STONY BROOK
STATE UNIVERSITY OF NEW YORK

CEMS

NSLS II – Earth and Environmental Sciences Workshop:

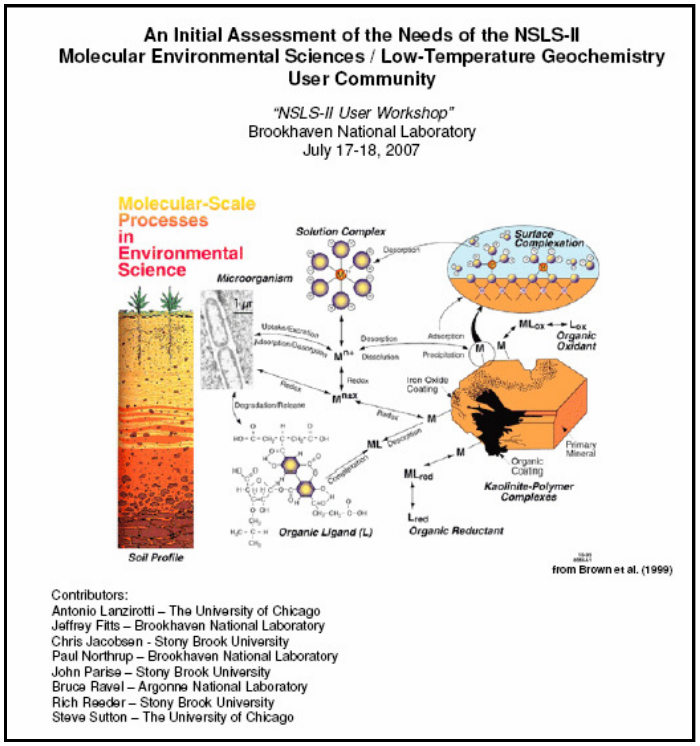
Trends in Environmental and Geosciences Synchrotron Research

Richard J. Reeder
Department of Geosciences
Center for Environmental Molecular Science
Stony Brook University

Previous Footsteps

• Earth and Environmental Science session at NSLS II User Workshop
17-18 July 2007 (BNL)

• EnviroSync Workshop: Assessing Synchrotron Radiation Capabilities and Future Needs for Molecular Environmental Science and Low-Temperature Geochemistry
23-24 July 2007 (Rockville, MD)



An Initial Assessment of the Needs of the NSLS-II Molecular Environmental Sciences / Low-Temperature Geochemistry User Community

"NSLS-II User Workshop"
Brookhaven National Laboratory
July 17-18, 2007

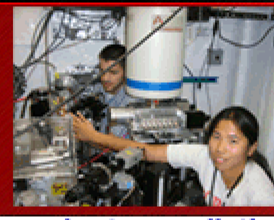
from Brown et al. (1999)

Contributors:
Antonio Lanzirotti – The University of Chicago
Jeffrey Fitts – Brookhaven National Laboratory
Chris Jacobsen - Stony Brook University
Paul Northrup – Brookhaven National Laboratory
John Parise – Stony Brook University
Bruce Ravel – Argonne National Laboratory
Rich Reeder – Stony Brook University
Steve Sutton – The University of Chicago

Report:
"An Initial Assessment of the Needs of the NSLS-II Molecular Environmental Sciences / Low-Temperature Geochemistry User Community"

EnviroSync

An organization of environmental science users of synchrotron radiation facilities



- **Grass-roots user organization**
- **Main functions are to:**

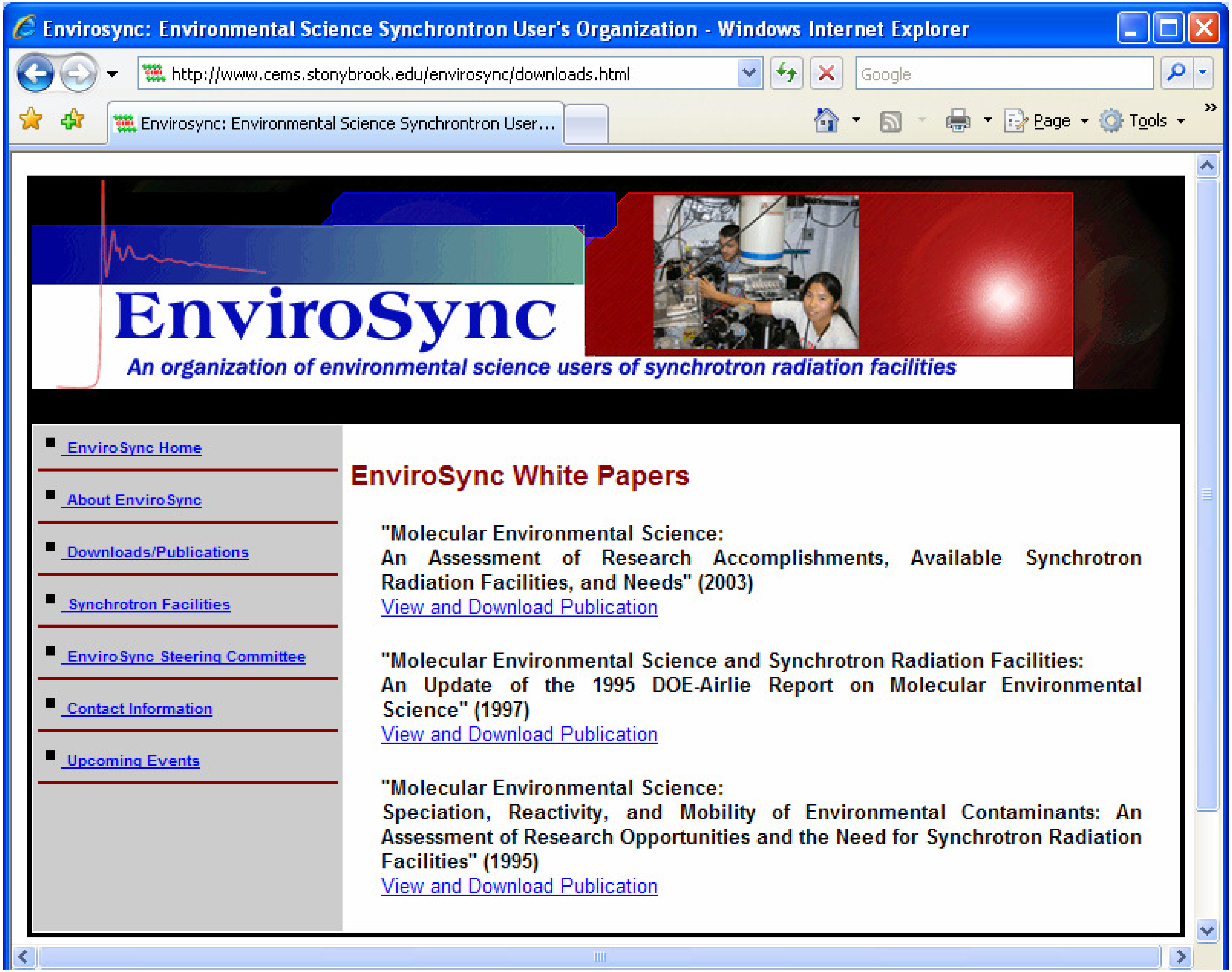
(1) serve as an advocate for the MES-SR community

