Applications of the Advanced Light Source to Problems in the Earth, Soil, and Environmental Sciences

Report of the Workshop

San Francisco, California

December 11, 1991

Organized by:

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Workshop Announcement

Applications of the Advanced Light Source to Problems in the Earth, Soil, and Environmental Sciences

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The GeoSync Committee (affiliated with the Mineral Physics Division of the American Geophysical Union), the Consortium for Advanced Radiation Sources (The University of Chicago), and the Advanced Light Source (ALS) are convening a workshop to discuss the potential uses of the facility for research in the earth, soil, and environmental sciences. The ALS—a next-generation synchrotron source of ultrabright x-ray and ultraviolet radiation—is under construction in Berkeley, California, at the Lawrence Berkeley Laboratory in the hills above the University of California campus. The planned start-up date is set for spring, 1993. The workshop will be held at the San Francisco Civic Auditorium in conjunction with the fall meeting of the American Geophysical Union. A tour of the ALS is planned.

Topics

ALS Status and Research Opportunities
(A. Schlachter, ALS Scientific Program Coordinator)

ALS Applications to Geological Materials
(D. Perry, LBL)

Earth Science at Existing and Planned Synchrotron Facilities
(J. V. Smith, Executive Director of the Consortium for Advanced Radiation Sources, The University of Chicago)

Applications in the Soil and Environmental Sciences
(D. Schulze, Agronomy Department, Purdue University)

X-Ray Spectroscopy
(G. Brown, Jr., Chairman, Department of Geology, Stanford University)

X-Ray Microprobe Analysis
(M. Rivers, Department of the Geophysical Sciences, the University of Chicago)

All interested persons in the earth, soil, and environmental sciences communities are invited to attend

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Preface

With the availability of synchrotron sources such as the Advanced Light Source (ALS) and the Advanced Photon Source (APS), many new opportunities open themselves to researchers in the geological sciences. Synchrotron radiation affords an extension of regular laboratory-based experimental equipment that uses traditional x-ray, ultraviolet, or electron beam sources. Nondestructive synchrotron radiation is more intense than these traditional sources, as well as pulsed, collimated, polarized, and tunable with respect to its wavelength.

Because of the versatility of synchrotron sources, many experimental areas are available to the geological researcher. X-ray-related spectroscopies, for example, include x-ray photoelectron, Auger, X-ray emission, x-ray absorption near edge structure (XANES), and extended x-ray absorption fine structure (EXAFS) spectroscopy. Analytical compositions of geological materials can be obtained using x-ray fluorescence microprobe analysis; not only can qualitative and quantitative elemental analyses be obtained using this technique, but also elemental mapping of a sample can be effected. In addition, X-ray scattering studies can be conducted on a wide range of geological systems.

The scope of research involving the geosciences can be grouped into three general areas: geological materials, liquids, and processes. Materials include rocks, minerals, and glasses, while liquids may encompass melts, geothermal brines, and fluid inclusions. Geological processes that are amenable to study include chemical reactions (and their mechanisms), nucleation processes, precipitation, formations of gels, and adsorption processes.

Synchrotron research can also be directed at geologically related fields that have strong social impact. The research disciplines of toxic and nuclear waste, for example, can make extensive use of the techniques mentioned above. Again, processes in geology come into play in a wide range of systems in these fields—processes involving chemical transport (in which adsorption can play a major role), chemical phase alterations, and dissolution/precipitation. Chemical reactions in these environmental systems have been shown to be exceedingly complex, and researchers will find facilities such as the ALS and APS to be invaluable tools in gaining a good understanding of how heavy metals, radioactive elements, and organic compounds interact with geological materials and fluids.

In summary, synchrotron radiation will find many and varied applications in the field of geosciences from both a basic and applied research standpoint. New approaches of an experimental nature will be opened to investigators by which they may obtain data related to materials and processes in the earth's domain—data that have heretofore been unobtainable with such a high degree of precision. These investigations will be limited in most cases only by the imaginations of the experimenters.

ALS Status and Research Opportunities

Alfred S. Schlachter

Lawrence Berkeley Laboratory

The Advanced Light Source (ALS) will begin operations in spring 1993—generating the world's brightest synchrotron radiation in the extreme ultraviolet and soft x-ray regions of the spectrum (<10 eV to ~10 keV). This $99.5 million facility, funded by the U.S. Department of Energy, is available to qualified researchers from industry, universities, and government laboratories.

Light from the ALS possesses special characteristics that make it a research tool of great versatility:

- Very high brightness
- Linear or circular polarization
- Tunability
- Pulsed nature
- High degree of coherence.

Of these, the unique characteristic is the light's high brightness, a measure of its spatial and spectral concentration (see Fig. 1). That is, the light has a high photon flux per unit source area and per unit solid angle into which the source radiates. (Flux is the number of photons delivered per second.)

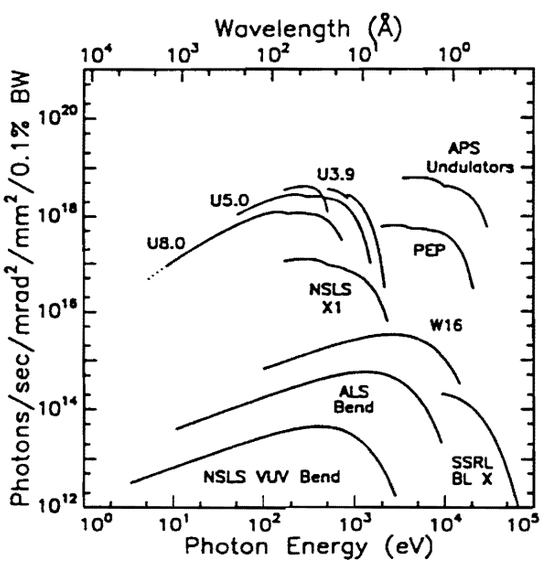

Figure 1. Plots of spectral brightness are shown for three ALS undulators, an ALS wiggler, the ALS bending magnets, undulators planned for the Advanced Photon Source (APS), and representative insertion-device and bending-magnet sources at the National Synchrotron Light Source (NSLS) and Stanford Synchrotron Radiation Center (SSRL and PEP). The discontinuities in the undulator curves represent shifts from the fundamental to the third harmonic or from one harmonic to the next.

As a consequence of high brightness, very high spatial resolution becomes possible because many photons can be focused on an extremely small spot. With help from beamline optics, the ALS is expected to achieve spot sizes as small as 200 Å.

Another effect of high brightness is high spectral resolution. By narrowing the slits of a monochromator, one can select a very narrow range of wavelengths from a beam of synchrotron radiation and still have a sufficient number of photons to use for imaging or measuring the properties of a sample. Many experiments that were previously impractical because of insufficient resolution or long measurement times become feasible using light from the ALS. Figure 2 illustrates the improvement in spectral detail possible with high spectral resolution.

Apart from the issue of spectral resolution, the tunability of light from the ALS is important in itself. From the range available in a beam, one can select specific photon energies, for example, to probe the K and L shells of light elements of interest in the earth, soil, and environmental sciences.

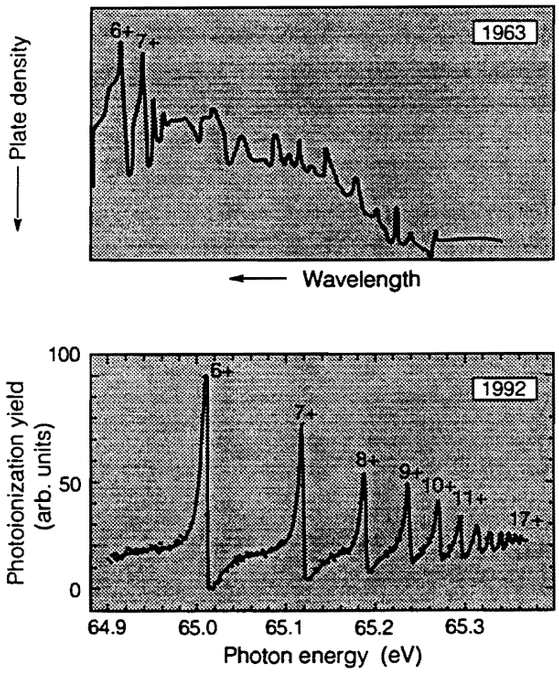

Figure 2. Synchrotron radiation of certain photon energies absorbed by helium atoms leads to the simultaneous excitation of two electrons into a series of distinct quantum states. A 1992 measurement of this phenomenon, made at the Stanford Synchrotron Radiation Laboratory, had the advantage of a tenfold improvement in resolution and considerably higher flux over the original measurement made in 1963. In addition, the more recent experiment measured ionization, whereas the 1963 experiment measured absorption. Work done by T. Reich, Z. Hussain, E. Moler, G. Kaindl, D. A. Shirley, and M. Howells (bottom) and R.P. Madden and K. Codling (top).

Light from the ALS is naturally pulsed because the electrons producing the radiation travel in bunches (see Fig. 3). Standard pulses are 35 ps wide (FWHM) and occur at intervals of 2 ns. This time structure can be varied by injecting one or a few electron bunches into the storage ring. In the few-bunch mode, the ALS delivers pulses at intervals up to 656 ns. The pulsed nature of the light, the high flux, and the ability to vary the interval between pulses make it possible to perform time-resolved studies, for example, on the kinetics of a chemical reaction or the lifetime of excited states of atoms or molecules.

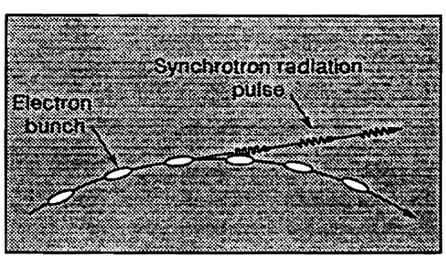

Figure 3. Schematic illustration of the bunched structure of the electron beam circling the ALS storage ring and the corresponding pulsed nature of the synchrotron radiation. Up to 250 electron bunches circle the ring. Each has a duration of about 35 ps. The time interval between bunches, dictated by the rf frequency, is 2 ns.

The ALS storage ring consists of 12 arc sectors alternating with 12 straight sections. The arcs are embedded in a lattice of bending and focusing magnets that force the beam into a curved trajectory and constrain it to a tight ellipse, 40 μm × 200 μm (σ). The three bending magnets in each arc cause the electron orbit to curve and thus generate synchrotron radiation. The straight sections can accommodate insertion devices—undulators and wigglers—that also generate synchrotron radiation, but with enhanced characteristics. Undulators and wigglers consist of two arrays of permanent magnets that create a magnetic field of alternating polarity perpendicular to the electron beam. One array is installed above and the other below the vacuum chamber. The alternating magnetic field causes the beam to curve horizontally from side to side as it passes between the rows of magnets. As the electrons curve back and forth, they emit synchrotron radiation.

Undulators and wigglers differ in the amount of angular deflection their magnets produce. The angle at which a wiggler's magnets deflect the electron beam is large compared with the natural emission angle of synchrotron radiation. As a result, a wiggler produces a continuous spectrum of radiation, similar to that produced by a bending magnet that has the same magnetic field strength—but more intense. The angle at which an undulator's magnets deflect the electron beam is close to the natural emission angle of the radiation. Consequently, the waves of light emitted at each pole in the array reinforce or cancel one another to enhance the

emission of certain wavelengths. For this reason, undulator radiation at the enhanced wavelengths is extremely bright—brighter than either bending-magnet or wiggler radiation. Furthermore, because it emerges in a narrow cone (see Fig. 4) and is partially coherent, it is similar to the light from a laser. Also, it is linearly polarized. Circularly polarized radiation can be produced by using specialized undulators or wigglers, or by a bending magnet.

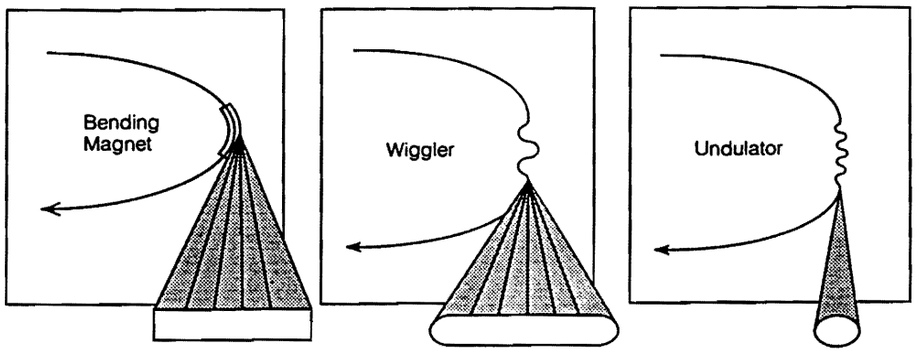

Figure 4. Bending magnets and wigglers generate fan-shaped beams of synchrotron radiation, whereas undulators emit pencil-thin beams.

The ALS will support an extensive research program in the many scientific disciplines that use x-ray and ultraviolet radiation to study and manipulate matter: atomic and molecular physics, chemistry, the life sciences, materials science, and earth science. When the facility begins operations in 1993, five beamlines will deliver photons to experimental stations: three with undulator sources and two with bending-magnet sources. By 1995, an additional five beamlines will be in operation.

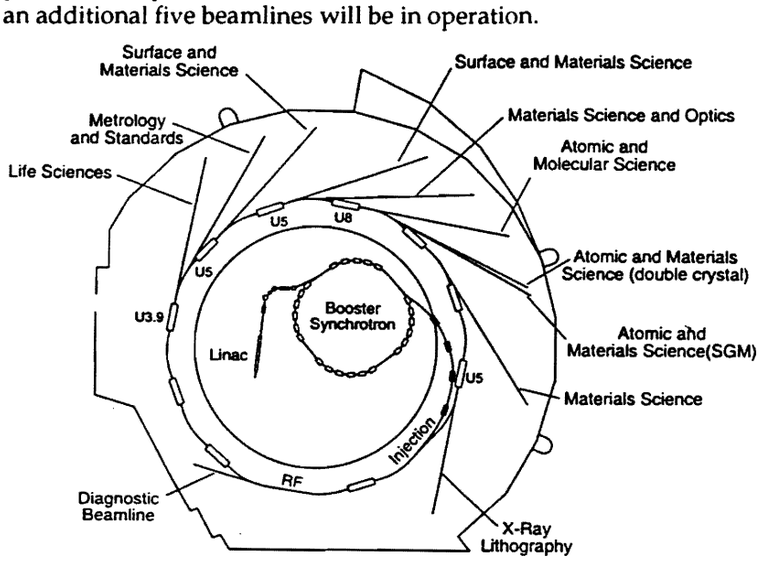

Figure 5. ALS floor plan showing locations of insertion devices and beamlines, and their applications.

Lawrence Berkeley Laboratory and ALS management have a commitment to making access to the beamlines as convenient as possible. We are developing efficient systems for user registration and training in order to minimize the time it takes users to meet institutional requirements and maximize the time for productive work. Construction of essential laboratory facilities for users is under way, and space has been made available for offices, a library, and a shop dedicated to users. Our goal is to see high-quality research conducted at the ALS, starting on the first day of operations.

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ALS Status and Research Opportunities

(A. Schlachter, ALS Scientific Program Coordinator)

The Advanced Light Source: vacuum-ultraviolet and x-ray beams of unprecedented brightness

- x rays as a probe of matter
- generating x rays with a synchrotron
- The ALS status
- opportunities in earth, soil, and environmental sciences

Fred Schlachter
Scientific Program Coordinator
Advanced Light Source

The ALS will be the world's brightest synchrotron radiation source in the extreme ultraviolet and soft x-ray regions of the spectrum when it opens its doors for research in April 1993.

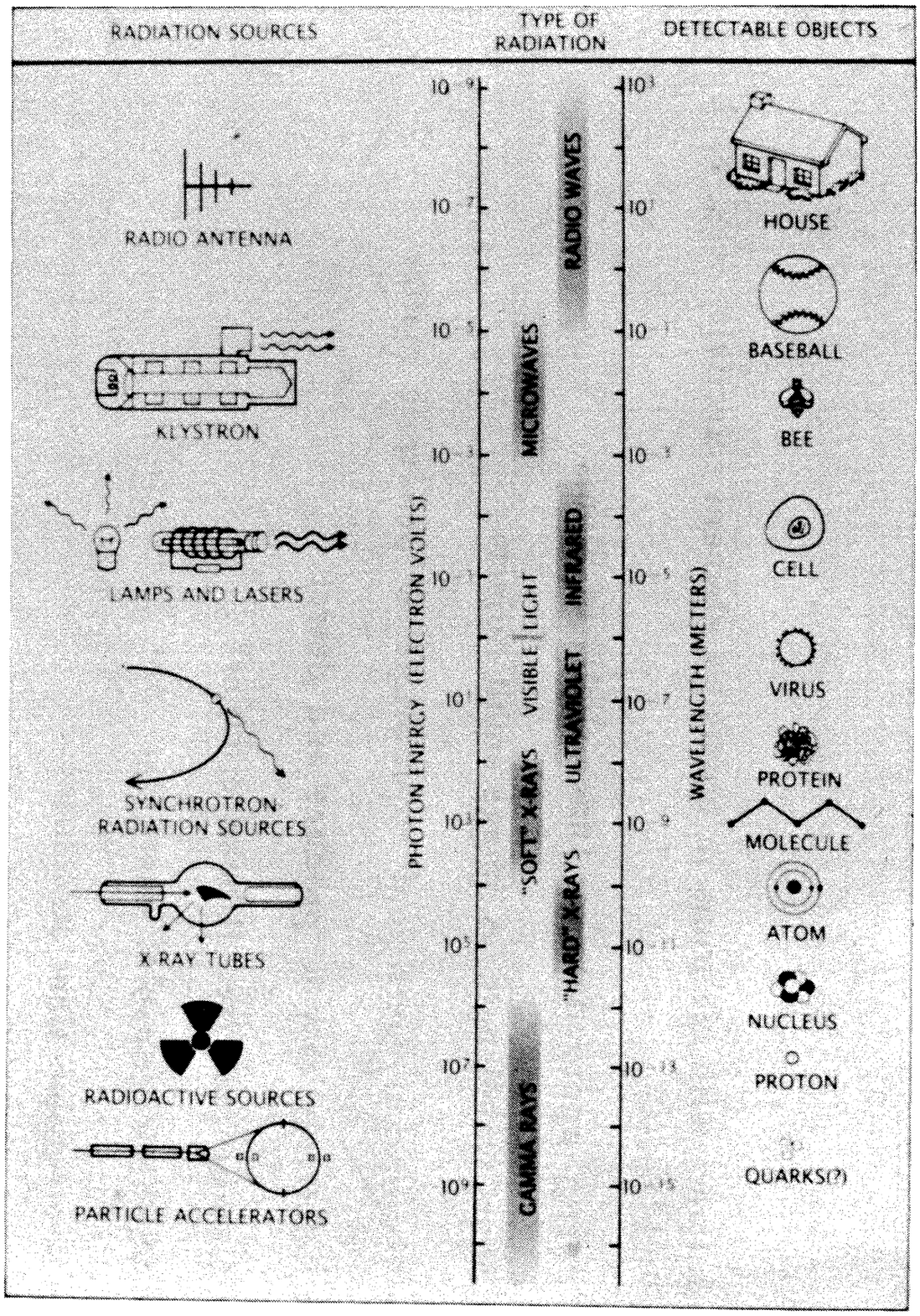
December 11, 1991

THE ALS: OUTLINE OF TALK

- X rays are a useful probe of matter
- The ALS is the first of a new generation of synchrotron radiation sources
- High brightness is the main feature of the ALS
- The ALS provides exciting new opportunities for research
- The ALS is progressing on schedule
- A diverse scientific program is in place
- The ALS will be user friendly

X-RAYS ARE AN IMPORTANT PROBE OF MATTER

- Interact with electrons in atoms ⇒ element selectivity (e.g., K, L edges)
- Energy appropriate for inner shells of atoms
- Short wavelength ⇒ image small objects
- Absorption coefficient appropriate ⇒ penetrate matter
- Relatively easy to produce and detect
- Can be polarized (linear, circular)
- Variable (tunable) energy
- Short-pulse time structure

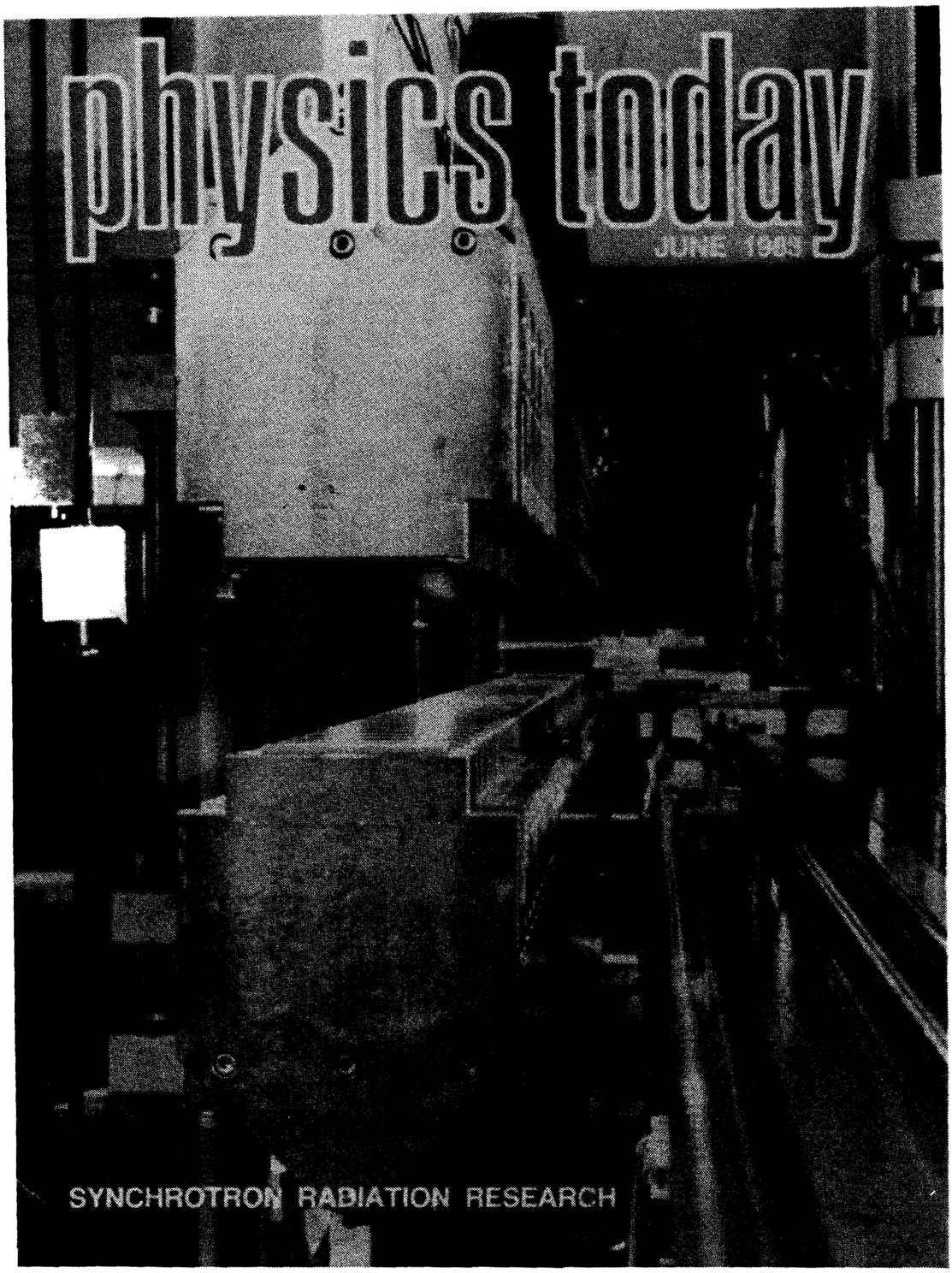

RADIATION SOURCES
TYPE OF RADIATION
DETECTABLE OBJECTS
RADIO ANTENNA
KLYSTRON
LAMPS AND LASERS
SYNCHROTRON RADIATION SOURCES
X RAY TUBES
RADIOACTIVE SOURCES
PARTICLE ACCELERATORS
PHOTON ENERGY (ELECTRON VOLTS)
RADIO WAVES
MICROWAVES
INFRARED
VISIBLE LIGHT
ULTRAVIOLET
"SOFT" X-RAYS
"HARD" X-RAYS
GAMMA RAYS
WAVELENGTH (METERS)
HOUSE
BASEBALL
BEE
CELL
VIRUS
PROTEIN
MOLECULE
ATOM
NUCLEUS
PROTON
QUARKS(?)

THE ADVANCED LIGHT SOURCE: OVERVIEW

ALS

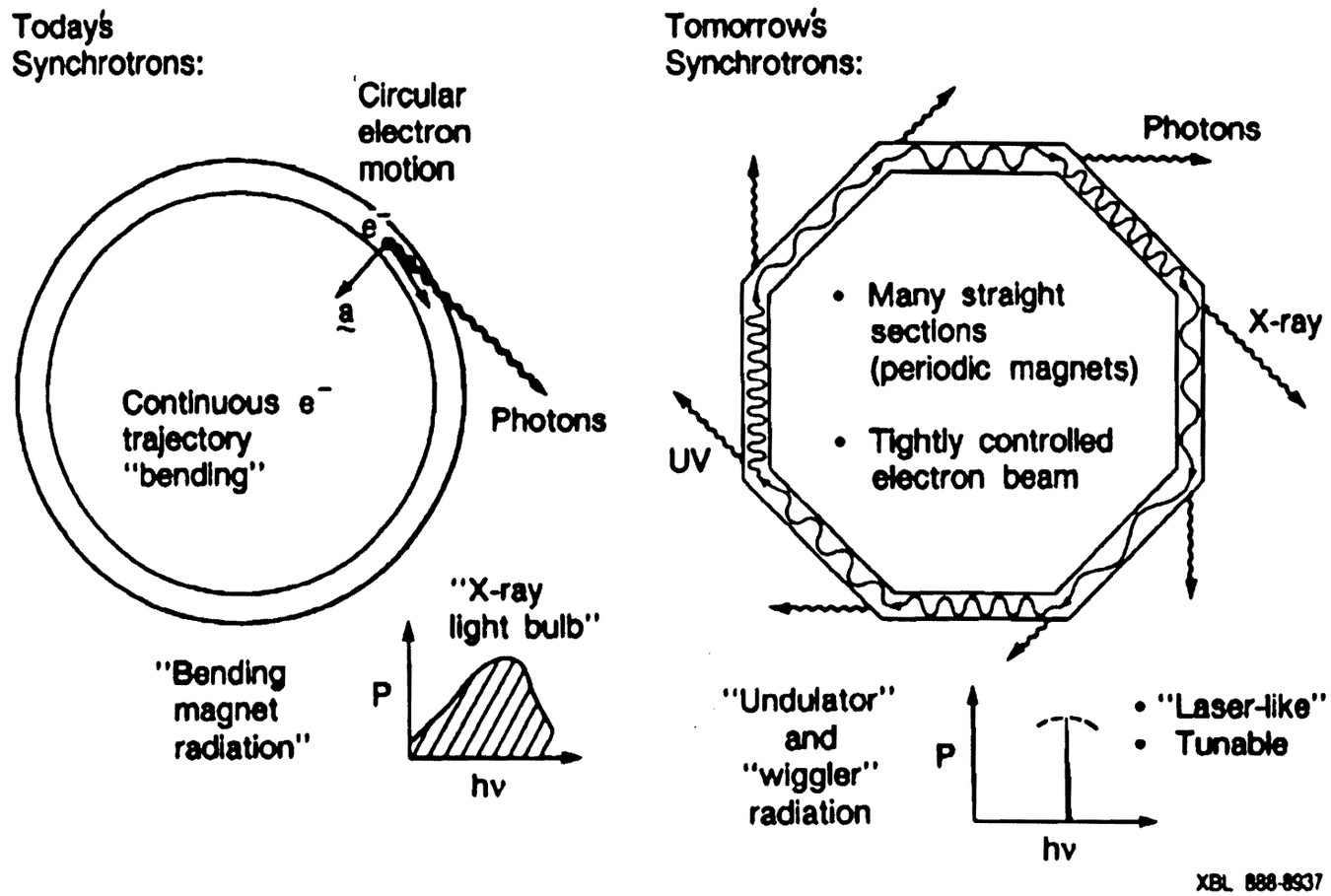
- National user facility
- Provides UV and soft x-ray beams of unprecedented brightness: (<10eV to ~10 keV)
  - Broadly tunable with narrow spectral features (resolution 10,000)
  - Partially coherent (optics, interference)
  - 35 psec time structure (life times, time of flight)
  - Polarized (linear, circular)
- Utilized by researchers from industry, academic, and national laboratory communities:
  - Materials and surface science
  - Atomic and molecular physics
  - Chemistry
  - Life sciences
  - Technology

  ] overlap with spectral range of lasers
- Construction project began in late 1986
- Begin operations in spring 1993
- Construction cost – $99.5 million


physics today
JUNE 1985
SYNCHROTRON RADIATION RESEARCH

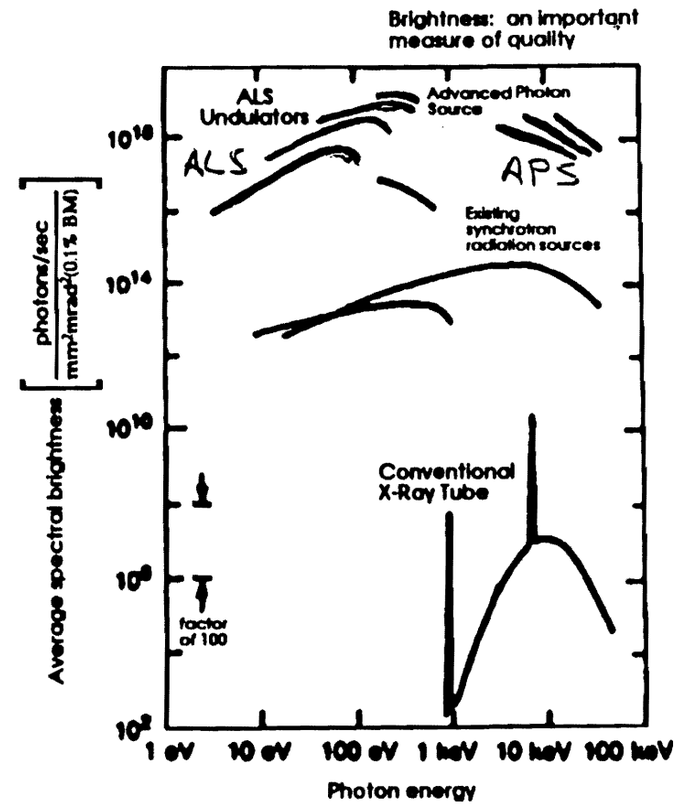
EVOLUTION OF SYNCHROTRON RADIATION

ALS



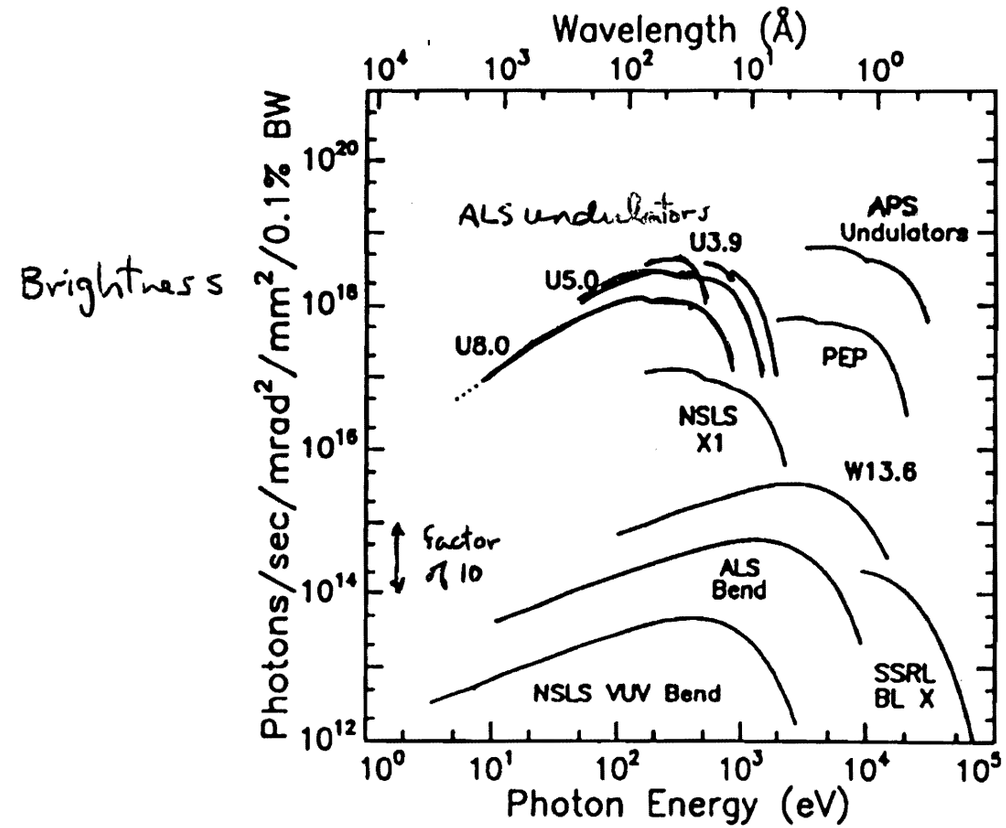
HIGH BRIGHTNESS IS THE MAIN FEATURE OF THE ALS

- High flux onto a small spot
- High resolution
- Ease of focussing ⇒ microscopy
- Element-specific sensitivity
- Partial coherence
- Broad tuning range
  (< 10 eV to > 1 keV)
- Short pulses



THIRD-GENERATION SYNCHROTRON-RADIATION SOURCES HAVE HIGH BRIGHTNESS

ALS



- **ALS undulators produce a beam which is a factor of 10,000 brighter than that from bend magnets**

An Undulator Produces a Very Bright Beam of VUV or X Rays

ALS

- Coherent superposition of radiation from electrons bent many times in periodic permanent-magnet structure

- Properties of undulator radiation:

  — High brightness
  — Tunable photon energy
  — Partial coherence
  — High linear polarization
  — Picosecond time structure

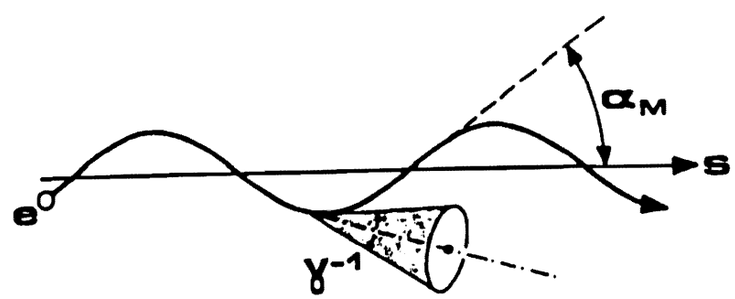
An undulator is a tunable soft-x-ray picosecond strobe light with laser-like properties

UNDULATORS AND WIGGLERS ENHANCE X-RAY PRODUCTION

- Both are periodic magnetic structure
- Radiation is emitted at each bend into angle $1/\gamma$

