Invited Review

Small is beautiful: The analysis of nanogram-sized astromaterials

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Abstract–The capability of modern methods to characterize ultra-small samples is well established from analysis of interplanetary dust particles (IDPs), interstellar grains recovered from meteorites, and other materials requiring ultra-sensitive analytical capabilities. Powerful analytical techniques are available that require, under favorable circumstances, single particles of only a few nanograms for entire suites of fairly comprehensive characterizations. A returned sample of >1000 particles with total mass of just 1 μg permits comprehensive quantitative geochemical measurements that are impractical to carry out *in situ* by flight instruments. The main goal of this paper is to describe the state-of-the-art in microanalysis of astromaterials.

Given that we can analyze fantastically small quantities of asteroids and comets, *etc.*, we have to ask ourselves, how representative are microscopic samples of bodies that measure a few to many kilometers across? With the *Galileo* flybys of Gaspra and Ida, it is now recognized that even very small airless bodies have indeed developed a particulate regolith. Acquiring a sample of the bulk regolith, a simple sampling strategy, provides two critical pieces of information about the body. Regolith samples are excellent bulk samples because they normally contain all the key components of the local environment, albeit in particulate form. Furthermore, because this fine fraction dominates remote measurements, regolith samples also provide information about surface alteration processes and are a key link to remote sensing of other bodies. Studies indicate that a statistically significant number of nanogram-sized particles should be able to characterize the regolith of a primitive asteroid, although the presence of larger components (*e.g.*, chondrules, calcium-aluminum-rich inclusions, large crystal fragments, *etc.*) within even primitive meteorites (*e.g.*, Murchison) points out the limitations of using data obtained from nanogram-sized samples to characterize entire primitive asteroids. However, the most important asteroidal geological processes have left their mark on the matrix, because this is the finest-grained portion and therefore most sensitive to chemical and physical changes. Thus, the following information can be learned from this fine grain size fraction alone: (1) mineral paragenesis; (2) regolith processes; (3) bulk composition; (4) conditions of thermal and aqueous alteration (if any); (5) relationships to planets, comets, meteorites (*via* isotopic analyses, including O); (6) abundance of water and hydrated material; (7) abundance of organics; (8) history of volatile mobility; (9) presence and origin of presolar and/or interstellar material. Most of this information can be obtained even from dust samples from bodies for which nanogram-sized samples are not truly representative.

Future advances in sensitivity and accuracy of laboratory analytical techniques can be expected to enhance the science value of nano- to microgram-sized samples even further. This highlights a key advantage of sample returns—that the most advanced analysis techniques can always be applied in the laboratory and that well-preserved samples are available for future investigations.

INTRODUCTION

We are entering a new and golden age of sample return missions. In the coming decade, we will harvest samples from Comet P/Wild II and interstellar dust courtesy of the Stardust mission (Brownlee *et al.*, 1997), asteroid 1989ML by the ISAS Muses-C mission (ISAS, 1996), and solar wind by the Genesis mission. A sample return from Mars is also envisioned as early as 2008. It is, however, sobering to realize that Muses-C aims to return 3–10 g of sample, Stardust will provide micrograms of comet and interstellar dust, and Genesis will harvest only few micrograms of atoms. The diminutive size of the returning samples may be a source of concern for petrologists used only to looking at hefty lunar rocks and meteorites.

From the Apollo missions, the new resource of 380 kg of lunar samples drove development of new, more sensitive and precise sample analysis techniques. We might expect the same thing to occur for

Stardust and Muses-C samples. However, we cannot assume that these developments will occur, given the different political climate for science as compared to 30 years ago. Now is the time to push developments of new analysis techniques and increase the precision and sensitivity of existing instruments.

Despite the fact that some future missions will be returning gram-sized quantities of sample, not micro- or nanogram quantities, the samples will nonetheless be precious and should be treated as such. Approaching analyses this way will ensure that the samples receive the greatest possible dissemination, while at the same time guaranteeing that adequate material will remain following the preliminary classification to curate and thus be available for future instrument developments we all desire. Also, if we can conclusively tie a specific meteorite type to any returned sample, then we can always turn to meteorites for further characterization of larger petrographic features that might be lacking in the space-returned samples.