(2) assess the state of existing SR facilities for MES research on a continuing basis

(3) assess the SR needs of the MES community on a continuing basis

(4) serve as an advisory group to federal agencies concerning the need for new SR facilities in the MES area

(5) co-sponsor MES workshops (Synchrotron Environmental Science series)



Envirosync: Environmental Science Synchrontron User's Organization - Windows Internet Explorer
http://www.cems.stonybrook.edu/envirosync/downloads.html
Google
Envirosync: Environmental Science Synchrontron User...
Page
Tools
EnviroSync
An organization of environmental science users of synchrotron radiation facilities
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EnviroSync Steering Committee
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Upcoming Events
EnviroSync White Papers
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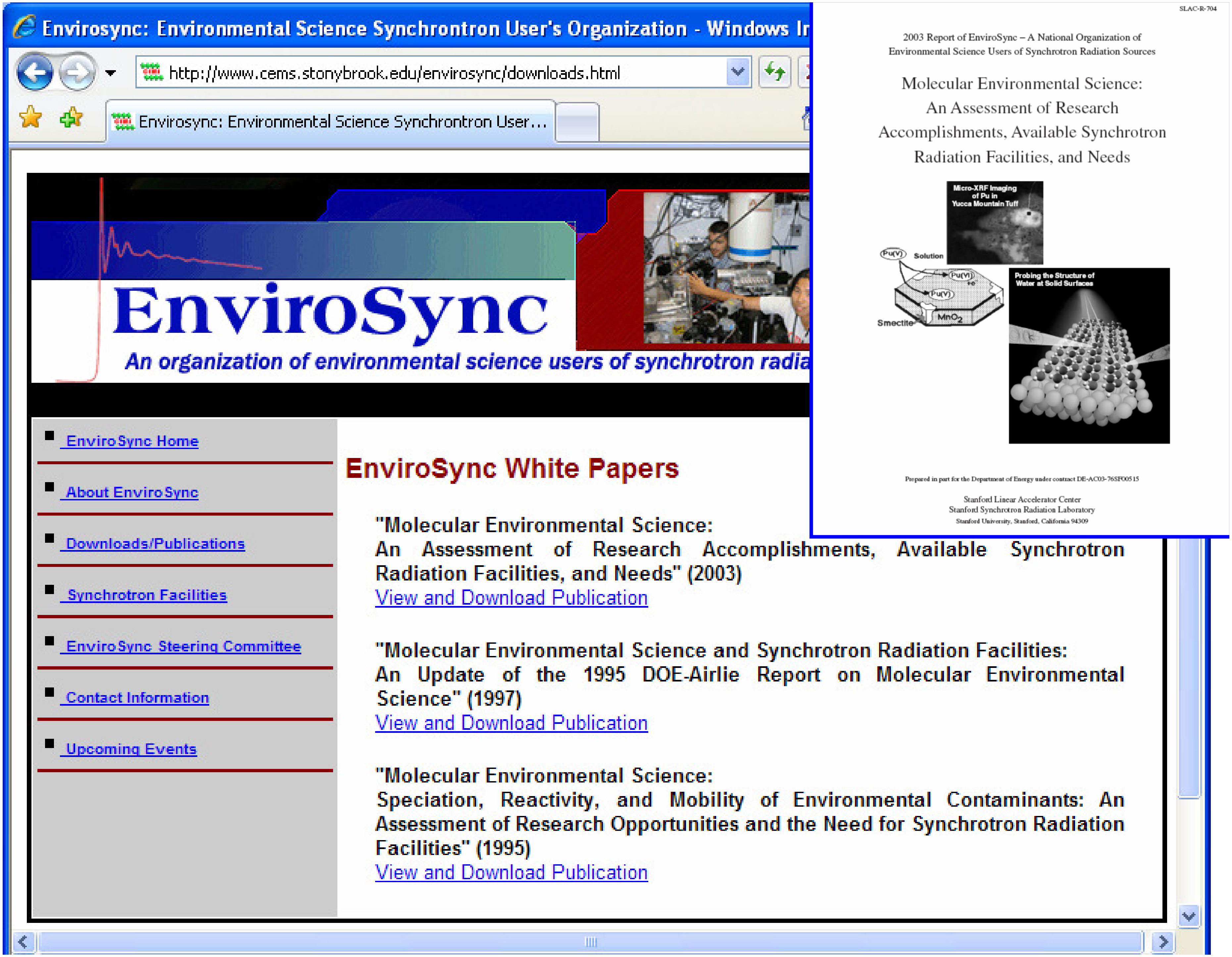
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http://www.cems.stonybrook.edu/envirosync/downloads.html
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An organization of environmental science users of synchrotron radia
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Micro-XRF Imaging of Pu in Yucca Mountain Tuff
Pu(V)
Solution
Pu(VI)
Pu(V)
MnO2
Smectite
Probing the Structure of Water at Solid Surfaces
Prepared in part for the Department of Energy under contract DE-AC03-76SF00515
Stanford Linear Accelerator Center
Stanford Synchrotron Radiation Laboratory
Stanford University, Stanford, California 94309

