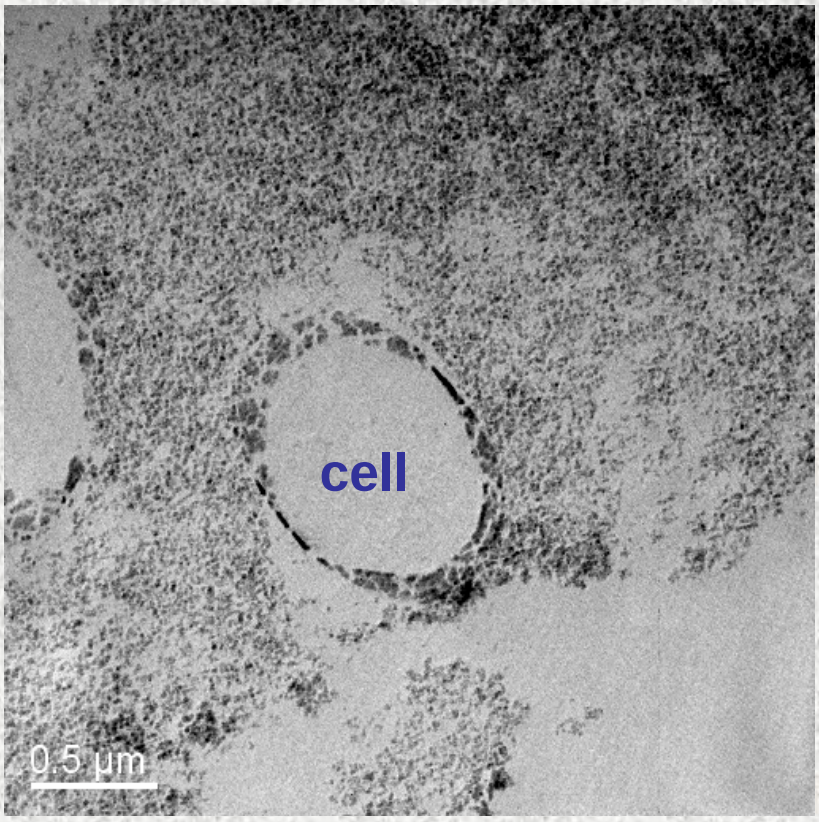
cytoplasmic membrane

inside cell

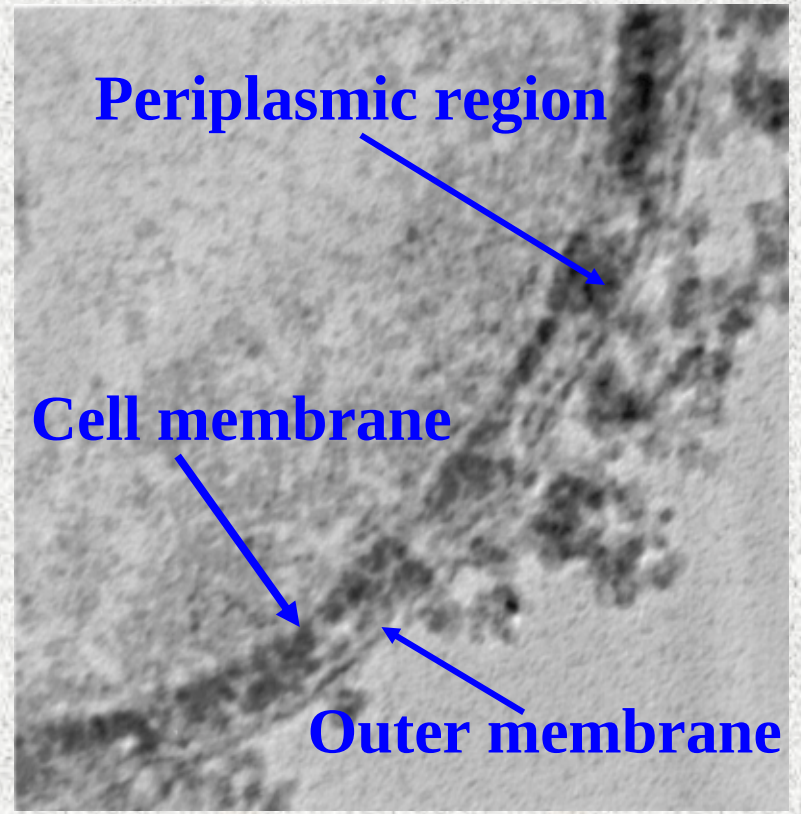


UO_2 Accumulates Extracellularly and in the Periplasm of CN32 Cells