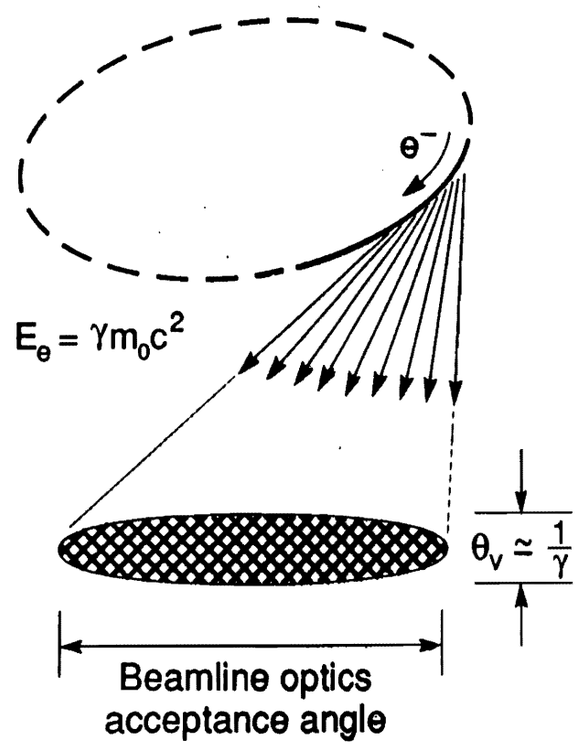
  ($1/\gamma \sim 1/3$ milliradian for 1.5 GeV electrons)

- Wiggler produces high flux:
  - Electrons deflected through large angles ($\alpha > 1/\gamma$, or $K > 1$)
  - Incoherent superposition of radiation
  - Like a collection of bend magnets
- Undulator produces high brightness:
  - Electrons deflected through small angles ($\alpha < 1/\gamma$, or $K < 1$)
  - Coherent superposition of radiation leads to interference
  - Produces small spot of nearly monochromatic radiation

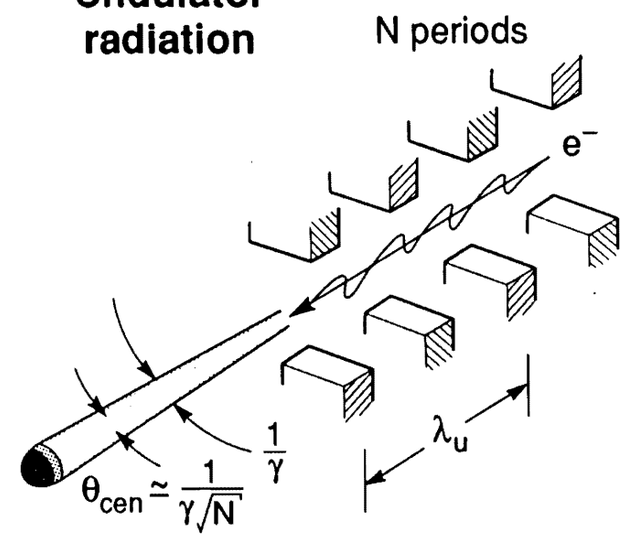


The ALS Has Both Undulators and Bending Magnets

Bending magnet radiation (sweeping searchlight)



Undulator radiation



$$\lambda_x = \frac{\lambda_u}{2\gamma^2}\left(1 + \frac{K^2}{2} + \gamma^2\theta^2\right)$$

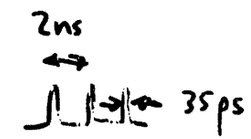
in the central radiation cone:

$$\frac{\Delta\omega}{\omega} \simeq \frac{1}{N}$$

$$\theta_{cen} \simeq \frac{1}{\gamma\sqrt{N}}$$

TIME STRUCTURE IS USEFUL FOR SOME EXPERIMENTS

- **Time structure of storage ring is different from that of laser**
  - CW laser
  - Pulsed laser
    - Low repetition rate
    - Pulsed length depends on laser (μs to fs)
  - Storage ring (ALS)



    - High repetition rate (500 MHz)
    - 35-ps pulse at 2-ns intervals standard
    - Variable filling pattern changes pulse spacing (e.g., single bunch with 650 ns between pulses; pseudo-random filling pattern)
- **Select physical problems on ps, or longer, time scale**
- **Can use multiple photons with time delay (pump-probe)**
  - Laser synchronized with storage ring
  - Photons from undulator and bend magnet
- **Energy per pulse is lower with SR than with laser**
  - Laser: high-pulse energy for harmonic generation
  - SR: low-pulse energy; undulator output includes harmonics

NEW CAPABILITIES, NEW RESEARCH

A L S

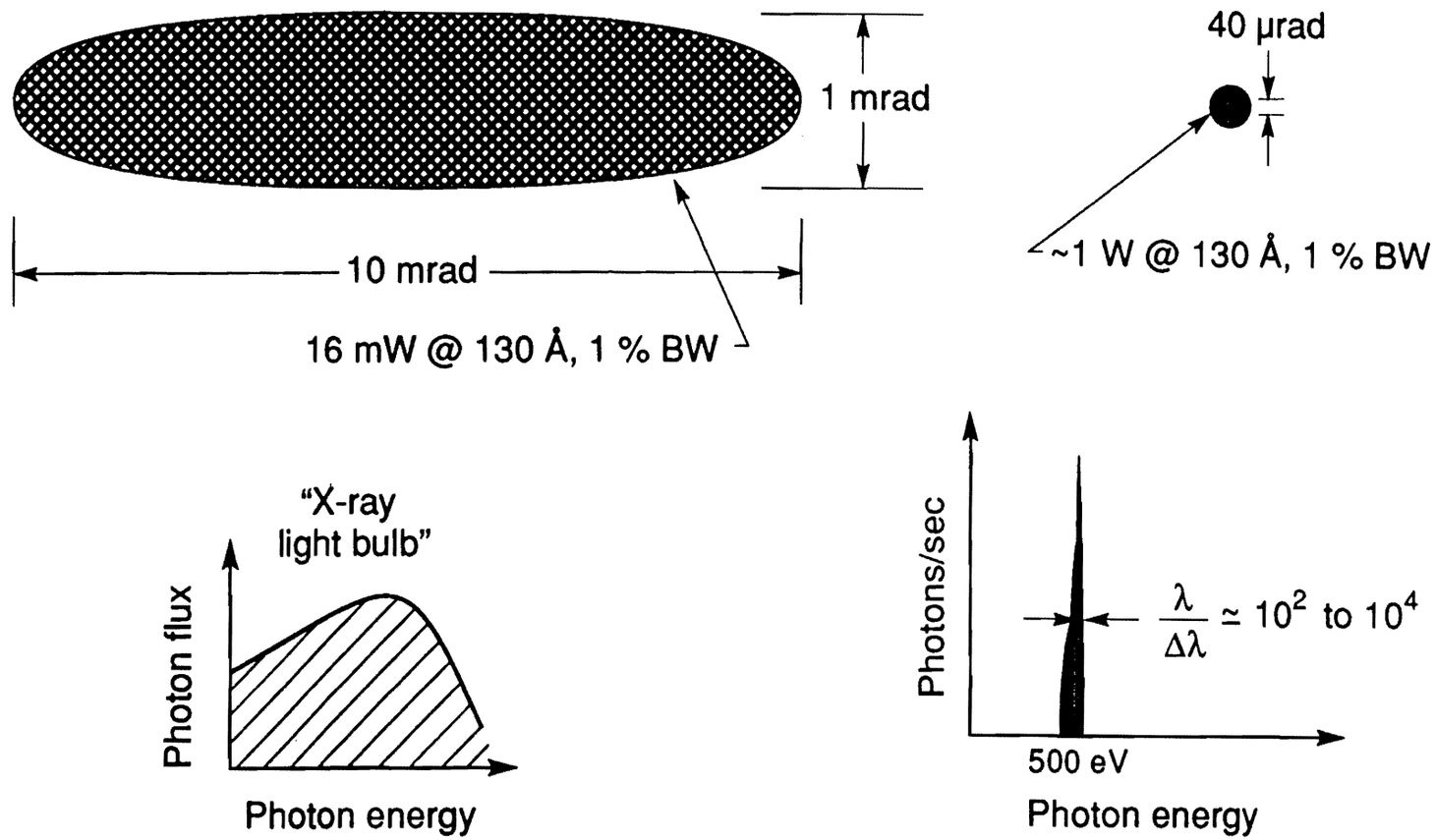
Next-Generation VUV Synchrotron-Radiation Facility Optimized for Insertion Devices

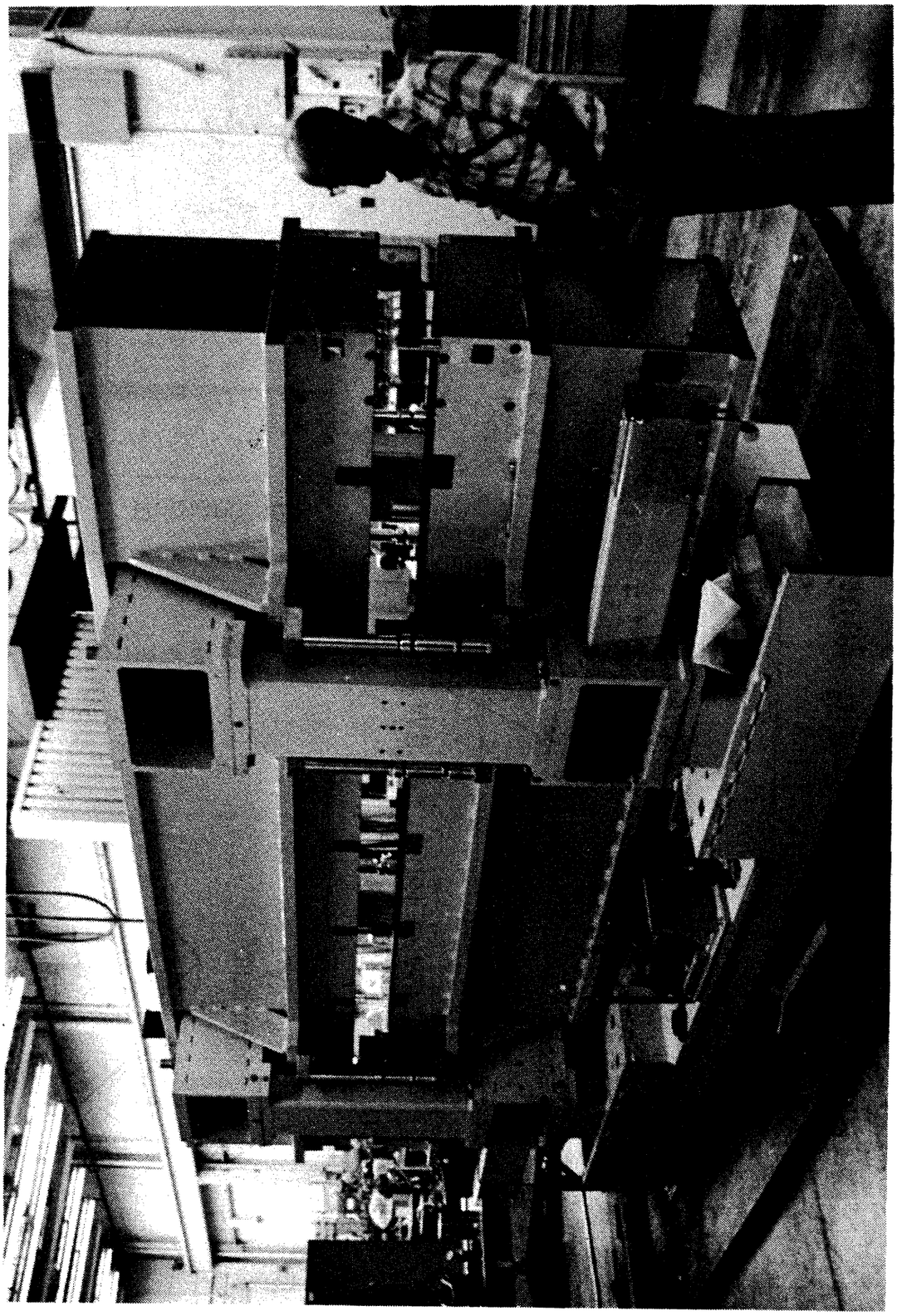
- INTENSITY, BRIGHTNESS
- COHERENCE
- Polarization
- SHORT PULSES: 35 ps *(35 trillionths of a second)*
- TUNABILITY

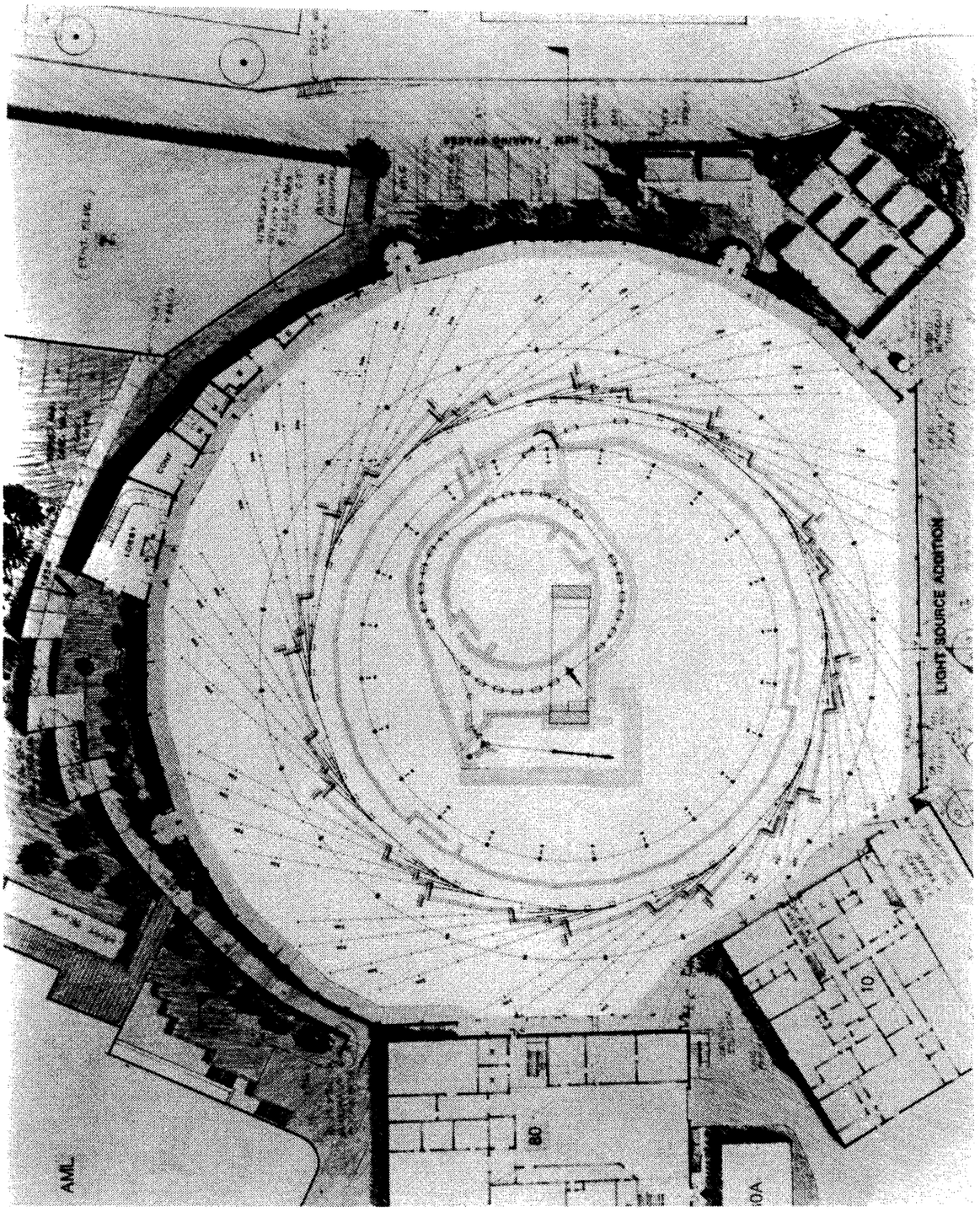
$\Longrightarrow$

- Biological imaging
- Measurements on small or dilute samples
- Studies of ultrafast processes
- Studies of dynamic processes in biological systems
- Bond-selective chemistry
- High-spatial-resolution studies
- Lithography for chip fabrication

Angular Divergence of Bending Magnet and Undulator Radiation



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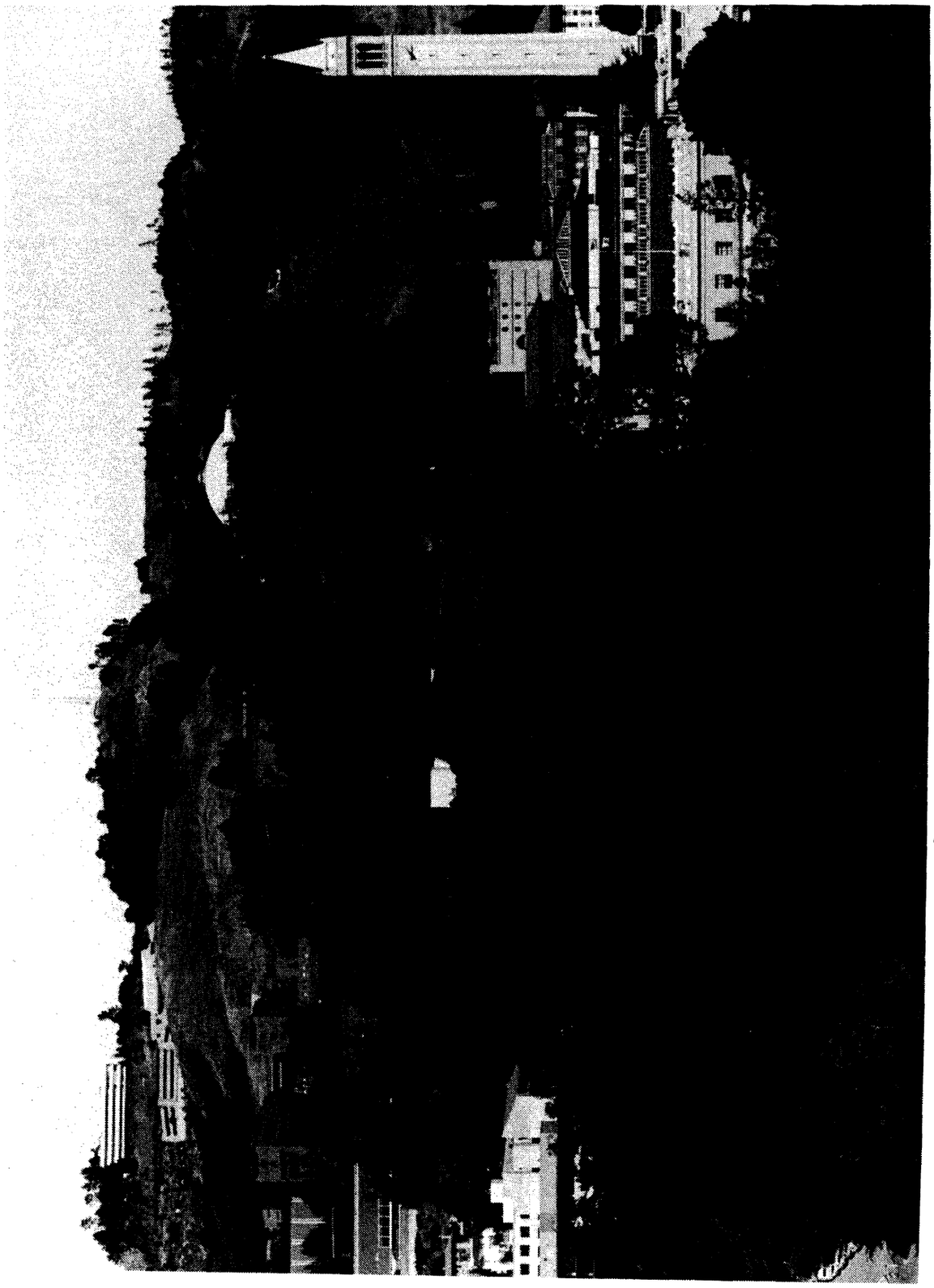
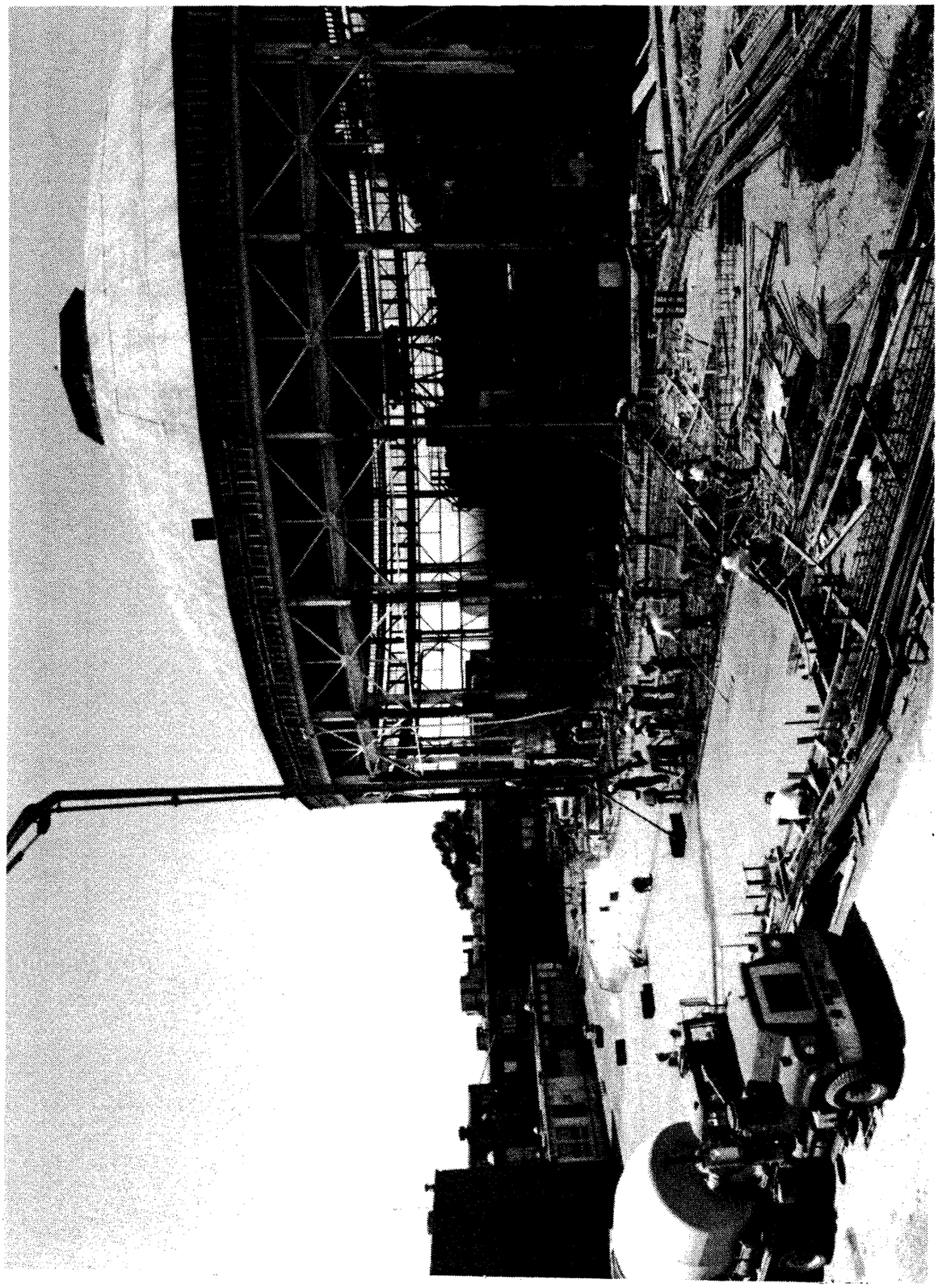
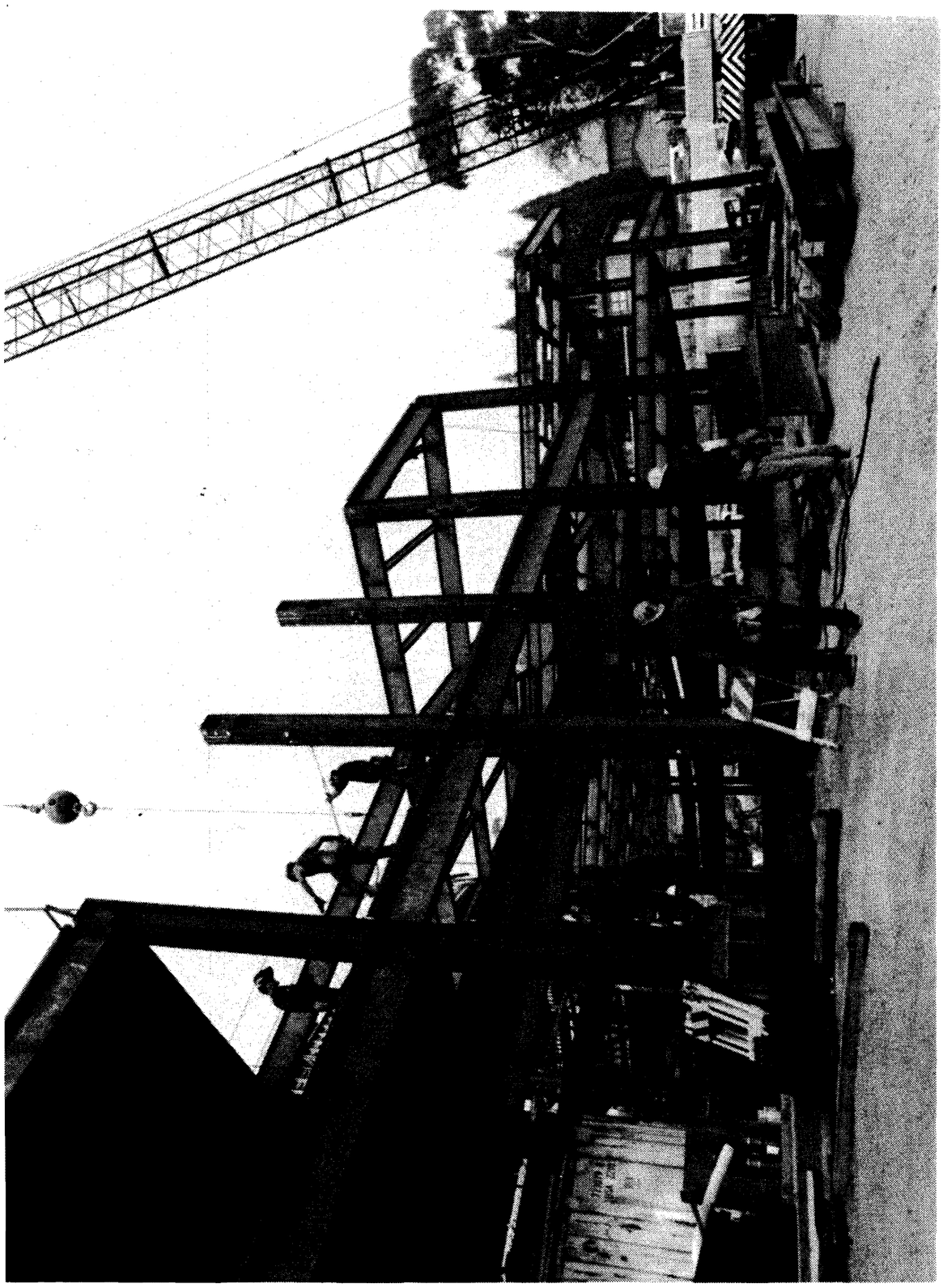
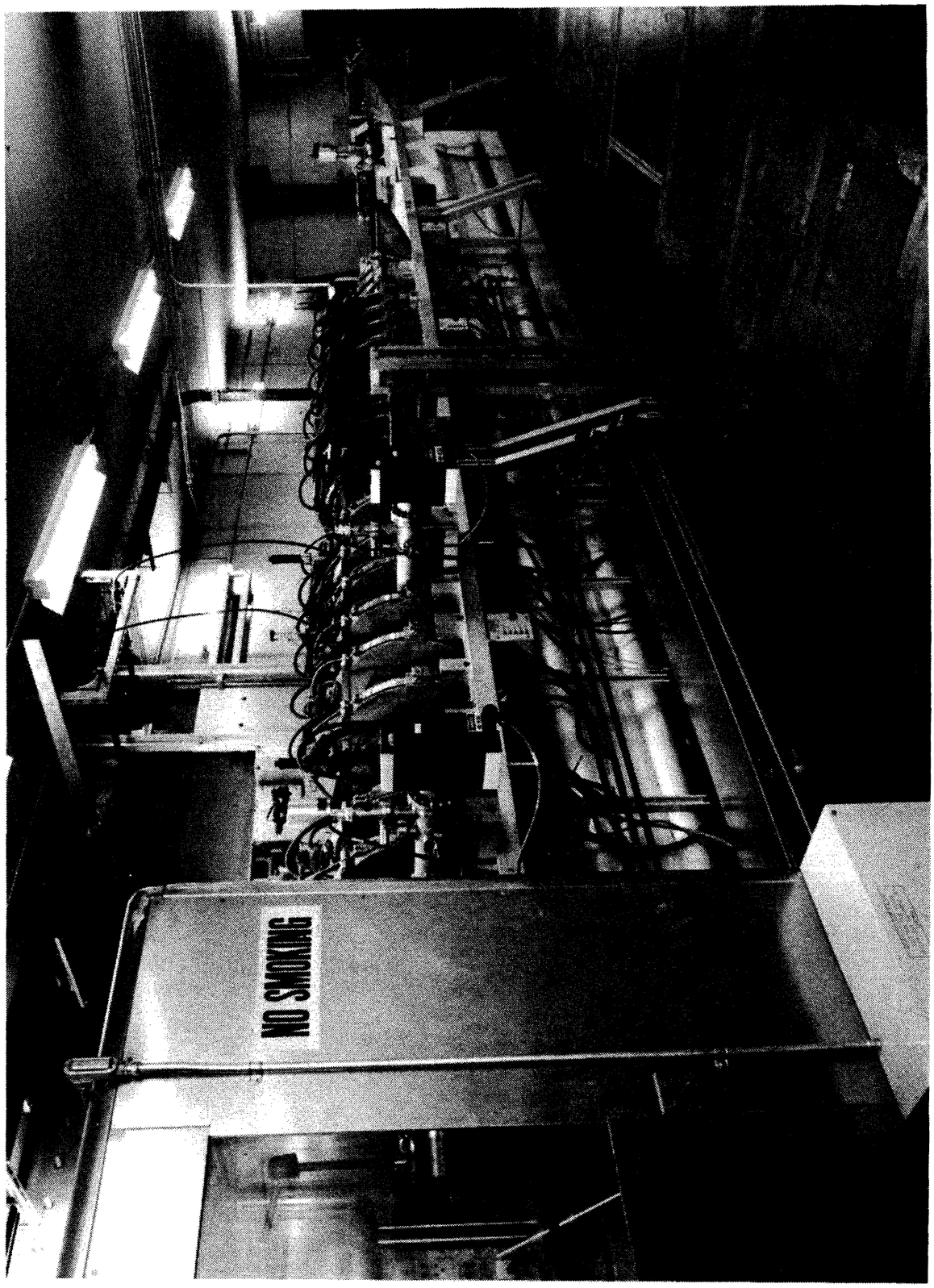
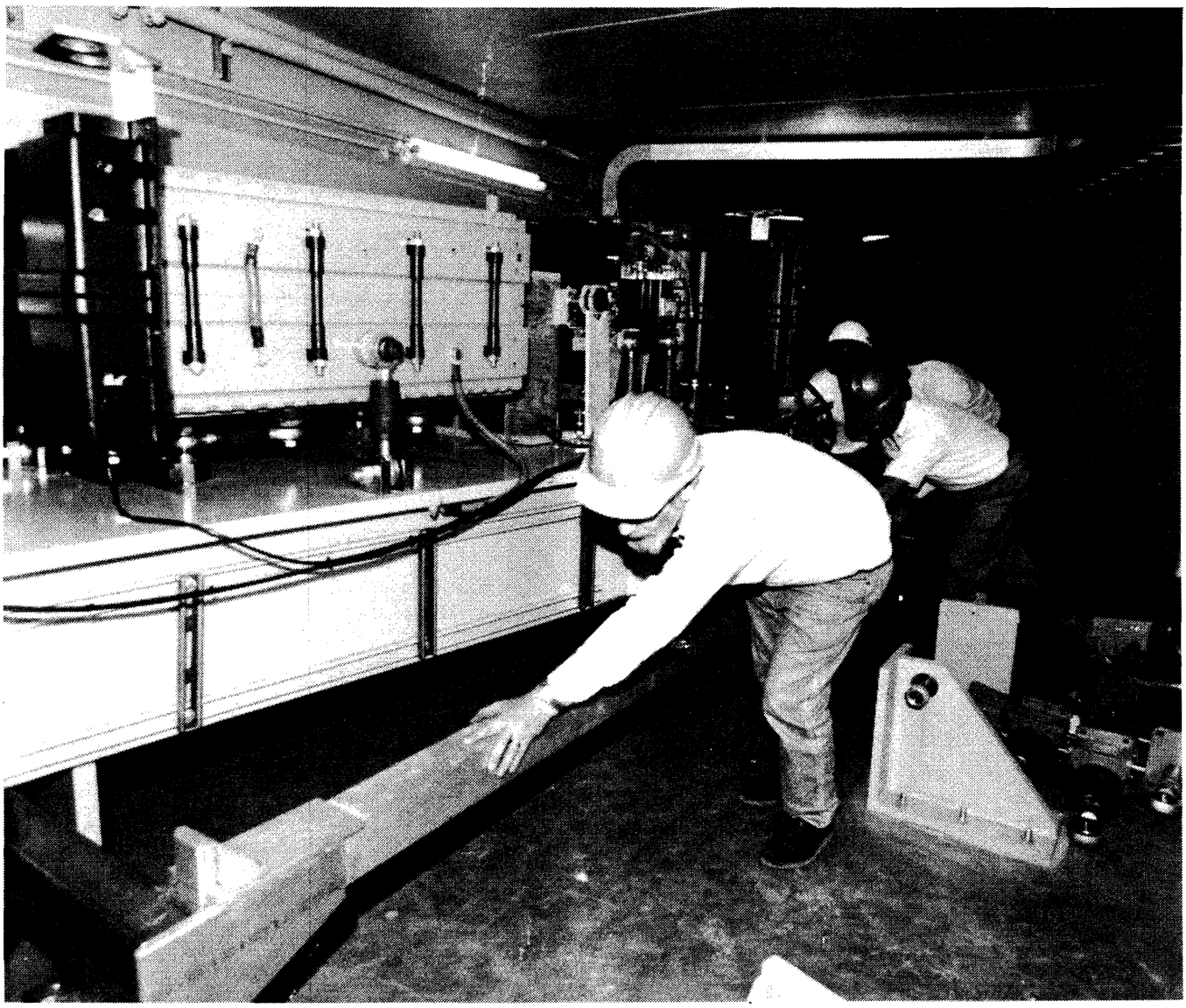
10
LIGHT SOURCE ADDITION








