

ADVANCED ANALYTICAL  
FACILITIES

REPORT OF THE  
PLANETARY MATERIALS  
AND GEOCHEMISTRY  
WORKING GROUP



**LPI Technical Report Number 88-11**

LUNAR AND PLANETARY INSTITUTE 3303 NASA ROAD 1 HOUSTON, TEXAS 77058



ADVANCED ANALYTICAL FACILITIES

REPORT OF THE  
PLANETARY MATERIALS  
AND GEOCHEMISTRY  
WORKING GROUP

Lunar and Planetary Institute      3303 NASA Road One      Houston, Texas 77058-4399

LPI Technical Report Number 88-11

Compiled in 1988 by the  
LUNAR AND PLANETARY INSTITUTE

The Institute is operated by Universities Space Research Association under Contract NASW-4066 with the National Aeronautics and Space Administration.

Material in this document may be copied without restraint for library, abstract service, educational, or personal research purposes; however, republication of any portion requires the written permission of the authors as well as appropriate acknowledgment of this publication.

This report may be cited as:

Planetary Materials and Geochemistry Working Group (1988) *Advanced Analytical Facilities Report*. LPI Tech. Rpt. 88-11. Lunar and Planetary Institute, Houston. 38 pp.

Additional copies of this report are available from:

Don Burnett  
Geological and Planetary Sciences  
California Institute of Technology  
Pasadena, CA 91125

## SUMMARY

The Planetary Materials and Geochemistry Working Group has conducted a study on the role of advanced analytical facilities. We have reached the following conclusions:

\* The analytical techniques presently used by the Planetary Materials and Geochemistry Program will continue to produce excellent science. This core program must continue to be supported; however, it needs to be both upgraded and supplemented with advanced techniques.

\* Upgrading is necessary because, due to funding limitations in the past decade, there has been a slow and steady erosion in program analytical capabilities relative to state of the art laboratories, e.g., in the major European geochemistry research institutes.

\* A significant fraction (approximately half) of the analytical instruments utilized by Program PIs are of pre-1980 vintage; some are much older.

\* Advanced instrumentation is required in order to maintain a worldwide leadership role in research on planetary materials.

\* Most of the instrumentation utilized in Program laboratories has been funded from non-Program sources.

\* Given the history of level Program funding and the need to upgrade present Program capabilities, development of advanced instrumentation requires supplemental funding.

\* Advanced instrumentation or techniques should be developed as facilities with the goal of broad and convenient community access once adequate development and testing has been carried out. At this stage program planning must allow for adequate operation and

maintenance costs.

\* From the Agency point of view advanced facilities are necessary to accomplish NASA sample return mission objectives as well as those for planetary materials. These facilities should be regarded as flight instruments for the sample return missions.

\* The greatest need is for microanalytical facilities, i.e., those capable of providing compositional data for small grains. This would be of great importance for all of the proposed NASA sample return missions, e.g., the space station particle collector, comet nucleus sample return, Mars sample return, etc. Such facilities would also greatly enhance the research programs on the present interplanetary particle collections, meteorites, and lunar samples.

\* Potentially interesting advanced facilities appear to be in the general areas of (1) secondary ion mass spectrometry, (2) induced X-ray trace element microanalysis, (3) transmission electron microscopy, and (4) resonance ionization mass spectrometry. Some program activity already exists in all areas except 4. This activity should be maintained, and the issue of broader community access should be investigated.

\* Study groups with broad PI representation should be formed to develop detailed technical and budgetary plans which can form the basis for supplementary funding requests for advanced facilities.

## Table of Contents

|   |     |
|---|-----|
| Summary   | iii |
| I. Background   | 1   |
| II. The Facilities Approach                                 | 5   |
| III. Upgrade/Replacement of Existing Instruments            | 16  |
| IV. Advanced Facilities                                     | 16  |
| V. Relation of Advanced Facilities to<br>Present Program    | 17  |
| A. Maintain the core program                                | 17  |
| B. Develop advanced facilities for<br>small sample analysis | 18  |
| VI. Possible Facilities: a Strawperson Payload              | 20  |
| A. Ion probes   | 20  |
| B. Induced X-ray microanalysis                              | 21  |
| C. Transmission Electron Microscopy                         | 24  |
| D. Accelerator mass spectrometry                            | 28  |
| E. Advanced mass spectrometry                               | 28  |
| VII. Recommendations  | 37  |
| Committee membership  | 38  |



## I. BACKGROUND

The tradition of post-war experimental science in the United States has been for individual laboratories to build or, more recently, buy the instruments and equipment required for research. In all physical science fields, strongly decreasing per-capita support for science has caused the old system to be highly strained, if not entirely broken down. These national problems have even stronger validity for the Planetary Materials and Geochemistry Program.

Because funding has lagged behind inflation for the past decade, the Planetary Materials and Geochemistry Program at present is dependent on special university funds, State legislatures, or spinoff from NSF equipment funds for improvements in laboratory capabilities. This is documented in Table 1, using the six largest (in terms of number of PIs) universities or research centers in the Planetary Materials and Geochemistry program as examples. It is fair to say that these locations have the best instrumented Program laboratories. The year of acquisition and primary source of funding for instruments utilized by these program PIs are tabulated on Table 1. Table 1 shows that over half of the instruments used are pre-1980. The JSC column is a special case, as only NASA funding is possible, but an attempt has been made to distinguish Program and "other NASA" funding. The table shows that only 13/57 instruments used by program PI's were actually acquired with Planetary Materials and Geochemistry funds, and only 3 such instruments have been

Table 1. Summary of analytical instrumentation in largest program laboratories (a)

|                                    | Cal. Inst.<br>Tech.                                   | Washington<br>Univ.                                      | Univ. of<br>Chicago                                     | Univ. Cal.<br>San Diego    | Univ. Ariz.<br>Tucson | Johnson Space<br>Center (b)       |
|------------------------------------|---|--|---|----------------------------|-----------------------|-----------------------------------|
| Solid source mass spectrometers    | 1967 - NSF<br>1970 - int.                             | 1986 - int.  | -----   | 1979 - NSF<br>1986 - int.  | 1982 - int.           | 1970 - P<br>1970 - P<br>1987 - oN |
| Light element mass spectrometers   | 1954 - AEC<br>1960 - AEC<br>1968 - NSF<br>1970 - NASA | -----  | 1959 - int.<br>1973 - NASA<br>1980 - int.<br>1985 - NSF | 1986 - NSF                 | -----                 | -----                             |
| Ion probes                         | 1976 - NASA   | 1983 - int.  | 1974 - NSF  | -----                      | -----                 | -----                             |
| Noble gas mass spectrometers       | -----   | 1970 - int.<br>1972 - int.<br>1976 - int.<br>1981 - int. | 1963 - NASA<br>1984 - NASA                              | 1962 - AEC                 | -----                 | 1968 - P<br>1972 - P              |
| Electron microprobes               | 1986 - NSF  | 1981 - int.  | 1968 - NSF<br>1986 - NSF                                | 1978 - NSF                 | 1974 - int.           | 1982 - P                          |
| Scanning electron microscopes      | 1978 - NASA<br>1987 - NSF                             | 1987 - int.  | 1980 - int.   | 1987 - int.                | -----                 | 1982 - P<br>1986 - oN             |
| Laser ionization mass spectrometer | -----   | 1986 - int.  | -----   | -----                      | -----                 | -----                             |
| Neutron activation facility        | -----   | 1978 - int.  | 1975-<br>1980 - NASA                                    | -----                      | 1978 - int.           | 1987 - oN                         |
| Atomic absorption spectrometer     | 1984 - NSF  | 1980 - int.  | -----   | 1986 - int.<br>1986 - int. | -----                 | -----                             |
| ICP spectrophotometer              | 1987 - NSF  | -----  | -----   | -----                      | -----                 | -----                             |
| PIXE facility                      | -----   | -----  | -----   | -----                      | -----                 | -----                             |
| Transmission electron microscope   | -----   | 1987 - int.  | -----   | -----                      | -----                 | 1975 - P                          |
| X-ray fluorescence                 | 1982 - int.   | -----  | -----   | 1978 - int.                | -----                 | -----                             |

a Approximate year of acquisition and primary source of funding. Most NSF awards are cost-sharing, up to 50%. Instruments are those used by program PIs. Laboratories selected on basis of number of PIs. int. = internal funding.