EnviroSync Workshop: Assessing Synchrotron Radiation Capabilities and Future Needs for Molecular Environmental Science and Low-Temperature Geochemistry
23-24 July 2007 (Rockville, MD)

Participants: 60+ researchers, beamline scientists, instrument designers, SR facility directors, funding agency program managers

Purpose:

1. Assess current capabilities for MES/LTG research at US synchrotrons
2. Assess current usage of these facilities by community
3. Identify SR needs for future MES/LTG research, including new directions
4. Propose and prioritize recommendations to meet community needs

Working groups: bulk spectroscopy, hard x-ray microprobe/tomography, spectromicroscopy, bulk scattering, and surface & interface scattering

Dissemination of workshop findings:

1. "White paper" (in prep) for program managers, facility directors, broader community
2. Summary articles published in EOS, SRN
3. Focused reports (for individual synchrotron facilities, etc.)

Sponsorship: DOE-BES, DOE-BER, NSF Geosciences

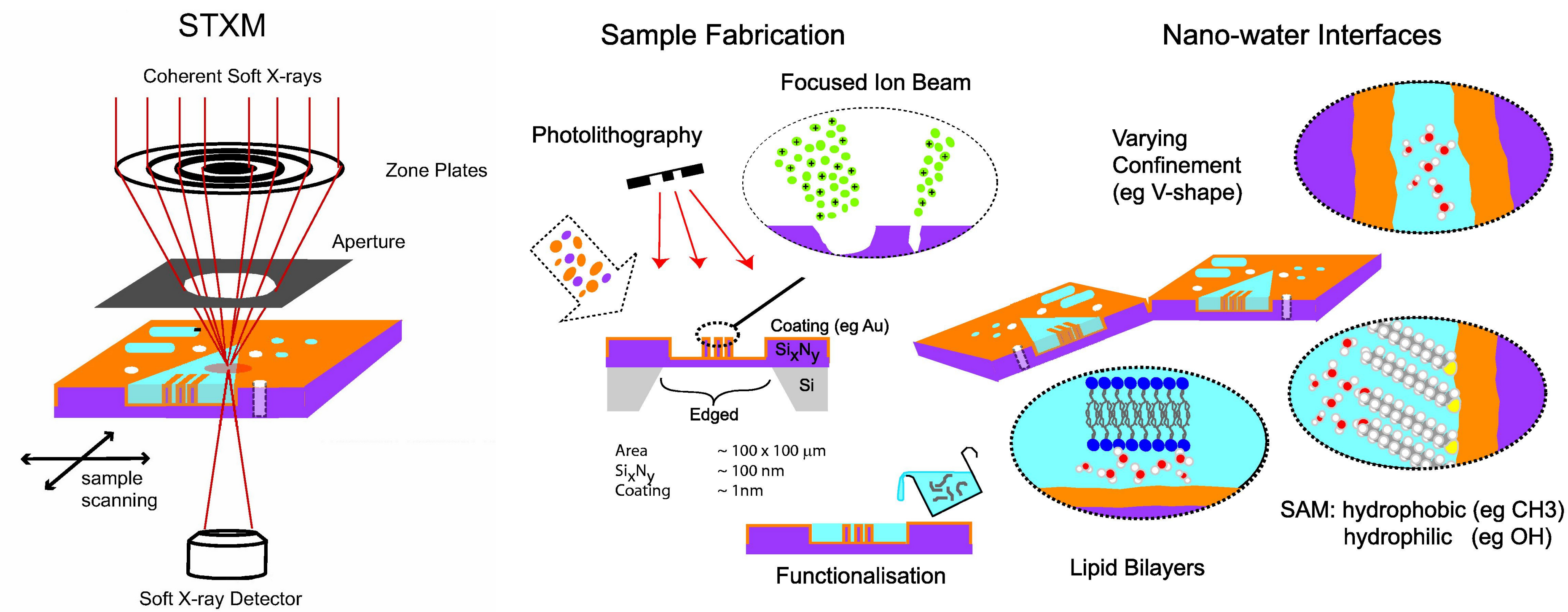
Science Drivers and Future Challenges

Broad scope of environmental science/geoscience research

- Amorphous and poorly crystalline solids – stability, role in reaction processes
- Solutes in liquids – aqueous complexes, nucleation/precipitation
- Properties of fluids in confined pores, geometries (incl. nanopores)
- Fluid flow and transport processes at pore and sub-pore scales (tomography)
- Nanoparticles and colloids – stability, transport and cycling of toxic substances
- Time-resolved studies of dynamic processes – nucleation/precipitation, nanoparticle nucleation, ripening and shape change
- In situ studies and integration of useful sample cells – mimic real conditions
- Transport and bioavailability of contaminants and nutrients
- Chemical speciation of contaminants – esp. beyond model systems
- Environmental genomics – gene modification to direct biologic interaction with contaminants, nutrients, etc.

Fundamental SR Research – Nano-Water in Confined Geometries and Membranes (A. Nilsson)

- Energy from 100-1000 eV, good performance at the O K edge
- 10-30 nm spatial resolution and vertical/horizontal polarization
- Temperature control at the sample stage 250-335 K
- External electric and magnetic fields at the sample stage
- Fast images for dynamical studies
- Internal tube for fast mixing of solutions at the sample stage



Courtesy of D. Shuh

Science Drivers and Future Challenges

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Science Drivers and Future Challenges

Interfaces – “nearly all reactions occur at interfaces”

- Two phases (model systems): mineral-water, mineral-microbe, mineral-gas
- Multiphase: mineral-biofilm-water, mineral-humic substance-microbe-water, etc.
- Structure, hydration, role of defects at surfaces
- Dynamic processes at interfaces: redox, adsorption, dissolution/precipitation
- Nanoparticles – surface vs interior