NO SMOKING



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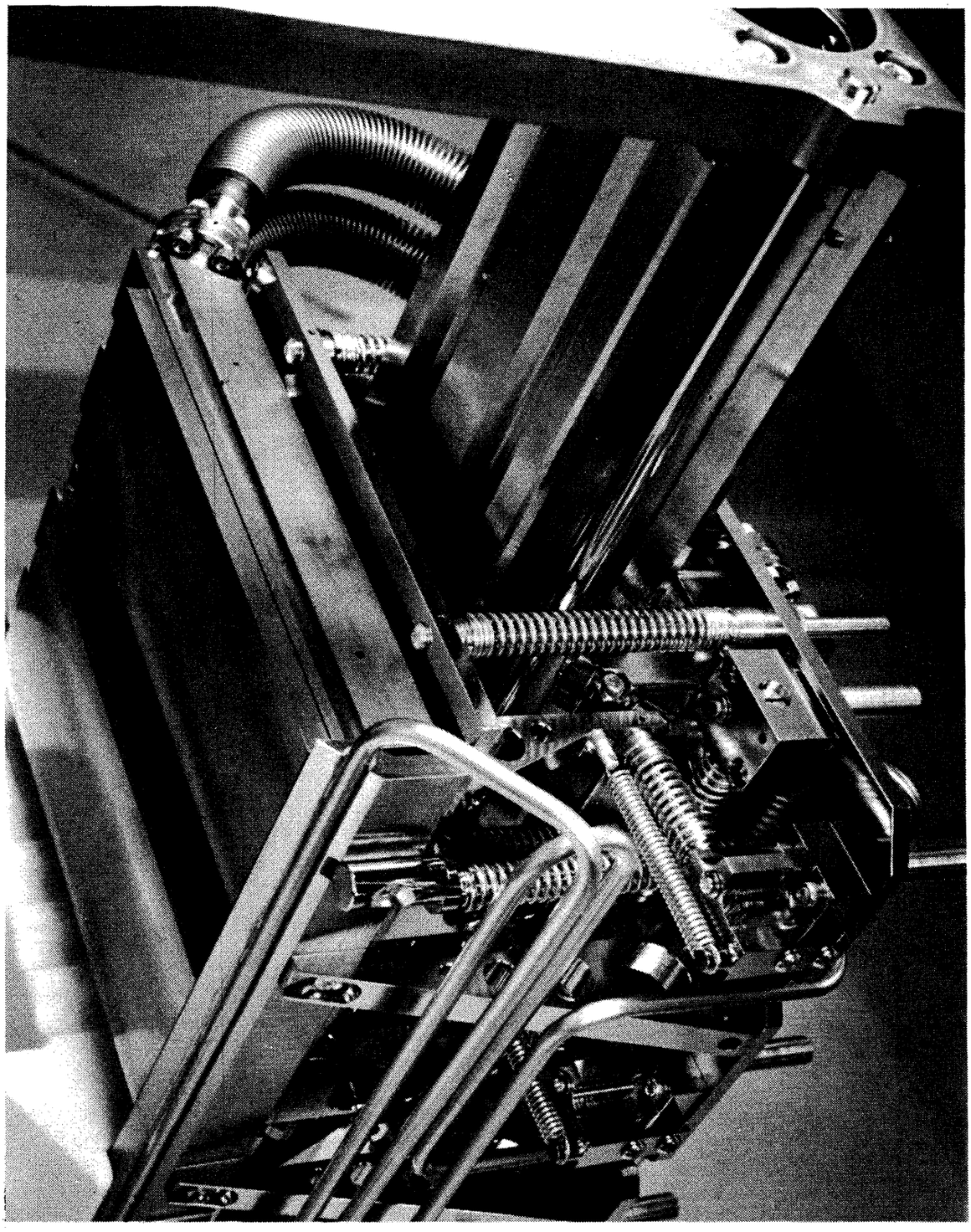
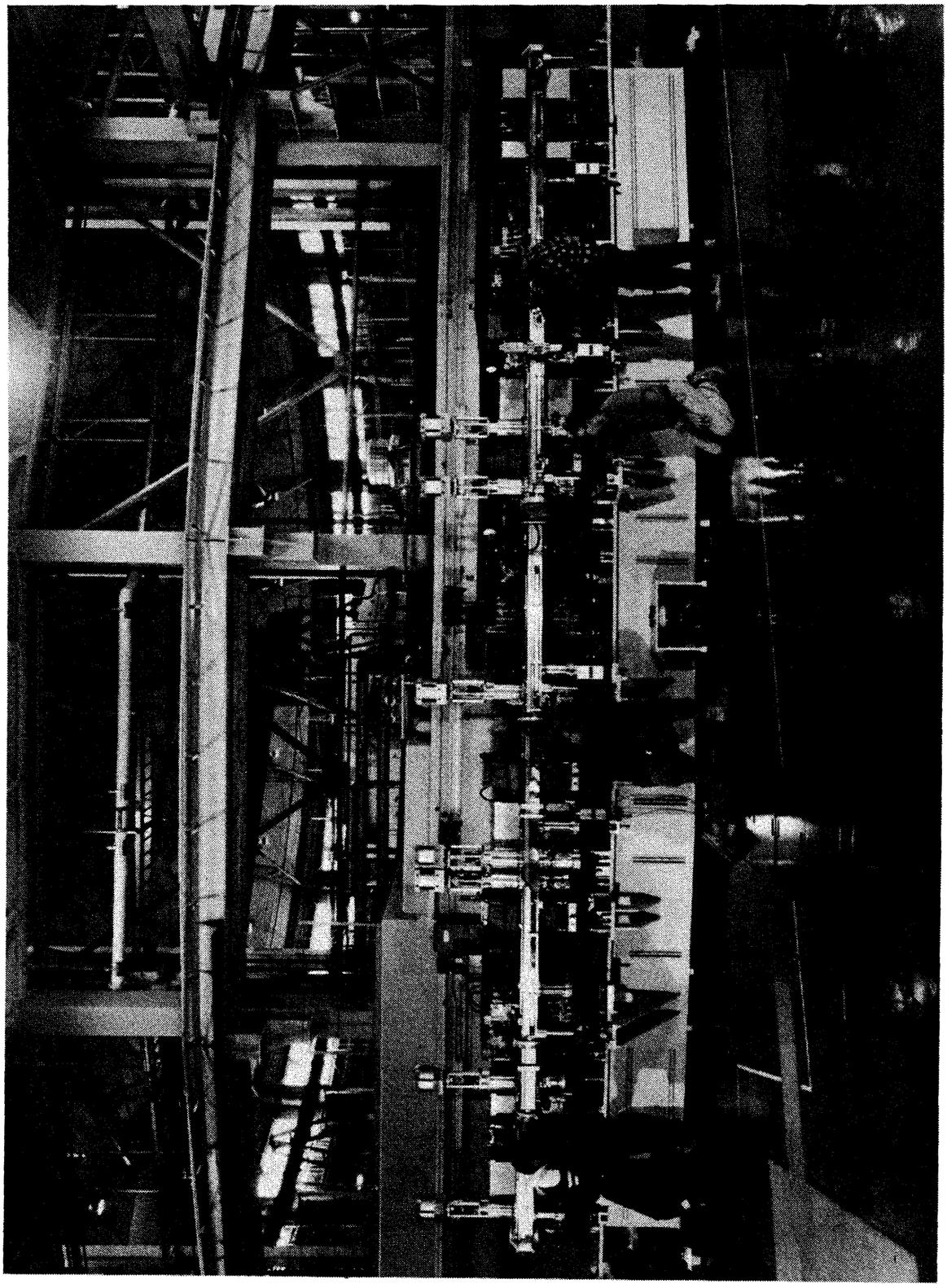




"PHOTONS—MOTHER NATURE'S FINEST TEST PROBES"

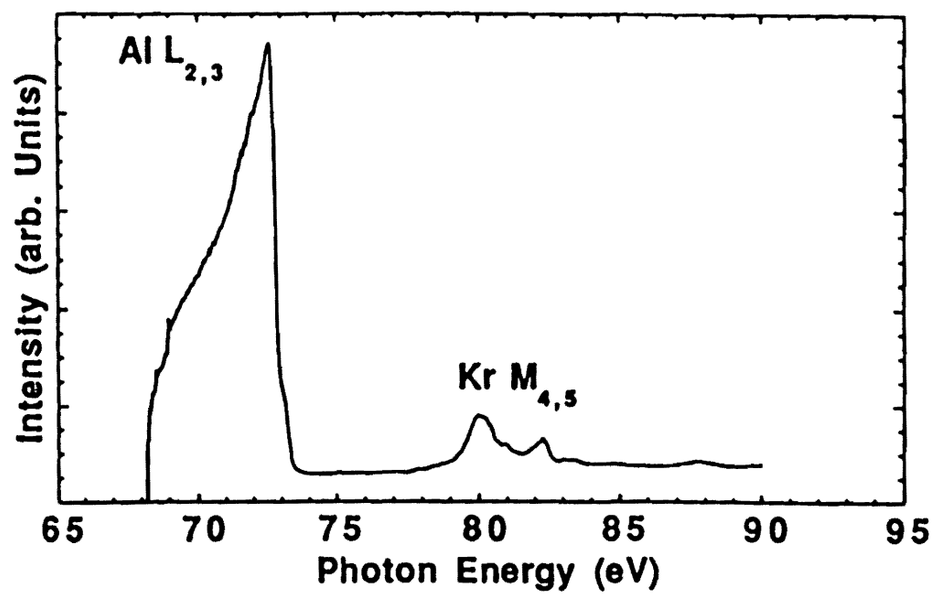
Dave Ederer

ALS

- X-ray fluorescence excited by x rays has several beneficial features

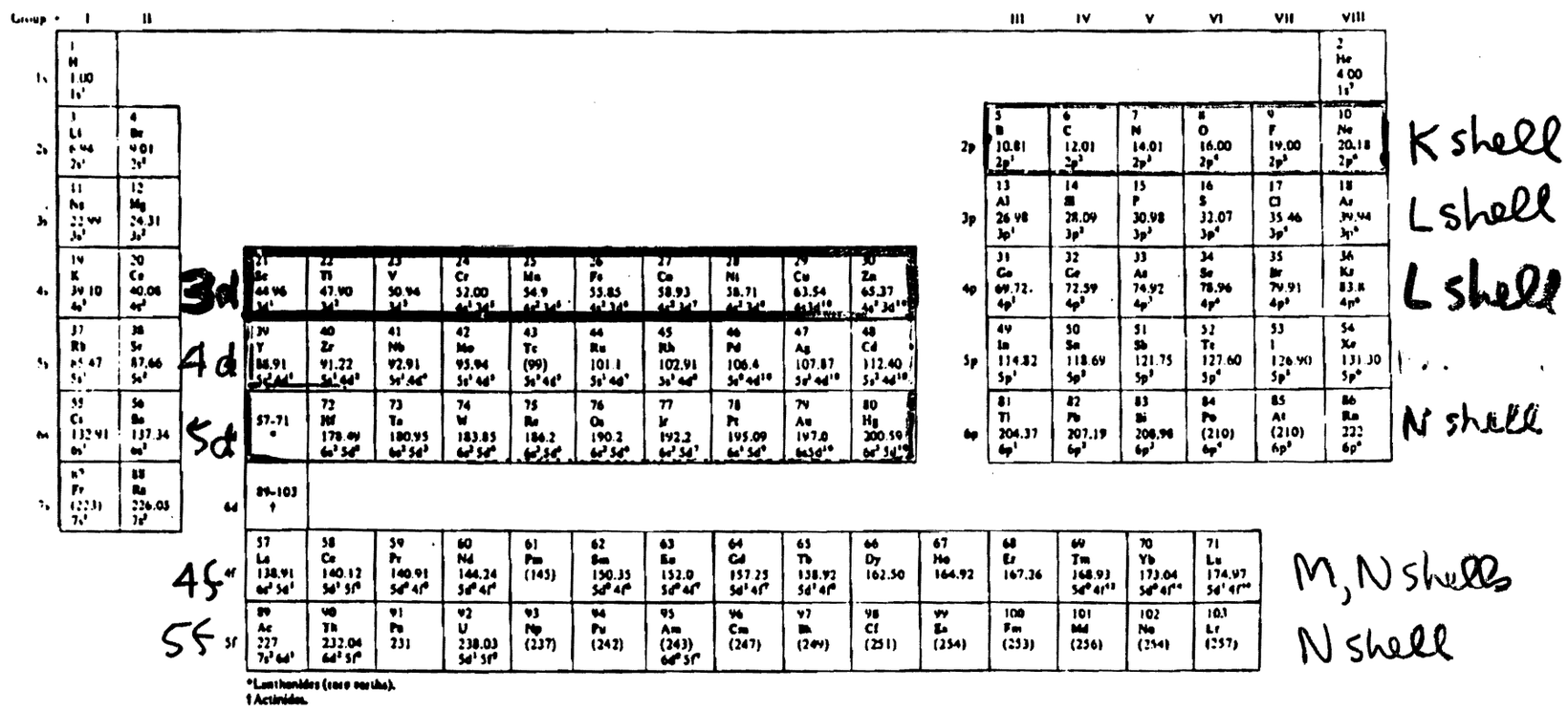
  — High spectral resolution
  — Low background
  — Easy to polarize photons
  — Low damage to samples by photons
  — Ultrahigh vacuum not required
  — Can be bulk or surface sensitive

e.g., photons are a perfect nondestructive probe for atoms buried in a substrate as illustrated by 10% krypton implanted in aluminum, where the krypton forms little balls about 1000 Å below the surface (Ref: D. Ederer, NIST, 1991)

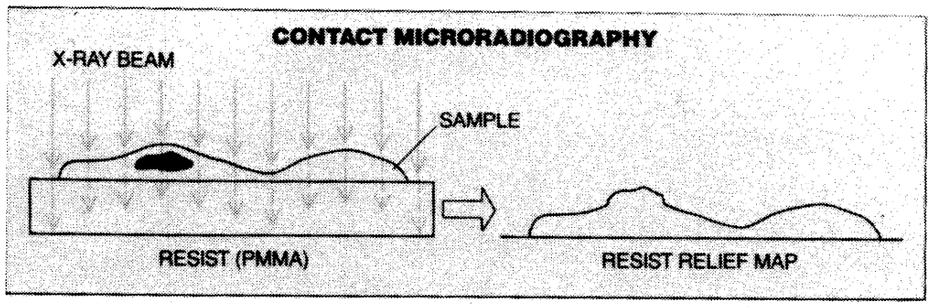


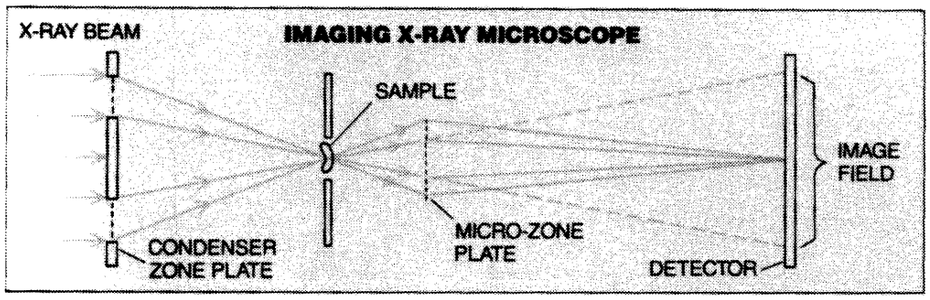
ALS Can Access Core Levels of Essentially All Elements: (200 - 1200 eV)

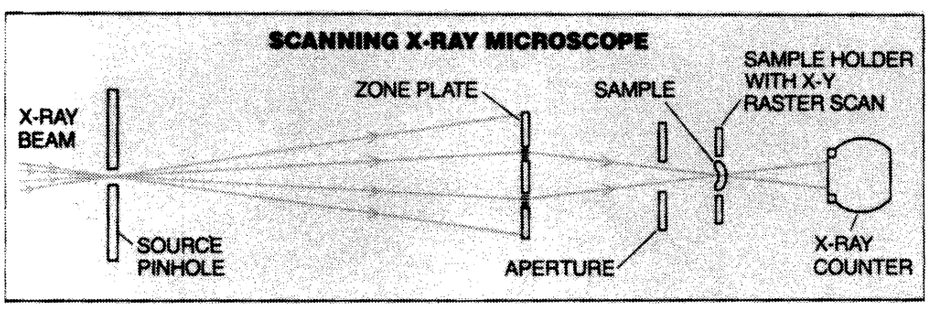
PERIODIC TABLE OF THE ELEMENTS

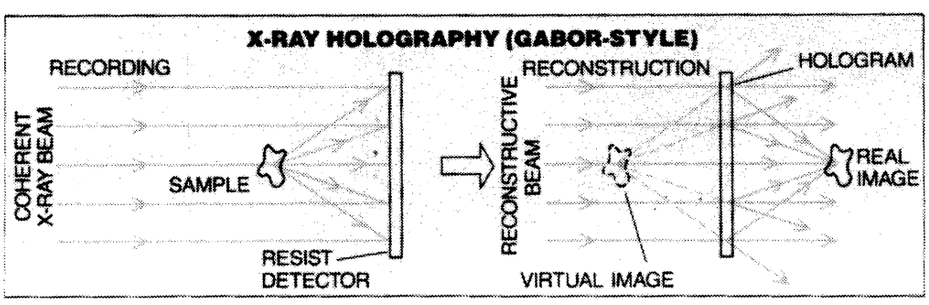


*Lanthanides (rare earths).
† Actinides.

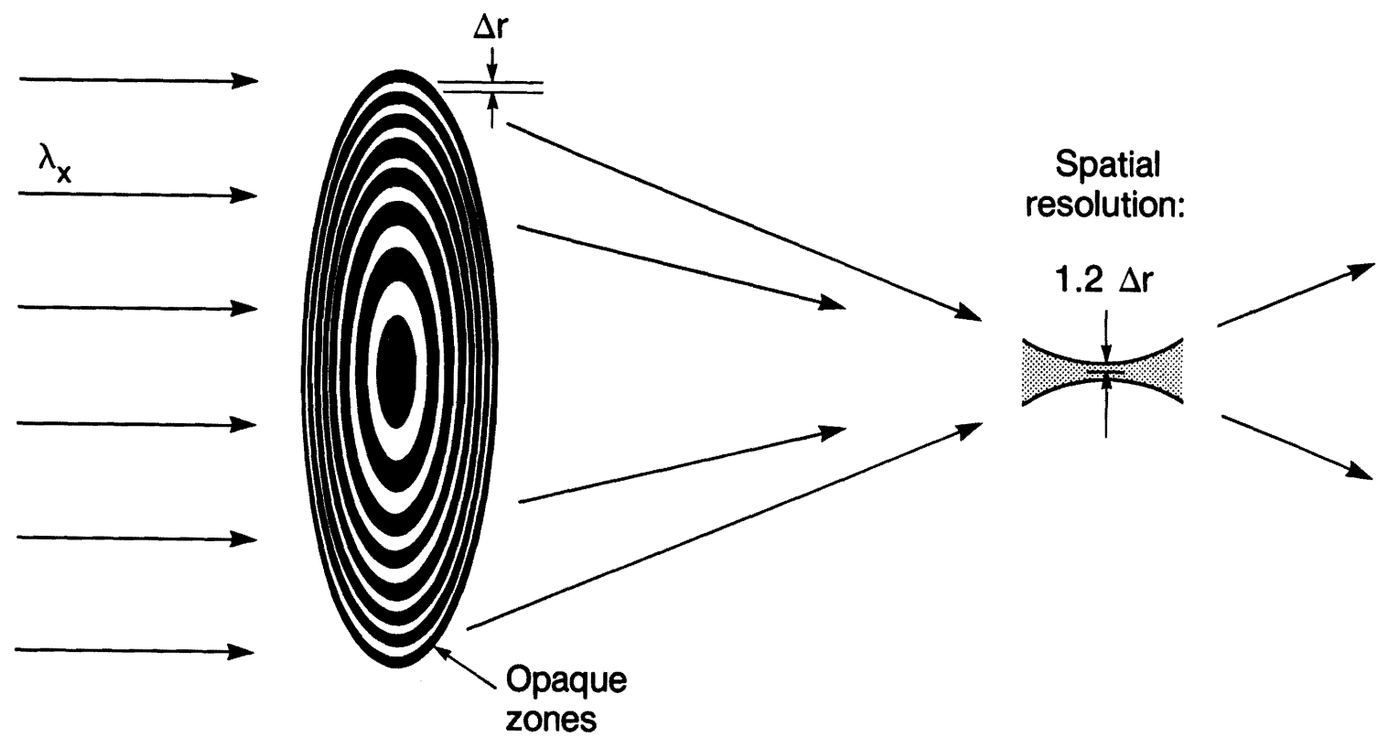

CONTACT MICRORADIOGRAPHY
X-RAY BEAM
SAMPLE
RESIST (PMMA)
RESIST RELIEF MAP


X-RAY BEAM
IMAGING X-RAY MICROSCOPE
SAMPLE
IMAGE FIELD
CONDENSER ZONE PLATE
MICRO-ZONE PLATE
DETECTOR


SCANNING X-RAY MICROSCOPE
X-RAY BEAM
ZONE PLATE
SAMPLE
SAMPLE HOLDER WITH X-Y RASTER SCAN
SOURCE PINHOLE
APERTURE
X-RAY COUNTER

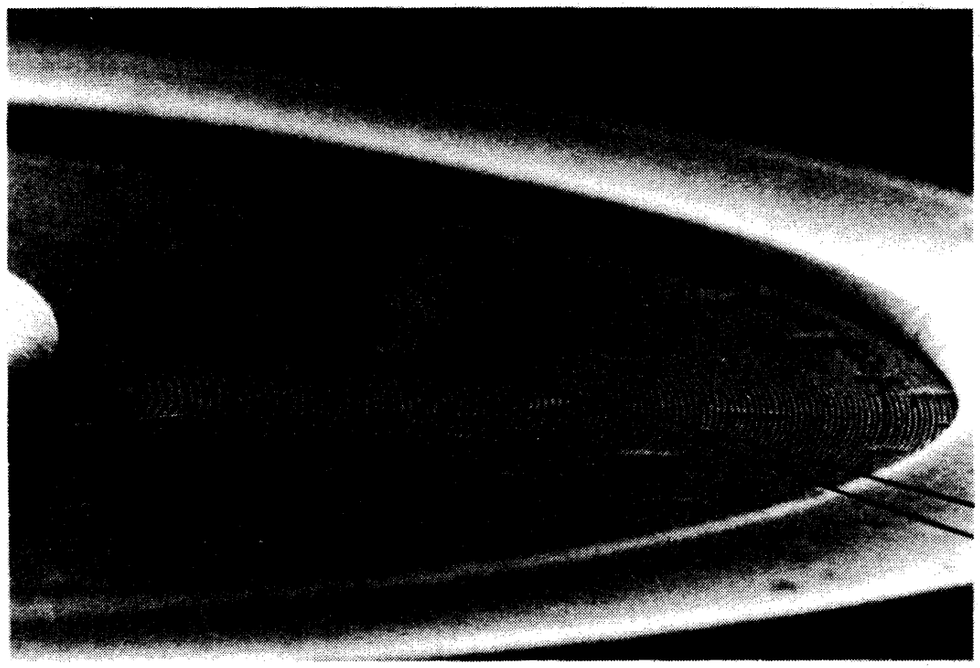

X-RAY HOLOGRAPHY (GABOR-STYLE)
RECORDING
COHERENT X-RAY BEAM
SAMPLE
RESIST DETECTOR
RECONSTRUCTION
HOLOGRAM
RECONSTRUCTIVE BEAM
REAL IMAGE
VIRTUAL IMAGE

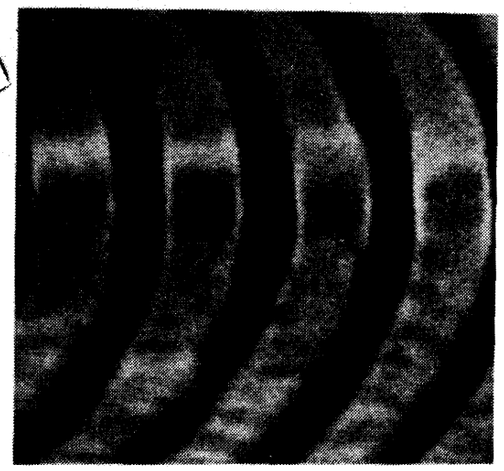
Fresnel Zone Plate Lens for Diffractive Focusing of X-Rays:



XBL 842-9405

500 Å Zone Plate for High Resolution X-ray Microscopy



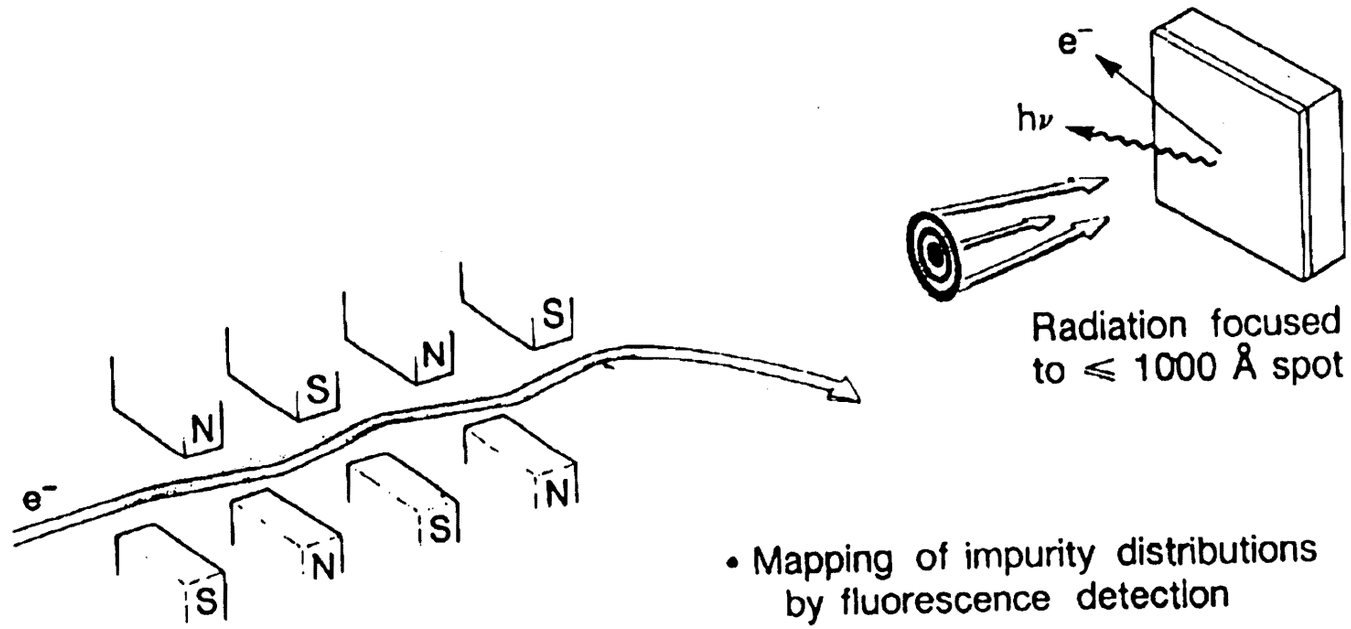


500 Å Fresnel zone plate
700 Å/300 Å bar/space ratio
1200 Å gold on 1000 Å silicon nitride
6000 Å thick apodized region
Outer diameter : 62μm
1 mm focal length at 31 Å

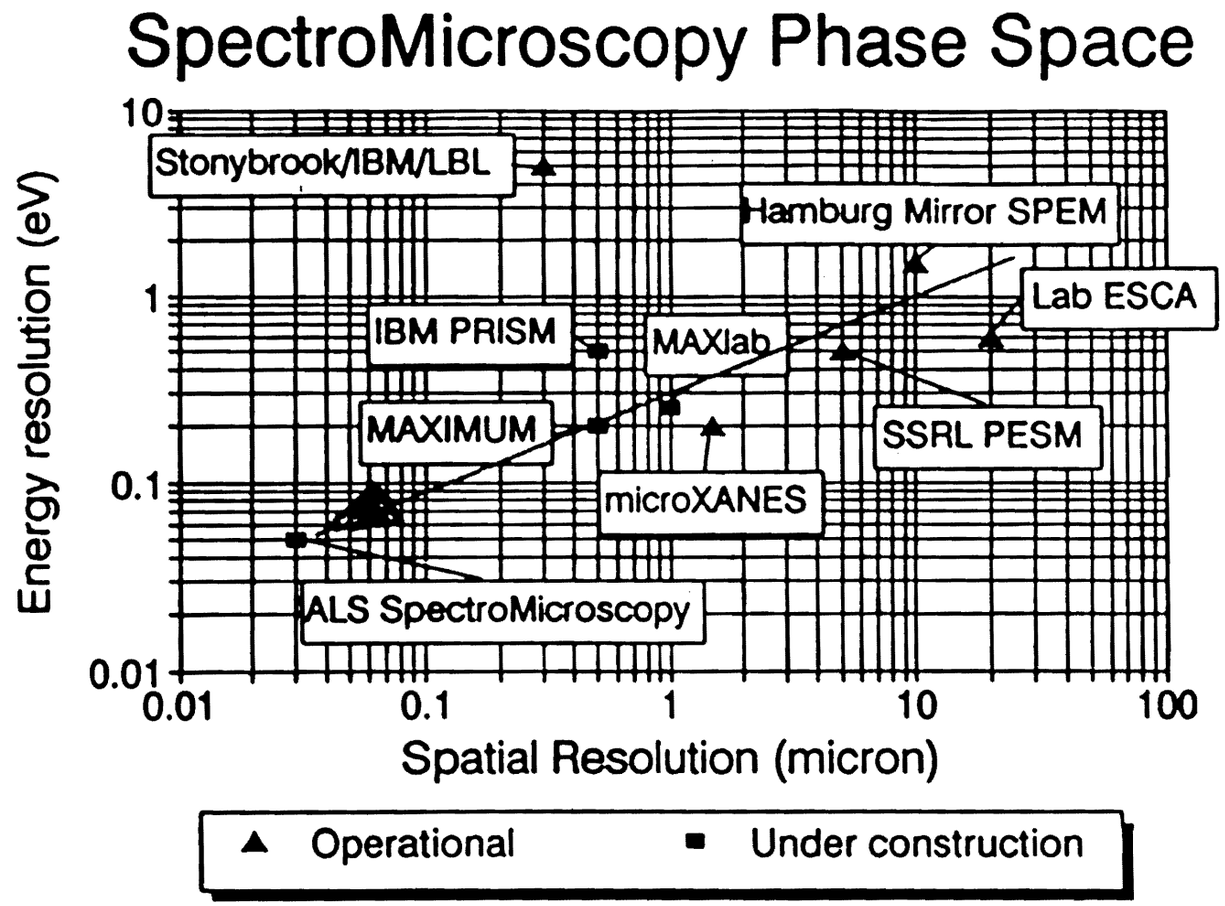
Spatially Resolved Spectroscopies for Dilute Impurity and Defect Systems

Spectromicroscopy

ALS



- Mapping of impurity distributions by fluorescence detection
- Mapping of bonding defects by photoemission

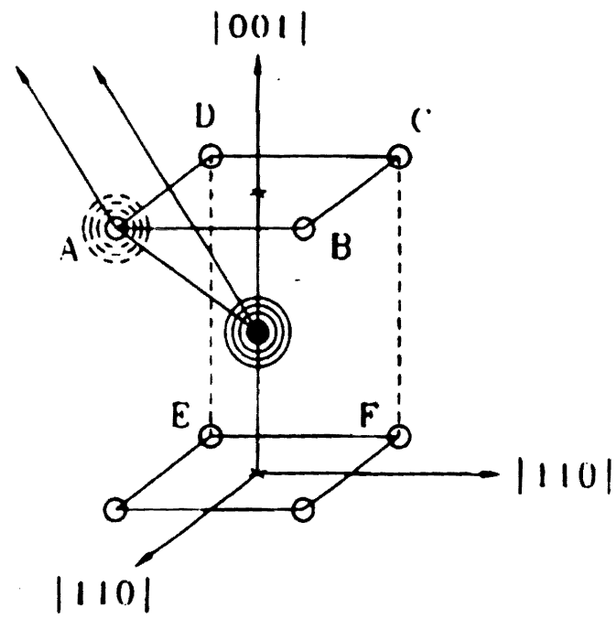


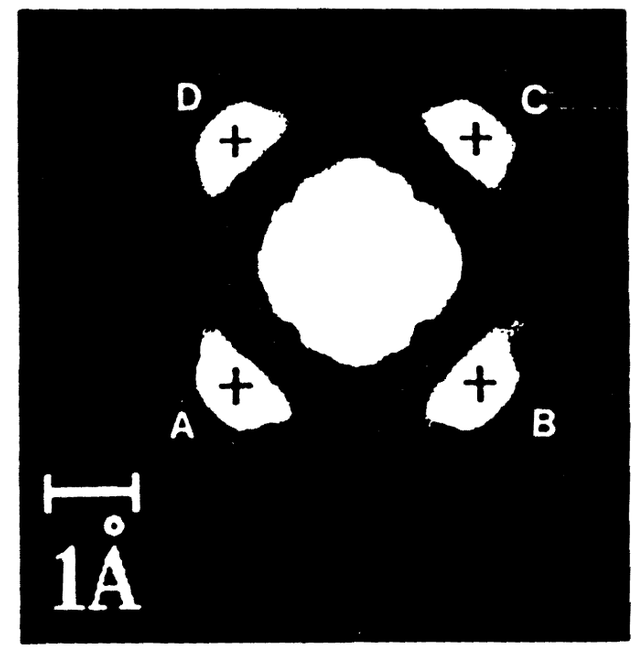
Spectromicroscopy at ALS:
- high energy resolution
- high spatial resolution.