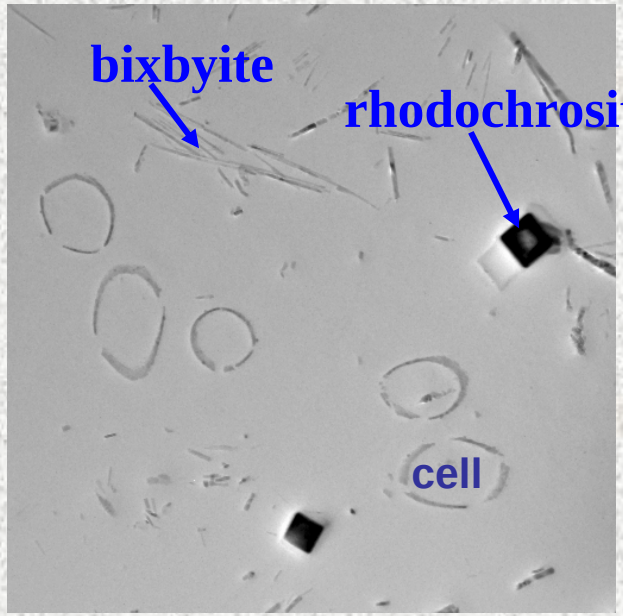
TEM Image of Unstained Thin Section

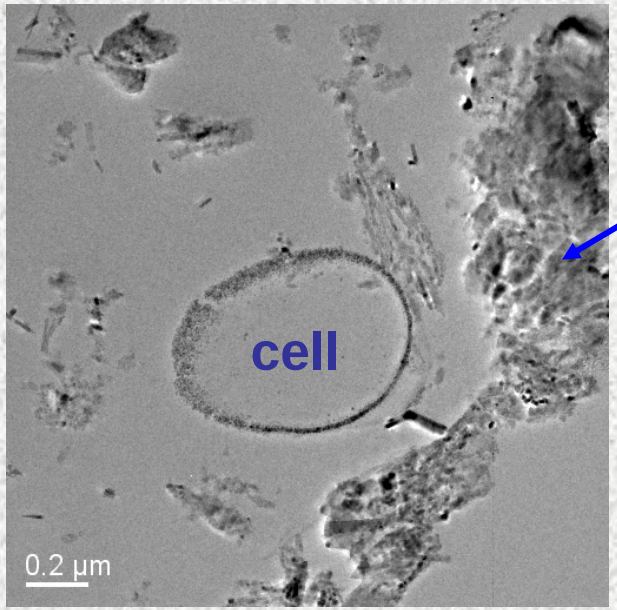


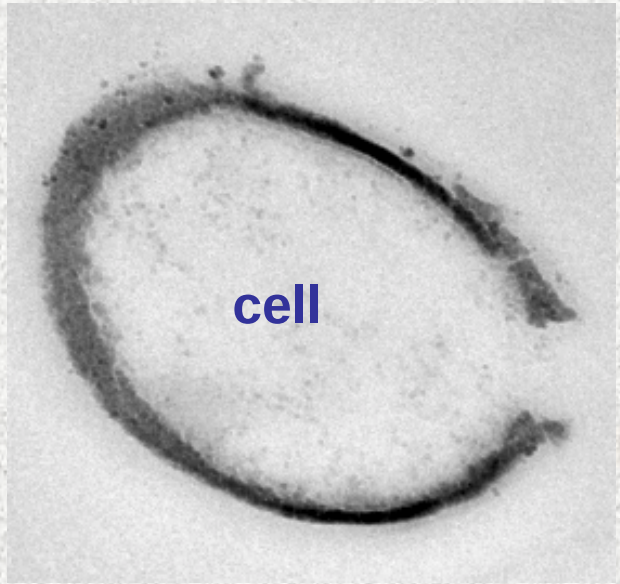