b All instrumentation acquired from NASA funding, but Planetary Materials support (P) is distinguished from other NASA sources (oN), mostly JSC internal funds.

purchased since 1980. Considering only the five universities, these figures change to 6/47 and 1.

Despite the obvious handicap illustrated in Table 1, the quality of scientific research performed in the Planetary Materials and Geochemistry Program is very high. This is primarily because of the dedication and abilities of individual scientists, both in research and in being able to find non-NASA sources of instrumentation funding. However, as documented by Table 2, we have also been successful because to some extent we can list the results of very sophisticated foreign laboratories as accomplishments in our field. The numbers of instruments of different types given in Table 2 were obtained by an informal survey but should be reasonably accurate. As in Table 1, data for six laboratories emphasizing geochemical research are given. Of these six laboratories, five have major efforts in research on extraterrestrial materials. Only instruments acquired in the 1980s or upgraded to state-of-the-art capabilities are entered in Table 2, so a direct comparison of the total number of entries in Tables 1 and 2 is not fair. An appropriate U.S.-foreign comparison of state-of-the-art instrumentation is given in the final two columns of Table 2, where the sum of foreign instruments of a given type is tabulated along with the numbers of state-of-the-art instruments in Program laboratories, as compiled from Table 1. The foreign dominance in terms of number of instruments is large, and the gap is especially prominent in terms of the

Table 2. Summary of major analytical instrumentation in foreign laboratories (a).

|                                      | Univ. of Paris | Planck Inst. Mainz | Planck Inst. Heidelberg | Univ. of Bern | Cambridge Univ. | Australian Natl. Univ. | State-of-the-art instruments:<br>foreign Program |
|--------------------------------------|----------------|--------------------|-------------------------|---------------|-----------------|------------------------|--|
| Solid source mass spectrometers      | 3              | 5                  | ---                     | 2             | 2               | 2                      | 14 4   |
| Light element mass spectrometers     | 2              | ---                | ---                     | ---           | ---             | ---                    | 2 3  |
| Ion probes                           | 1              | 1                  | 1                       | 1             | *               | 1(*)                   | 7 1  |
| Noble gas mass spectrometers         | 2              | 3                  | 2                       | 4             | 3               | 2                      | 16 2   |
| Electron microprobes                 | 1              | 1                  | 1                       | ---           | 1               | 1                      | 5 4  |
| Scanning electron microscopes        | 1              | 1                  | 1                       | 1             | 1               | 1                      | 6 6  |
| Laser ionization mass spectrometers  | ---            | ---                | 2                       | *             | *               | *                      | 5 1  |
| Neutron activation facilities        | ---            | 1                  | ---                     | ---           | ---             | 1                      | 2 1  |
| Atomic absorption spectrophotometers | 1              | ---                | ---                     | 1             | ---             | ---                    | 2 4  |
| ICP spectro-photometers              | ---            | ---                | ---                     | ---           | ---             | 1                      | 1 1  |
| PIXE facilities                      | ---            | ---                | 1                       | ---           | ---             | ---                    | 1 0  |
| Transmission electron microscopes    | 1              | ---                | 1                       | ---           | ---             | 1                      | 2 1  |
| X-ray fluorescence                   | ---            | ---                | ---                     | ---           | ---             | 2                      | 2 1  |

a Number of instruments acquired since 1980 or upgraded to state-of-the-art.

\* Being purchased or developed.

most advanced instrumentation such as ion microprobes and laser ionization mass spectrometers. The same information and comparisons, compiled in the form of histograms, are shown in figures 1-5.

## II. THE FACILITIES APPROACH

Accepting that the present situation requires organizational changes, this report proposes the development of collective use laboratories, i.e., "facilities." For the purpose of this report a facility is defined as instrumentation and/or laboratories "open" to use of "qualified" members of the Planetary Materials and Geochemistry Program research groups in a hands-on, but user-friendly, mode. Facility scientists need not be research collaborators with outside users, but they can be. Many successful examples for this mode of operation with accelerators and telescopes can be cited.

In specific situations whether to adopt a facilities mode is strictly a matter of money. Below some level, \$10K at present, even Planetary Materials PI's can afford their own equipment (e.g. furnaces, polishing equipment). This level is unhealthy, and should be raised to about \$100K by regular core program instrumentation augmentations. At higher levels, \$100-500K(?), facilities installation and operation costs could be shared on a local or regional level (electron microprobes?). Above around \$500K(?), we must think of national facilities. It is our opinion that we must adopt the facilities mode or, at best, stand still. Ideally the

### **Figure 1**

This histogram shows the decade of acquisition of instruments utilized by PI's in the Planetary Materials and Geochemistry (PMG) Program for six U.S. institutions surveyed. The ordinate is number of instruments. Instruments acquired in the 1980s are regarded as state-of-the-art. Approximately 1/2 of the instruments utilized are of pre-1980 vintage, with some going back into the 1950s.