ATOMIC-RESOLUTION ELECTRON HOLOGRAPHY

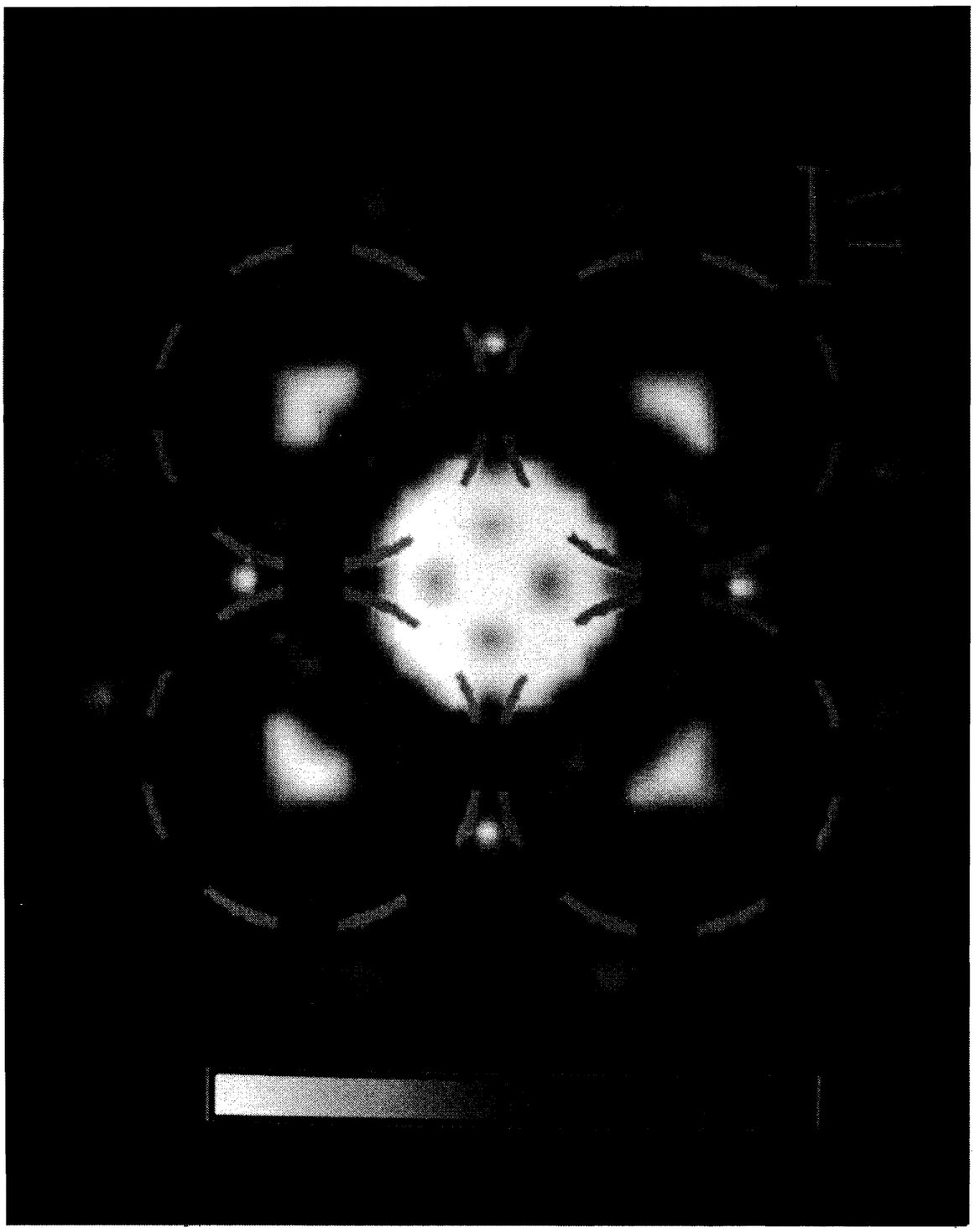
ALS

- Image near-neighbor environment of specific chemical species in three dimensions
- Measure photoelectron diffraction pattern produced by x ray to select chemical species
- High resolution needed to resolve chemical shifts



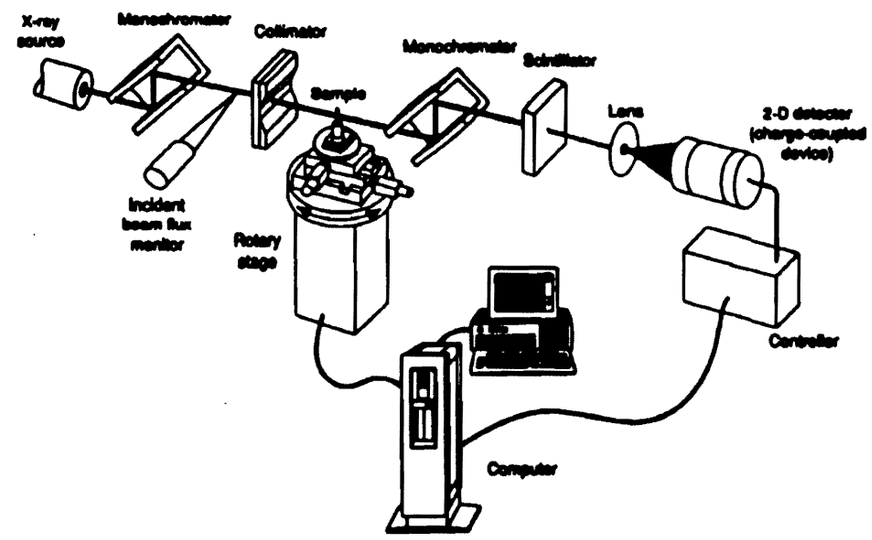


Holographic reconstruction of Cu (001)
Ref: Harp et al., *Phys. Rev. Lett.* 65, 1012 (1990); *Phys. Rev. B* 42, 9199 (1990)



ELEMENTAL ANALYSIS WITH X-RAY MICROPROBE/TOMOGRAPHY

- Fluorescence detection for element specificity
- Femtogram sensitivity
- Lateral resolution: microns



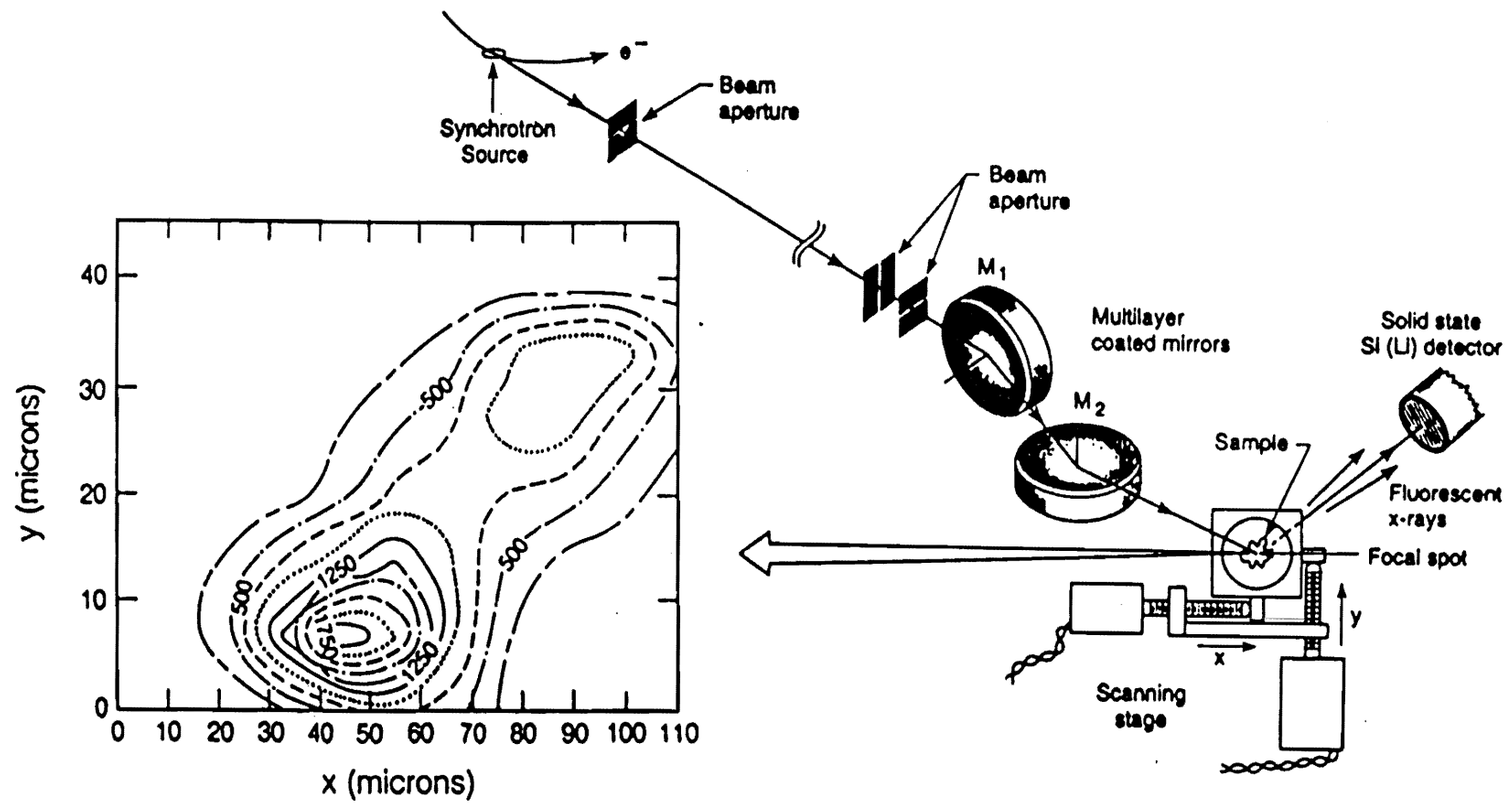
- Example: microtomography map of fiber composite material (silicon carbide fibers with graphite cores in a calcium alumino-silicate matrix)

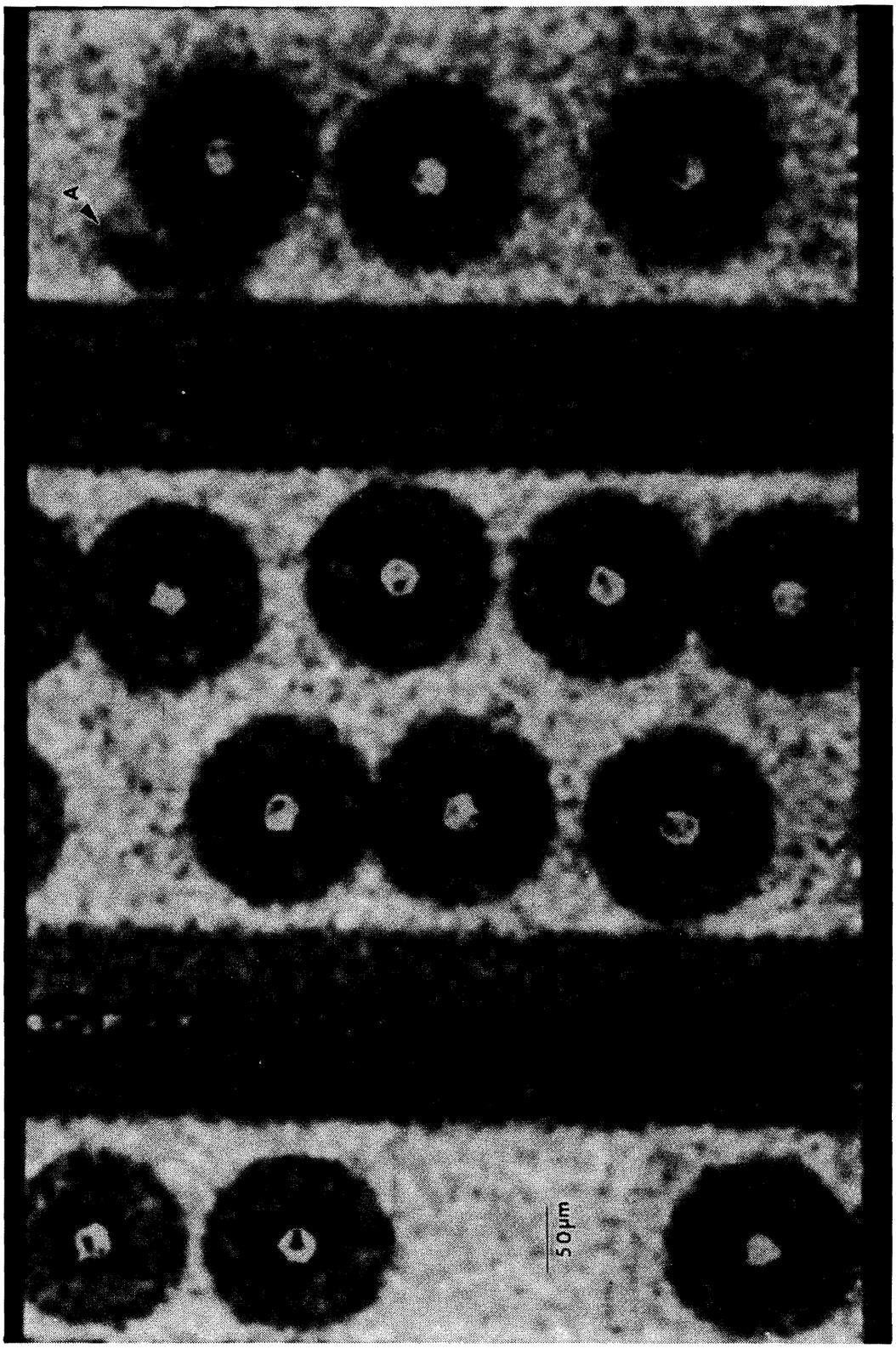
X-RAY MICROPROBE FOR THE EARTH SCIENCES

ALS

- Fluorescence microprobe provides high-sensitivity, nondestructive elemental mapping with micrometer, spatial resolution in ambient environments

  e.g., two-dimensional distribution of calcium in a fluid inclusion embedded in geophysical quartz (Ref: A. Thompson, LBL, 1987)

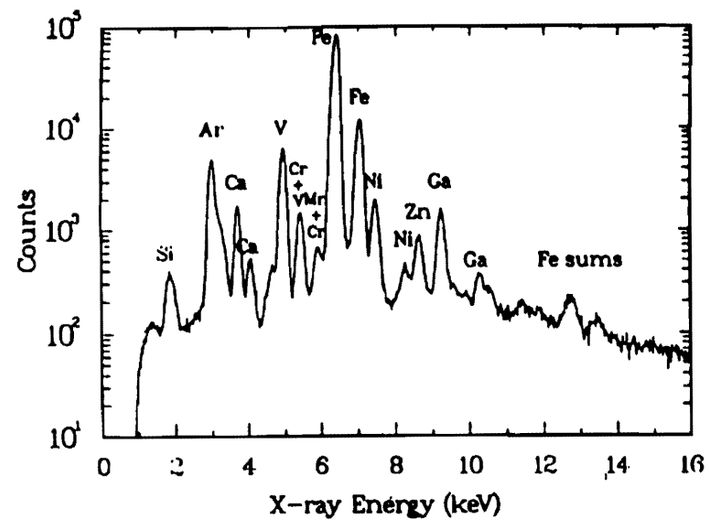



A
50 µm

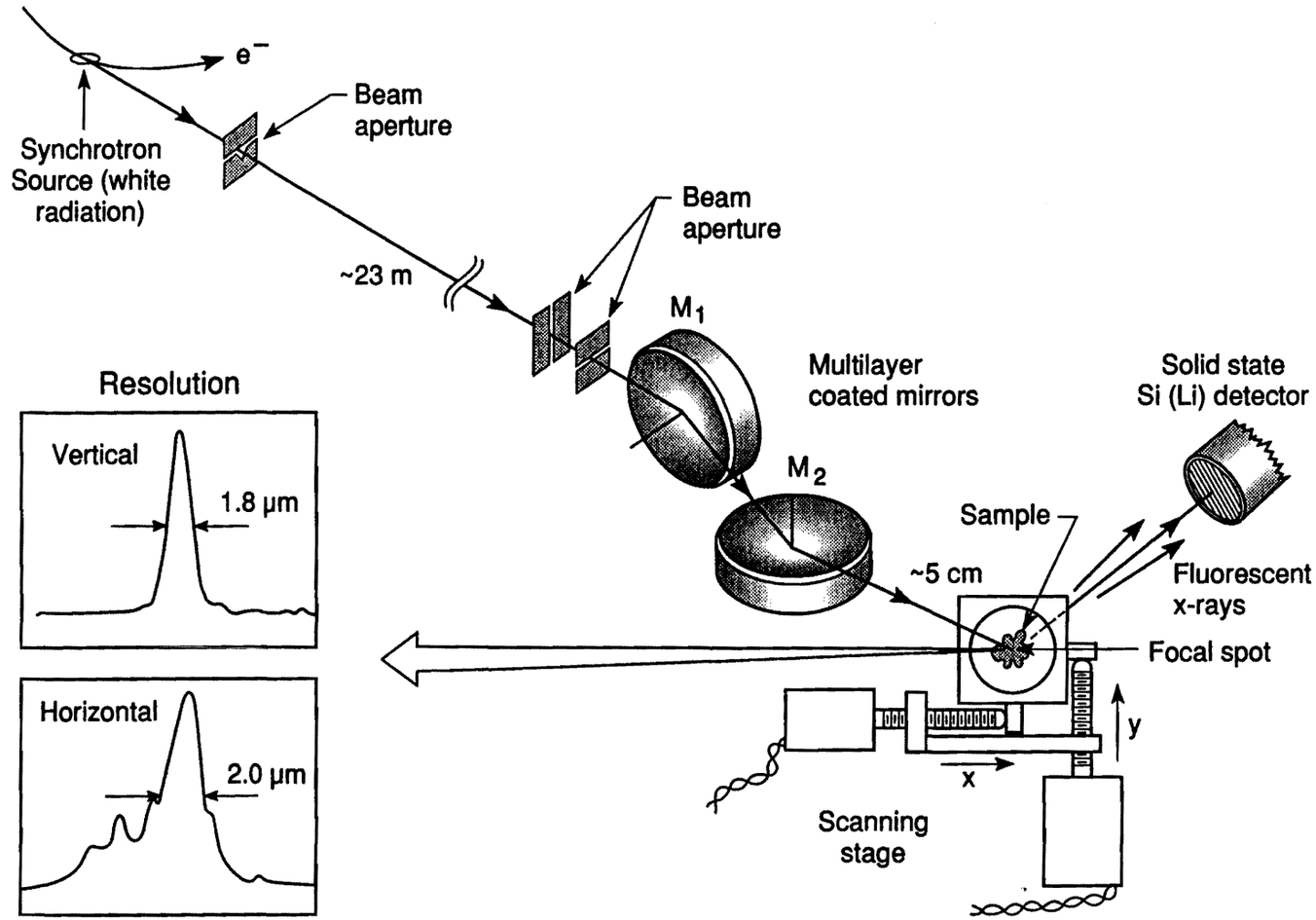
X-RAY MICROPROBE FOR THE EARTH SCIENCES

- Fluorescence microprobe provides high-sensitivity, nondestructive trace-element analysis in geochemical systems

  e.g., trace-element composition of kaolinite in anthracite coal (Ref: S. Mattigod, (PNL) and M. Rivers and S. Sutton (Univ. of Chicago, 1990)



X-Ray Microprobe Using Synchrotron Radiation



XBL 903-5796

PARTICIPATING RESEARCH TEAMS (PRTs)

Insertion Device Teams

Insertion Device	Scientific Focus	Spokesperson	Date Ready
U10	Chemical dynamics	Tomas Baer, U. of North Carolina Yuan Lee,LBL	Future
U8.0	Atoms, molecules, ions	Denise Caldwell, U. of Central Florida	1993
U8.0	Pump-probe, timing, dynamics experiments	R. Stanley Williams, UCLA	Future
U5.0	Surfaces and interfaces	B. Tonner, U. of Wisconsin	1993
U5.0	Surfaces and interfaces	Joachim Stöhr, IBM Almaden Research Center	1993
U5.0	Optics characterization	Nate Ceglio, LLNL	1994
U3.9	X-ray imaging and optics for the life and physical sciences	Dave Attwood, LBL Steve Rothman, UCSF	1994
W16	Atomic, molecular, optical physics, materials science	Bernd Crasemann, U. of Oregon Phil Ross, LBL	Future
W16	Life sciences	Stephen Cramer, UCD Sung Hou Kim, LBL	Future

Bend Magnet Teams

Scientific Focus	Spokesperson	Date Ready
EUV and soft x-ray spectroscopy; x-ray optics	James H. Underwood, LBL	1994
Infrared spectroscopy; fast IR detectors	Gwyn P. Williams, Brookhaven National Laboratory	Future
Polarized photon studies; biology	Stephen Cramer, LBL	Future
Materials studies and optical component characterization	Marvin Weber, LLNL	1993?
High-resolution studies in materials and chemical sciences	Charles Fadley, LBL	1993
Microprobe	Al Thompson, LBL	1993
Atomic and materials sciences	Dennis Lindle, University of Nevada, Las Vegas	Future

DOING RESEARCH AT THE ALS *ALS*

- Research opportunities

  - join a PRT
  - form a PRT
  - independent investigator

- Additional information

Fred Schlachter
Scientific Program Coordinator, Advanced Light Source
Lawrence Berkeley Laboratory, MS 46-161
Berkeley CA 94720

phone: (510)486-4892
fax: (510)486-4873
e-mail: FRED@LBL.GOV

11dec91

Advanced Light Source Applications to Geological Materials

Dale L. Perry

Lawrence Berkeley Laboratory

INTRODUCTION

The field of geological sciences has many examples of materials, many of which are commercially important. Many minerals act as the principal ores for heavy metals, for example, most of which are industrially and militarily significant. Some materials such as coal have obvious impacts on national energy needs and policy. Other types of materials of interest include soils, sediments, and rocks.

The Advanced Light Source (ALS) at Lawrence Berkeley Laboratory will afford an excellent opportunity to perform a wide variety of research studies on geological materials. The x-ray fluorescence microprobe, for example, can be used to not only detect trace amounts of elements but also to laterally map their concentrations on a sample of material. Another area of study that will be possible is that of electronic state studies of elements contained in rare minerals; this in turn will be related to other aspects of the elements contained in the mineral, such as the coordination and bonding details of the central metal atom.

Chemical alteration processes of geological materials will be readily amenable for study. Such processes include both natural ones (such as in weathering) and environmentally-induced ones. A good example of the latter type of process is that of the chemical interaction of nitrogen and sulfur oxides with the materials. Other types of reactions that can be studied are thermal and photolytic reactions that can also occur in nature as well as the laboratory.

Another area of tremendous importance is that of research into the actual processing of the materials themselves—one being that of strategically important ores. Many significant aspects of their chemical processing lend themselves to study, including such seemingly simple (although indeed exceedingly complex) processes as the air oxidation of a sulfide ore. Other interests in this general area include the interactions of heavy metal ions, organic acids, and other aqueous system interactions with the mineral ores during the course of flotation and depression reactions.

Geothermal-based reaction systems are quite amenable to study at the ALS. Scales formed under geothermal conditions include those involving sulfides (such as lead, iron, copper, etc.), carbonates, and silicates. While they are not geological, geothermal tubing corrosion processes are extremely important. Easily one of the most technically and socially important areas of study that is possible at the ALS is that of toxic and nuclear waste chemistry—with a strong emphasis on interactions of these chemical species with geological materials. Actinide chemistry involving such species as uranium, thorium, and plutonium and spent fuel fission products such as nickel—intensive investigations of these species interacting with soils, minerals, etc.—are all extremely important in gaining an understanding of the actions and movements of these chemical systems in the ground. Some of these heavy metal systems that constitute toxic waste are not radioactive but exhibit other toxicologic effects. Metals in this class are ones such as cadmium, lead, chromium, and nickel. Additionally, the chemistries of these metals in conjunction with toxic organic compounds (and a detailed knowledge of them reacting with geological materials) are also extremely important.

Purpose of Workshop

- Introduction to synchrotron research
- Overview of applications to geology and geology-related fields
- Request for input from the earth, soil, and environmental science communities
  - What research topics are of interest?
  - How can we at the Advanced Light Source help the scientific community plan its research using the facility?

This input will be important in the design and construction of beam lines and obtaining the appropriate funding.

Types of Information Obtained Using Synchrotron Radiation

- Chemical
  - Elements
  - Oxidation states
  - Functional groups
- Structural
  - Lattice
  - Surface

Applications of the Advanced Light Source (ALS) to Geological and Geological-Related Research

- Natural alteration processes
- Mineral processing
- Geothermal energy technology
- Nuclear waste
- Toxic waste

Geological Materials

- Soils
- Sediments
- Minerals
- Rocks
- Ores
- Coal
- Volcanic ash

Types of Studies Involving Materials

- Structure
- Electronic states
- Reaction chemistry products
- Analysis

Natural Alteration Processes

- Chemical
  - Natural vs. environmental
  - Rock/water interaction
- Thermal
- Photolytic

Mineral Processing

- Oxidation of ores
- Organic interactions with ores
- Heavy metal interactions with ores
- Geological material interactions with acids

Geothermal Energy Technology

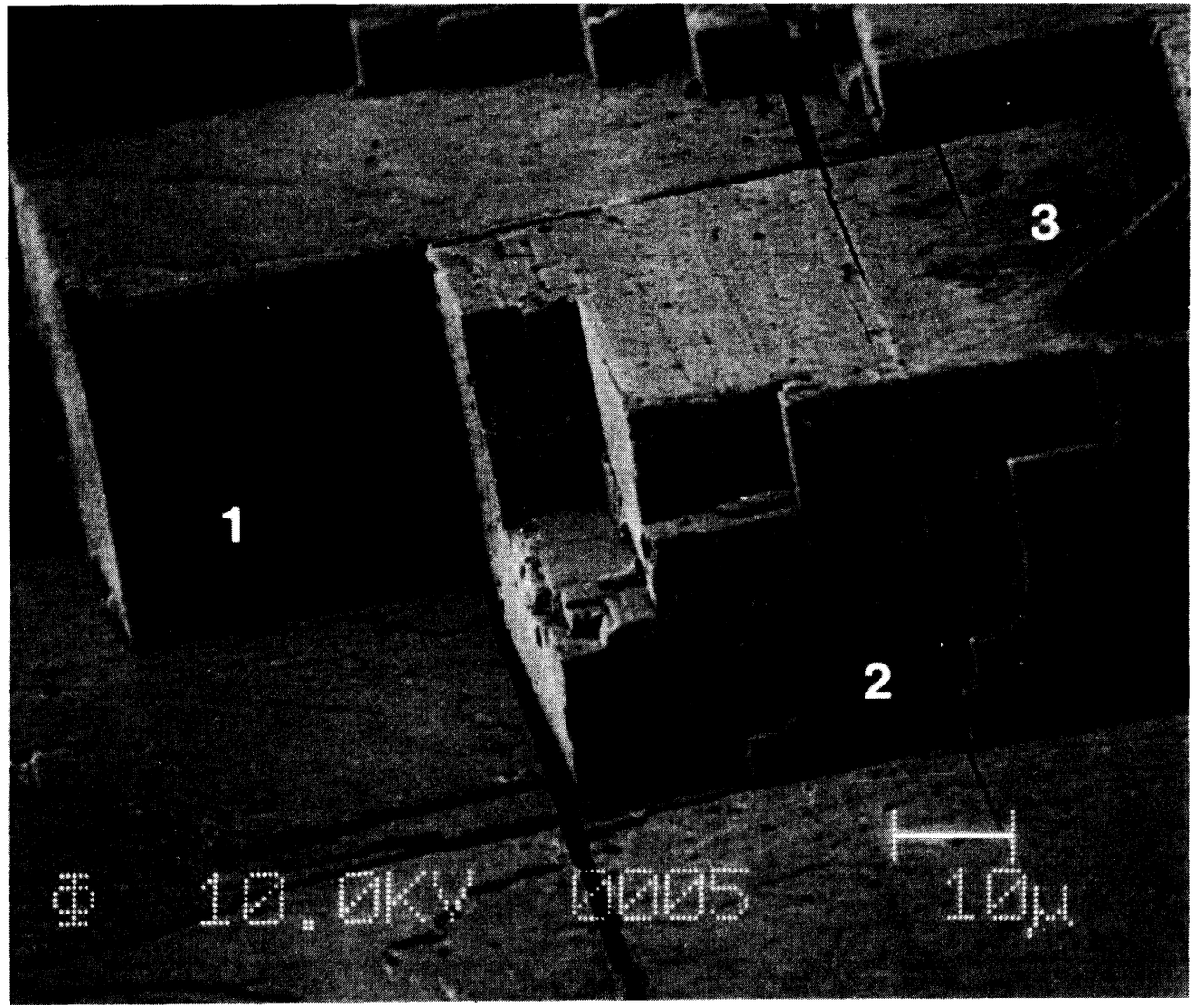
- Scaling
  - Sulfide systems (copper, iron, lead minerals)
  - Carbonate systems
  - Silicate systems
- Corrosion

Nuclear Waste

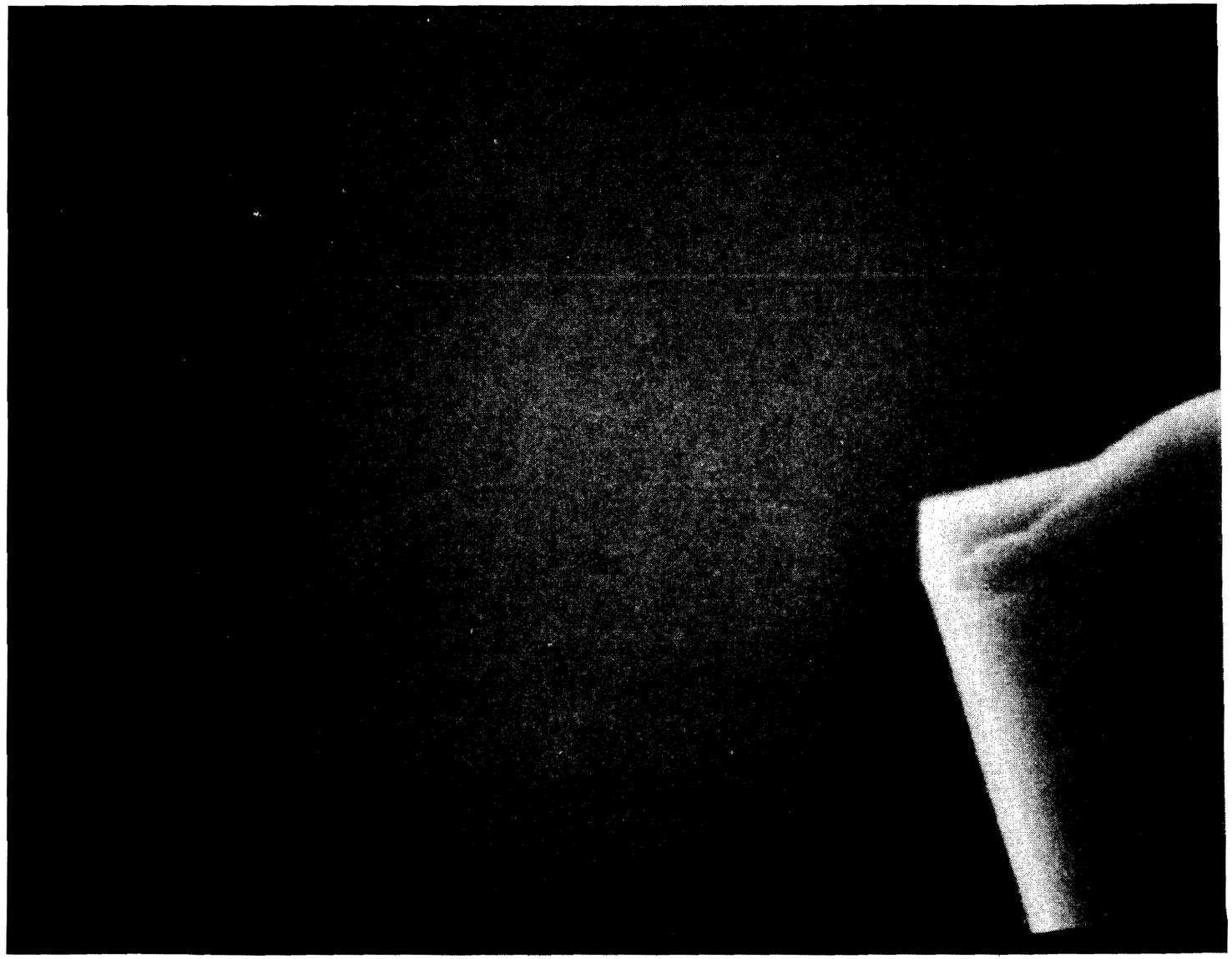
- Actinides
  - Uranium
  - Plutonium
  - Thorium
- Nuclides (Non-Actinide)
  - Nickel
  - Tin
  - Cobalt
- Radionuclide-substituted minerals
- Naturally altered radioactive minerals
  - Uranium oxides
  - Thorium oxide

Toxic Waste

- Heavy metal systems
  - Chromium
  - Cadmium
  - Lead
- Heavy metal-organic systems
  - Metal/organic complexes
  - Metal/organic interactions with geological materials



Magnified surface of galena, PbS.



Magnified surface of galena, PbS, that has undergone interaction with the chromium ion.

Applications in the Soil and Environmental Sciences

Darrell C. Schulze

Purdue University

INTRODUCTION

The chemistry of the low Z elements is extremely important to the agricultural and environmental sciences. Nitrogen, phosphorous, and potassium are major plant nutrients, and the soil chemistry of these three elements has been extensively studied from the standpoint of increasing crop production. Environmentally, there are increasing concerns as current agricultural practices can sometimes lead to the leaching of nitrate into ground water and the erosion of nutrient-rich sediments into surface waters.

Although widely studied, the chemistry of N, P, and K in soils is not completely understood, and a molecular level understanding of the chemistry of these elements in soils is still lacking. Take phosphorous, for example. Soil solution P is only a small part of the total P in soils, but it is the only P fraction which can be taken up by plants. Fertilizer P quickly becomes unavailable to crops and must be added yearly to sustain maximum crop growth. On the other hand, phosphorous sorbed onto mineral particles can be desorbed when the particles are eroded into lakes and streams. The complex sorption-precipitation and desorption-dissolution reactions controlling P availability to plants and P release from sediments are generally understood only in terms of adsorption models based on bulk measurements. Solid phases believed to control P solubility have only rarely been identified. Synchrotron-based microanalytical techniques may prove useful to unravel the reactions of soil P. X-ray absorption spectroscopy may be particularly useful because many of the P-containing phases apparently exhibit only short-ranged order.

Silicon and aluminum are important elements in soil weathering studies. While plants take up silica without any apparent deleterious effects, aluminum can be quite toxic. Aluminum solubility increases as soils become more acid during normal soil weathering processes. Aluminum toxicity is a major constraint to crop production on some soils, and the chemistry of soil aluminum is an active area of soils research. Silica and aluminum are common in the major clay-sized minerals in soils. Aluminum substituted goethites, for example, should be relatively easy to study using x-ray absorption spectroscopy. Aluminum substitutes for iron in the iron oxide minerals which form during soil weathering. Aluminum-substituted goethites and hematites have been studied extensively using both natural and synthetic systems, but it is not known whether the Al is randomly distributed throughout the structure or whether it is in Al-rich domains. X-ray absorption spectroscopy could provide the answer.

Magnesium and sodium are important exchangeable cations on clay surfaces. Spectroscopic studies of these two elements would be of interest in studies of clay swelling and cation exchange.

A major constraint to the study of low Z elements using x-ray based techniques is the need to place the samples in a high vacuum. This should not be a major problem for studying many mineral phases, but it would be a problem if one chooses to study poorly crystallized materials or sorption-desorption reactions on mineral surfaces. Most of the important soil chemical reactions occur in an aqueous medium. Hydrated samples would provide much more useful information than samples which have been dried in a high vacuum. The use of the ALS for soil and environmental studies would be greatly enhanced by the development of procedures for analyzing small amounts of fully hydrated samples.

Applications in the Soil and Environmental Sciences

Important Chemical Elements ($Z \leq 15$):

P - a major plant nutrient, constraint to crop production in developing countries
- environmental pollutant

Si - weathering studies

Al - weathering studies, toxic to plants under certain conditions

Mg - exchangeable cation on soil clays, plant nutrient

Na - important exchangable cation in arid soils, can result in poor soil physical properties

F - substitutes for OH in some layer silicate minerals

C - soil organic compounds, carbonates

N - major plant nutrient

B - plant micronutrient

Sorption of Cations by Layer Silicates

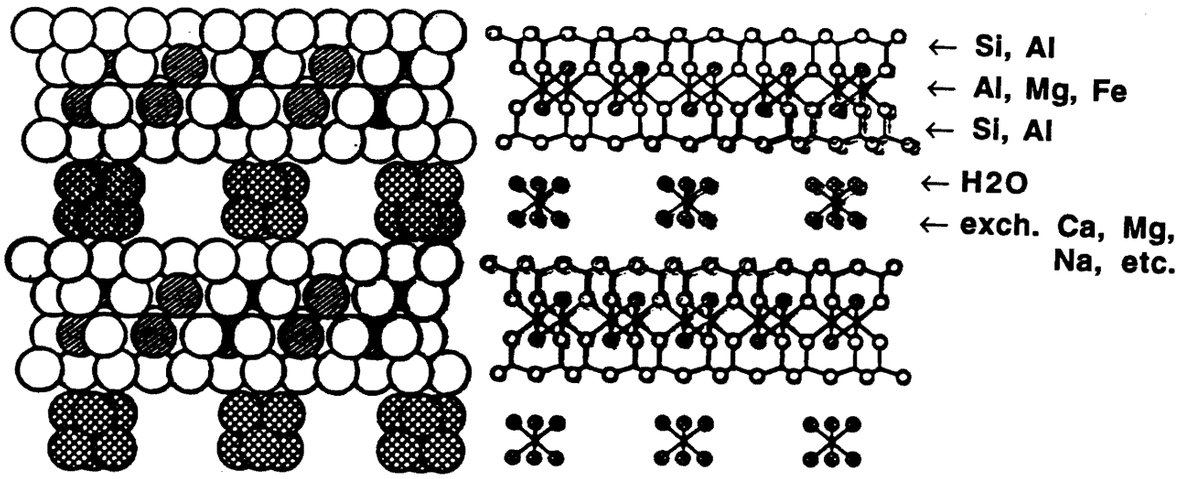
- Ca, Mg, K, Na
- study in an aqueous system?