Stained Section

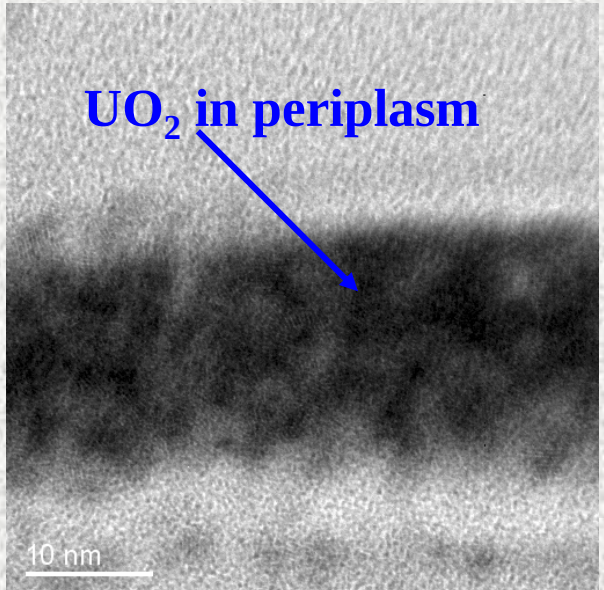


UO_2 Accumulates Exclusively in the Cell Periplasm in the Presence of Mn Oxides

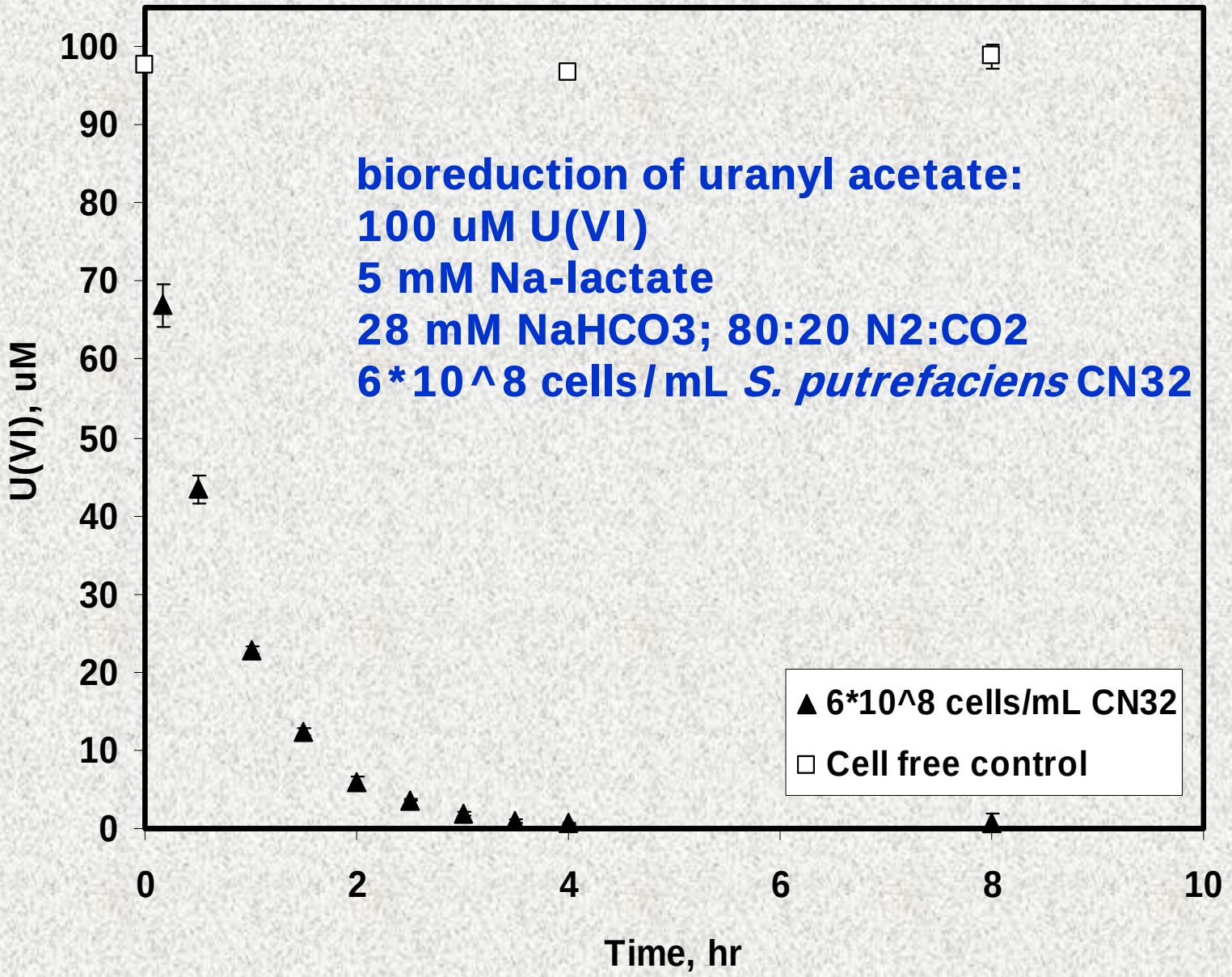