# Age of PMG Instruments

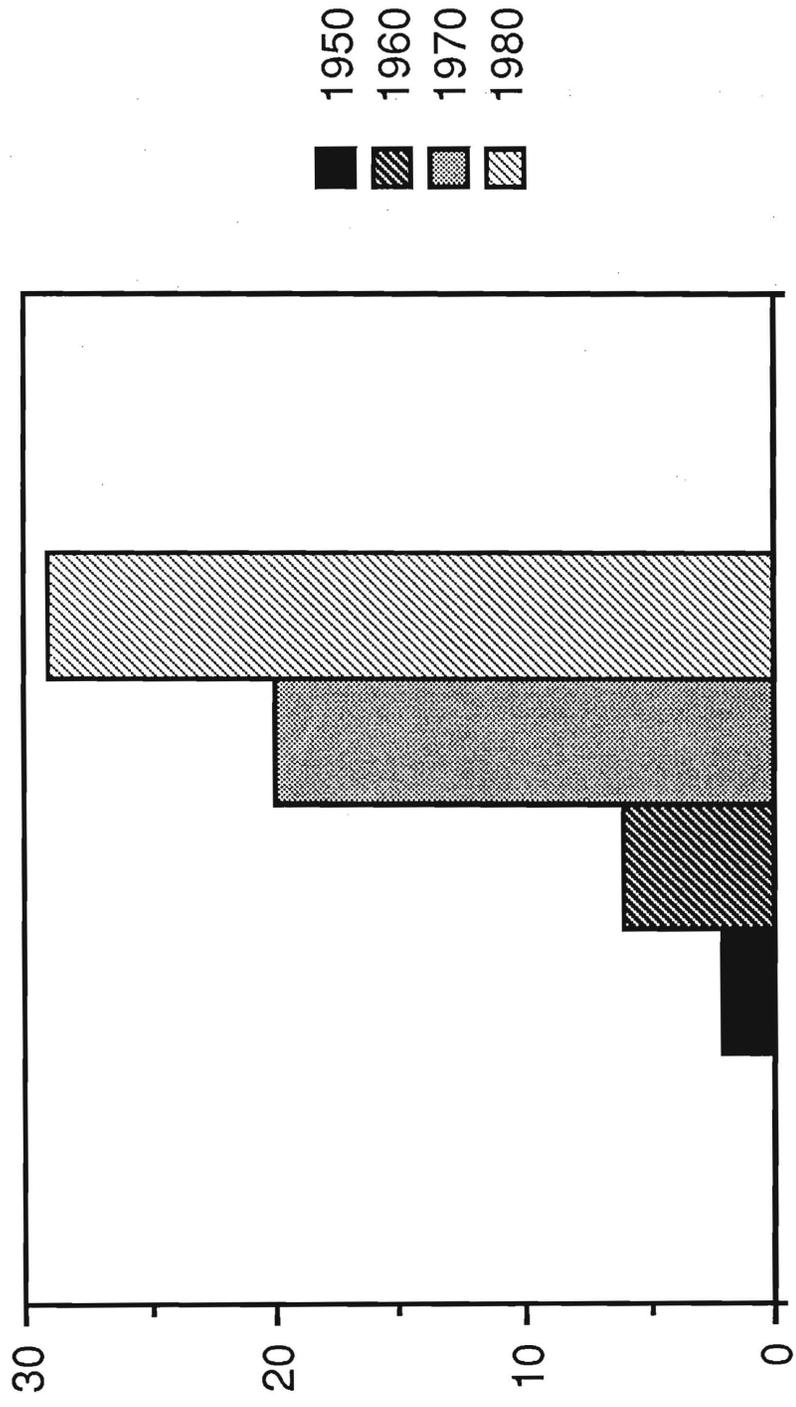


FIGURE 1

## Figure 2

This histogram shows the primary source of funding for the acquisition of the instruments used by the PMG Program institutions surveyed. The ordinate refers to number of instruments. The NSF is the most common source of other federal funding. Only a fraction of the instruments utilized were funded by PMG or previous NASA extraterrestrial materials analysis programs, including the Apollo program.

# Sources for Program Instruments

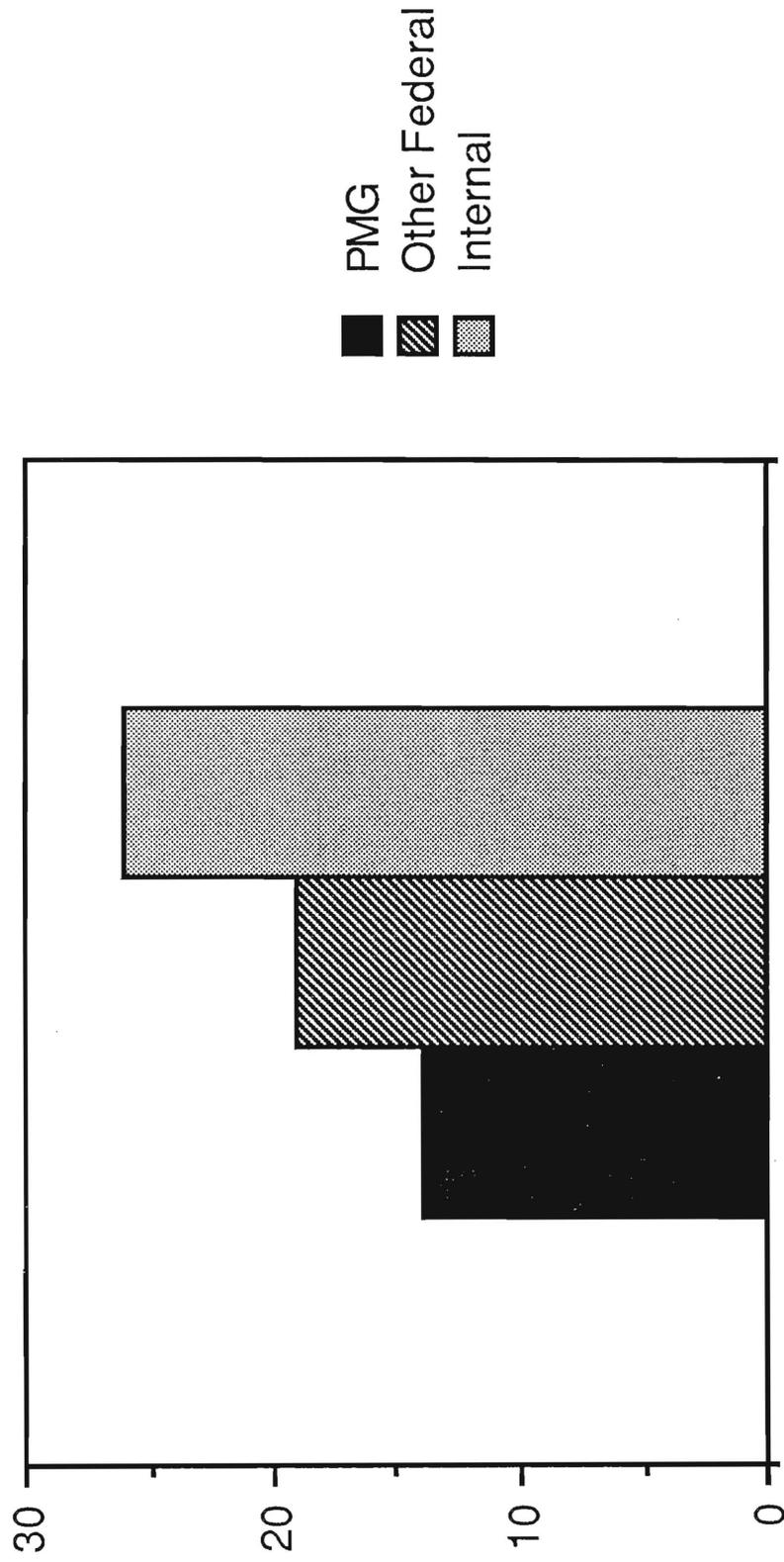


FIGURE 2

### **Figure 3**

This histogram is the same as Fig. 2, except that only state-of-the-art instruments are tabulated. Only a few modern instruments have been funded by the PMG program.