Fundamental SR Research – Ion Sorption at Mineral-Water Interface

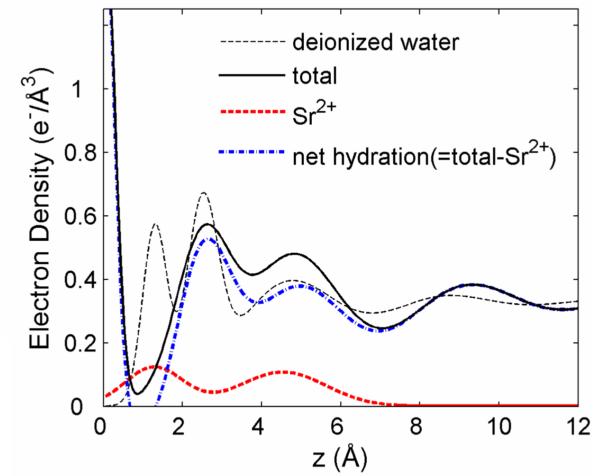
Advanced Photon Source
Argonne National Laboratory

PRL **97,** 016101 (2006) PHYSICAL REVIEW LETTERS week ending 7 JULY 2006

Hydration and Distribution of Ions at the Mica-Water Interface

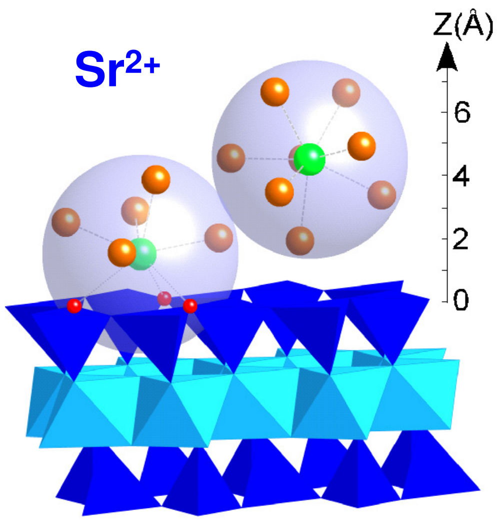
Changyong Park,[1,*] Paul A. Fenter,[1] Kathryn L. Nagy,[2] and Neil C. Sturchio[2]
[1]*Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439, USA*
[2]*Department of Earth and Environmental Sciences, University of Illinois at Chicago, Illinois 60607, USA*
(Received 20 March 2006; published 5 July 2006)

Molecular-scale structures of mica surfaces in electrolyte solutions reveal how ion and interfacial hydration control cation adsorption. Key differences are obtained for Rb^+ and Sr^{2+} using resonant anomalous x-ray reflectivity: Rb^+ adsorbs in a partially hydrated state and incompletely compensates the surface charge, but Sr^{2+} adsorbs in both fully and partially hydrated states while achieving full charge compensation. These differences are driven by balancing the energy cost of disrupting ion and interface hydration with the electrostatic attraction between the cation and charged surface.

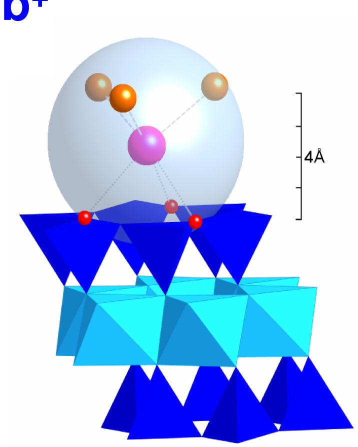


Resonant anomalous X-ray reflectivity (RAXR)

Sr^{2+}



Rb^{+}



Sr^{2+} sorbs as both inner- and outer-sphere complex on muscovite basal plane

Rb^{+} sorbs as inner-sphere complex only

<u>Fundamental questions raised:</u>

- **Are mixed modes of adsorption common?**
- **Do mixed sorption modes vary from one mineral and/or surface to the next?**
- **Do outer-sphere species represent a “reservoir” of weakly bound species?**
- **What controls the stabilities and concentrations of IS and OS species at the mineral-water interface?**

Courtesy of P. Fenter

Opportunities in Growth Areas for MES and Geoscience SR Users

Societal Impact of our Research is Significant

- Environmental and human health (medical geology) – chemical speciation and bioavailability, nutrient cycling, soil pollution and agriculture

- Climate science – element cycling, paleo-proxy verification

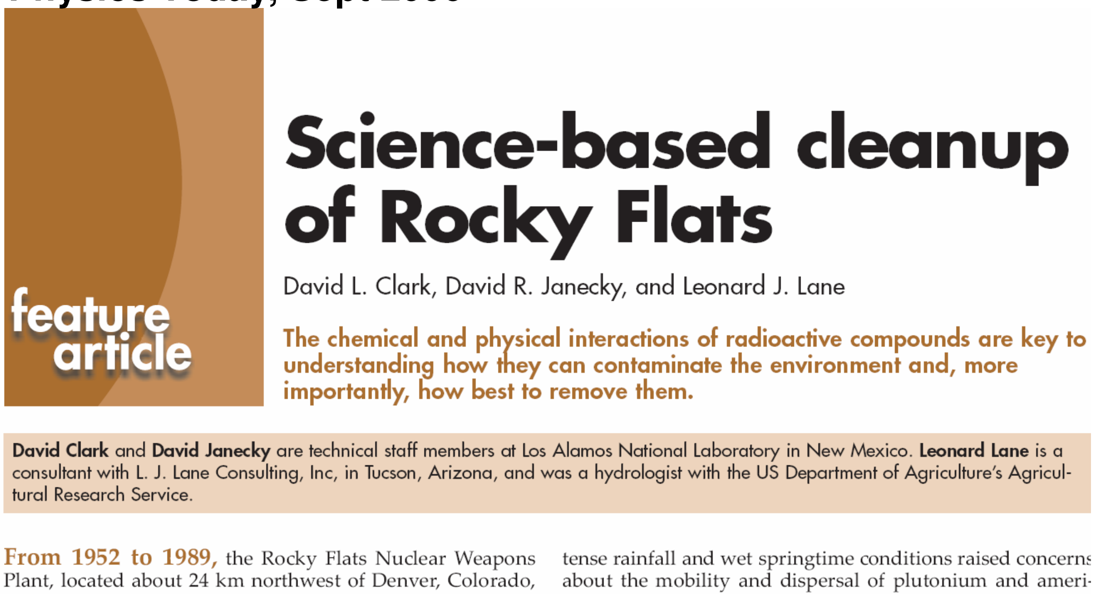
- Nanoparticles and colloids – fundamental properties and reactivity, pollution, element cycling and transport, human health aspects, etc.
  Esp. airborne particles, transport and speciation of toxicants, disease vectors