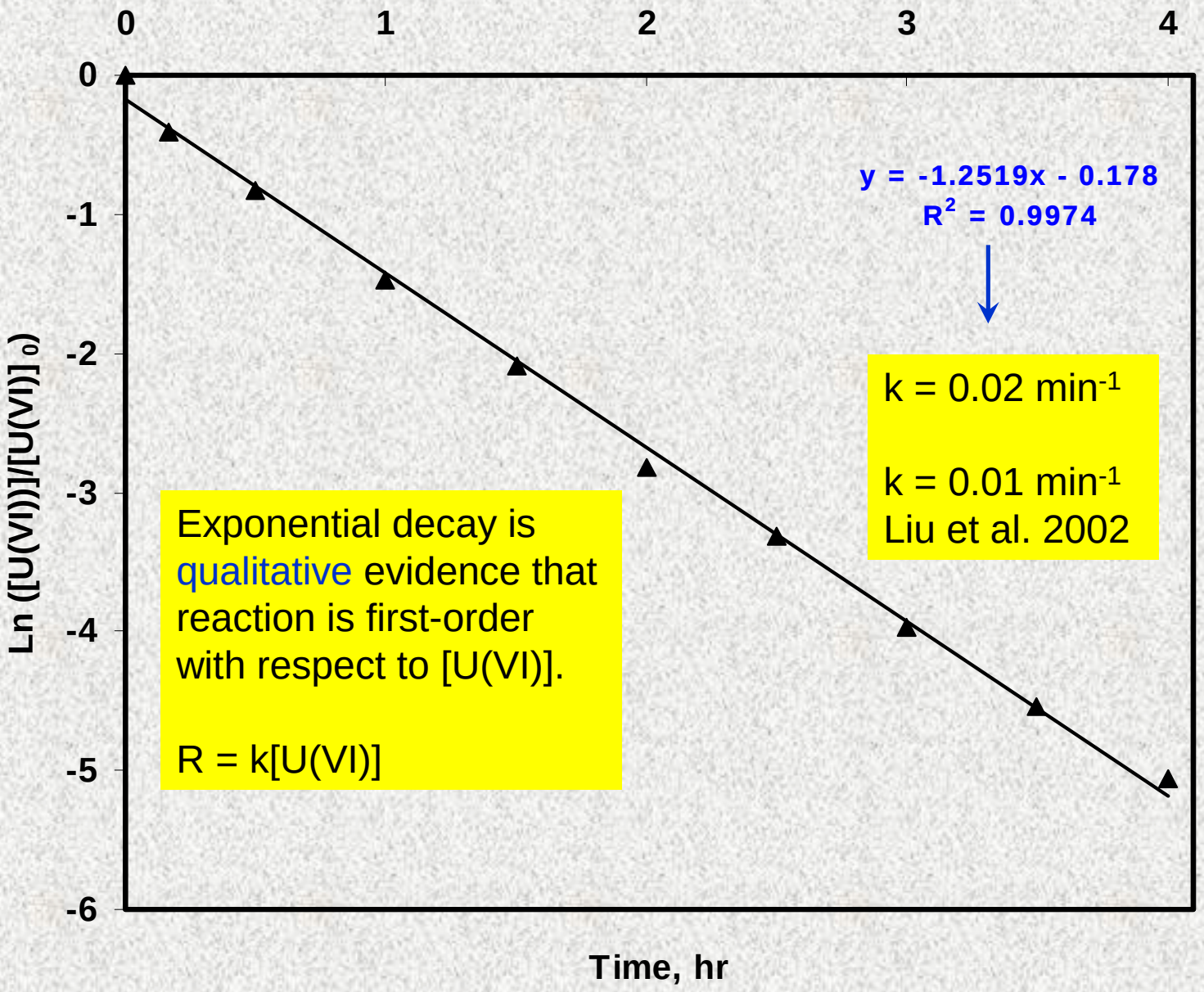




Kinetic data used to determine reaction rate



Quantitative assessment of reaction rate



Reaction Rate Formulations