# Support for Program Instruments

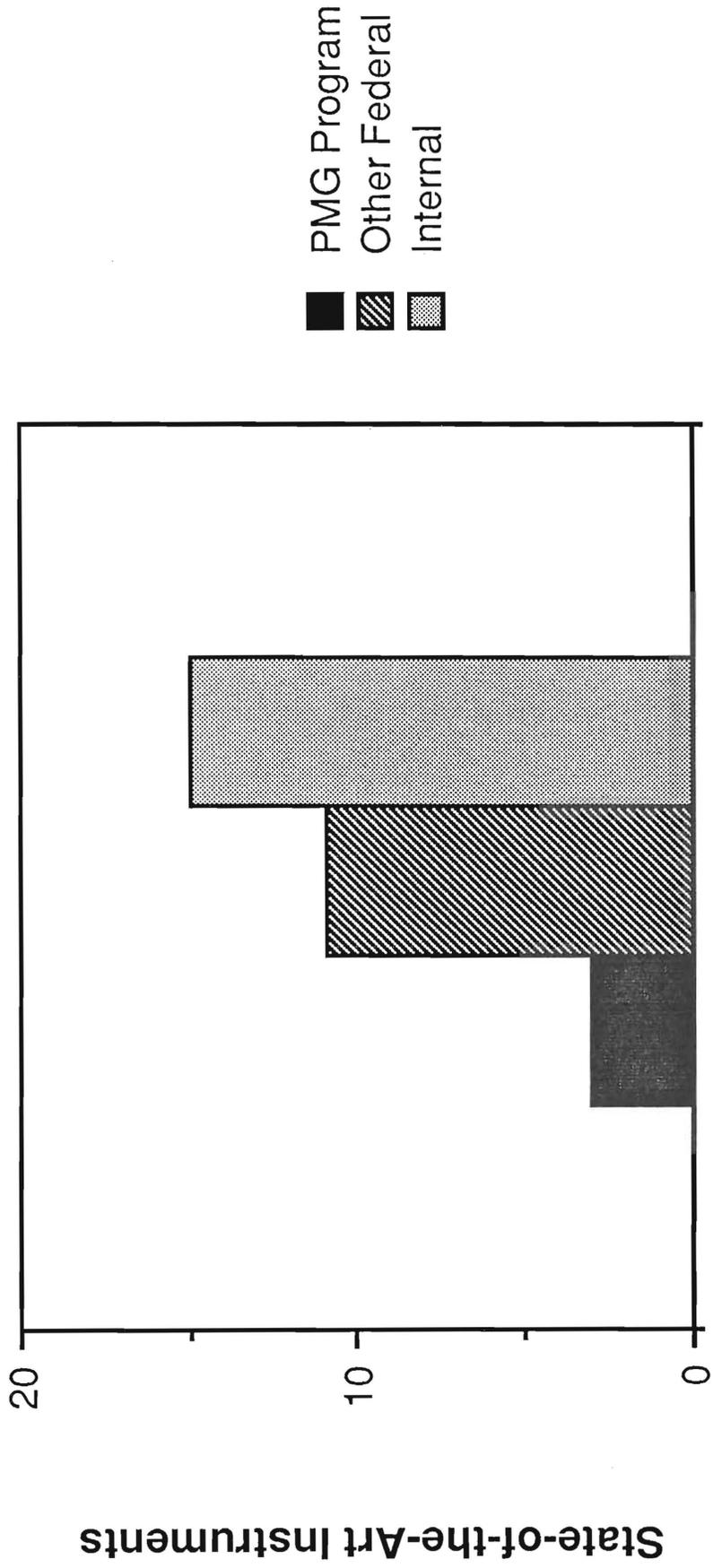


FIGURE 3

#### **Figure 4**

For 13 categories of instruments surveyed, the histogram compares the number of state-of-the-art instruments in six major foreign geochemical analysis laboratories with the 6 U.S. institutions surveyed. In essentially every category foreign laboratories are better equipped.

1. Solid Source M.S.
2. Light Element M.S.
3. Ion Probes
4. Noble Gas M.S.
5. Electron Microprobe:
6. TEM Facilities
7. Laser Ionization M.S.
8. Neutron Activation
9. Atomic Absorption
10. ICP Spectrometers
11. PIXE Facilities
12. TEM Facilities
13. X-Ray Fluorescence

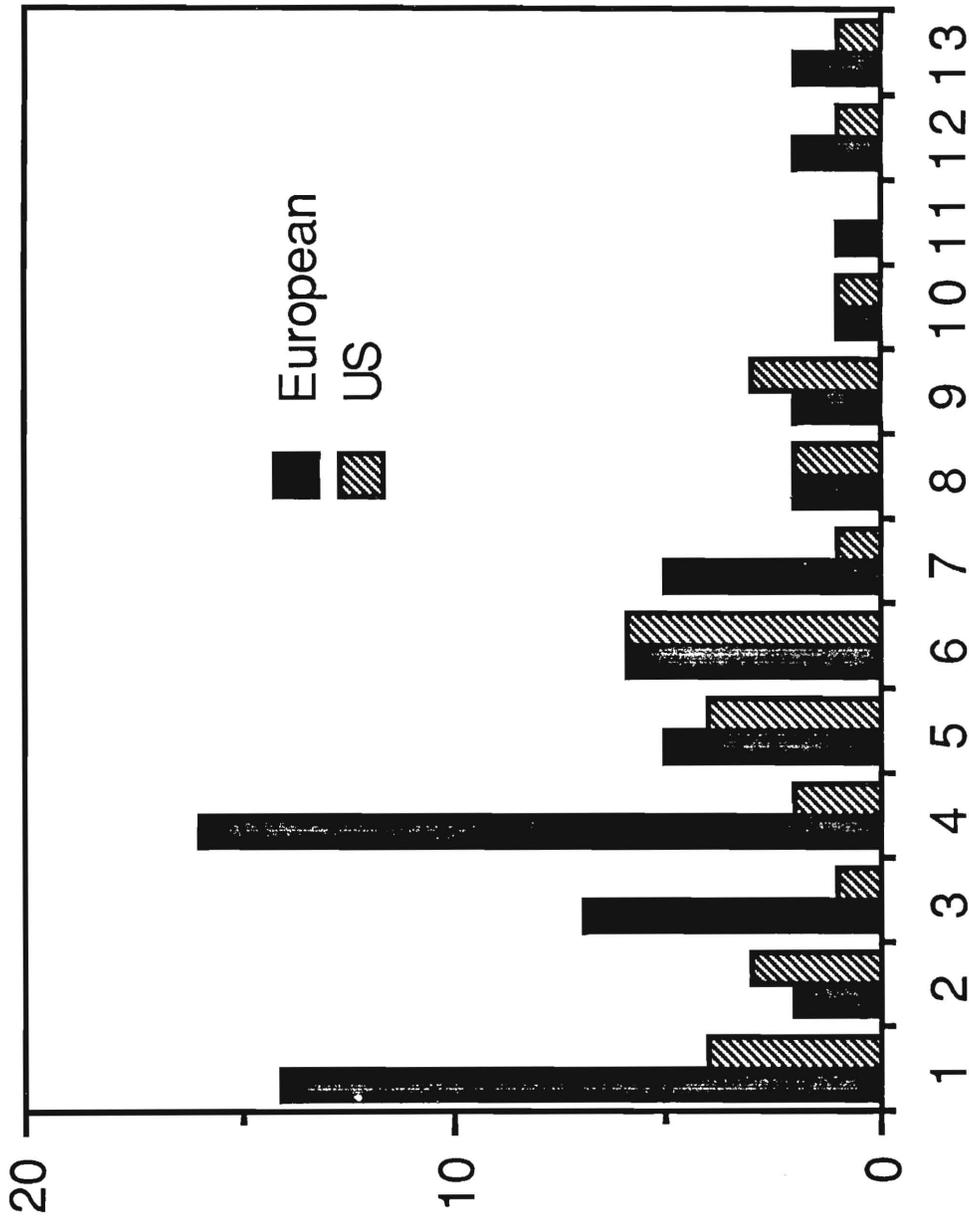


FIGURE 4

### Figure 5

Using the same format as in Fig. 4, this histogram consolidates the data into five major categories of instruments. Mass spectrometry in general is a core technique in PMG research, and the foreign dominance is very high. Ion microprobes and laser ionization mass spectrometry are discussed as advanced techniques for PMG in this report, but all of the foreign laboratories surveyed already have these instruments, at least in the development stage. The erosion of PMG capabilities is most clearly displayed in columns 1, 2, and 3.