- Water – fundamental properties, pollution and remediation, contaminant transport

- Energy – environmental impact, subsurface CO_2 storage, fluid transport, radioactive waste storage and stewardship

Applied SR Research – Radionuclide Remediation

Physics Today, Sept 2006



feature article

Science-based cleanup of Rocky Flats

David L. Clark, David R. Janecky, and Leonard J. Lane

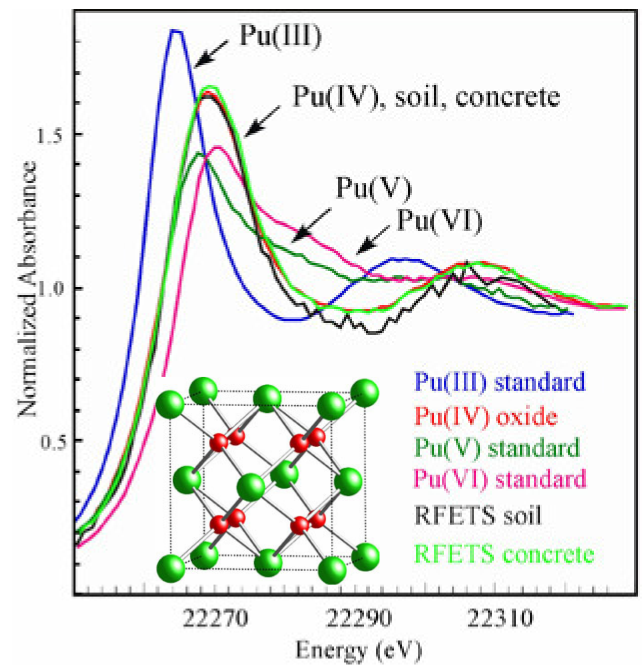
The chemical and physical interactions of radioactive compounds are key to understanding how they can contaminate the environment and, more importantly, how best to remove them.

David Clark and **David Janecky** are technical staff members at Los Alamos National Laboratory in New Mexico. **Leonard Lane** is a consultant with L. J. Lane Consulting, Inc, in Tucson, Arizona, and was a hydrologist with the US Department of Agriculture's Agricultural Research Service.

From 1952 to 1989, the Rocky Flats Nuclear Weapons Plant, located about 24 km northwest of Denver, Colorado, tense rainfall and wet springtime conditions raised concerns about the mobility and dispersal of plutonium and ameri-

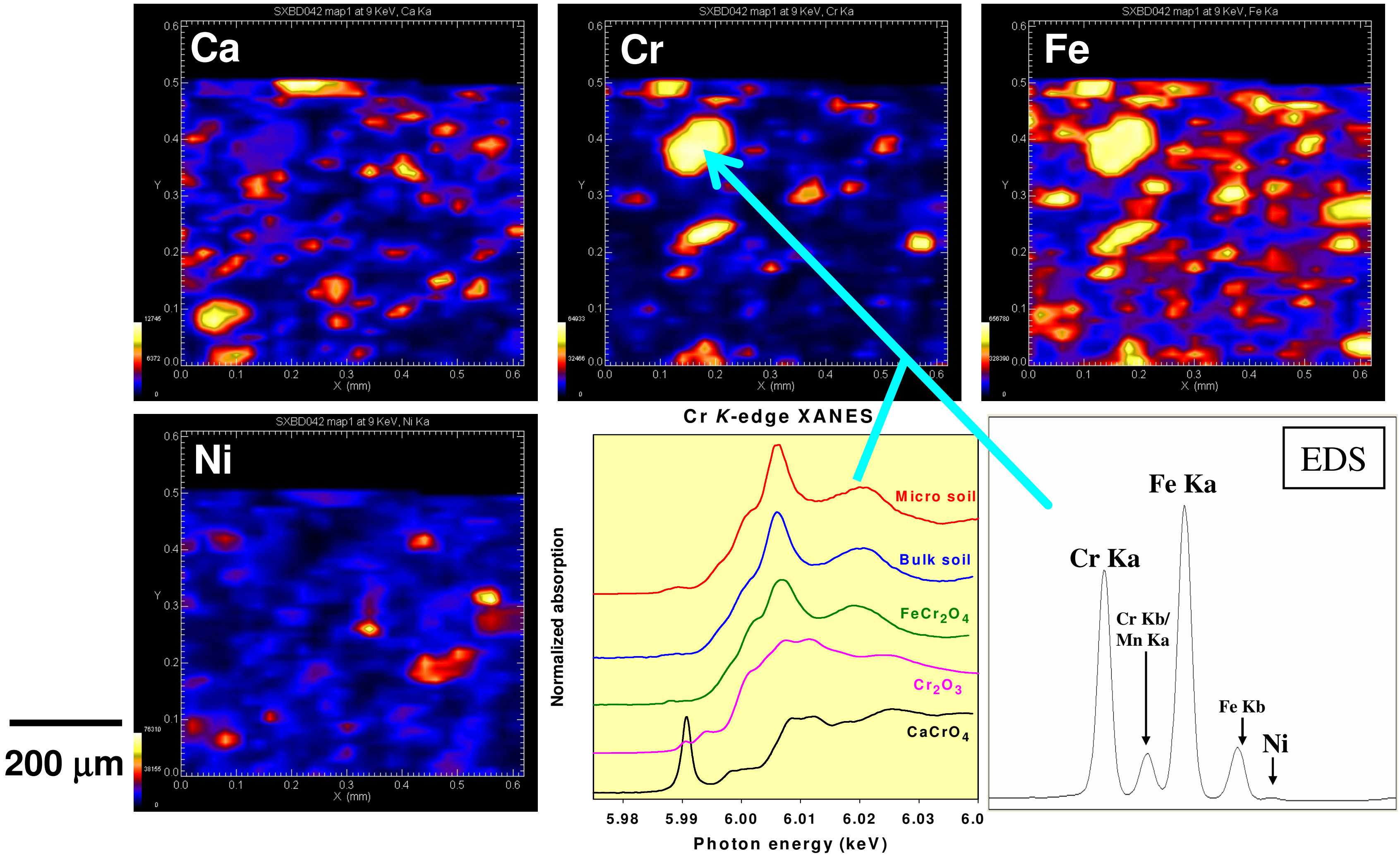
Remediation of Pu contamination in soils at Rocky Flats Site
D.L. Clark, S. Conradson, & collaborators, LANL