Reactions of Phosphorus in Soils

- total P averages ~ 600 ppm
- P available to plants is only a small part of total
- study in an aqueous system?

The absorption of cations by layer silicates and the reactions of phosphorous in soils are two research areas which would benefit from the ALS if approaches can be developed to study aqueous systems.

Vermiculite and Smectite



The layer structure common to the phyllosilicate minerals vermiculite and smectite. Both minerals are common in soils and sediments. Exchangeable cations with various degrees of hydration reside between the clay layers.

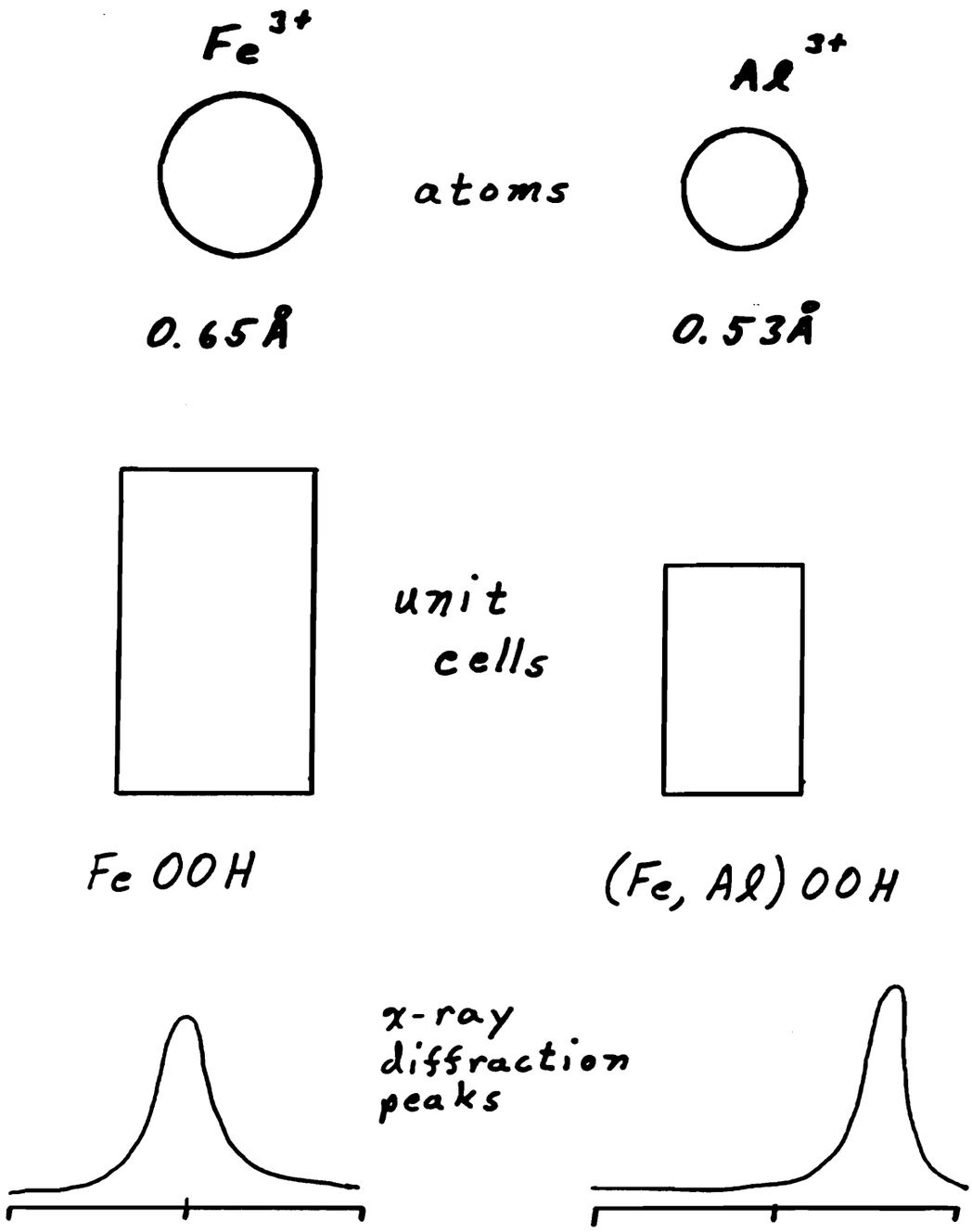
Al substitution in Iron Oxides

- up to ~33 mole % Al in goethite ($FeOOH$)

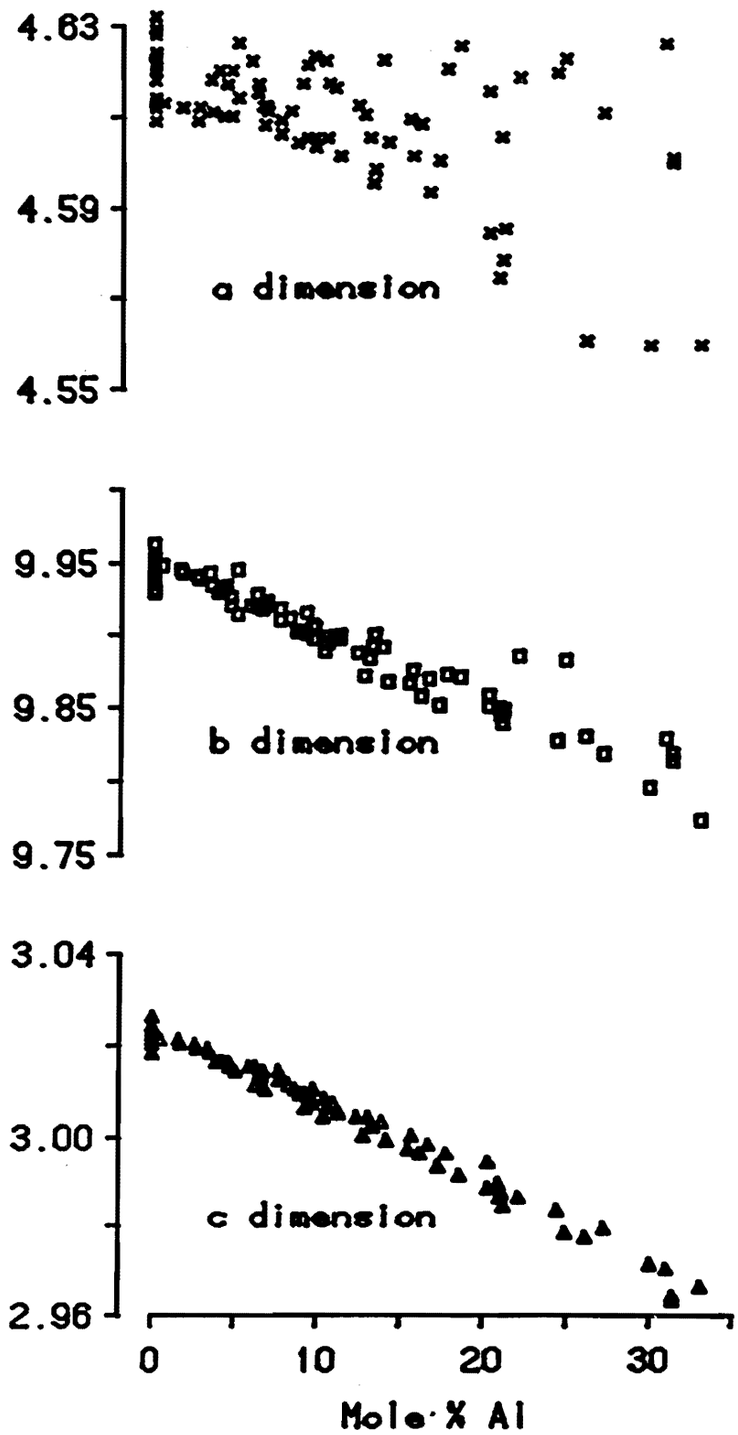
- up to ~15 mole % Al in hematite (Fe_2O_3)

- Al substitution varies with the environment of formation

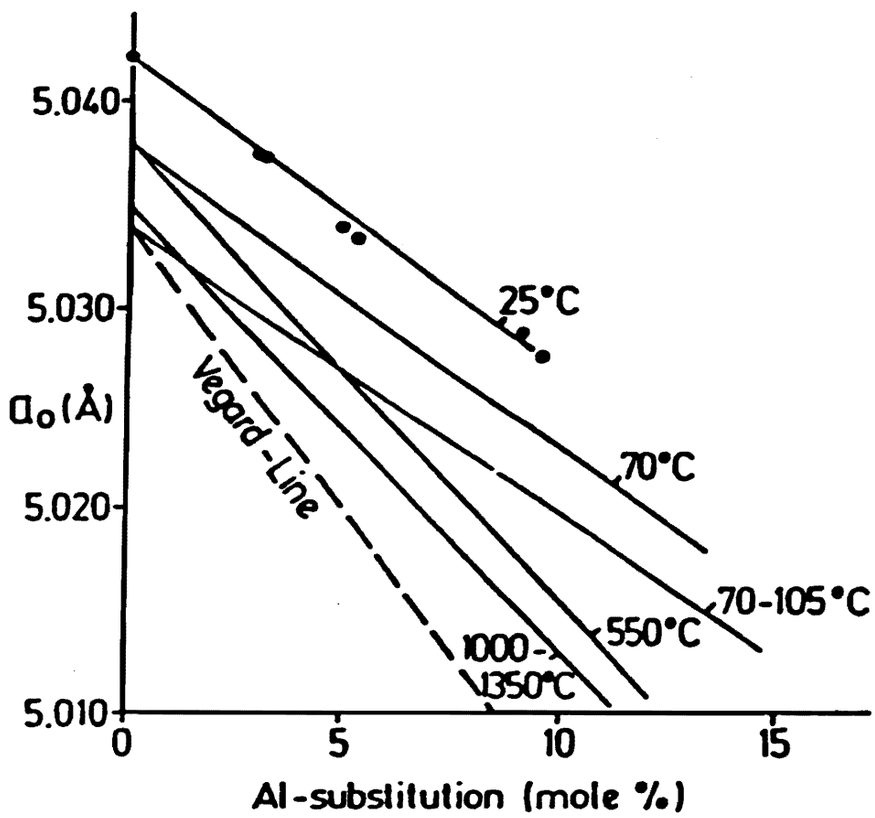
The substitution of Al for Fe in iron oxides can be appreciable and varies with the soil environment in which the mineral formed.



The smaller size of Al^{3+} versus Fe^{3+} results in smaller unit cell dimensions for Al-substituted minerals and results in a shift of x-ray diffraction line position.



If Al-substitution were the only factor influencing the unit cell dimensions of goethite, then all three cell dimensions should vary as a smooth function of Al substitution. The a-dimension shows considerable variability not related to Al substitution.



Hematite cell dimensions vary as a function of synthesis temperature (from Schwertmann, U. 1988. Some properties of soil and synthetic iron oxides. p. 203–250. In J. W. Stucki, B. A. Goodman, and U. Schwertmann (eds.) Iron in soils and clay minerals. D. Reidel Publishing Co., Boston.)

Questions

- is Al randomly distributed throughout the structure?

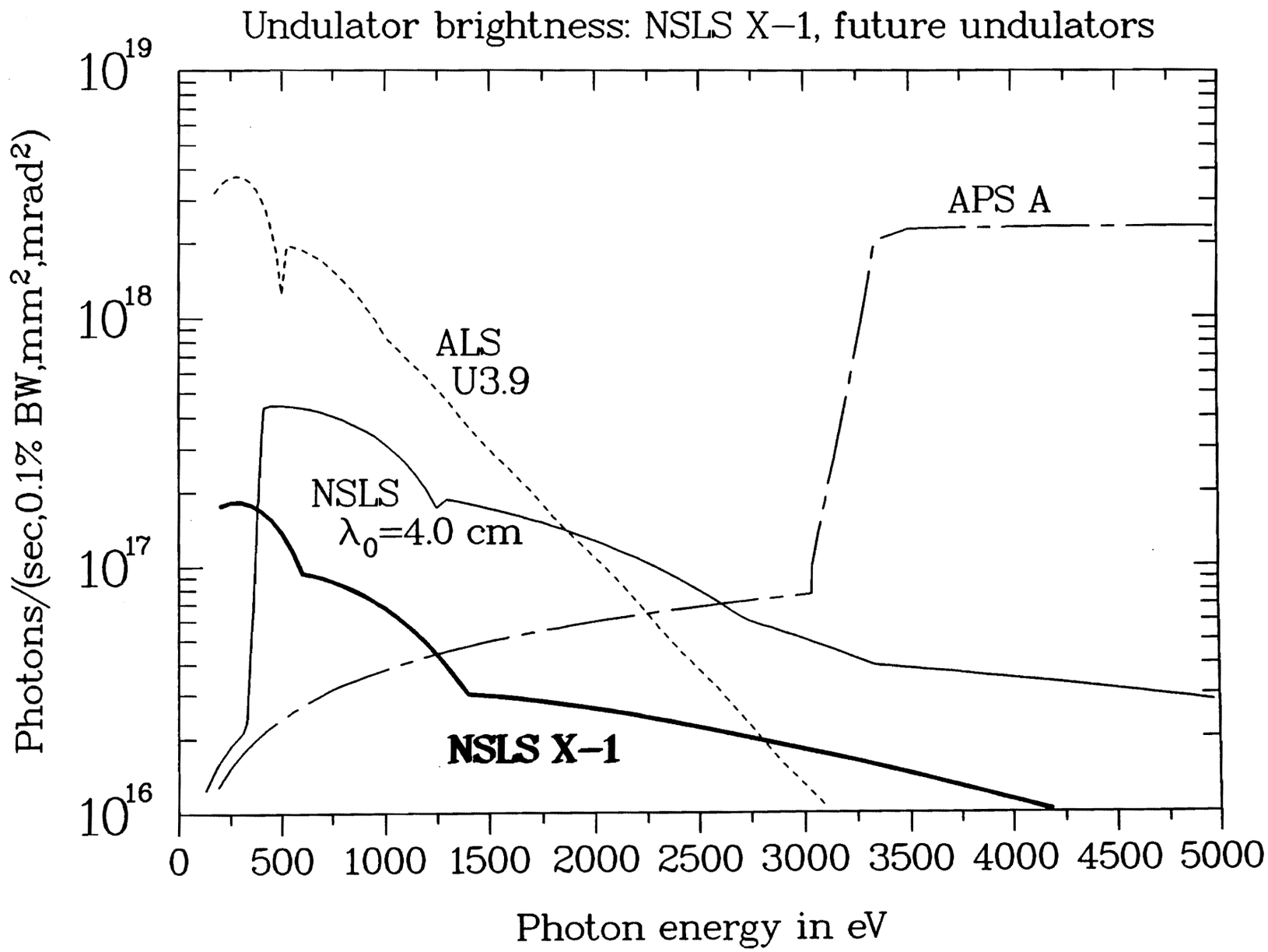
- is non-stochiometric OH preferentially associated with Al?

X-ray absorption spectroscopy should be useful in determining if Al is randomly distributed within the iron oxide structure. There is also evidence that non-stochiometric OH is preferentially associated with the Al rather than with the Fe. X-ray absorption spectroscopy may provide useful information for testing this hypothesis as well.

X-Ray Microprobe Analysis

Mark Rivers

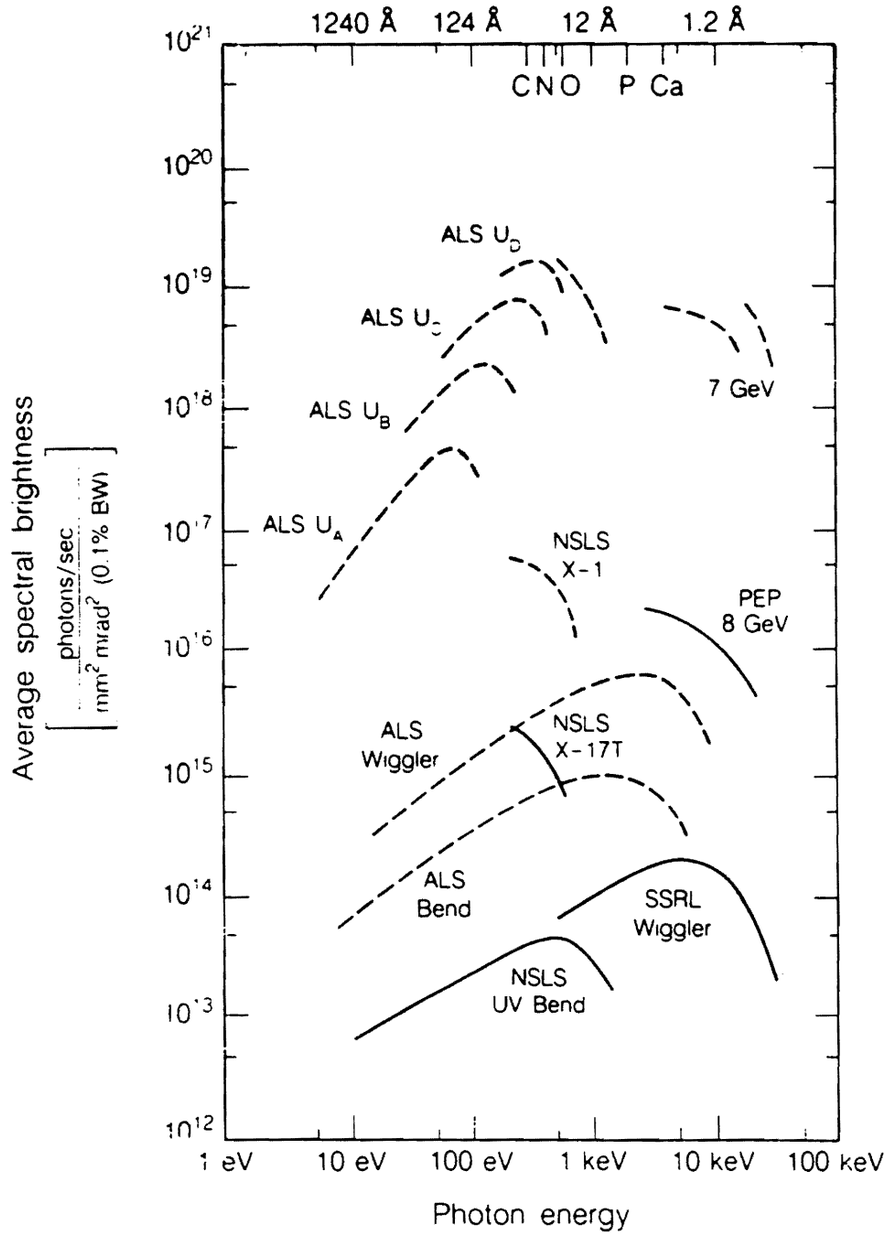
Brookhaven National Laboratory


Undulator brightness: NSLS X–1, future undulators
Photons/(sec,0.1% BW,mm^2,mrad^2)
10^{19}
10^{18}
10^{17}
10^{16}
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
Photon energy in eV
APS A
ALS
U3.9
NSLS
λ_0=4.0 cm
NSLS X–1

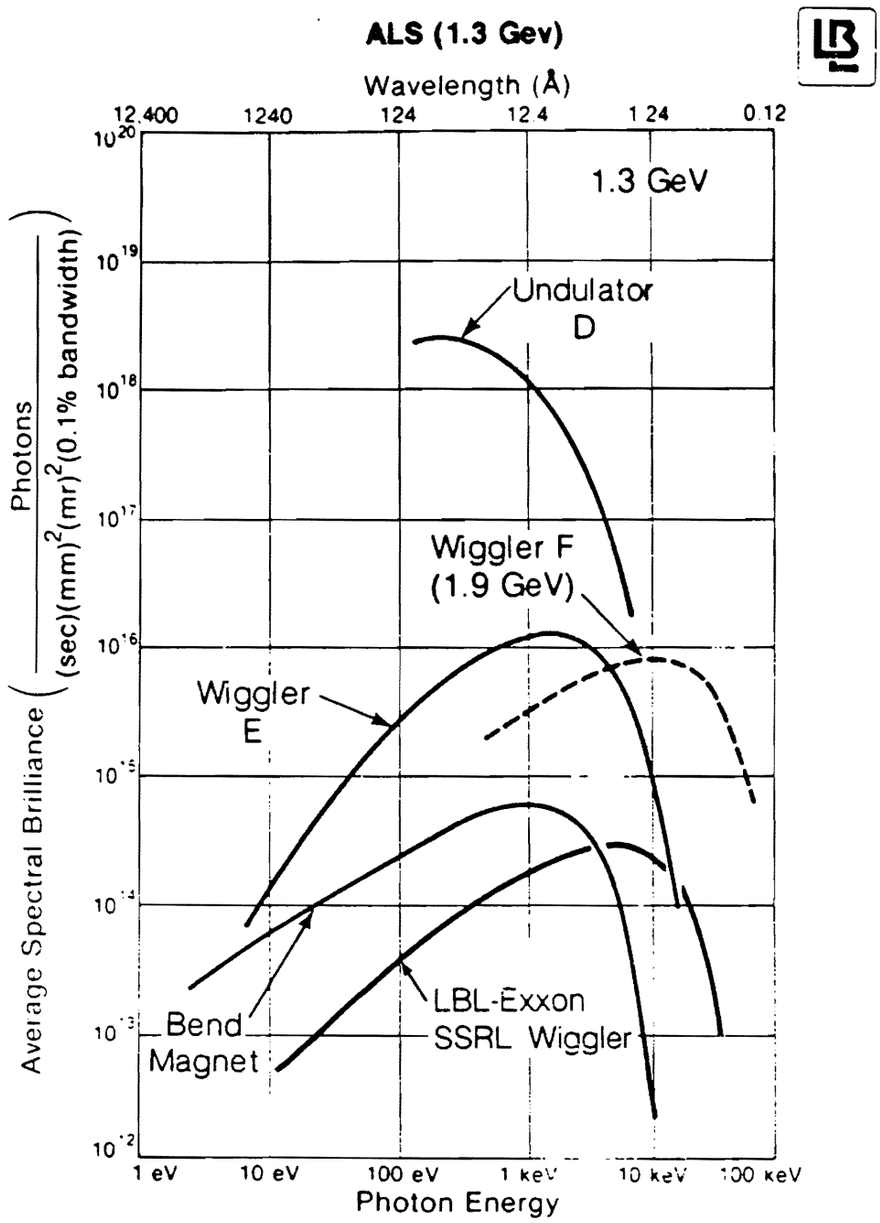
$$P_T[\mathrm{kW}] = 0.633\, E^2[\mathrm{GeV}] B_0^2[\mathrm{T}] L[\mathrm{m}]\, I[\mathrm{A}]$$

For bending magnets, B_0^2 in the above expression must be replaced by $2B^2$, where B is the magnetic field in the bending magnet. The angular distribution of the radiated power is

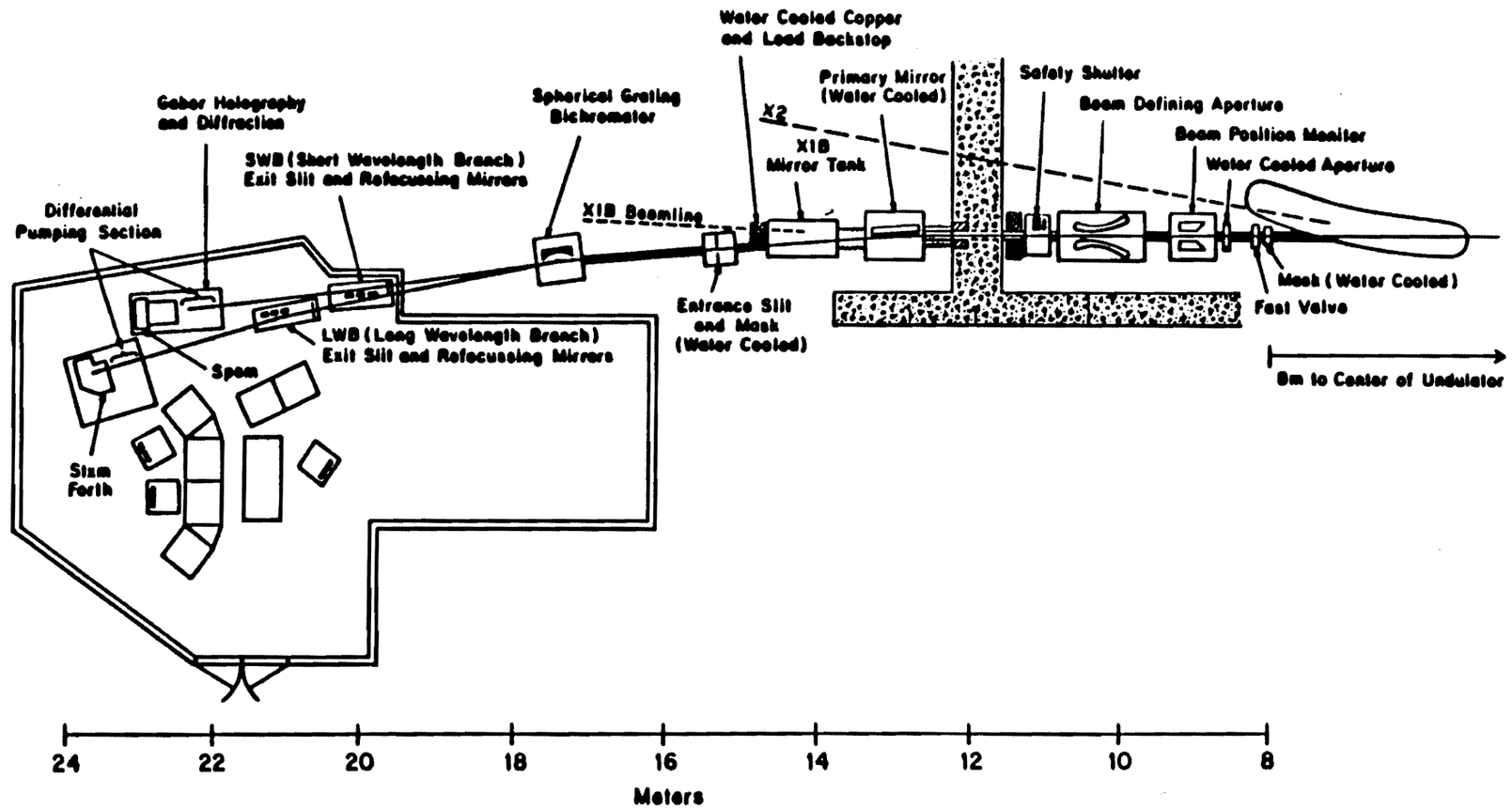
$$\frac{d^2P}{d\theta d\psi} = P_T \frac{21\gamma^2}{16\pi K} C(K) f_K(\gamma\theta, \gamma\psi),$$

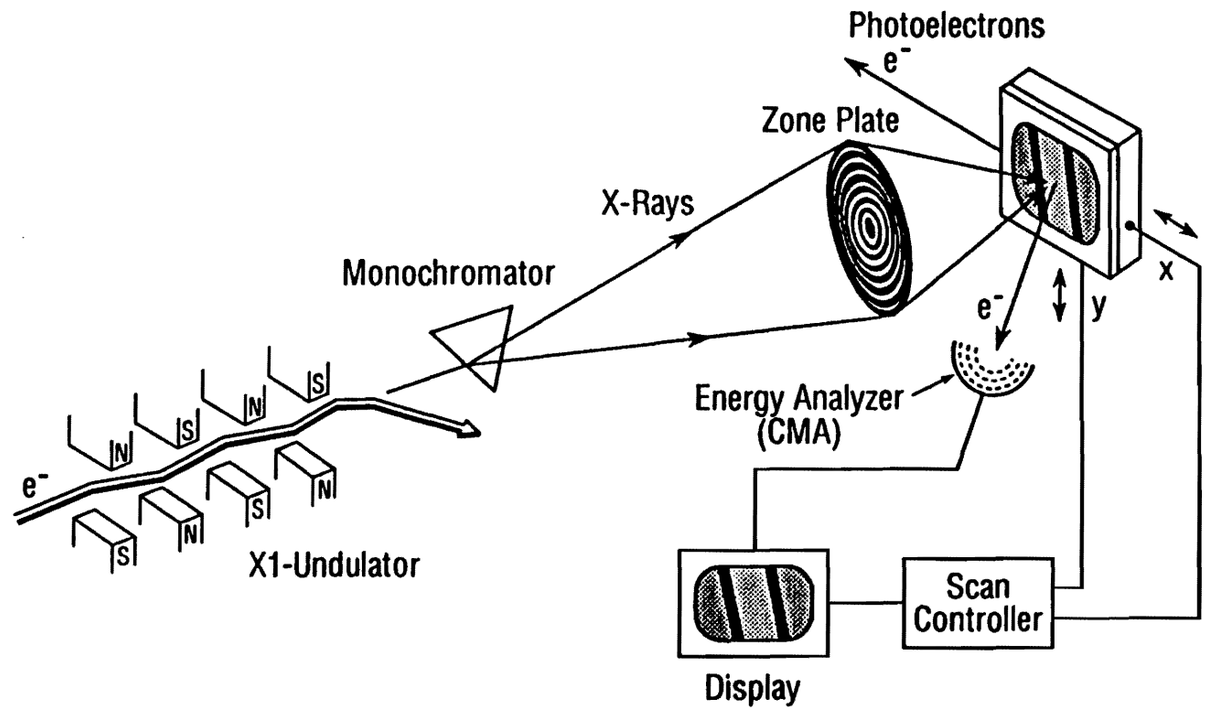


Average spectral brightness within a 0.1% bandwidth, as a function of photon energy, for a variety of synchrotron radiation sources.



XBL 842-9403D


Water Cooled Copper
and Lead Backstop
Primary Mirror
(Water Cooled)
Safety Shutter
Beam Defining Aperture
Beam Position Monitor
Water Cooled Aperture
X2
X1B
Mirror Tank
Spherical Grating
Bichromator
X1B Beamline
Gabor Holography
and Diffraction
SWB (Short Wavelength Branch)
Exit Slit and Refocussing Mirrors
Differential
Pumping Section
Entrance Slit
and Mask
(Water Cooled)
Mask (Water Cooled)
Fast Valve
LWB (Long Wavelength Branch)
Exit Slit and Refocussing Mirrors
Spam
Sizm
Forth
8m to Center of Undulator
24
22
20
18
16
14
12
10
8
Meters

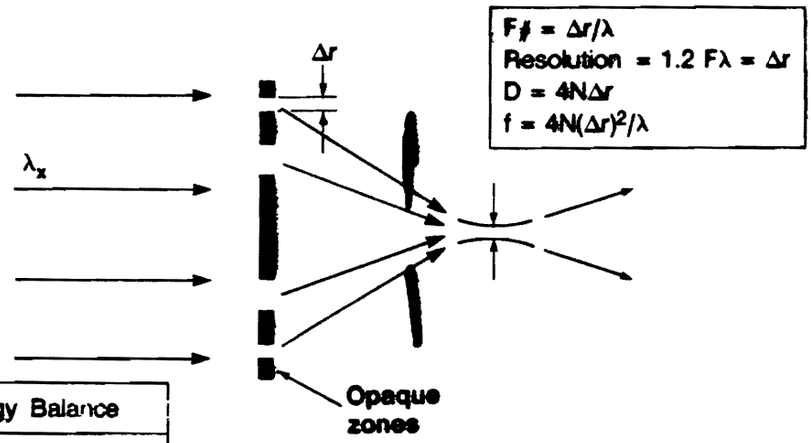


High-Resolution Scanning Photoelectron Microscope

M. Rowe - H. Ade 1a 8/22/91 j.o.

Fresnel Zone Plate Lens for Diffractive Focusing of X-Rays:

(Feature sizes of order λ_x)



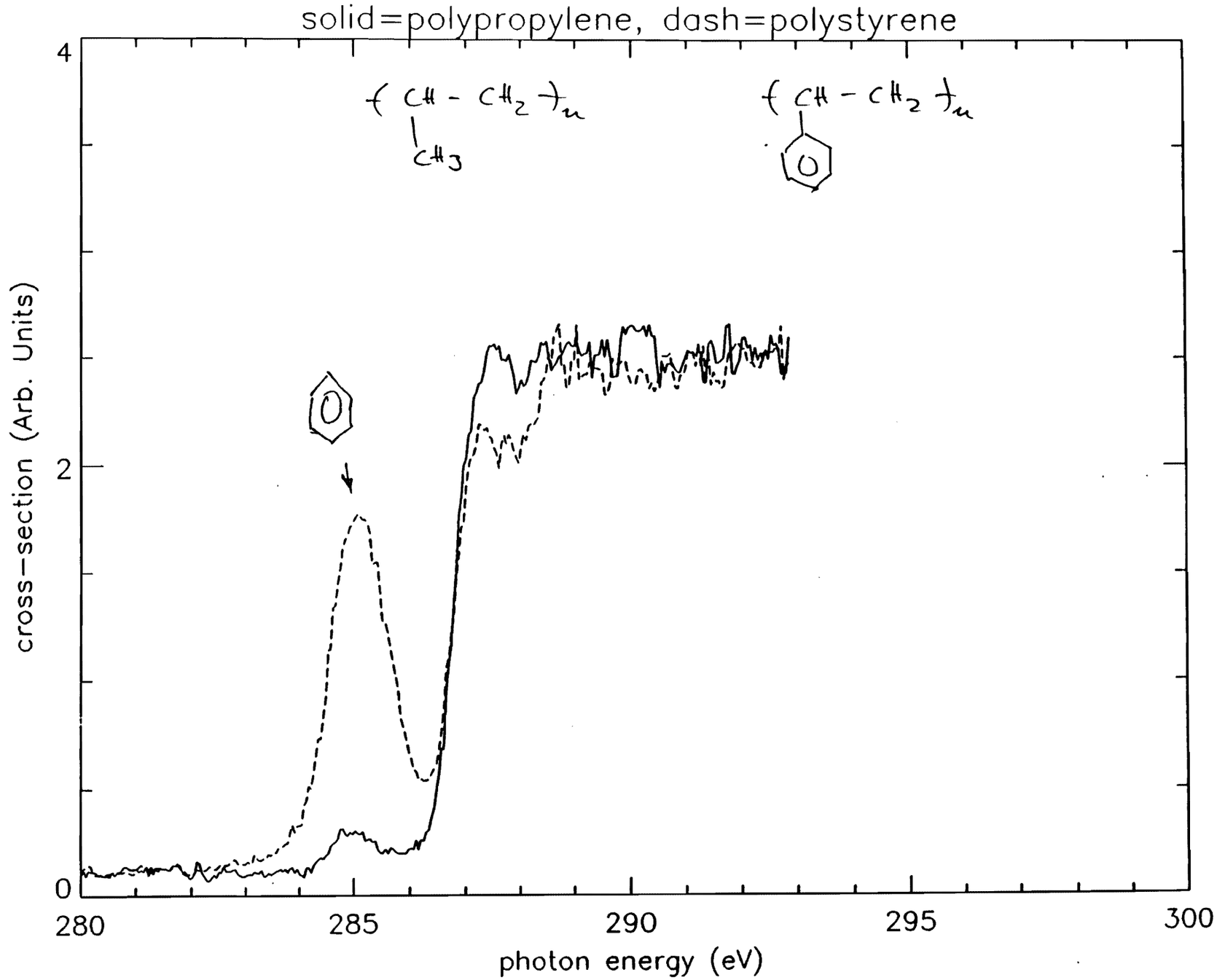
Energy Balance	
10%	1st order focus
50%	absorbed
25%	undiffracted
15%	other foci