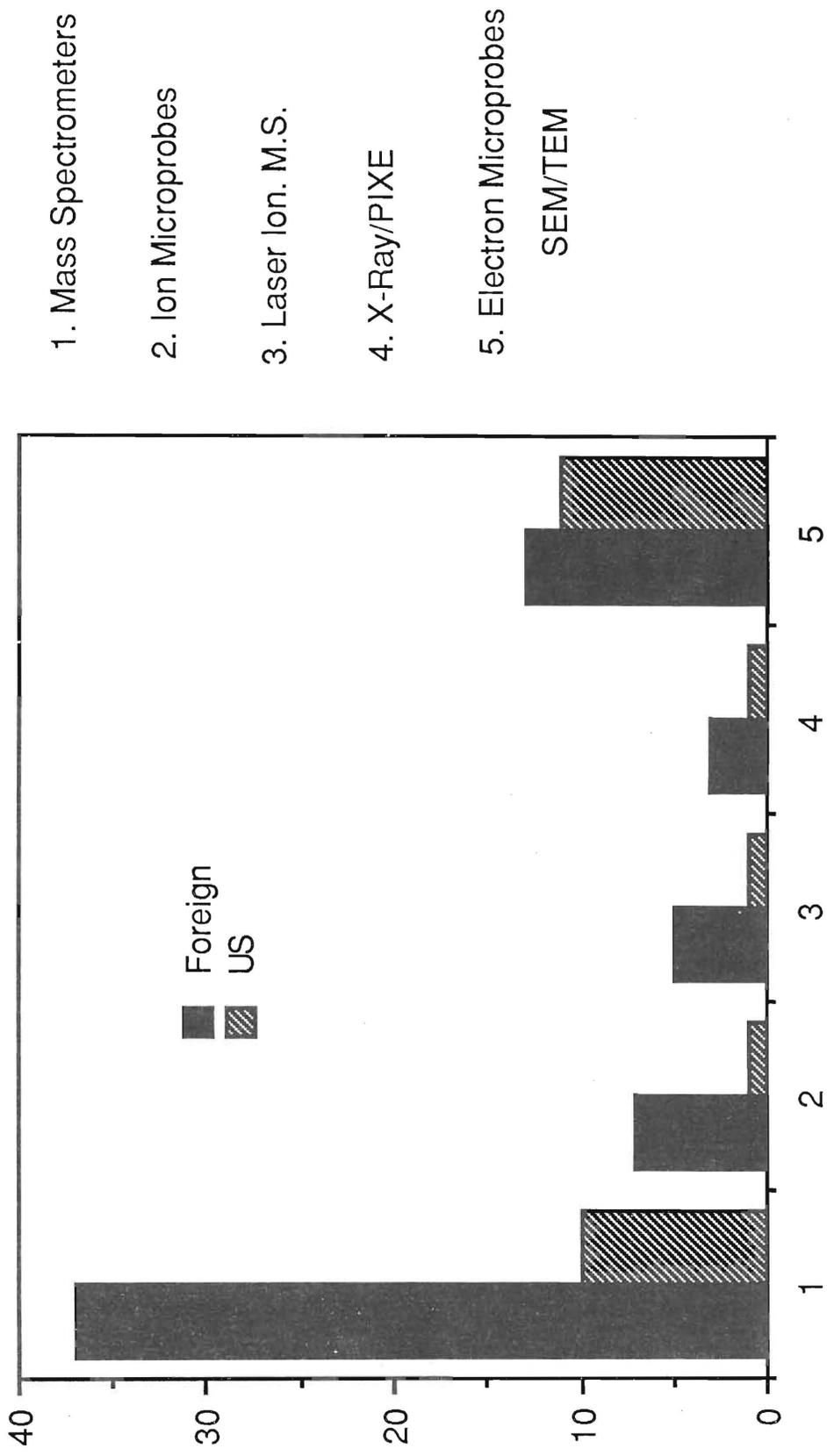


FIGURE 5

facility should be dedicated to planetary materials research, but compromises on this will probably be necessary in view of funding realities. Sharing of facilities with other research programs may also be desirable in some cases, because it may permit more convenient regional facilities.

### **III. UPGRADE/REPLACEMENT OF EXISTING INSTRUMENTS**

The present Program philosophy is, by necessity, "Maintenance/Repair" of laboratories at typically 1975-1980 levels. This philosophy has caused, and will continue to cause, an erosion of the importance of at least the laboratory analysis portions of our work. The increase in the number of overview/interpretational/modeling talks at our meetings is in part a reflection of this erosion.

Bringing our laboratories to 1988 state-of-the-art levels is of great importance. Although they have been unsuccessful, we acknowledge and appreciate the efforts made by our program managers to obtain equipment funding. These efforts are of great importance and should continue. However, in addition the Working Group recommends that "Advanced" facilities should be established. The advanced facilities are needed to unlock the secrets of extraterrestrial materials.

### **IV. ADVANCED FACILITIES**

"Advanced" is not a clean concept, but, as a working definition, it is either (1) a new technique or type of data or (2) an old technique with a major improvement in data quality. We regard improvements in old techniques that

provide greater amounts of data with essentially the same quality as in the past as "state-of-the-art".

Advanced facilities are probably best established by special one-shot funding in the name of the whole Program. Program augmentations for "equipment" are most appropriately allocated to individual PI's for state-of-the-art level improvements. Individual PI equipment and facilities should not be viewed as trade-offs; both are essential. It may be better to seek support separately for these two areas.

Because the advanced facilities would be major technical efforts, initial multiple-year funding would be essential. Much of the initial funding period would probably be spent in instrument development as opposed to analysis.

It must also be clearly understood that, eventually, the maintenance and operating costs of successful facilities must come from the annual program appropriation, and this must be allowed for in Program planning.

#### **V. RELATION OF ADVANCED FACILITIES TO PRESENT PROGRAM**

Proper selection of advanced facilities requires definition of the scientific objectives to be addressed and a philosophy concerning how the advanced facilities will relate to the existing research efforts. On these issues we recommend:

##### **A. Maintain the core program**

We must have an ongoing program that provides the scientific context to utilize sensibly any advanced technologies. The data from the core program will not be

obsolete; they simply need to be enhanced. Specifically by "core program" we mean primarily research based on data from: conventional ( $Z > 10$ ) electron microprobes, scanning electron microscopes, experimental petrology, thermal ionization mass spectrometry, gas mass spectrometry, and neutron activation.

#### B. Develop advanced facilities for small sample analysis

If we are going to understand the first-formed materials in the solar system and isolate pre-solar interstellar material from interplanetary dust particles, returned cometary material, chondritic matrix phases, fine-grained Ca-Al-rich inclusion (CAI) material, etc., the ability to analyze individual small grains is crucial. Equivalent capabilities are required to obtain complete chemical and isotopic characterization of individual mineral phases in planetary rocks or complex regolith/soil samples, as might be obtained from a Mars sample return mission. Ideally we need to be able to determine the mineralogical/structural properties as well as the chemical and isotopic abundances of any desired element on small grains.

In evaluating small grain analyses there are two important guidelines:

1. The number of submicrogram grains available for analysis is infinite. Therefore, sample selection/separation schemes ("petrography") are very important. But, even with great skill and cleverness in sample selection, it will be important to have rapid analytical throughput.