- **Up to 1,450 pCi/g in soils from leaking drums at 903 Pad**
- **>90% of the Pu is within upper 10-12 cm of soils**
- **XAS & Ultrafiltration: Pu occurs as hydrated PuO_2 colloids that are insoluble, strongly bound to soil matrix**
- **Risk dominated by erosion. Mitigation by soil removal.**
- **Science-based site closure accomplished ahead of schedule at a cost savings of b*illions* of dollars**



Complexity – Unique Challenges Posed by Samples

Cr- and Ni-rich soils, El Dorado County, California (Y. Tang and J. Morrison)



- Multiple techniques needed for study, esp. micro-beam techniques
- In situ, non-destructive, special environmental sample cells

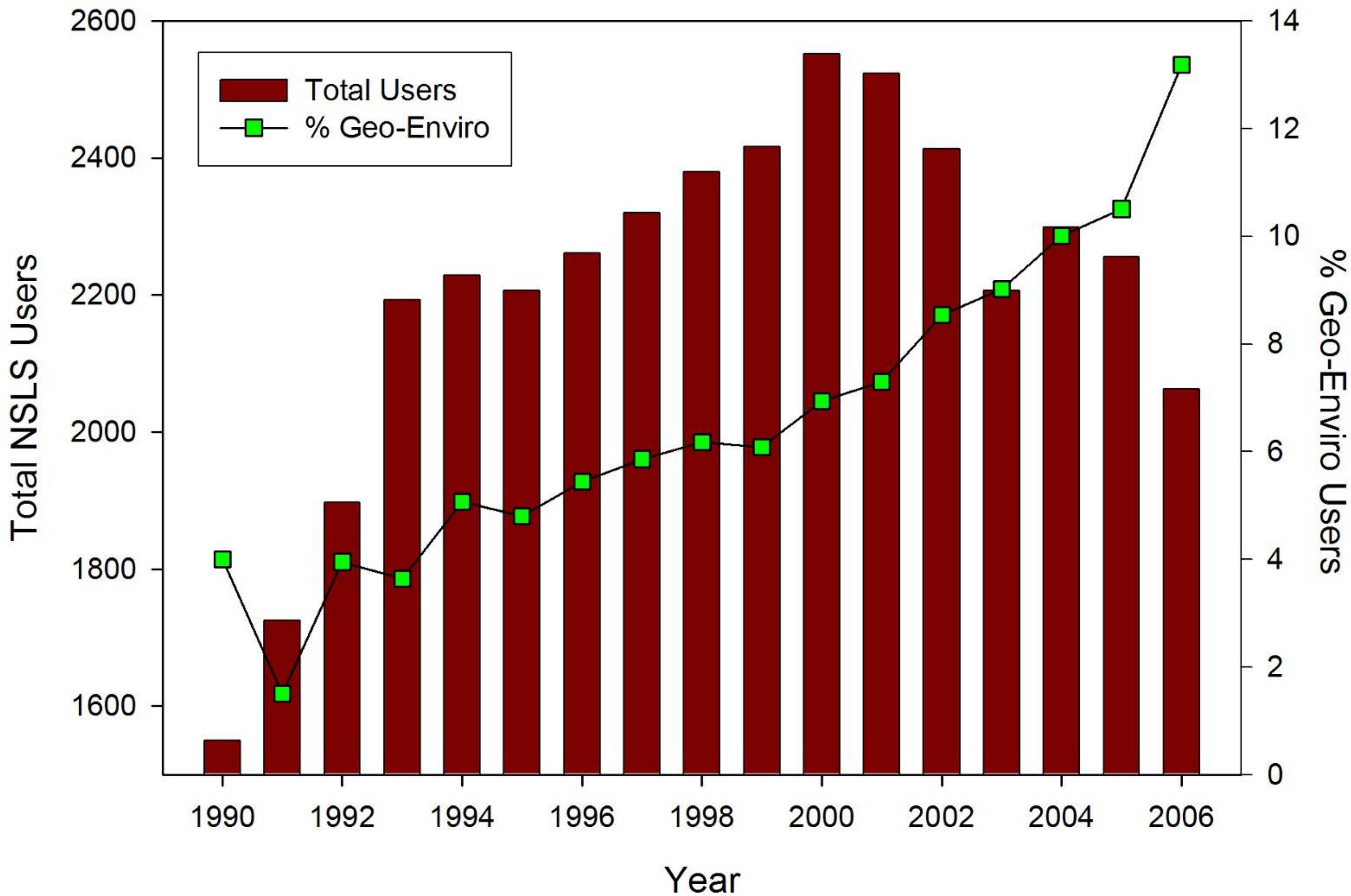
User Demand and Challenges

Current user demand far exceeds available beamtime at almost all beamlines/sectors used for MES research at the four DOE-supported SR facilities

Average oversubscription:

ALS	**190 %**
APS	**175 %**
NSLS	**170 %**
SSRL	**170 %**

Growth of Enviro-Geosciences Usage at NSLS



From T. Lanzirotti

Demand at NSLS Beamlines Used for MES Research

Beamline	*Techniques*	*Equivalent MES*	*Oversubscription Factor*
X26A	Microprobe	1	3.2
X27A	Microprobe	0.6	1.3
X1A	STXM	0.33	0.6
X11A/B	EXAFS	0.45	1.8
X18B	EXAFS	0.1	2.7
X19A	EXAFS	0.2	2.0
X23A2	EXAFS	0.1	2.4
X15B	EXAFS	0.9	1.1
X10C	EXAFS	0.1	0.7
X7B	XRD	0.18	2.8
X16C	XRD	0.12	0.5
U2B	FTIR	0.1	1.4
U10B	FTIR	0.15	1.4
		4.3	**7.2 beamlines needed**

NSLS NATIONAL SYNCHROTRON LIGHT SOURCE (Data from T. Lanzirotti)

Demand at APS Sectors Used for MES Research

Sector/ Beamline	*Techniques*	*Equivalent MES beamlines*	*Oversubscription factor*
2	Microprobe, XAS, diffraction	0.2	2.5
5	XSW, SAXS, XAFS	0.3	1.3
10	XAFS, microprobe	0.45	2.0
11	PDF, Surface scattering	0.75	1.5
12-ID	Surface scattering, SAXS	0.25	2.0
12-BM	XAFS	0.3	1.5
13	Microprobe, XAFS, IXS, Surface scattering	1.0	2.5
20-ID	Microprobe, XAFS	0.45	3.0
20-BM	XAFS	0.6	1.5
Other		0.1-0.4	
		~4.5	**8.6 beamlines needed**

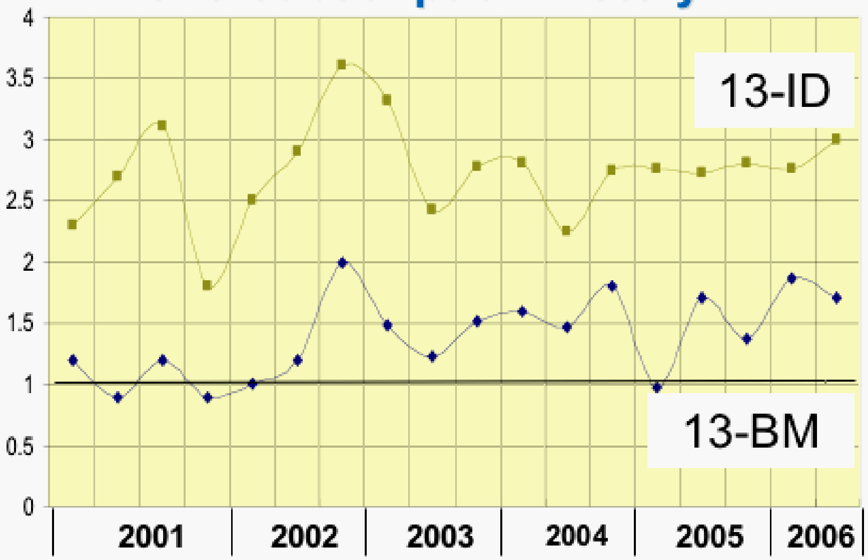
Beamtime Proposals and Oversubscription

• 1,095 beam time proposals submitted since 2001 for work at GSECARS.

•Oversubscription rates fairly steady at 2.8 for 13-ID and 1.6 for 13-BM

•Oversubscription managed by allocating fewer days than requested to limited numbers of investigators

Oversubscription History



•Oversubscription rate is constant and a self-limiting process

•Anecdotal evidence that some of the "new/potential" researchers are getting frustrated because not getting access to facility and have abandoned the incorporation of synchrotron radiation in their research or are going elsewhere.

•MES/LTG wants to grow but its growth is being restrained

•Beam time access has been and is at capacity

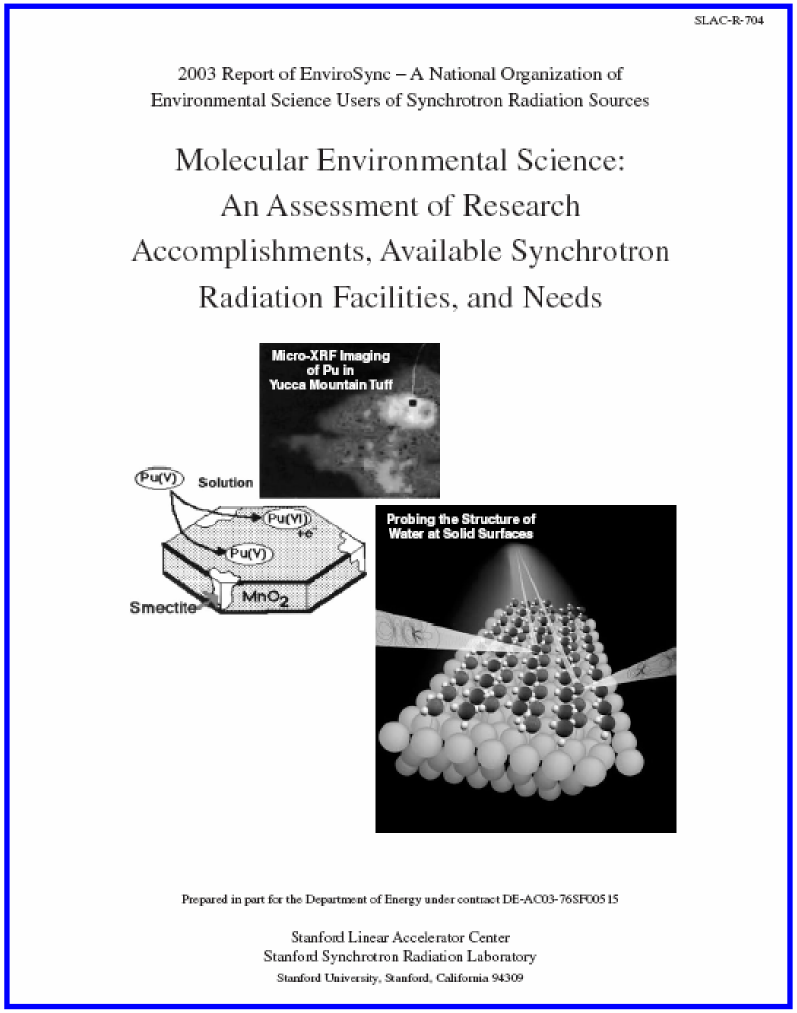
MES and Geoscience Funding Challenges

"The breadth of societally important issues addressed by SR-based MES and geoscience research starkly contrasts with the narrow funding base that supports it."