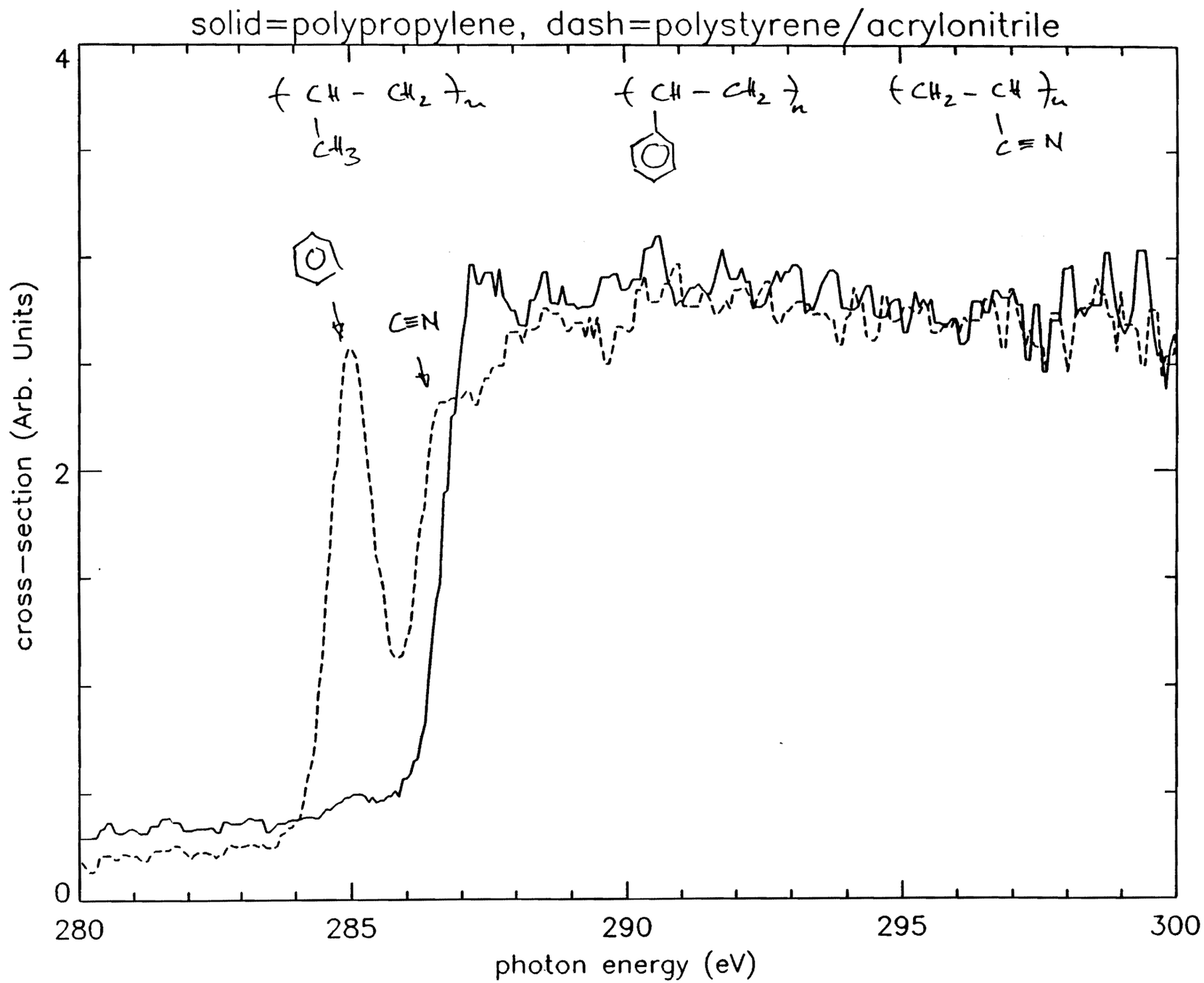
30°

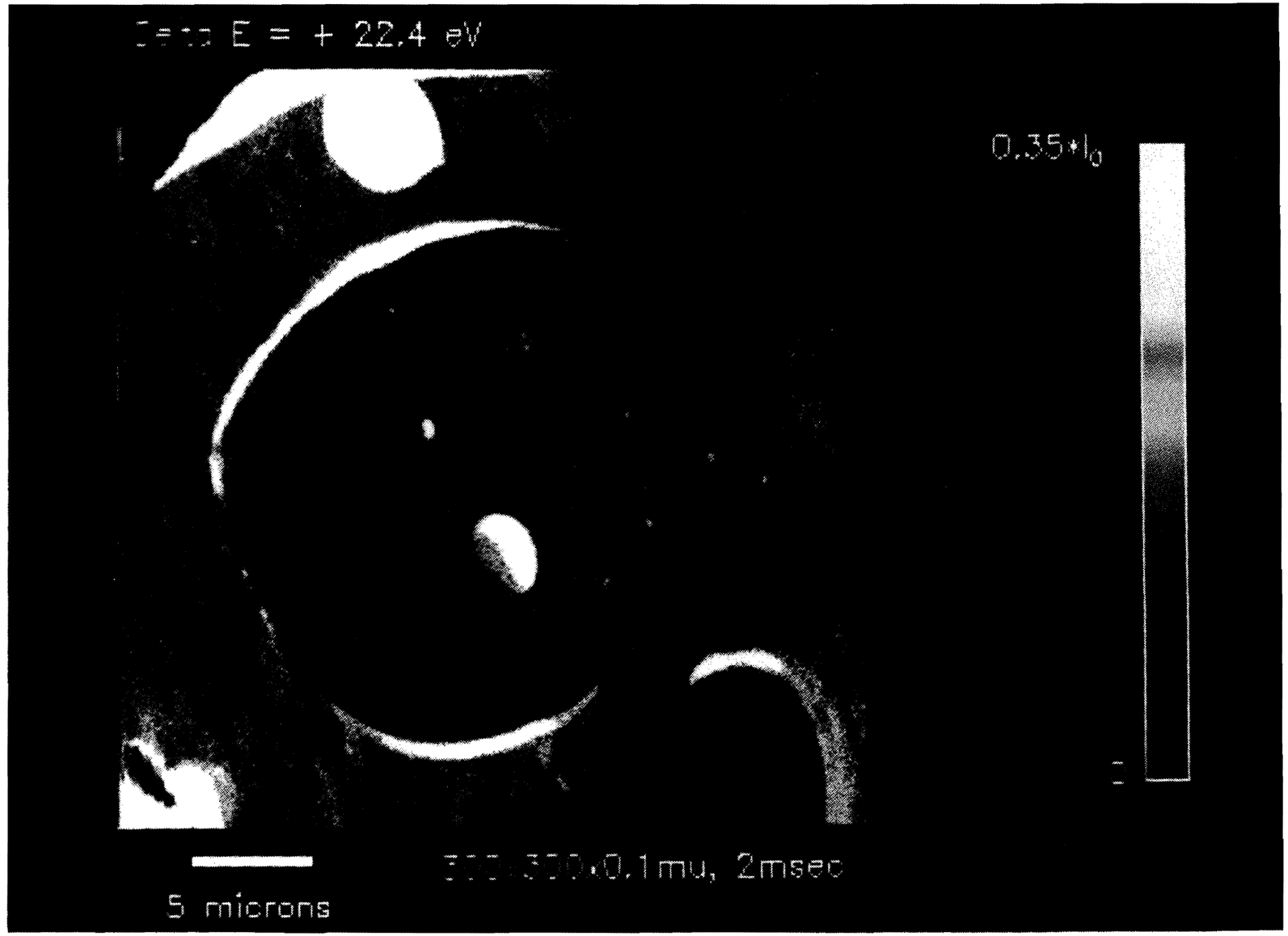
References:

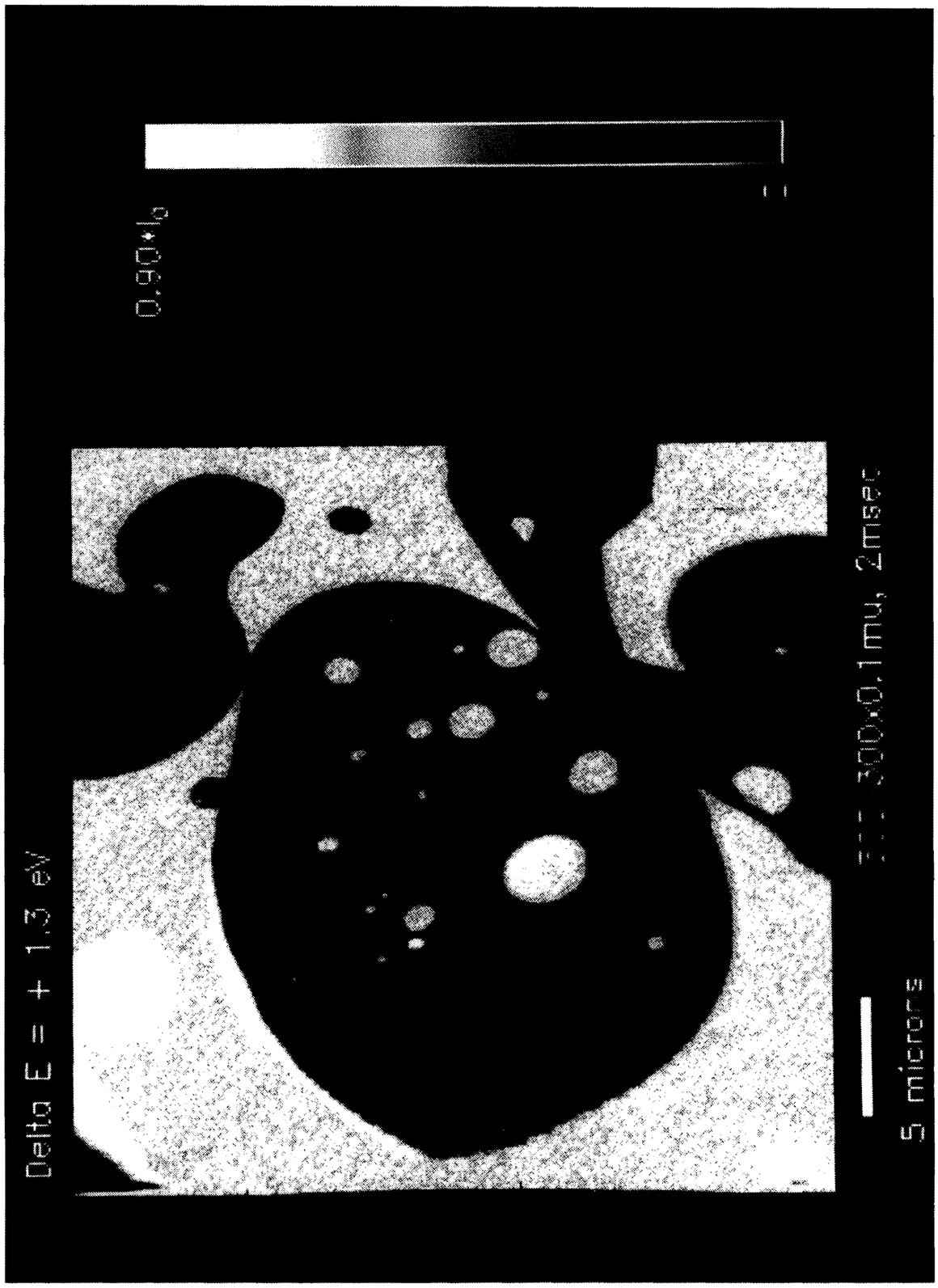
A. V. Baez, J. Opt. Soc. Am. 51, 405 (1961)
J. Kirz, J. Opt. Soc. Am. 64, 301 (1974)
N. M. Ceglio and H. I. Smith, LLNL, (1977)

XBL 842-9405


solid=polypropylene, dash=polystyrene
cross-section (Arb. Units)
photon energy (eV)
0
2
4
280
285
290
295
300


solid=polypropylene, dash=polystyrene/acrylonitrile
cross-section (Arb. Units)
photon energy (eV)
0
2
4
280
285
290
295
300
C≡N


E = + 22.4 eV
0.35*I0
0
5 microns
0.1mu, 2msec


Delta E = + 1.3 eV
0.90*Io
1
300x0.1mu, 2msec
5 microns

Potential Applications of the ALS in Soil and Environmental Sciences

Paul M. Bertsch

University of Georgia

INTRODUCTION

The elucidation of distinct molecular forms of atoms of an element or clusters of atoms of different elements, a process termed chemical speciation, has become a cynosure in environmental and earth sciences. It has been over two decades since the importance of chemical speciation in natural waters was formally recognized (Garrels and Thompson, 1962), yet the significance of this fundamental concept was not fully appreciated by investigators working in diverse disciplines until the late 1970's to early 1980's. Today it is widely accepted that chemical speciation determines the behavior and mobility of chemical constituents in the environment, as well as their bioavailability and toxicity. Furthermore, it has become increasingly evident that specific information regarding the molecular forms of adsorbate elements and the nature of adsorbent surfaces is prerequisite to developing clearer mechanistic descriptions of solid-solution interfaces from which more powerful predictive transport models can be developed and from which molecular level information on mechanisms of metal toxicity can be derived. Unfortunately, advances in the *concept* of chemical speciation have developed more rapidly than the analytical capabilities to determine it, thus resulting in applications where macroscopic data is interpreted at a microscopic level and is often incorporated into microscopically based mechanistic models.

In recent years, a number of spectroscopic techniques have been utilized to provide molecular level information on the chemical speciation of both soluble and surface sorbed constituents, including x-ray photoelectron spectroscopy (XPS), nuclear magnetic resonance spectroscopy (NMR), infrared spectroscopy (IR), electron spin resonance spectroscopy (ESR), and x-ray absorption spectroscopy (XAS). Applications of XAS utilizing synchrotron sources have begun to provide a much clearer picture of the solid solution interface and have greatly advanced the knowledge of how contaminant metals interact with important mineral phases common in soils and sediments. The ability to extract specific information concerning valence state, interatomic distances, coordination numbers, and identities of nearest and second nearest neighbors make XAS a most powerful tool for probing the nature of the adsorbate-adsorbent environment and for providing structural information on poorly crystalline solid phases common in soils and sediments. A number of recent examples of EXAFS investigations on heavy element contaminant mineral interactions have appeared in the literature and these have provided such molecular level information, heretofore unavailable (see chapter by Gordon Brown).

The ALS will allow these capabilities to be extended to lighter elements (K edge < 2.5 keV) that are quite relevant to soil and environmental science (see chapter by Darrell Schulze), yet are difficult to study or cannot be studied at current synchrotron facilities. Of particular interest are applications involving elucidation of structural environments in poorly crystalline Al containing solid phases including Al-substituted oxyhydroxides, poorly crystalline aluminosilicates (e.g., allophane and imogolite) and the Al hydroxy interlayered components of the hydroxy interlayered 2:1 phyllosilicate minerals. Additionally, there has been great interest in Al remobilization in soils and sediments as related to acidic precipitation and on Al toxicity to both aquatic and terrestrial organisms. Direct speciation of Al on mineral exchangers and on biological surfaces, therefore, could provide important information required to predict Al mobility and to elucidate specific mechanisms of Al toxicity.

Discussion

- Elucidation of structural environments in poorly ordered oxides and aluminosilicates:
  - Al-substituted
  - Allophanes and imogolites
  - Al-interlayered 2:1 phyllosilicates
- Probing environments of sorbed Al and Al complexes:
  - Minerals and model exchangers
  - Biological samples

Poorly ordered aluminosilicate phases are quite common in soils formed in volcanic ash, but have been increasingly described in a wide range of soils and may be important phases in more highly weathered soils common throughout the Southeastern USA. Because of their extremely high surface areas (~1,000 m^2 g^{-1}), these phases may be very important in controlling contaminant behavior in these soils, even when present in relatively small quantities by weight. The structural model of the poorly ordered aluminosilicate imogolite suggests that the Al is arranged in a curved or spherical gibbsite sheet (10–12 gibbsite unit cells) to which monomeric or isolated orthosilicate groups are bound through OH groups surrounding an unoccupied octahedral site in the Al-hydroxide sheet (Fig. 1). Imogolite consists of tubes with an inner diameter of ~1 nm which assemble into thread-like structures varying in diameter from 10 nm to 30 nm and extending up to a couple of microns in length. Allophane is another poorly ordered aluminosilicate, consisted of hollow spheres having diameters between 3.5 nm to 5 nm and a variable Si/Al ratio, typically between 1:2 and 1:1, although other poorly ordered aluminosilicate phases with differing Si/Al ratios have been proposed. ^{27}Al NMR data on imogolite and allophane have generally supported the existence of mostly octahedral Al in imogolite while most allophanes examined have both octahedrally and tedrahedrally coordinated Al. There has, however, been a number of conflicting reports in the literature concerning the coordination of Al in these phases.

Both XANES and EXAFS investigations would provide the specific information required to refine the structural models of imogolite and allophane and elucidate the specific coordination environments of Al and Si within these structures and indicate how these may vary between samples. The surface chemistry of these materials has also been problematic, with observed inconsistencies in surface charge properties as probed by ion sorption and electrophoresis, and as inferred from structure (Su et al., 1992). One possibility that may explain these anomalies is that some untreated polynuclear Al (having a residual positive charge) is specifically adsorbed to the poorly ordered aluminosilicate phases during synthesis (Fig. 2). Two Al polynuclear structures are believed to be important one having only octahedral Al with shared OH bridges between units (basic unit of the gibbsite structure) and the second having a tetrahedrally coordinated Al in the center of a cage-like structure consisting of 12 octahedrally coordinated Al sharing both common edges and vertices (the tridecameric or Al_{13} polynuclear). It is well established that the Al_{13} polynuclear forms readily in partially neutralized Al solutions, over a wide range of concentration and synthesis conditions (Parker and Bertsch, 1992). It is likely that this polynuclear is formed during synthesis of laboratory prepared allophane and imogolite, and it is possible that a fraction of this polynuclear is either specifically sorbed or structurally associated to or with the outer

regions of the allophane spheres or the imogolite tubes. The chemical shift representative of the tetrahedral Al in the Al_{13} polynuclear and tetrahedral Al within the allophane structure are indistinguishable in the ^{27}Al MASNMR spectra. EXAFS experiments would provide the information on bond lengths and second nearest neighbor identities that could resolve these uncertainties.

We have also been investigating the chemical speciation of Al on mineral and biological surfaces and probing the local environment of exchangers by multinuclear NMR spectroscopy. The data collected to date suggest that we can differentiate between inner and outer-sphere associated Al on model exchanger and mineral surfaces (Figs. 3-8). Figure 4 demonstrates the ^{27}Al NMR spectra for Al sorbed to Al loaded (4c—both outer and inner-sphere Al) and Ca-Al exchanged (4d—two inner-sphere environments) chelex resin where both outer-sphere Al and two types of inner-sphere Al environments are postulated. Additionally, it is possible to distinguish between mono and Al_{13} polynuclear Al adsorbed to sulfonic (4b) and chelex (4c) exchangers. A comparison of these spectra to that for the saturating solution (4a) suggests that the exchangers have a preference for the mono vs. the polynuclear Al, a trend that was also observed for sorption to a smectite (SWy-l) (Fig. 6). The relaxation and linewidth data for the sorbed Al species suggest that their motion is greatly restricted on a number of exchangers (Figs. 7 and 8). Distinct sorption environments on a sulfonic resin were indicated for Al-Cs exchange data where relaxation (T_1 and T_2) data demonstrated different dynamics (rotational motion) of the Cs in less specifically interacting (site I—greater mobility and higher symmetry) and more specifically interacting (site II—lower mobility and symmetry) sites (Figs. 9 and 10). We have also begun to examine Al species sorbed to cell walls and membranes. Using ^{27}Al and ^{19}F we have demonstrated the ability to speciate mono and polynuclear and fluoro-Al complexes on both mineral and biological surfaces (e.g., Figs. 11 and 12) and have begun to collect molecular level information on Al interactions at these surfaces that could be relevant to mechanisms of Al toxicity. EXAFS experiments would provide the information required to support the proposed interactions, supply additional structural information that is currently not available, yet critical for developing a clearer mechanistic picture, and would allow these experiments to be conducted at much lower surface Al concentrations.

In summary, the availability of the ALS will facilitate XAS experiments that will provide more specific molecular information that will greatly enhance our ability to understand interactions of lighter elements with a variety of surfaces. Such information is prerequisite to understanding the behavior of such elements in the environment and their specific role in either biological function or toxicity.

References

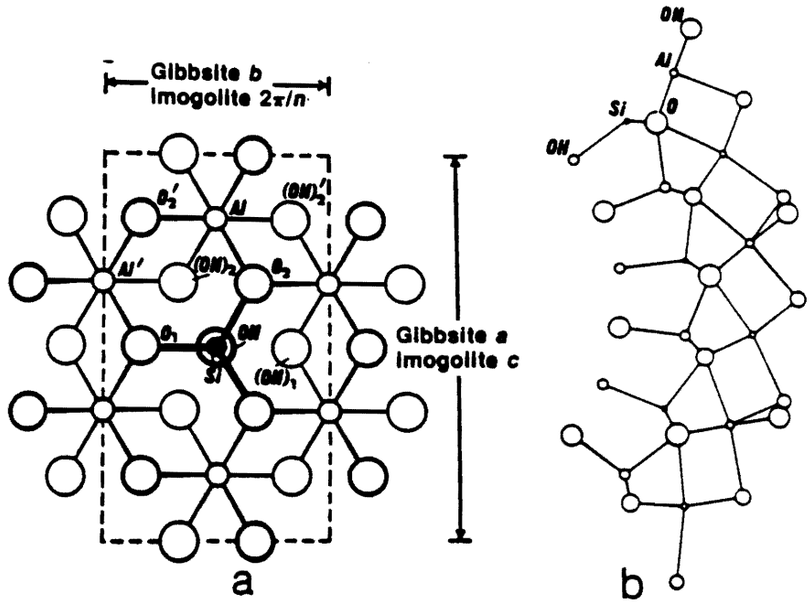
Garrels, R.M. and Thompson, M.E., 1962. A chemical model for seawater at 25°C and one atmosphere. Am. J. Sci. 260: 57-66.

Su, C., James B. Harsh and Paul M. Bertsch, 1992. Sodium and chloride sorption by imogolite and allophanes. Clays and Clay Miner (in press).

Parker, D.R. and P.M. Bertsch. 1992. Formation of the Al_{13} tridecameric polycation under diverse synthesis conditions. Environ. Sci. Technol. 26: 914-921.

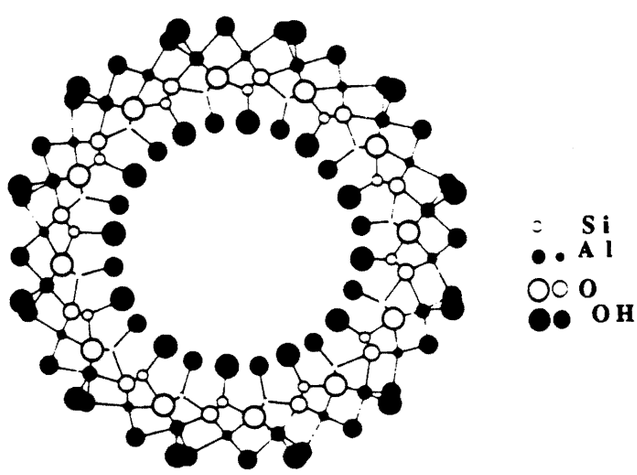
Wada, 1989

ALLOPHANE AND IMOGOLITE



(a) Postulated relationship between the structure unit of imogolite and that of gibbsite. SiOH groups that would lie at the cell corners in imogolite are omitted from the diagram. (b) Curling of the gibbsite (hydroxide) sheet induced by contraction of one surface to accommodate SiO_3OH tetrahedra; projection along the imogolite *c*-axis. Reprinted from Cradwick et al. (1972).

Goodman et al., 1985



A cross-section of the structure of an imogolite tube

Fig. 1

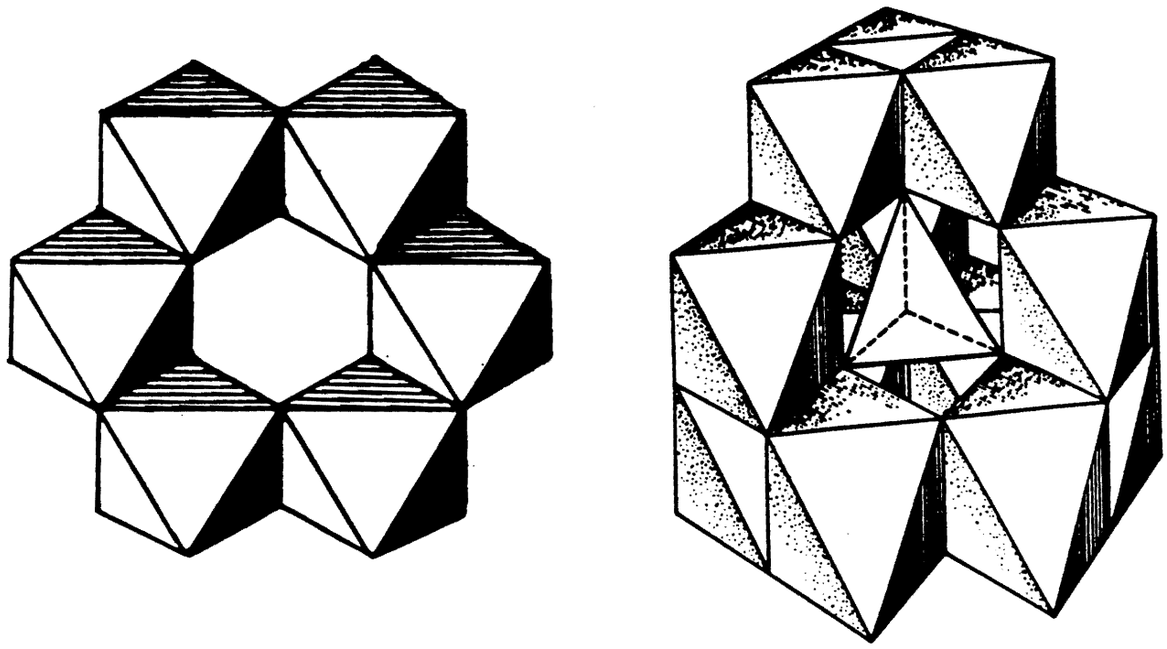


Fig. 2

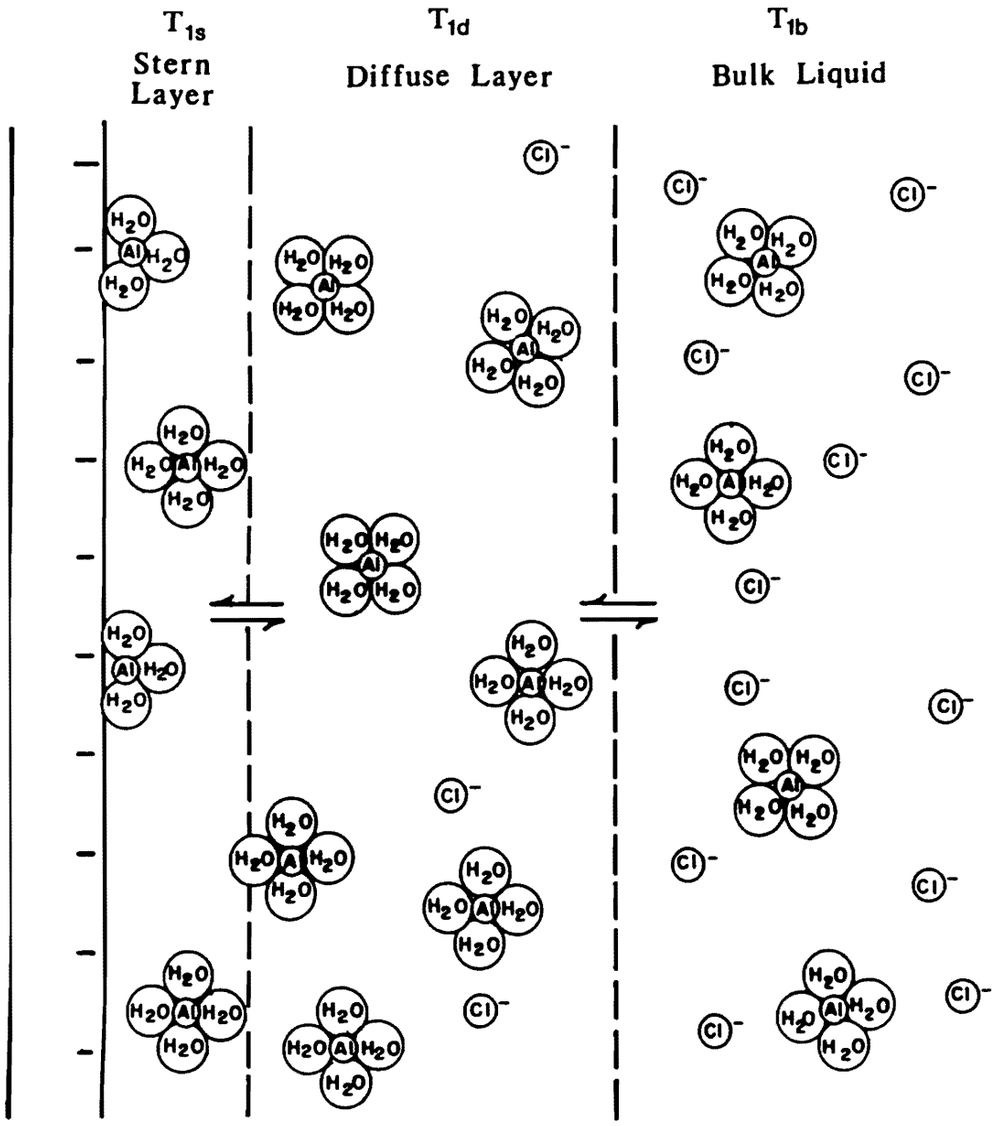


Fig. 3

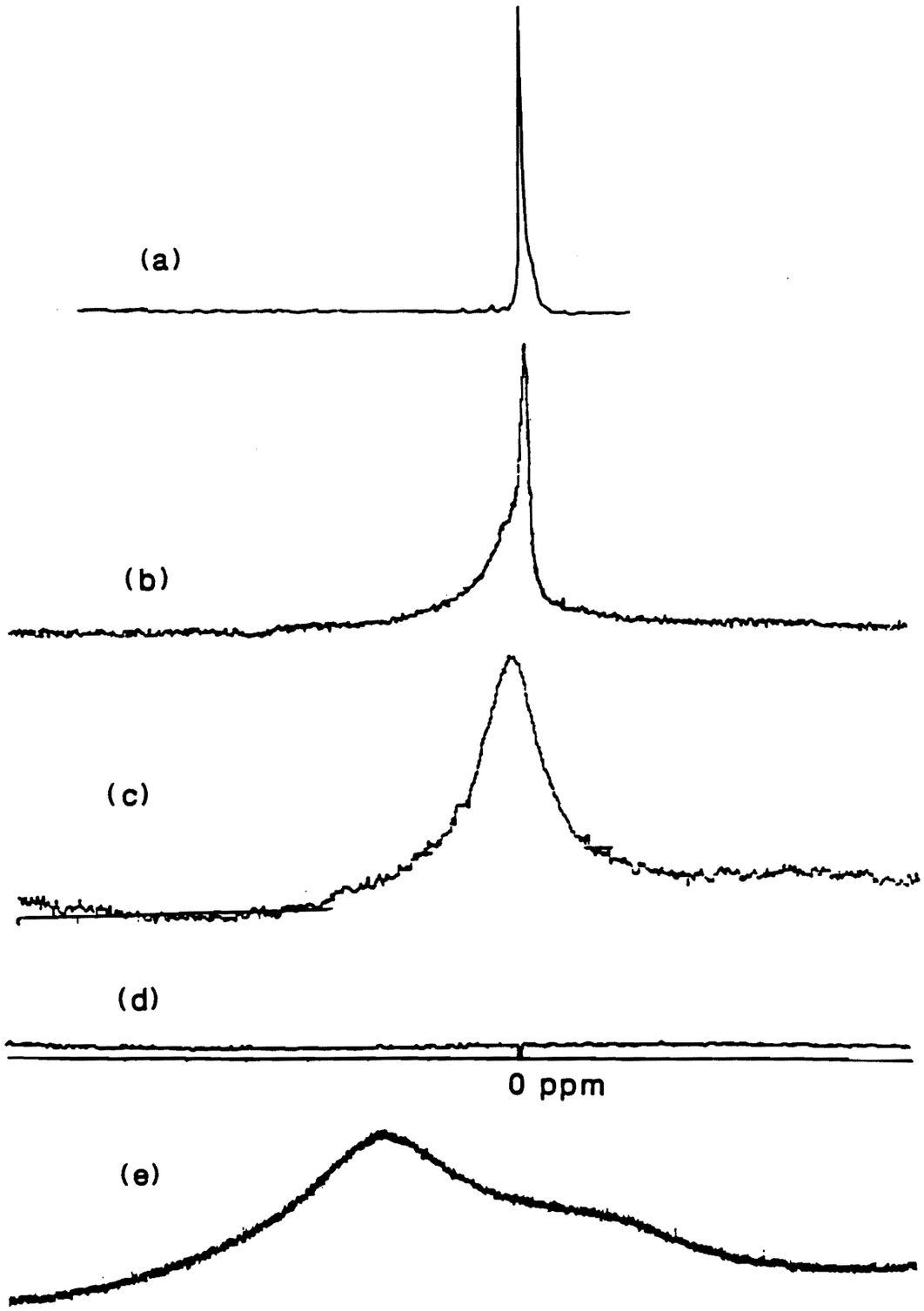


Fig. 4

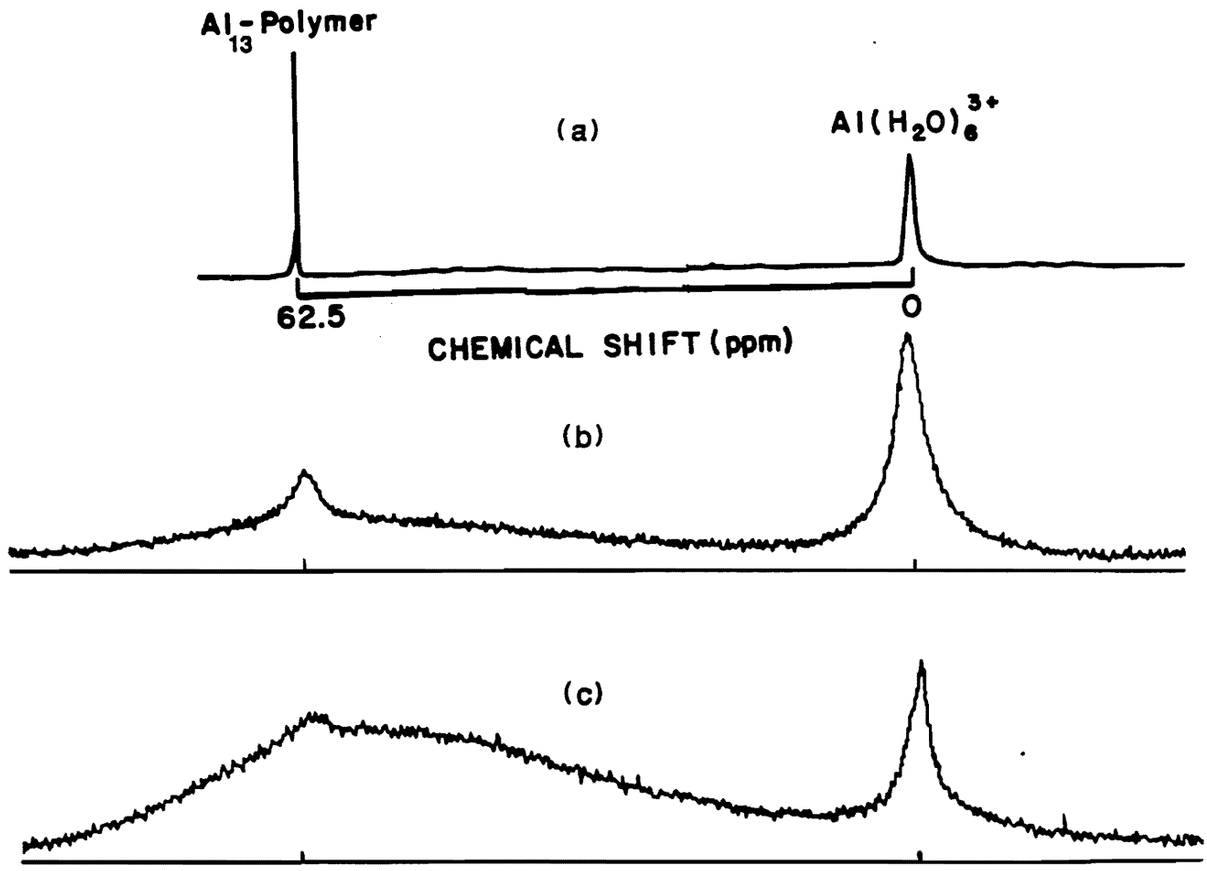


Fig. 5

^{27}Al NMR on Partially Neutralized Stock Solution and On SWy-1

component	Integral	$V_{1/2}$	Al_{13}/Al^{3+}
Al^{3+}	61.3	63.0	
Al_{13}	68.9	15.4	1.12
	Surface Sorbed		
Al^{3+}	90.2	257.8	
Al_{13}	41.6	143.3	0.46