2. New instruments should complement the capabilities of

thermal ionization mass spectrometers and present generation Cameca-class ion probes. With respect to isotopic analyses that would complement thermal ionization mass spectrometers, the focus should probably be on techniques with high throughput, even at the expense of precision, i.e., the focus should be on searching for large (>1%) anomalies. For elemental analysis the emphasis should be on high sensitivity (<100ppm or <10<sup>11</sup> atoms, whichever is more appropriate), high accuracy (+-3%), and a broad element repertoire. To some extent the Cameca-class ion probes already accomplish at least the isotopic precision and sensitivity objectives, and the capabilities of any advanced facility must be evaluated relative to these instruments, as discussed further below.

A precise generic specification of "small" is difficult and probably not necessary at this stage. In essence the requirement is that there be a major improvement over present capabilities. The ultimate limit is the number of atoms of a given element. Consequently the limit depends on whether one is concerned with major or trace elements and whether isotopic or elemental analysis is the goal. For example a rare earth element at ppm levels in a 1 micron grain corresponds to roughly 10<sup>4</sup> atoms. Isotopic analysis with 1% or better precision would probably be impossible. An elemental analysis to about 3% would still be possible, but in most cases multielement analysis is desirable, thus the sample should not be consumed in the analysis of one element. For major elements, analysis of smaller grains is possible.

For example there are enough atoms in a 0.1 micron carbon grain for a C isotopic analysis. The most challenging task is the analysis of individual minerals in chondritic interplanetary dust particles which are in many cases closer to 0.01 micron in size and contain few atoms. Only transmission electron microscopy appears capable of functioning at this level. However, a 1 micron particle of this type contains  $10^6$  grains of 0.01 micron size. This is equivalent to a 1 g sample size for a rock with a 100 micron average grain size. From this point of view, "total rock" chemical and isotopic measurements of small polymineralic grains would still be important and interpretable, as well as being the only possible type of measurement.

## **VI. POSSIBLE FACILITIES: A STRAWPERSON PAYLOAD**

This list is ordered approximately in terms of technical feasibility. No other prioritization is intended. There is not a good correlation of feasibility and cost, and it would be important to develop a parallel cost ranking, but this is not attempted here. Also, it should be emphasized that everything below is the result of a brief committee study. More work would have to be done on most of the listed items before specific supplemental funding requests could be submitted.

### **A. Ion Probes**

By ion probes we mean a focused primary beam secondary ion mass spectrometer. Including these as advanced facilities is somewhat arbitrary because such instruments are already

making significant contributions and head any list ordered by practicality. As indicated above, present generation Cameca-class instruments already meet many of the desired specifications. These instruments are clearly here to stay, and continued Program support is important. Broader PI access to ion probes should be arranged. An additional facility could be justified, but the purchase, installation, and operation of present commercial instruments is very expensive. Further, such a proposal may not be viewed as very imaginative and might be hard to sell. Our recommendation is to propose new facilities that are different but complementary to existing Cameca-class instruments, but it should be emphasized that an advanced form of ion probe is not ruled out by this recommendation.

#### B. Induced X-ray microanalysis

Two viable techniques will be considered briefly: (1) synchrotron X-ray fluorescence (SXRF) and (2) proton-induced X-ray emission (PIXE):

(1) SXRF. Synchrotron radiation photons (10-100 keV) from a GeV-energy electron storage ring ("X-ray ring") can be collimated/focused to produce a small spot (potentially micron-sized) with sufficient intensity to induce usable rates of fluorescent X-rays from trace elements. In principle focusing can be combined with dispersion so that the incident synchrotron radiation spectrum can be controlled. A dedicated beam line at the Brookhaven National Synchrotron Light Source (NSLS) X-ray ring has been

established. The partial support from the Planetary Materials and Geochemistry Program given to the NSLS effort is important and should be continued. This facility is evolving to its ultimate configuration, and a relatively small, one-shot investment of equipment money would expedite installation of specific instrumentation (e.g., a microscope viewing system or a crystal spectrometer) important to us. A greater investment should also guarantee us a greater amount of beam time with what should be a very successful facility, but one which could potentially have a very high user demand.

(2) PIXE. Beams of Mev-energy protons can be highly focused with currents of up to 100 nanoamps on 10-100 micron spots. Ionizing proton-electron collisions result in secondary X-ray production analogous to an electron microprobe and with similar cross sections. However the signal-to-noise ratio is better for protons by factors of 10-1000 depending on details of the sample analyzed.

Several members of the Planetary Materials and Geochemistry Program have used the Los Alamos PIXE equipment on a special arrangement basis. Enough work has been done to demonstrate that useful quantitative data can be obtained, but it is not a user-friendly operation at present. This is a situation where a similar, relatively low cost arrangement with Los Alamos, as the Program now has with Brookhaven for SXRF, could guarantee significant access for Program PI's in a user-friendly environment.

(3) Comparison of SXRF and PIXE. The ultimate sensitivity

of SXRF is better, but at present both techniques have similar limitations set by the maximum total count rate and the relatively poor energy resolution of Si(Li) detectors. A major difference at present is that for SXRF the incoming photons and emitted X-rays are not strongly absorbed for trace elements heavier than Ni. To be infinitely thick, samples need to be millimeters in thickness. Consequently, at present, SXRF samples need to be on pure backing materials, or ideally unbacked, and need to be of known thickness, if not of mm thicknesses. PIXE depth resolution is set at 10-30 microns by proton energy loss. Polished thick sections can be analyzed, and it is quite possible that many previously prepared thin sections can also be used. Both techniques, but particularly SXRF, would benefit by the higher energy resolution of crystal spectrometers, because the depth resolution would now be set by the crystal spectrometer rather than by X-ray attenuation. Also, the complication of diffraction peaks in SXRF would be minimized.

(4) Comparison of X-ray and ion probe techniques. The basic physics determining X-ray production for both SXRF and PIXE is well understood, so there is no problem in principle in obtaining quantitative analyses, and present data analysis schemes have yielded good quantitative results. The situation for the ion probe is more complicated because the basic physics of the processes controlling matrix effects on ion yields is not adequately understood. However, studies to date on REE analyses in Ca-rich phases have been very

successful. At least empirically it appears that only relatively simple standards are necessary, at least in the systems studied, provided that analyses are confined to the high energy secondary ions. In any case some type of standard will always be required for ion probes but not for PIXE or SXRF. The general sensitivities of SXRF and ion probe (with strong energy filtering) are apparently comparable and higher than PIXE, although the potential sensitivity of SXRF has not yet been realized.

### C. Transmission Electron Microscopy (TEM)

Mineralogy and petrology studies of small particles and fine-grained regions in rock samples are essential, both for their own sake and for proper interpretation of the results of sophisticated chemical and isotopic measurements. Scientists of the Planetary Materials and Geochemistry Program have pioneered such multi-technique "consortium" studies for rare and/or complex types of lunar samples and meteorites.

Infa-red and visible spectrometry have made important contributions to the study of interplanetary dust particles, and advances in this area are possible. However, electron microscopy will probably remain as the primary characterization tool. Scanning electron microscopy (SEM) is an important reconnaissance tool, giving textural and chemical information on individual grains down to about 1 micron in size; however, this does not appear to be an important area for an advanced facility.