MES and Geoscience communities must be more effective in communicating:

- importance of SR methods to our research activities
- societal impact of our research
- needs of community for conducting research

Thank you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Pu(V)
Solution
Pu(VI)
Pu(V)
Smectite
MnO2
Probing the Structure of
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Prepared in part for the Department of Energy under contract DE-AC03-76SF00515
Stanford Linear Accelerator Center
Stanford Synchrotron Radiation Laboratory
Stanford University, Stanford, California 94309

2003


Elements
An International Magazine of Mineralogy, Geochemistry, and Petrology
Volume 2, Number 1
User Research Facilities
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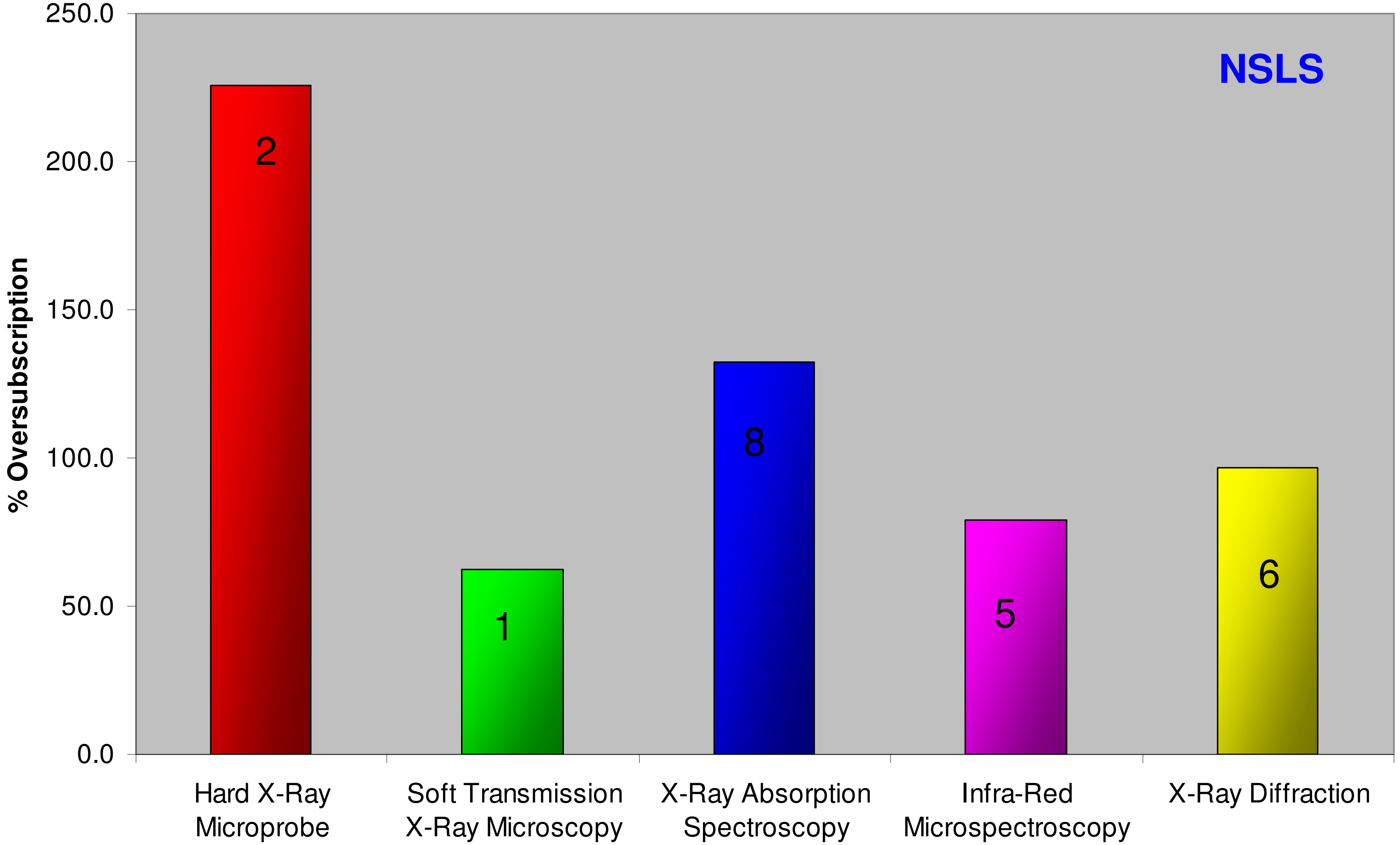
X-ray, Neutron, and Mass Spectrometry Techniques
Scientific Advances Made Possible by User Facilities
Accessing User Facilities
New Opportunities at Emerging Facilities

2006

Oversubscription by Technique
Cycle 2, FY07, Jan-Apr 2007



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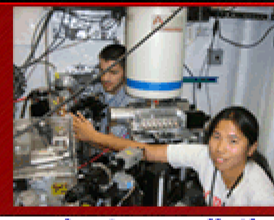

2007 EnviroSync Workshop:

Assessing Synchrotron Radiation Capabilities and Future Needs for Molecular Environmental Science and Low-Temperature Geochemistry

23-24 July 2007 Rockville, MD

U.S. DEPARTMENT OF ENERGY

Sponsorship: DOE – BES (N. Woodward)
DOE – BER (R. Hirsch)
NSF – EAR (D. Lambert)

NSF

The breadth of scientific topics addressed by SR-based MES and geoscience research and their societal relevance are not reflected in its funding base.

In contrast to the breadth of important scientific topics addressed by SR-based MES and Geoscience research, the funding base that supports it is remarkably narrow.