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of the

ALS Users' Association Annual Meeting
Lawrence Berkeley Laboratory
Berkeley, CA,
June 2-3, 1988

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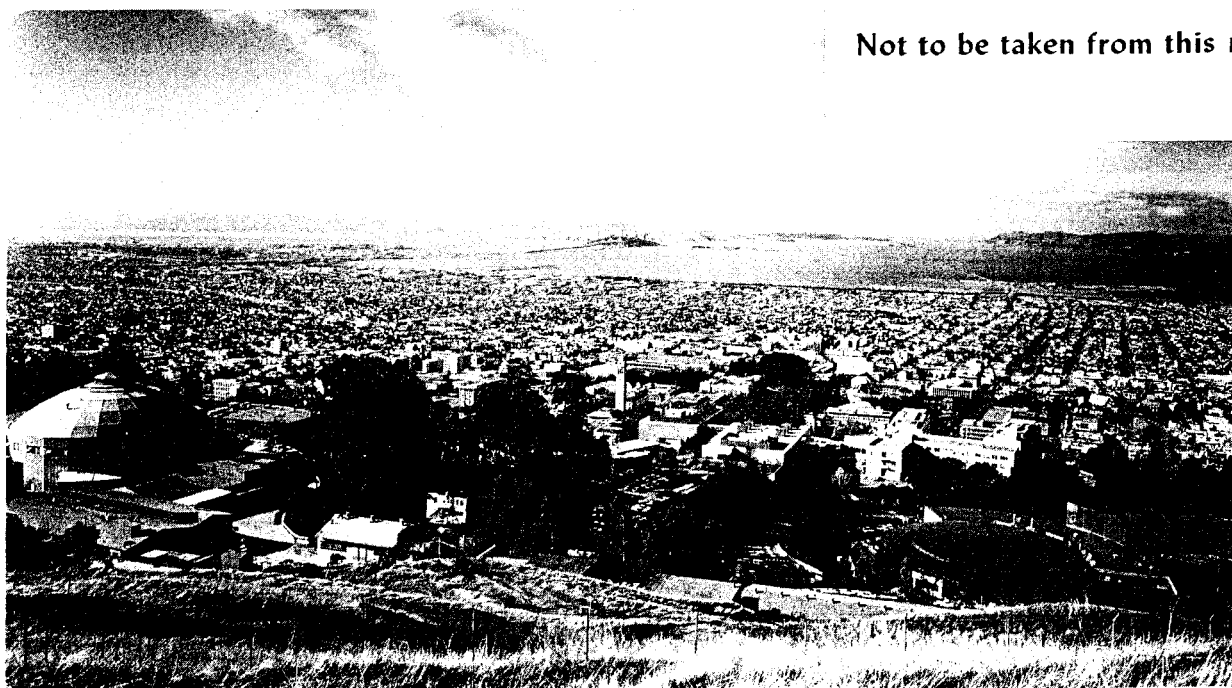
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J. Dillard, H. Wollenberg, D. Perry, R. Giaque, and A. Thompson

September 1988

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**Summary of Discussions of Uses of the Advanced Light Source (ALS)
for Earth Sciences Research: Workshop Report**

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September 1988

A workshop to discuss opportunities for research using the Advanced Light Source (ALS) was held as a part of the first annual ALS users meeting at the Berkeley Convention Center, Berkeley, California, June 2-3, 1988. The participants, listed below, were from university and governmental laboratories, and some of those attending had had experience using synchrotron light sources.

Participants

John A. Apps	Earth Sciences, Lawrence Berkeley Lab.	Berkeley, CA 94720
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Harold Wollenberg	Earth Sciences, Lawrence Berkeley Lab.	Berkeley, CA 94720

Because the Earth Science interests had not been voiced or considered in previous workshops or meetings of the ALS groups, it was the principal task of the group to explore the capabilities of the ALS appropriate to the Earth Sciences, to identify areas of research where the ALS would be of significant benefit, and to provide input regarding desired insertion devices.

Discussions of synchrotron radiation phenomena (1-3) and applications of synchrotron radiation in earth sciences have been highlighted in the literature (4-11) and in a recent report of a workshop held at Argonne National Laboratory (12), A

summary outline of some typical potential uses and the information to be gained from the use of synchrotron radiation is given below. This is not an exhaustive list of earth sciences applications, but indicates the breadth of applications that can be addressed.

- A. X-Ray Absorption Near Edge Structure (XANES) Spectroscopy**
Oxidation state of elements
Coordination number of metal ions

- B. Extended X-Ray Absorption Fine Structure (EXAFS) Spectroscopy**
Glasses and other disordered structures
Solutions
Gels - silicates, aluminates
Clays - swelling phenomena, intercalation chemistry
Adsorption - speciation, chemical reactions, kinetics
Polyhedral linkages - Fe, Mn oxides

- C. Energy Dispersive X-Ray Diffraction**
Mineral transformations vs temperature and pressure

- D. Small Angle Scattering**
Precipitation phenomena

- E. X-Ray microprobe**
Element mapping

Comments and discussion at the ALS meeting identified the principal areas of interest for earth scientists as:

- Adsorption Phenomena
- Nucleation Processes
- Gel Structure
- Reaction Mechanisms
- Temperature and Diffusion Effects

Geologic materials are chemically and physically complex. To be able to explore the research areas noted above, the ALS facility, with a bright tunable x-ray source, affords the opportunity to study trace and light elements, particularly their distribution, structural, and chemical state in minerals, at interfaces, and in solutions. The specific characteristics of geologic materials and the corresponding requirements for the ALS are summarized below:

Characteristics	Requirements
1. A wide range of elements occurs in a single sample	Tunability of source over a broad spectral range
2. Low-z elements make up the bulk of the earth	High x-ray flux at low energies (~ 3KeV)
3. Elements often distributed inhomogeneously, at micron to submicron scale	High x-ray brightness for high spatial resolution
4. Many elements are at very low concentrations (<1000 PPM, and often <1 PPM)	Extremely high flux
5. Many geologic processes of interest are time dependent	Use of the time structure of the source
6. Strong interactions occur at grain boundaries	High spatial resolution

Aware of the potential characteristics of minerals and other geologic materials that could be studied, the group discussed generic measurements based on interaction of x-rays with matter. The primary measurement areas identified were: x-ray absorption processes (surface chemical spectroscopies) and x-ray microprobe (element mapping).

X-Ray Absorption Processes

The principal information to be gained in these studies will be chemical information including oxidation states, coordination geometry, and relative concentrations of elements distributed in mineral phases (13-22). The ability to study minute areas of minerals will permit determination of element speciation of both metals and non-metals. The opportunity to study different core levels of elements will allow non-destructive depth profiling. Chemical information will also be attainable from examination of Auger transitions and from evaluation of the Auger parameter (13). Perry (14) and others (15-21) have discussed the advantages of combined x-ray photoelectron/Auger studies in minerals and of adsorbed or absorbed phases on minerals. Examples of mineral systems that might be studied are listed in Tables 1 and 2.

Chemical reactions at mineral surfaces play an important part in trace metal incorporation and reduction/oxidation processes on these surfaces (14,15,21,22). The availability of a pulsed tunable x-ray source will offer opportunities to study rapid reaction processes at mineral surfaces. The spatial resolution capability should also be valuable for studying migration processes and associated chemical changes that accompany diffusion or phase alterations in minerals.

The value of x-ray absorption studies for mineralogical application has been discussed by Brown and Waychunas (23) and Calas, et al. (4). XANES (4,11,23) and EXAFS (4-12,23) methods have provided valuable structural and chemical information for minerals and mineral-oxide melts at high temperatures (24) and high pressure (25). In addition, studies of trace elements in silicates (26) and electrolyte solutions have been cited (27). The availability of an x-ray source of high brightness and intense flux from the ALS should enhance the capability for studying chemical and structural changes at mineral interfaces.

Table 1. Possible Mineral Systems for X-Ray Photoelectron Studies Using the Advanced Light Source

Element	X-Ray Photoelectron Line	Mineral System or Mineral
Silicon	2p	Silicates
Phosphorus	2p	Phosphates
Carbon	1s	Carbonates
Aluminum	2p	Aluminates
Chromium	2p	Chromatite Chromite
Iron	2p	Goethite Pyrite
Vanadium	2p	Vanadinite Vanalite

Table 2. Possible Mineral Systems for Auger Studies Using the Advanced Light Source

Element	Auger Line	Mineral System or Mineral
Sulfur	KLL	Galena Chalcopyrite Sphalerite Pyrite
Silicon	KLL	Silicates
Aluminum	KLL	Aluminates Aluminosilicates
Molybdenum	LMM	Molybdenite Molybdite
Zirconium	LMM	Zircon
Bismuth	MNN	Bismoclite Bismite Bismutite
Lead	MNN	Litharge Cerussite
Mercury	MNN	Cinnabar

X-Ray Microprobe - Element Mapping

The synchrotron based x-ray microprobe provides the ability to analyze samples with small beam spot sizes and high trace-element sensitivity. X-ray spot sizes of $10\ \mu\text{m} \times 10\ \mu\text{m}$ have been achieved using multilayer x-ray mirrors arranged in a Kirkpatrick-Baez geometry (28,29). At the Brookhaven National Synchrotron Light Source (NSLS) an intensity of 3×10^9 photons/sec for 10 keV photons has been demonstrated when the storage ring was operating at 2.5 GeV and 150 mA. The energy bandpass of the mirrors was measured to be about 1 keV.

At the ALS it is planned that the beam spot size will be reduced to the range of $1\text{-}10\ \mu\text{m}^2$. The beam intensity on an ALS wiggler beam line will be comparable to those at NSLS. Using different sets of focussing mirrors, the focussed beam energy can be varied from 3 keV to over 10 keV. For typical geochemical samples, the trace element sensitivities for elements from K to Zr will be in the range of $1\text{-}50\ \mu\text{g/g}$ in a measuring time of 30 seconds.

Rapid two dimensional x-ray imaging of the major geochemical components such as sodium, magnesium and silicon will be possible. Quantitative analysis of these components will also be feasible.

Recommendations

The research concepts described briefly above establish the initial instrumental and insertion device requirements for the ALS facility for Earth Sciences applications. The minimum needs are:

- Two ports on a wiggler (EC ~ 3Kev); one dedicated to microprobe applications in collaboration with other users, one for other earth science applications;

- A dedicated bending magnet line.

ALS undulators will probably not provide the photon energy range needed for earth science applications. A wiggler will provide the optimum energy - brightness combination

It is clear that in the near future earth scientists should organize research teams in the areas of x-ray absorption and x-ray microprobe mapping, to better specify their interests, plan experiments, and to embark on securing funding for the projects.

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