Fig. 6

Spin-lattice Relaxation Times (T_1) and Line Widths ($V_{1/2}$) for Al-saturated clays

Sample	T_1(ms)	$V_{1/2}$(Hz)
Al-sat smectite	11.6	433.5
Al-sat Kaolinite	11.9	347.7
Al^{3+}-solution	140.0	3.6

Fig. 7

Spin-lattice Relaxation Times (T_1) and Line Widths ($V_{1/2}$) for Al-saturated Exchangers and Al^{3+}-Al_{13} Solutions

Sample	T_1(ms)	$V_{1/2}$(Hz)
Al-sat sulfonic	5. 0	205.0
Al^{3+}(Al-Al_{13}) sulfonic	2. 1	262.0
Al_{13}-sulfonic	4. 2	166.0
Al^{3+}-SWy1	11.6	433.5
Al^{3+}(Al-Al_{13})-SWy-1	4.5	327.6
Al^{3+}-solution	140.0	3.6
Al_{13}-solution	50. 0	2.4

Fig. 8

Cs exchanged Dowex

Site	τ_c	χ(MHz)
I	7.32×10^{-9}	0.139
II	1.10×10^{-8}	0.226

Fig. 9

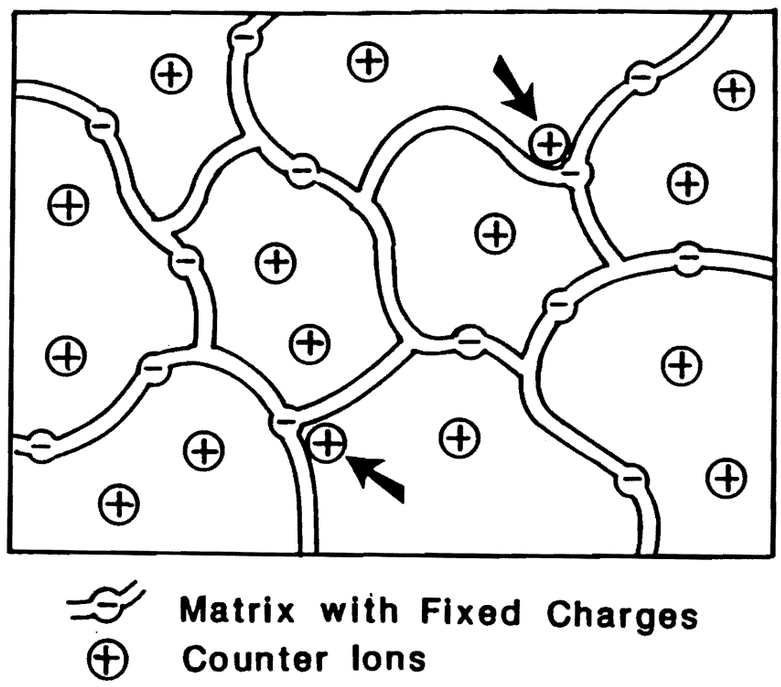


Fig. 10

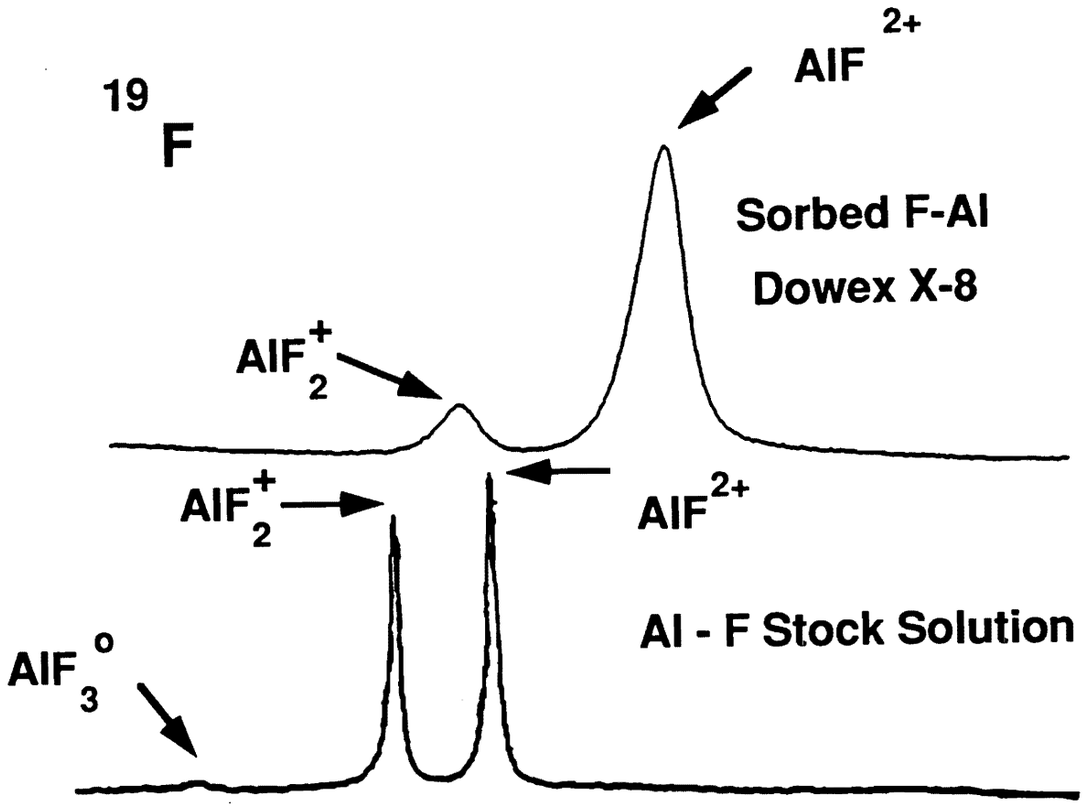

19 F
AlF 2+
Sorbed F-Al
Dowex X-8
AlF2+
AlF2+
AlF2+
Al - F Stock Solution
AlF3o

Fig. 11

^{19}F NMR on Stock Solution and On Sulfonic Resin

Sample	Integral	$\%F_T$	$\frac{AlF}{AlF_2}$
AlF^{2+}	146.9	53.8	
AlF_2^+	122.0	44.7	1.2
AlF_3^0	4.2	1.5	
	Surface	Sorbed	
AlF^{2+}	1234.9	89.0	
AlF_2^+	153.0	11.0	8.07

Fig. 12

X-Ray Spectroscopy Using Soft X-Rays: Applications to Earth Materials

Gordon E. Brown, Jr.

Stanford University

Key Points:

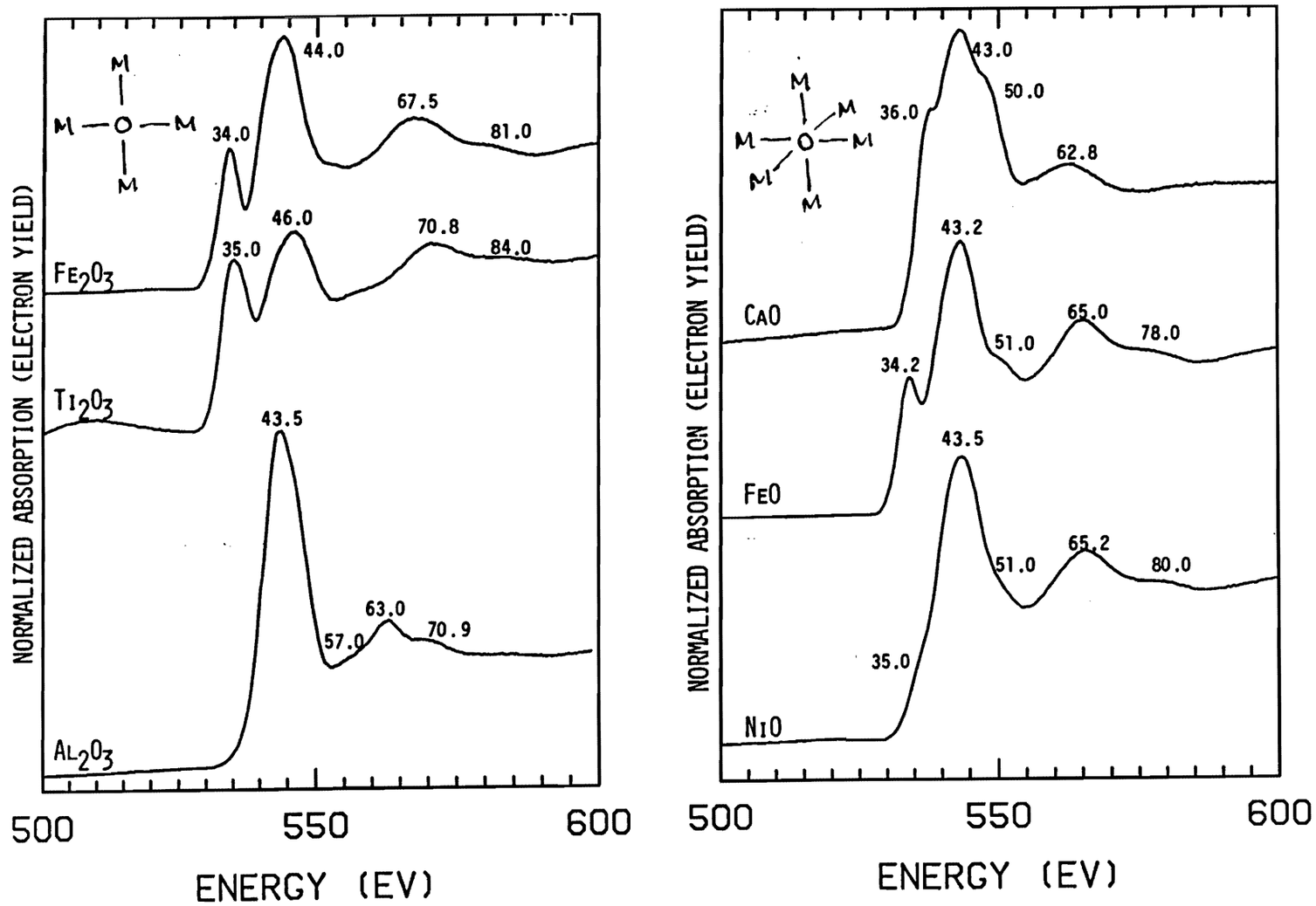
• Vacuum methods are required for these measurements due to the low energies of the x-rays and the fact that they are readily absorbed by an atmosphere.

• Detection of photoelectrons by electron yield detectors is typically used in these measurements

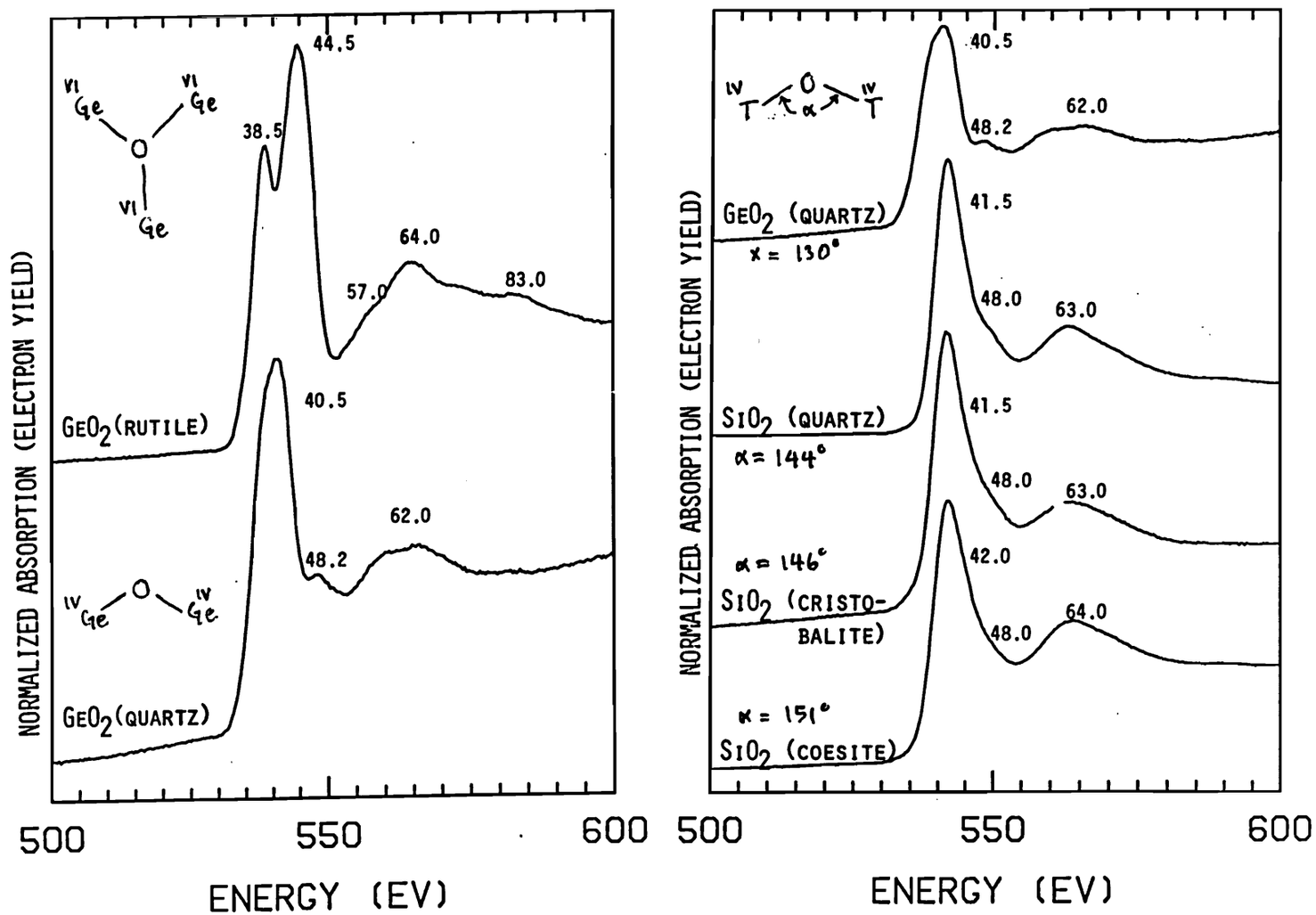
• Soft x-ray spectroscopy is inherently surface sensitive due to the shallow escape depths of photoelectrons of low energy from the sample surface. Surface EXAFS (SEXAFS) spectroscopy is well suited for studies of the geometric details of surface sites on oxides and of molecules sorbed on oxide and metal surfaces, particularly when the polarization of synchrotron light is utilized (i.e., polarized SEXAFS). Thus it is capable of providing quantitative structural information about organic molecules sorbed to mineral surfaces.

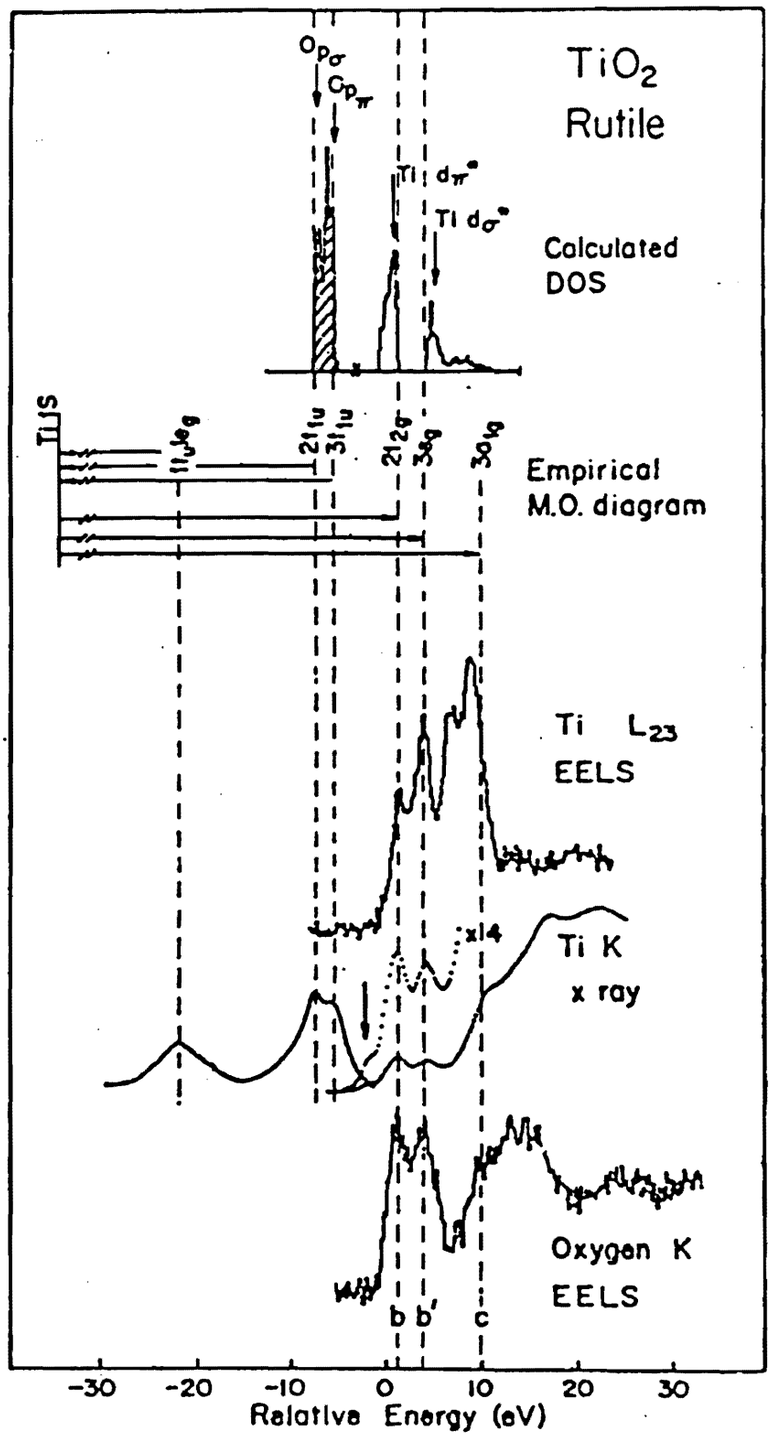
• Soft x-ray spectroscopy is applicable to many low Z elements of geological interest: C, O, F, Na, Mg, Al, Si, P, S, and Cl.

OXYGEN K-EDGE XANES



OXYGEN K-EDGE XANES (Brown et al., 1986)

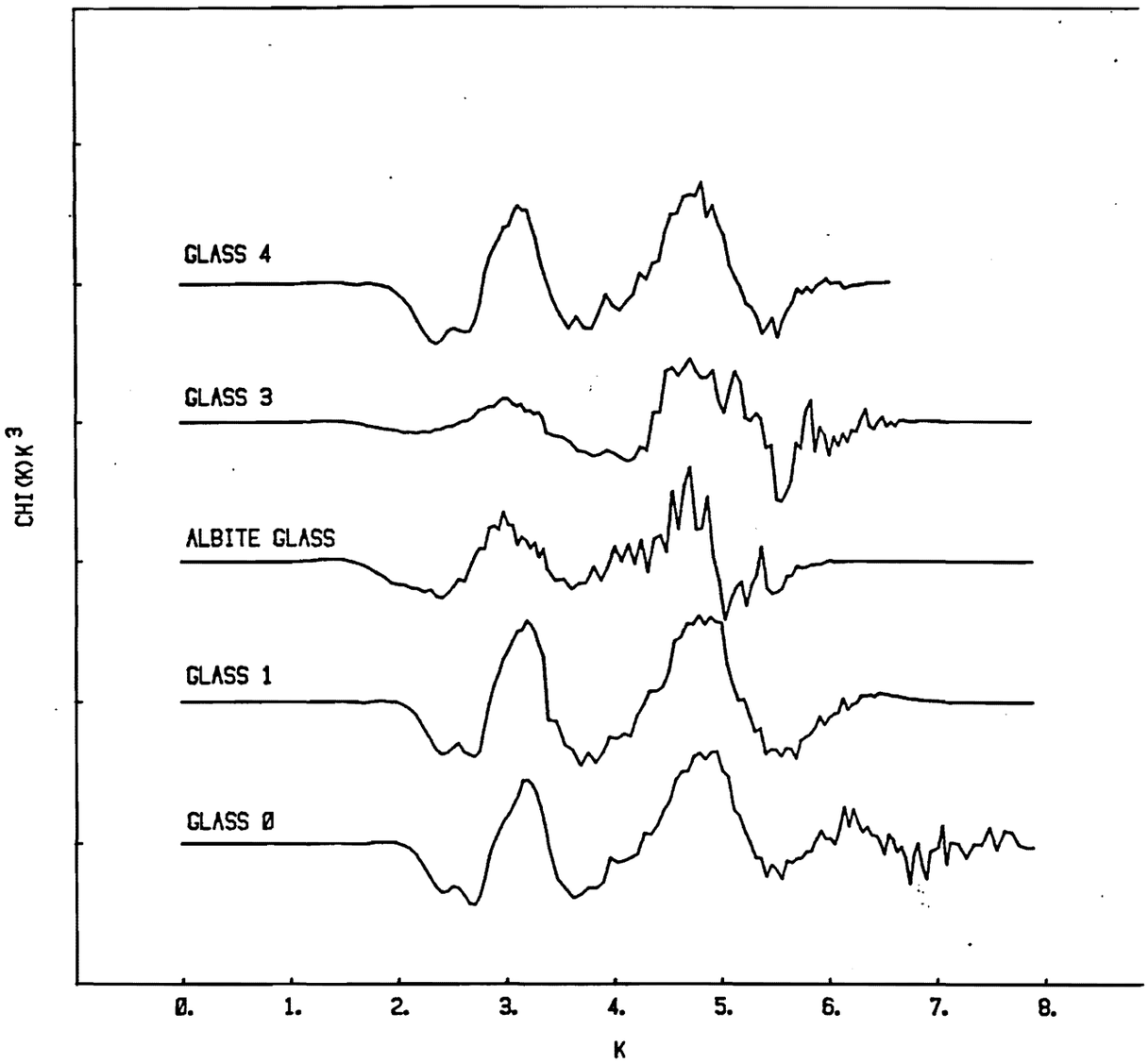




Grunes et al. (1982)

FIG. 16. Fine-structure peaks in the Ti L_{23}, Ti K, and O K edges in TiO_2 are aligned to construct an empirical MO energy-level diagram. The energy-level spacings are in good agreement with peaks in the calculated conduction-band DOS of Wilker and Hoffmann (Ref. 12). (The Ti K emission data at negative energies is from Ref. 16. EELS data from Refs. 4 and 12.)

NA EXAFS IN SELECTED NA-ALUMINOSILICATE GLASSES



Glass O: 7.6 oxygens at 2.60 Å

EXAFS FITS FOR THREE NA-ALUMINOSILICATE GLASSES

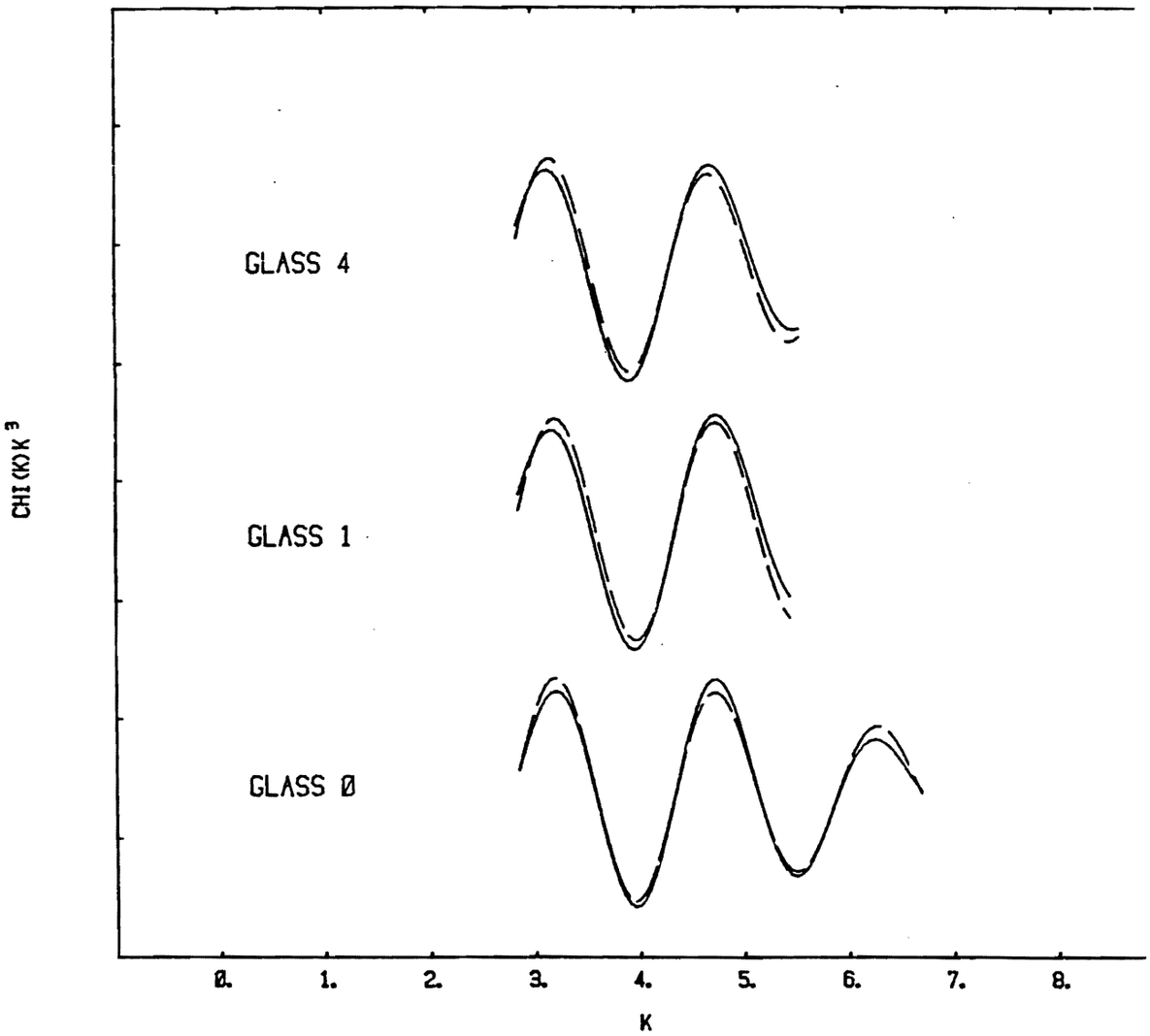


Table 2. $k^3\chi_{fit}(k)$ Refinements

Sample	χ^2(of fit)	σ^2	r	N
Nepheline	0.191	0.035Å^2*	2.57(1)Å	5.5(1)
Nepheline glass	0.008	0.0211(10)	2.62(1)	5.1(3)
$Na_2Si_2O_5$ glass	0.010	0.0109(6)	2.61(1)	6.4(1)
Glass 0	0.014	0.0215(2)	2.60(1)	7.6(1)
Glass 1	0.048	0.0133(1)	2.60(1)	6.8(1)
Glass 4	0.037	0.0241(116)	2.61(1)	5.7(1.2)

All refinements using s_0^2=0.45,
and $\Phi(k)$=1.137-1.106k-0.006k^2.
(standard deviations in parentheses)
* calculated parameter left constrained during refinement.

Greaves et al. (1981) $Na_2Si_2O_5$ Glass

Na environment : 5 oxygens at 2.3 Å

Measurements done in transmission on v. thin blown glass sample.

MIXED ALKALI EFFECT

Replacing one alkali cation by another in a series of glasses across a binary join, certain physical properties may be seen to vary in a non-linear manner.

VARYING PHYSICAL PROPERTIES

Density, Viscosity, Coefficient of Thermal Expansion, Ionic mobility, Electrical Resistivity

BASIS OF THEORIES

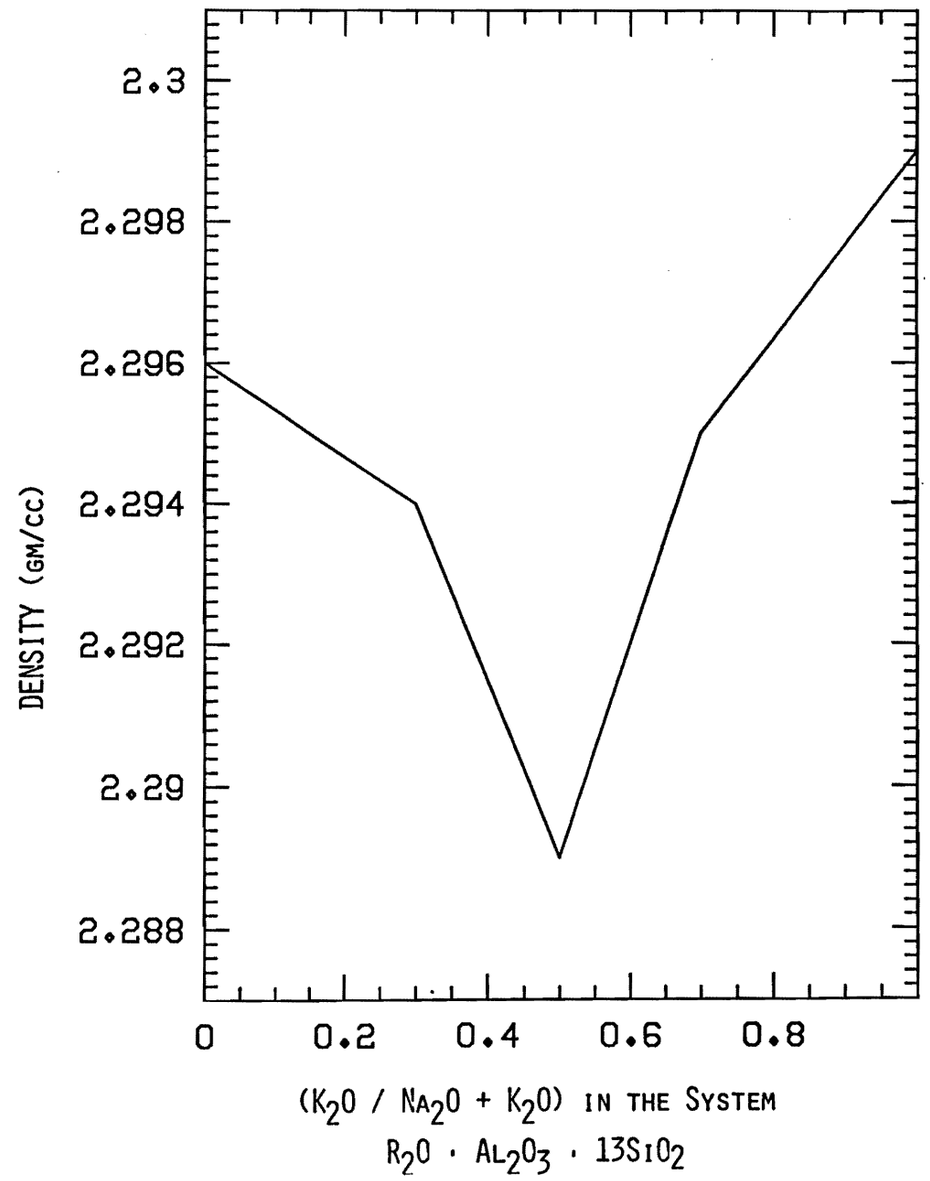
1. Alkali - alkali cation interactions.
2. Alkali cation size, mass, field strength, electronegativity differences.
3. Alkali cation bonding and coordination environment differences.
4. Phase separation and independent structures.
5. Anharmonic thermal vibrations.