$$4UO_2(CO_3)(aq) + CH_3COO^- + 4H_2O \Leftrightarrow 4UO_2(s) + 6HCO_3^- + 5H^+$$

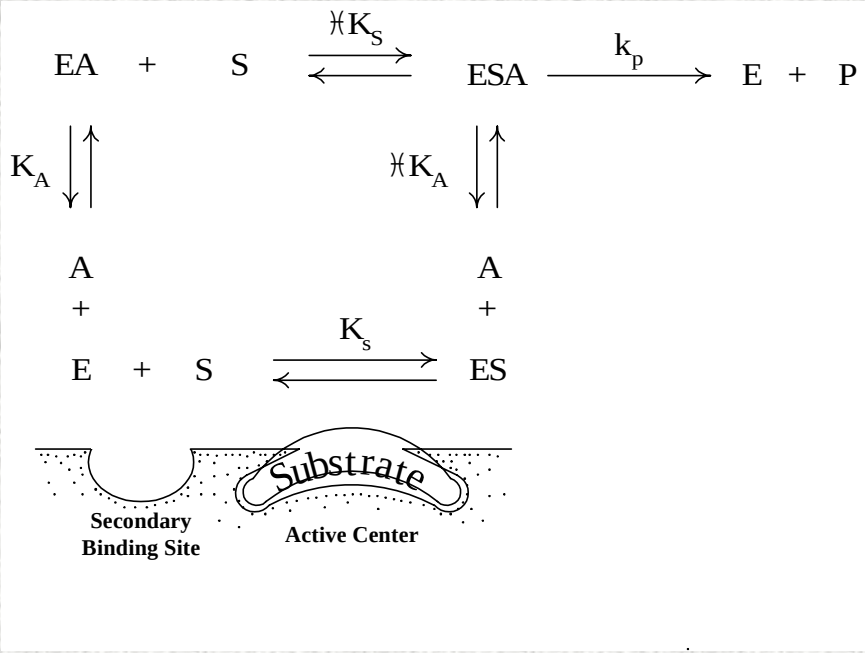
- Empirical Rate Formulation $R = k[U(VI)]$