Modern TEM instruments can provide spatial resolution for both imaging and electron diffraction studies better than 10 Angstroms and this is clearly an important technique for small particle study. Many 1-10 micron particles can be considered as rocks and, in the case of interplanetary particles, contain an extremely large number of individual crystals and crystallites. There are obvious practical problems in individual grain studies, but these should certainly be a long-term goal.

The recent development of techniques for making ultrathin sections of small particles is a major breakthrough, permitting a petrological as well as mineralogical approach to the study of small particles.

As Table 1 shows, TEMs are much less utilized by the Planetary Materials and Geochemistry PIs surveyed than is the case for SEMs. This is a valid conclusion for the Program as a whole. Thus, a Planetary Materials and Geochemistry TEM facility appears justified. This is not without precedent, as the NSF has extensive experience in the organization and management of TEM centers.

A current limitation with the study of small particles is that most work is done in a piggy-back mode with other TEM studies. There are relatively few instruments dedicated and staffed adequately for such work. Any desired instrumental modification can only be made with great difficulty. In a typical situation instrument time is allocated in half-day sessions. Samples must then be removed so someone else can

use the TEM, and days may pass before more time is available. A dedicated Program instrument deserves serious consideration.

Our basic conclusion is that state-of-the-art instruments with X-ray and electron energy loss analysis capabilities (AEMs) would probably be adequate. What is required is increased access by Program scientists. The study of small particles is difficult and specialized at present. Also, because TEM work itself is sufficiently mysterious to the average PI, the presence of an experienced, well-trained facility support staff would be especially important for a TEM facility.

Nevertheless, there are some advanced features that should be considered:

(1) Improved vacuum. Most current TEMs operate in the  $10^{-6}$  torr range, but instruments are available that have three orders of magnitude lower pressure. Advantages of such instruments are (a) less contamination, which is important in general, but especially significant for the study of carbonaceous materials and (b) more control of radiation damage effects.

Chemical reactions occur on sample surfaces under electron bombardment. The rates are highly dependent on chemical environment but can best be understood and controlled when adsorbed gases and carbonaceous deposits are minimized. This is best done with high vacuum operation. Limitation of radiation damage is critical for materials that are unstable

in the electron beam, as are some of the interplanetary particle phases.

(2) Higher energies. Most current TEMs operate at 100-200 keV, although higher voltage instruments are available. In principle higher energy electrons (smaller wave lengths) give better resolution. However some high voltage instruments are not optimized for high-resolution work, and so are of limited utility for the purposes of this report.

A major advantage of higher energy instruments is the ability to study thicker samples, although the use of ultra-thin sections makes this issue less significant. Other features of a higher energy instrument of possible significance are: (a) larger lateral areas can be imaged and (b) sample heating and radiation damage may be significantly reduced, thereby making a broader range of materials accessible to study. Also, larger currents may be used, making X-ray analysis more efficient and sensitive.

(3) Improved sample handling. This is a general need for all types of small particle study. For TEM work computer-controlled stages are required that would permit preliminary imaging and analysis. Such stages are widely available for SEMs, but requirements for control may be tighter for TEM work. It may also be useful to have an adjacent sample handling chamber so that material is not lost during transfers.

(4) Advanced analysis capabilities. Spectroscopic methods for studying surfaces, e.g., Auger electrons, should be

considered, although there may be problems on rough surfaces.

#### D. Accelerator Mass Spectrometry

This technique is already relatively well-established for high abundance ratio measurements as applied to  $^{14}\text{C}$ ,  $^{10}\text{Be}$ ,  $^{26}\text{Al}$ , etc. Such data have already made interesting and important contributions to our program. Program PI's have been able to gain access to existing facilities; further, there appears to be outside commitments to support such facilities. Consequently any effort in this area should focus on different goals, e.g., an ion probe with an accelerator as the mass spectrometer.

#### E. Advanced Mass Spectrometry

A large number of options are possible here, and the committee has not made a detailed study of these. In general, however, this area appears to have great promise. Most options discussed below are based on the use of laser resonance ionization because of the possibility of high sensitivity due to efficient, ideally 100%, ionization. Basic physics of resonance ionization mass spectrometry. Sample atomization is required. This can be done by (1) thermal evaporation, (2) ion beam sputtering, or (3) laser or electron volatilization. A laser then photoionizes specific elements by resonance ionization. Atomization with sputter ions or by laser volatilization appears much superior to thermal evaporation because high power laser beams must be pulsed, and synchronization of the atomizing and ionization is possible with methods (2) and (3).

Laser ionization from the atomic ground state is carried out in at least two steps: first, element-specific resonance excitation from the ground state to an excited state, and then absorption of one or two more photons to cause ionization. The photon energy required for the resonance excitation differs for each element, eliminating both isobaric and molecular mass interferences. This technique has high elemental sensitivity because the photoionization can be made essentially 100%, so it is plausible to expect that a high fraction (order 10%) of the atoms of a given element can be detected. Claims have been made that all elements, with the exception of He and Ne, can be analyzed in this way, and such claims seem to be borne out in practice.

There are two major problem areas: First the resonance excitation photon wave lengths for many elements lie in the ultra-violet or vacuum ultra-violet. Such wave lengths can be reached only by frequency multiplication and tuned dye lasers, involving relatively complicated and costly sets of processes. The least expensive approach is to use photons whose energies are exactly one-half of the required excitation energy. Excitation is then produced via an intermediate virtual state (i.e., one photon excitation to 1/2 the required energy), which lasts long enough to absorb a second photon, completing the transition. However, large photon fluxes (laser power) are required which cause line broadening and produce interferences, especially from molecular ions, reducing selectivity. Secondly, a separate

excitation scheme is required for each element, complicating multielement analysis. Some relief can be found in that the tuning range of dye lasers overlaps the excitation energies of large groups of elements. Nevertheless, four separate laser systems would probably be required for reasonable elemental coverage, and rapid re-tuning would be a feature that would need to be developed and incorporated into a useful system.

Noble gases present the greatest difficulty because the first excited states are very energetic. For Xe and Kr the more complicated and more costly approach is to do the mixing out of the active region with four-wave mixing. Multi-photon processes, involving repeated excitation and detection of single atoms have been demonstrated for Kr. Also, resonant charge exchange processes can eliminate some of the laser complexity in special cases. For example, excitation of a specific Kr or Xe transition can be induced by interacting an ionized sample with Cs atoms. Near-resonant charge exchange will occur leaving the neutral Kr or Xe in a range of excited states; however, most of these will decay to a metastable state accessible to photoionization with laser photons. A sweeping field is required to remove the remaining ions before photoionization.

Possible Instruments. Given a large number of options the proper approach would be to formulate the most important class of problems to be addressed and to use this as a means of setting design priorities for facilities components.

Proceeding from the discussion in Section V.B., a list of possible advanced mass spectrometric instruments is given below. This is not a complete list, but these options are regarded by the Working Group as the most promising. It is conceivable that all the desired features could be combined in one instrument, although this appears difficult. No prioritization is intended in the following order:

(1) Resonance ionization mass spectrometer using sputter or laser atomization with design emphasis on small spot (0.1 micron) isotopic analysis.

(2) Resonance ionization mass spectrometer with "conventional" (10 micron) spot size with design emphasis on isotopic ratio precision.

(3) Noble gas resonance ionization mass spectrometer.

(4) High sensitivity mass spectrometer for high accuracy isotopic dilution analysis:

(a) with resonance ionization,

(b) with accelerator,

(c) with plasma ion source.