THIS STUDY

Potassium K-EXAFS of glasses along Ab - Or join

OBSERVATIONS

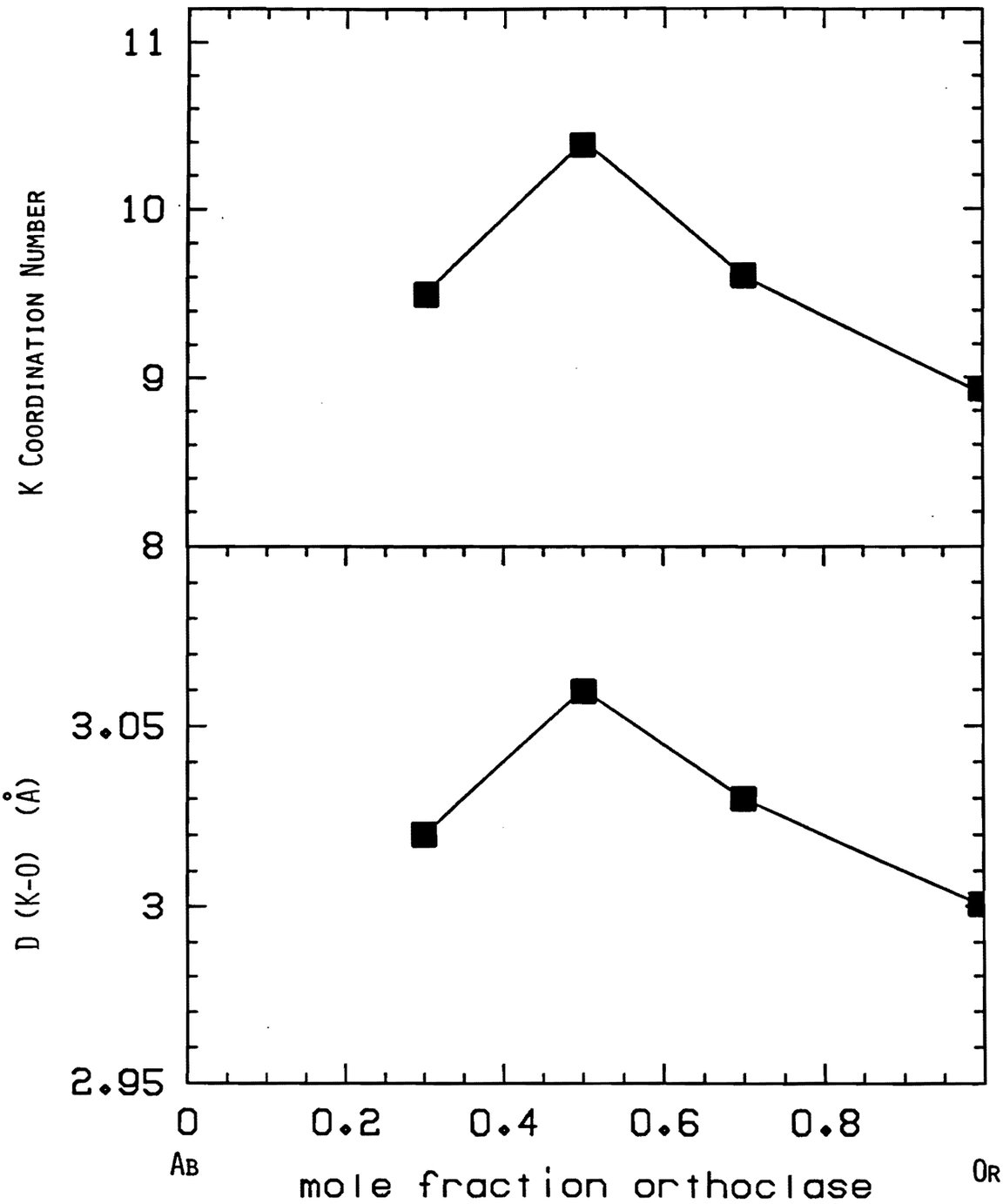
Maxima exhibited in both K-O coordination and bond distance across join. Edge features indicate glass structures based on interconnected 6 and 4 membered tetrahedral rings.



EXAMPLE OF THE MIXED ALKALI EFFECT ON DENSITY FOR NA-K ALUMINOSILICATE GLASSES

DATA FROM HAYWARD (1976)

K-O Distances and K Coordination Numbers of Mixed K - Na Glasses ($K_x Na_{1-x} AlSi_3O_8$) From EXAFS Fits



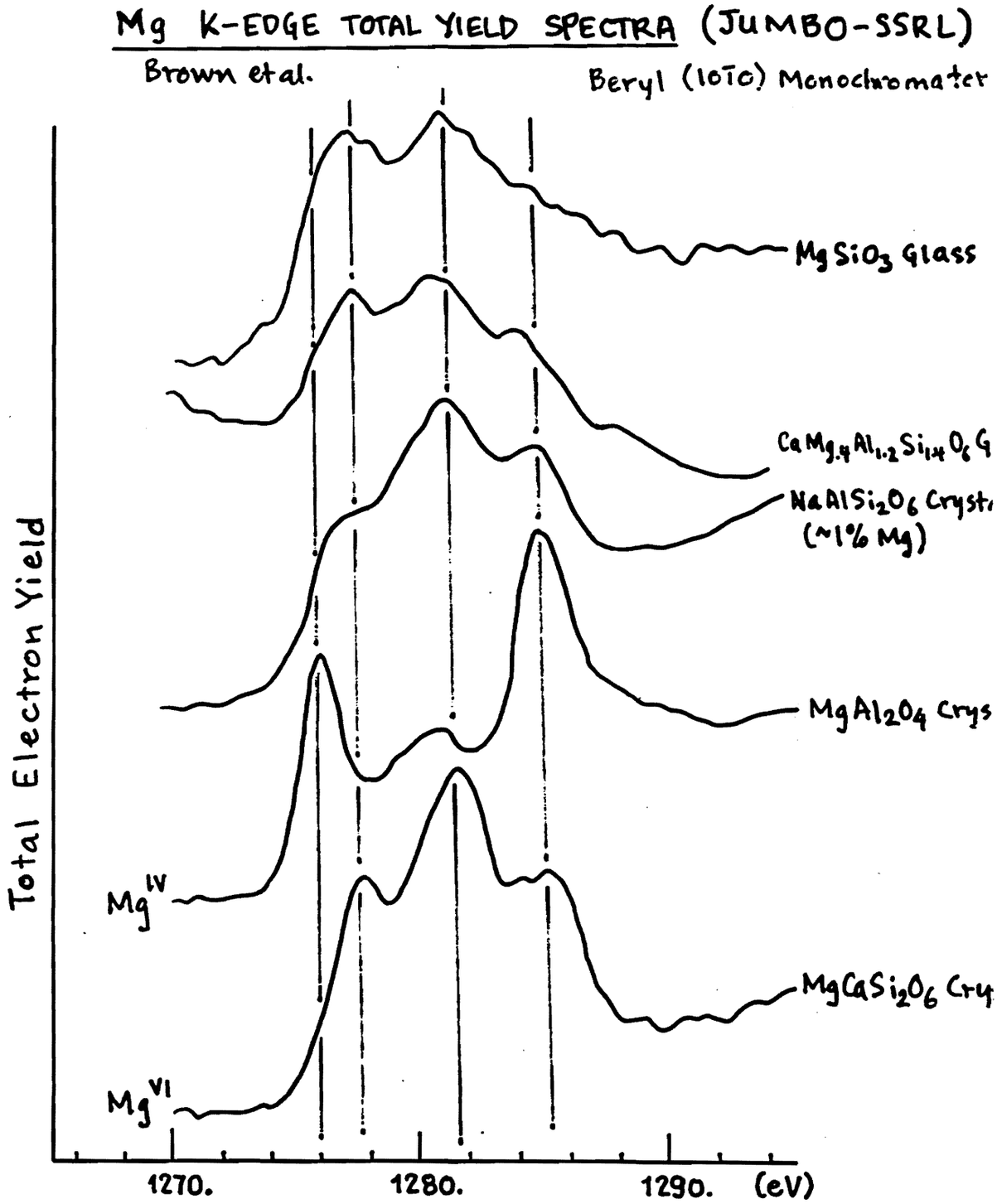
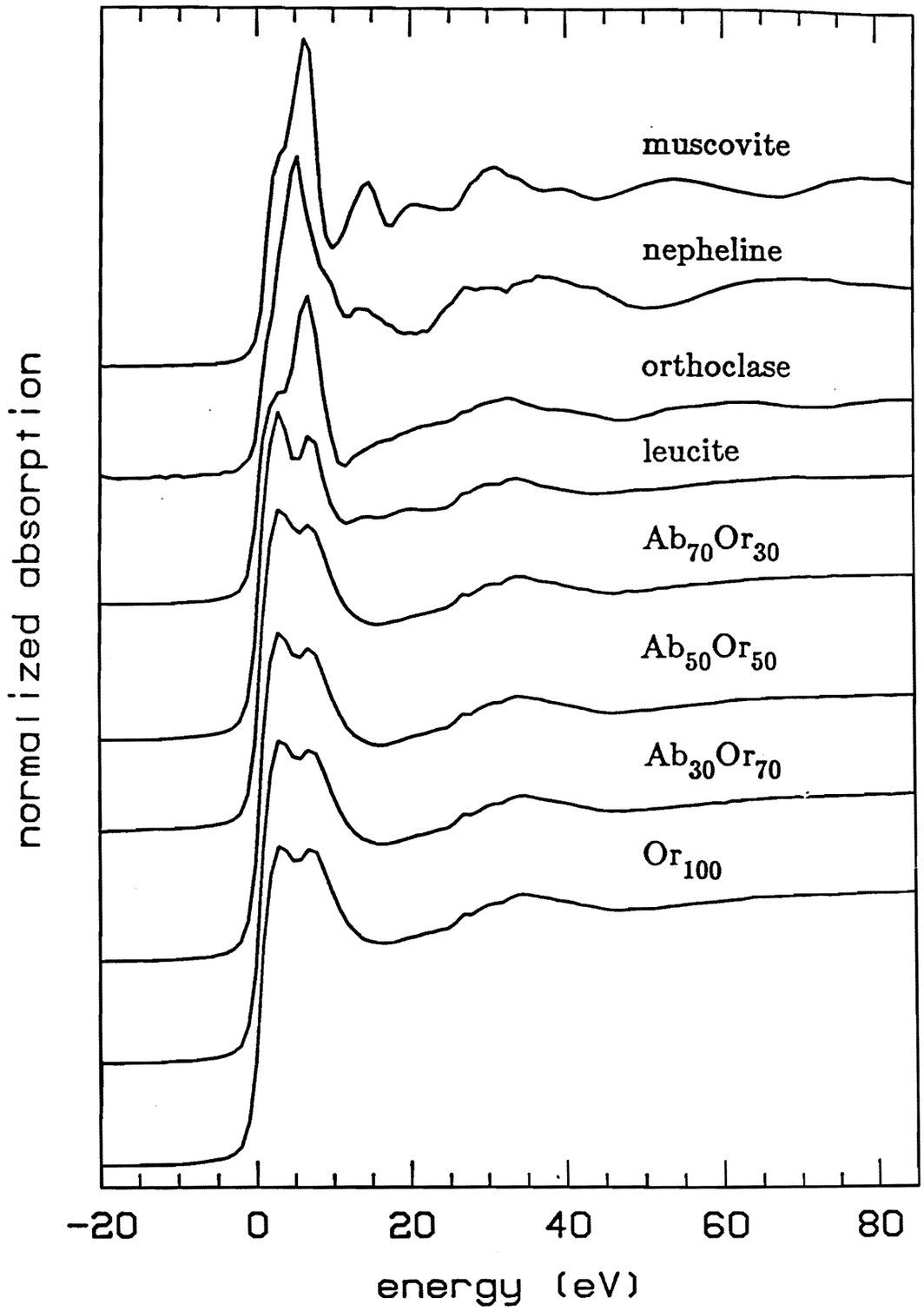
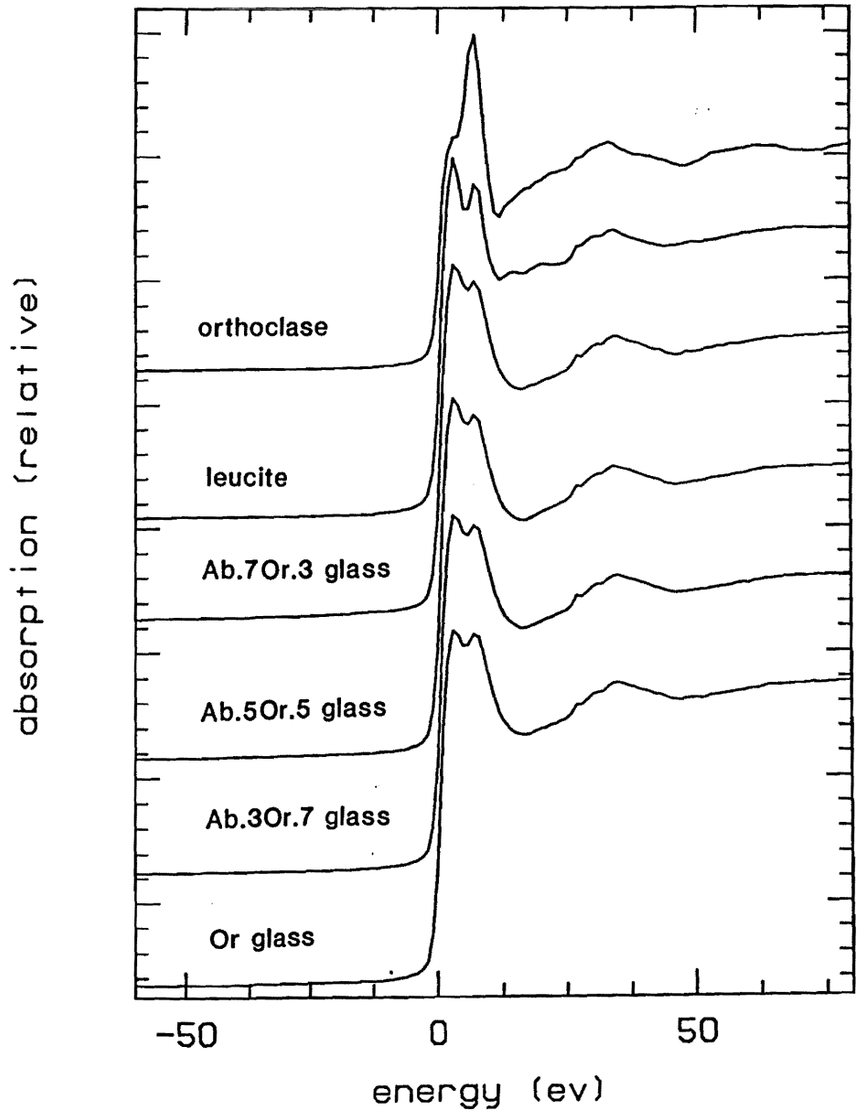

Mg K-EDGE TOTAL YIELD SPECTRA (JUMBO-SSRL)
Brown et al.
Beryl (10$\bar{1}$0) Monochromator
MgSiO3 Glass
CaMg.4Al1.2Si1.4O6 G
NaAlSi2O6 Cryst.
(~1% Mg)
MgAl2O4 Crys
MgCaSi2O6 Cry
Mg^IV
Mg^VI
Total Electron Yield
1270.
1280.
1290.
(eV)

Fig. 1: Jackson et al.

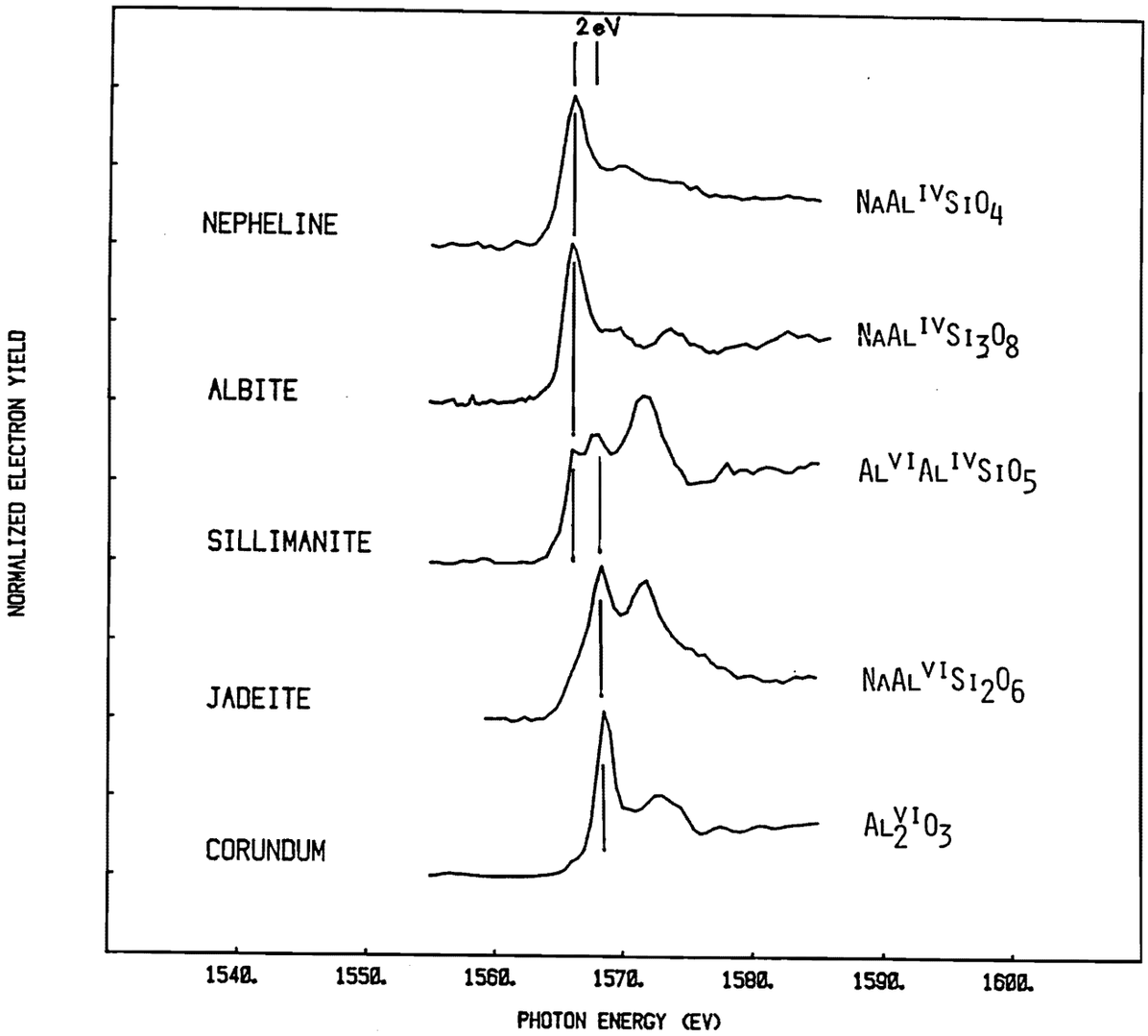




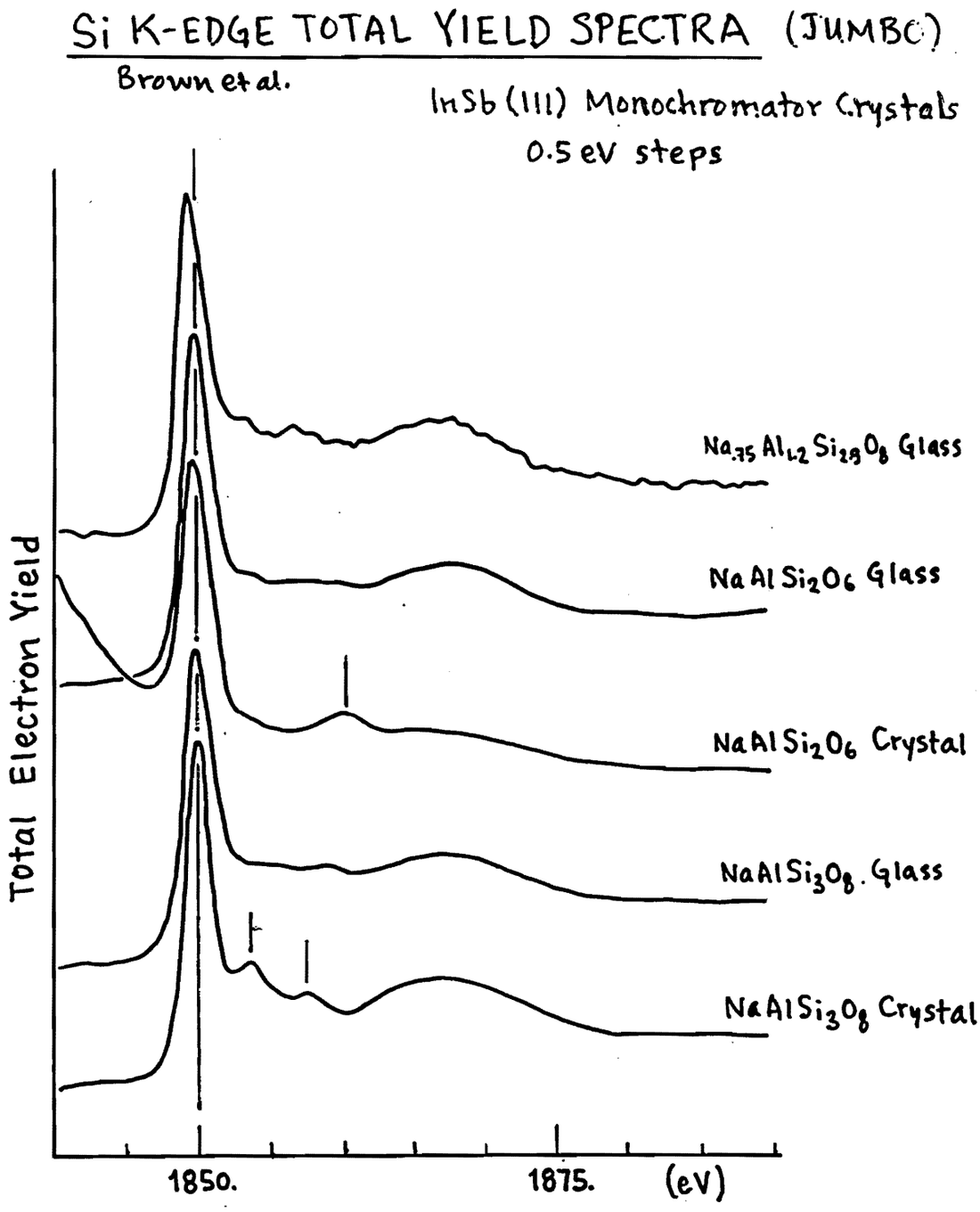
COMPARISON OF POTASSIUM K-NEXAFS FOR TWO CRYSTALLINE MODEL CPDS AND FOUR MIXED ALKALI GLASSES OF COMPOSITION

$(K_x\ Na_{1-x}\ Al\ Si_3\ O_8)$

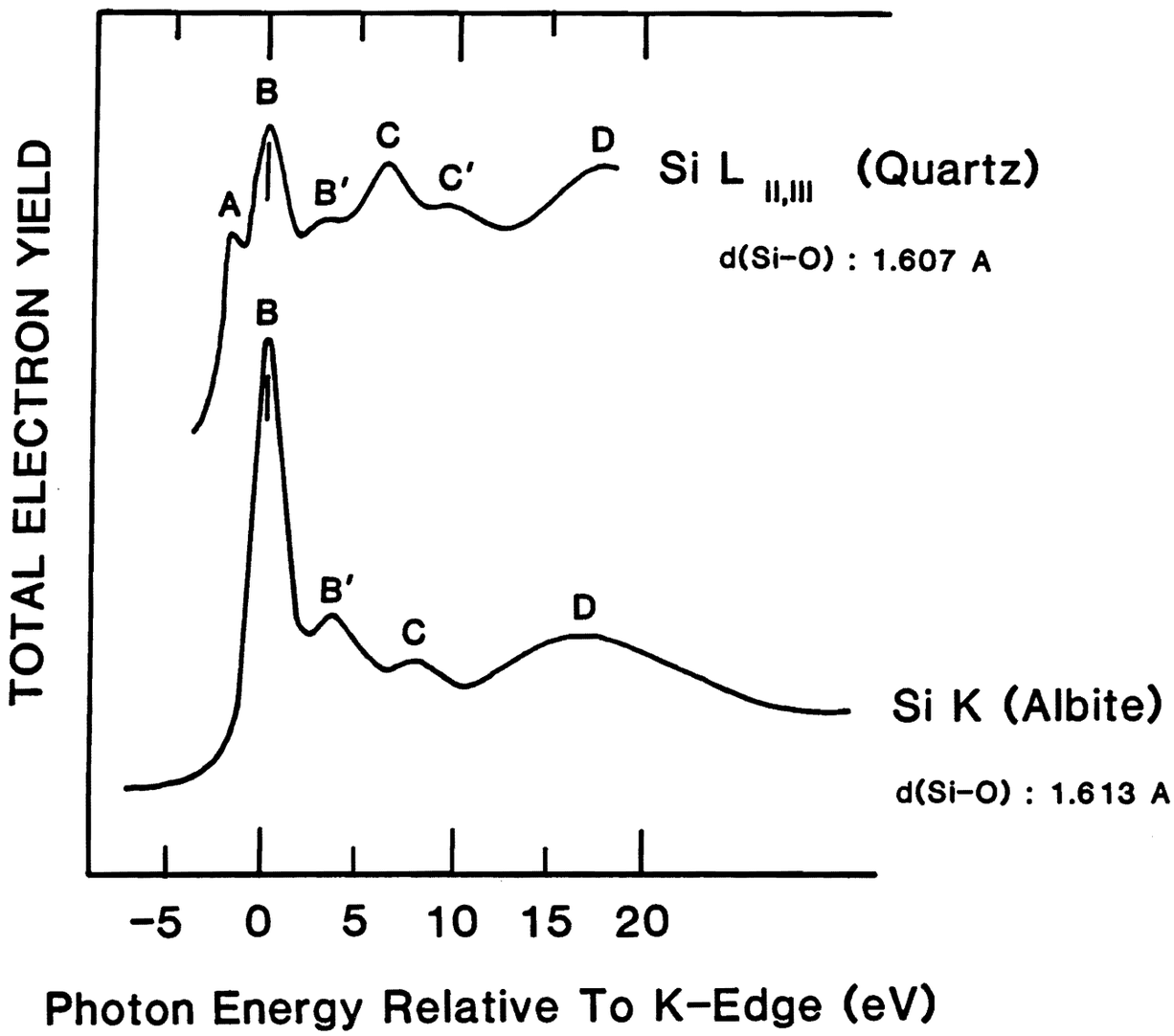
AL K-NEXAFS SPECTRA OF CRYSTALLINE AL OXIDES AND SILICATES



STUDY PERFORMED ON JUMBO (SSRL) USING TOTAL ELECTRON YIELD & QUARTZ (SiO_2) MONOCHROMATOR CRYSTALS


Si K-EDGE TOTAL YIELD SPECTRA (JUMBO)
Brown et al.
InSb (111) Monochromator Crystals
0.5 eV steps
Total Electron Yield
$Na_{.75}Al_{1.2}Si_{2.8}O_8$ Glass
$NaAlSi_2O_6$ Glass
$NaAlSi_2O_6$ Crystal
$NaAlSi_3O_8$ Glass
$NaAlSi_3O_8$ Crystal
1850.
1875.
(eV)

Brown et al.


TOTAL ELECTRON YIELD
A
B
B'
C
C'
D
Si L II,III (Quartz)
d(Si-O) : 1.607 A
B
B'
C
D
Si K (Albite)
d(Si-O) : 1.613 A
-5
0
5
10
15
20
Photon Energy Relative To K-Edge (eV)

ALKALI AND ALKALINE EARTH CATIONS IN SILICATE GLASSES

ALKALIS (NA AND K) AND CA TYPICALLY OCCUPY LARGE, HIGHLY-COORDINATED (7-12), DISTORTED SITES IN CRYSTALLINE SILICATES.

WHAT IS THEIR COORDINATION NUMBER AND AVERAGE BOND LENGTH WITH OXYGEN IN SILICATE GLASSES.

PROBLEMS:

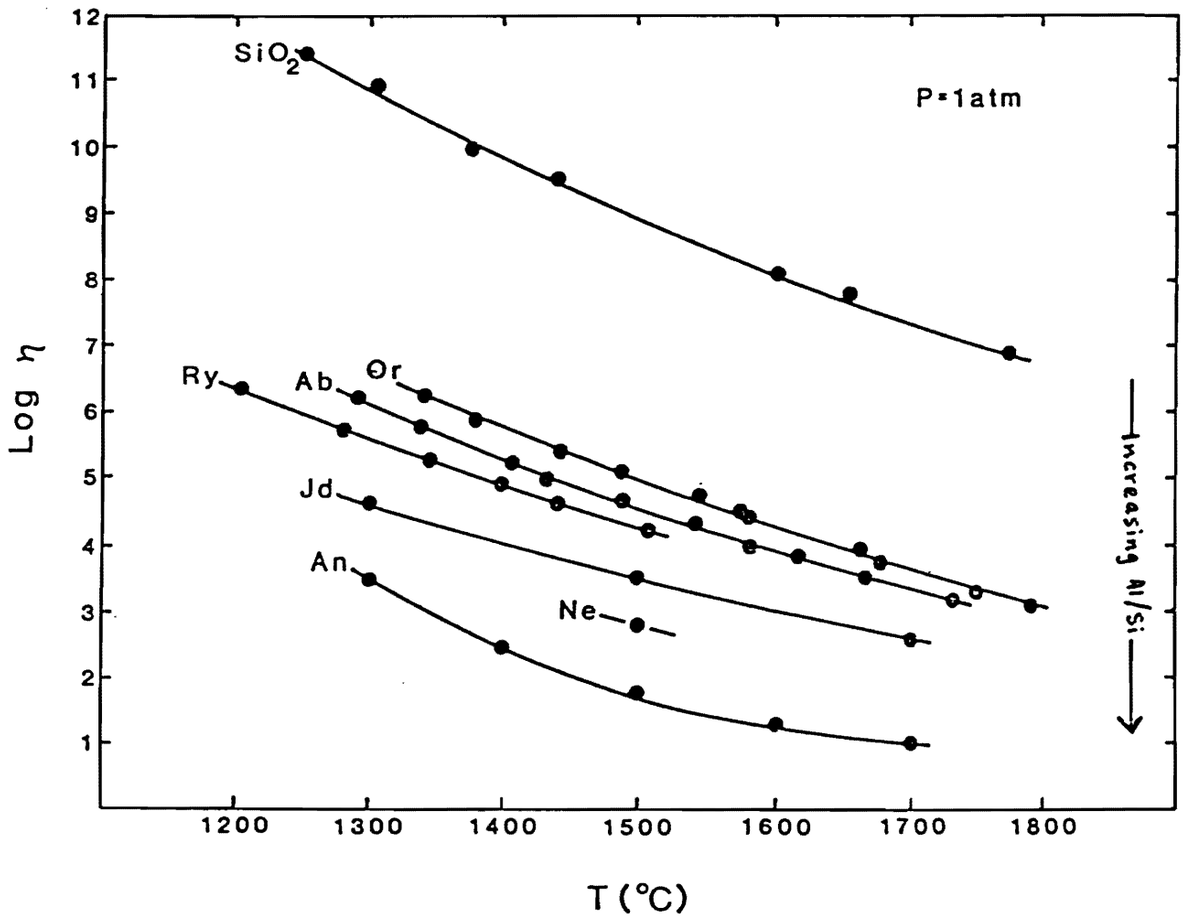
ADDITION OF SMALL AMOUNTS OF ALKALI TO SILICATE MELTS AND GLASSES CAUSES LARGE CHANGES IN PHYSICAL PROPERTIES.

NA-O, K-O, AND CA-O DISTANCES ARE DIFFICULT TO DETERMINE RELIABLY FROM X-RAY RADIAL DISTRIBUTION ANALYSIS.

LITTLE INFORMATION ON THE LOCAL COORDINATION GEOMETRY OF THESE ELEMENTS CAN BE DETERMINED FROM SPECTROSCOPIC METHODS SUCH AS RAMAN, FTIR, XPS, OR NMR.

EXAFS SPECTROSCOPY OF K AND CA (USING FLUORESCENCE TECHNIQUES) AND OF NA (USING TOTAL ELECTRON YIELD TECHNIQUES) IS A GOOD METHOD OF OBTAINING AVERAGE STRUCTURAL ENVIRONMENTS OF THESE CATIONS IN GLASSES.

EFFECT OF $MAlO_2 \rightleftharpoons SiO_2$ SUBSTITUTION ON VISCOSITY OF SILICATE MELTS - FROM HOCHELLA & BROWN (1984)



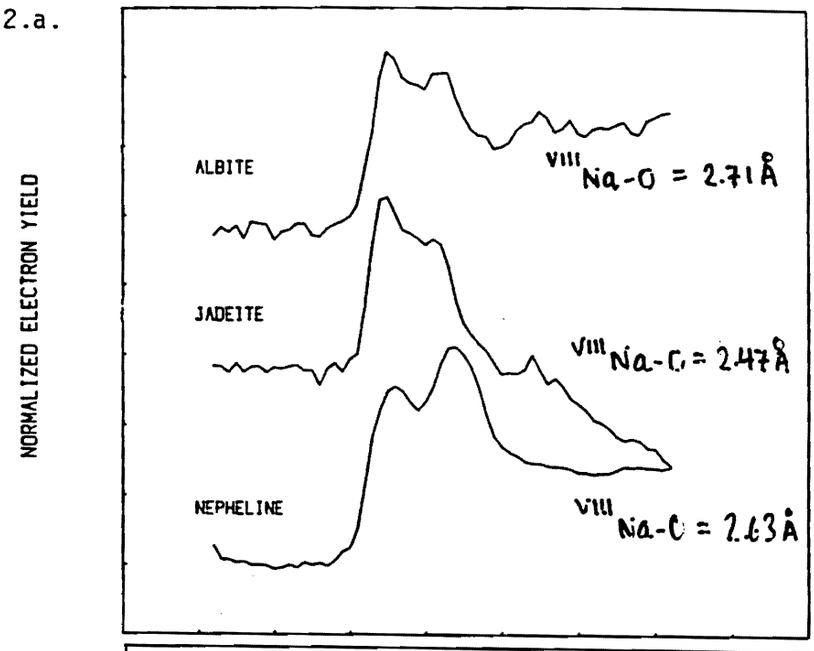
OR = $KAlSi_3O_8$ RY = RHYOLITE COMPOSITION

AB = $NaAlSi_3O_8$ JD = $NaAlSi_2O_6$

NE = $NaAlSiO_4$ AN = $\bar{C}aAl_2Si_2O_8$

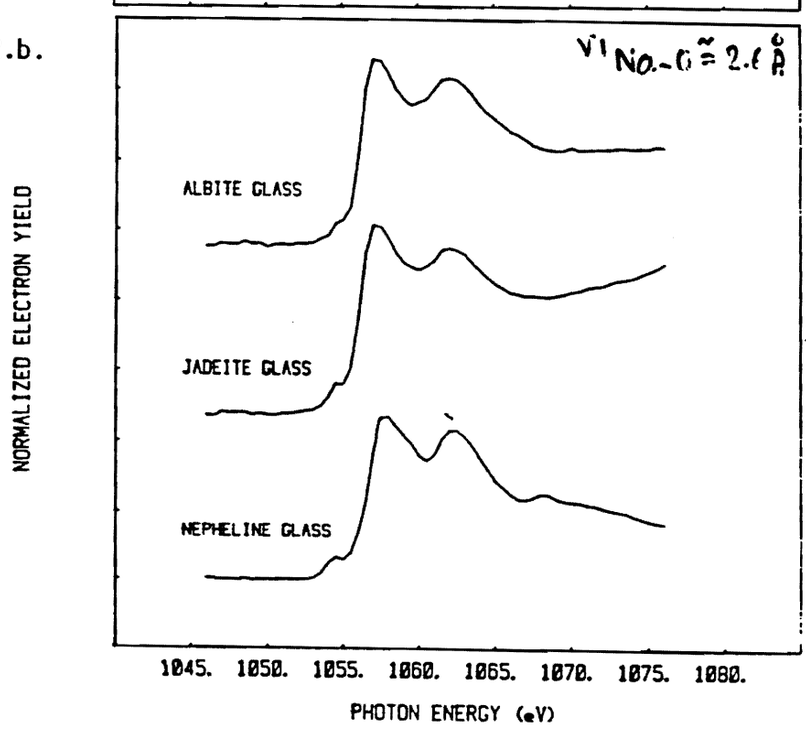
Na K-NEXAFS for Crystalline and Glassy Na Silicates

Figure 2.a.



Differences in Na environments in 3 crystalline phases is reflected by differences in edge structure.

Figure 2.b.



Na K-edges in glasses are similar suggesting similar Na environments

Na NEXAFS & EXAFS DATA TAKEN ON JUMBO (SSRL) USING TOTAL ELECTRON YIELD & BERYL MONOCHROMATOR CRYSTALS.