- Elementary Rate Formulation

$$R = k_f[UO_2(CO_3)]^4[CH_3COO^-] - k_b[HCO_3^-]^6[H^+]^5$$

- Mechanistic Rate Formulation →

$$R = V_{max}\frac{[UO_2CO_3]}{K_U + [UO_2CO_3]}\frac{[CH_3COO^-]}{K_D + [CH_3COO^-]}$$



Draft Report

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Draft Report

1 – mechanisms of metal reduction;

U(VI) Reduction

In an overly simplified sense, the mechanism of reduction of soluble metals involves the transfer of electrons from an enzyme (or electron carrier) to the metal. More specifics of the mechanisms involve the cellular location of the enzyme (e.g., bound in the outer membrane, within the periplasm, bound in the cytoplasmic membrane, or soluble electron carrier), the exact location of the enzyme active site (e.g., outside of the outer membrane; periplasmic side of outer membrane; within periplasm; periplasmic side of cytoplasmic membrane; cytoplasmic side of cytoplasmic membrane), and the location of the soluble metal (e.g., sorbed to the outer membrane, within the periplasm, within the cytoplasm). That said, "direct" microbially-mediated reduction of soluble metals like U(VI) can proceed through a variety of enzymatic mechanisms (D. Lovley):

1 - reduction of U(VI) by outer membrane proteins

2 - reduction of U(VI) by periplasmic proteins

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2 – rates of metal reduction;

organism	e- acceptor	e- donor	solution chemistry	reduction rate	comments	reference
S. putrefaciens CN32; $2x10^8$ cells/mL	500 uM uranyl chloride	10 mM Na-lactate, or H_2 overpressure	26 mM NaHCO3 at pH 6.8 under 80:20 N_2:CO_2 atm	k_1 = 0.01 min^{-1} with lactate; k_1 = 0.012 min^{-1} with H_2	UO_2^{2+} measured by KPA after 0.2 um filtration	Liu et al. 2002, Biotech. Bioeng. 80:637

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3 – comprehensive reaction network operative at the FRC site;

Reaction	Reaction constant(s)	Comments/reference
$4UO_2(CO_3)(aq) + CH_3COO^- + 4H_2O \Leftrightarrow 4UO_2(s) + 6HCO_3^- + 5H^+$		soluble-phase U(VI) reduction
$UO_2(OH)_2(s) + CH_3COO^- + 4H_2O \Leftrightarrow 4UO_2(s) + 5HCO_3^- + 4H^+$		solid-phase U(VI) reduction
$\equiv FeO\text{-}UO_2 + CH_3COO^- \Leftrightarrow UO_2(s) + HCO_3^- + 4H^+$		sorbed U(VI) reduction
U(VI)-organic acid (aq) + $CH_3COO^- \Leftrightarrow UO_2(s) + HCO_3^- + 4H^+$		complexed U(VI) reduction; complexants could include e.g. EDTA, citrate, humics
U(VI)-organic acid (aq) + $CH_3COO^- \Leftrightarrow$ U(IV)-organic acid + $HCO_3^- + 4H^+$		complexed U(VI) reduction; reduction leads to soluble U(IV) complex

Draft Report

4 – emerging research needs/knowledge gaps.

Participant Input Needed!

- list of publications from your research that contain rate data or mechanistic information
- list the reactions you have studied and plan to study
- specify whether you have detailed kinetic data
- can you propose a rate formulation with specific rate parameters?

Edit the draft report directly!