(5) Ion cyclotron resonance (Fourier transform) mass spectrometer.

Discussion. Numbering in this section refers to entries in the advanced mass spectrometer instrument list above:

(1) The primary objective here would be to distinguish individual interstellar grains in small meteoritic or interplanetary particles by their anomalous isotopic compositions. Very large isotopic variations might be

expected, so high precision mass spectrometry is probably not essential, but given the small number of atoms in a 0.1 micron grain, high sensitivity is important. In general the required sensitivity would be about  $10^4$ - $10^5$  atoms of the less abundant isotopes of the major lithophile elements, C, and O.

(2) This is essentially a state-of-the-art ion probe with a resonance ionization mass spectrometer. Allowing for the capabilities of present-generation Cameca-class ion probes, the primary science objective would be to utilize the elemental specificity of resonance ionization to make isotopic abundance measurements for nuclei involved in the isobaric decays used for dating, e.g.,  $^{87}\text{Rb}$ - $^{87}\text{Sr}$ ,  $^{176}\text{Lu}$ - $^{176}\text{Hf}$ ,  $^{187}\text{Re}$ - $^{187}\text{Os}$ , etc. This might permit single grain age measurements. The size grain that could be analyzed would depend on trace element levels. The major experimental problems would be to obtain highly reproducible mass fractionation and to obtain adequate accuracy in concentration measurements.

(3) For noble gases resonance ionization has the potential for few atom detection limits because of the possibility of multiple interrogation of the gas atoms in a laser cell. A disadvantage is that analysis of He and Ne would not be possible; however, with clever laser design, analysis of molecular gases might be possible. Design sensitivity requirements of about  $10^4$  atoms of heavy noble gases can be set in relation to existing techniques. There may be major problems in sample extraction, background and contamination

problems, and this type of instrument may be best left in the hands of individual PI's, rather than operated as a facility.

(4) This instrument would be designed for trace element analysis of small particles, either individual mineral grains from a rock or whole interplanetary particles. It may be that major element analysis of individual phases in small (<30 micron) multiphase particles can best be done by electron microscopy. But it will still be important to get accurate (e.g., 5% standard deviation or better) "total particle" chemical data for both major and trace elements. The need for the instrument discussed here can be seen by contemplating the problem of measuring a rare earth element pattern of a one micron grain of chondritic composition. Ideally one would like the total pattern, but, e.g., there are only 1000 Tm atoms. (Fortunately, there are 1000 times more Tm atoms in a 10 micron grain).

The basic idea is to dissolve the sample in the presence of multielement isotopic tracers, then deposit the dissolved sample in an approximately 1x1 mm area for isotopic analysis or inject the dissolved sample directly into a plasma ion source. For larger grains an ion probe or an electrostatic accelerator [options (b) and (c)] can be used for mass analysis, and some ion probe measurements using this approach have already been made. If deposition is on a metallic substrate, negative secondary ions can be used, which improves yields for some elements relative to the positive secondary ions typically used in ion probe work.

The accelerator has the advantage that it might be cheaper to set up a facility with this approach, especially if an existing accelerator is adapted. Use of multiple detector arrays or position-sensitive detectors after mass analysis could greatly increase analytical efficiency, and this may be more easily done with the MeV ions from an accelerator. The accelerator also has the advantage of being able to break up molecular ions.

Present inductively-coupled-plasma mass spectrometers using solution injection do not have sufficient sensitivity for the applications discussed here but could be useful for mg-sized samples because of the large number of elements that can be analyzed. Graphite furnace evaporation into the plasma ion source apparently has much greater sensitivity, and this approach might deserve further study.

For grains larger than 10 microns the induced X-ray techniques are competitive for bulk analyses. For grains smaller than 1-10 micron the potential sensitivity of resonance ionization is probably required. With experience it may be that a few isotopic ratios are sufficient for a good analysis, and throughput can be enhanced, at least for a given element.

The required chemical dissolution and spiking would require a parallel major effort in development of nanochemical techniques, even though the steps are conceptually very simple. Chemical processing blanks could be the practical limitation in this whole approach. Despite

these serious disadvantages, there is also an advantage here in that this type of analysis is well suited for a facility instrument. PIs can develop, either individually or collectively, nanochemical modules to process samples in their own laboratories, which will be then taken to the facility for analysis.

(5) Fourier transform mass spectrometry utilizes the mass dependence of the cyclotron resonance frequency of an ion undergoing circular motion (for a charge  $q$  in magnetic field,  $B$ , frequency =  $qB/m$ ). An element is ionized and injected into the magnetic field at a well-defined energy. Resonance ionization could be used as an efficient ion source. The ions are then accelerated in conventional synchrotron fashion by "chirping" the magnetic field. Each isotope orbits at its own specific frequency, and a time varying current is sensed by electrodes on the vessel walls. A frequency (mass) spectrum is obtained by taking the Fourier transform of the time-varying current. Each frequency component represents one specific isotope. The obvious advantage of this technique is that each ion can be sensed many times, increasing potential sensitivity.

At present there are a number of problems. Existing cells cannot contain more than about  $10^6$  total ions before the mass resolution is severely limited by space charge effects. This prevents measurement of low abundance isotopes in the presence of high abundance isotopes. Thus the injected ion population must be extremely clean, and for this reason, a

resonance ionization source would appear essential. It may also be difficult to get precise (even 1%) isotopic ratios, because the "peak" shape is inherently unfavorable, and present studies indicate non-linear and variable isotopic mass fractionations.

Summary. No specific Committee recommendation on the various possible options is made except that more study on each would be warranted. Combining resonance ionization, a small spot sputter source, and a suitable mass spectrometer might result in the ultimate ion probe facility. This would be quite expensive, and it may be that more modest initial steps should be taken, e.g., a resonance ionization facility based on the analysis of chemically-processed spiked samples with large area sputter atomization. The experience gained here, at a more modest cost, could be the basis for future growth.

## VII. RECOMMENDATIONS

The major conclusions and recommendations are contained in the summary section of the report. Although promising areas have been identified, the Planetary Materials and Geochemistry Working Group has not studied these options in sufficient detail to endorse specific new projects. (Program facility support is already being given for SXRF).

We do, however, endorse the facilities concept. A more thorough examination of the above areas, and perhaps others, could be carried out by small "study groups." Although not official proposals, the reports of these study groups should contain sufficient technical and budgetary detail that they could be used by Program managers to apply for supplemental funding from combinations of various internal NASA sources or, in the case of larger projects, as direct items in the Agency budget. The study groups could be organized by PI initiative or with management help and don't necessarily need to be subsidized by Program funds. In any case the study groups need not wait for official approval before acting.

In general a facility should serve at least 5-10% of the Planetary Materials and Geochemistry PI's, and ideally the study groups should contain about 3-5% of the PI's.

We also recommend that program managers seek to have such facilities defined as "flight instruments" and be eligible for competition in flight instrument development programs. The justification for this is strong: such facilities are required to complete successfully future NASA missions that involve sample return.

Planetary Materials and Geochemistry Working Group membership  
during preparation of this report

- K. Burke  
Lunar Planetary Inst.
- D. Burnett  
California Inst. of Technology
- P. Buseck  
Arizona State U.
- M. Drake  
U. Arizona
- T. Grove  
Mass. Inst. of Technology
- C. Hohenberg  
Washington U., St. Louis
- O. James  
U.S. Geological Survey
- G. Lugmair  
U. Calif. San Diego
- L. Rancitelli  
Battelle