NOBLE GASES BY MASS SPECTROSCOPY — Solar Exposure History

TEM / LAM-ICPMS / ION PROBE / ATOMIC FORCE MICROSCOPY / OPTICAL SPECTROSCOPY — Mineralogy, Petrography, Composition; Composition; Origin and History of Elements; Atomic and Magnetic Structure; Molecular Structure

ORGANIC CHEMISTRY BY MASS SPECTROSCOPY AND PHONON SPECTROSCOPY — History of Carbon, Origin of Life
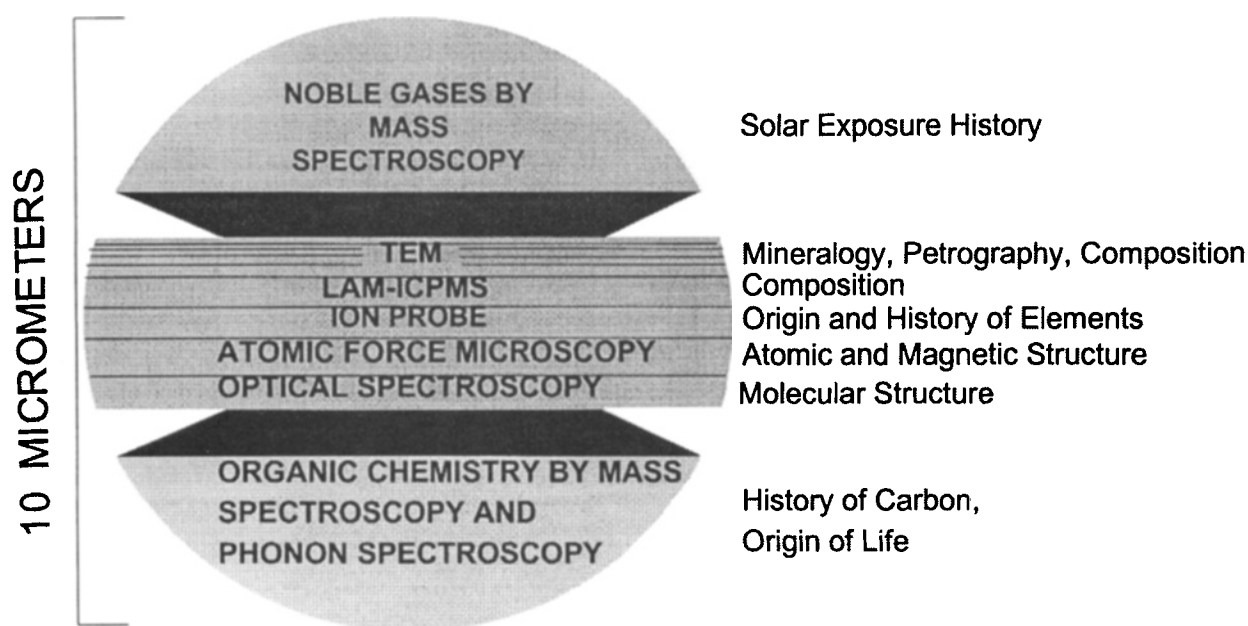
10 MICROMETERS

FIG. 1. A schematic showing the incredible amount of information that can be gained from careful dissection (by ultramicrotome) and consortium study of a single grain measuring 10 μm. Not all applicable techniques are even shown.

In Fig. 1, we present a schematic showing the incredible amount of information that can be gained from careful dissection (by ultramicrotome) and consortium study of a single grain measuring 10 μm (~1 ng) as an introduction to the state-of-the-art of study of fine-grained materials. Since 1981, NASA has supported asteroid and comet science by collecting dust grains from these bodies in the stratosphere and making them available for analysis in laboratories worldwide (Warren and Zolensky, 1994). Over the succeeding 17 years, many new techniques have been developed for these painstaking analyses by at least 24 different laboratories across the globe. Despite the fact that the particle supply has always exceeded the demand, the painstaking efforts required for most of the nanoscale analyses have resulted in only 1520 grains having been analyzed, with a total mass of only 0.52 μg. The work reported by Thomas *et al.* (1995) is a perfect example of this consortium mode of interplanetary dust particle (IDP) research, wherein six different analytical techniques in different laboratories were applied to a single, complex particle.

The purpose of this paper is to answer the following fundamental question: How much sample is really needed to achieve prime science objectives, while maintaining a cost-effective mission (Discovery class)? The range of geological processes that we will want to address with these samples is staggering, encompassing not merely the entire history of the solar system, but the history of the elements themselves. The interstellar processes include element formation, production and interactions with radiation, formation of organics, grain condensation and evolution, and interactions with magnetic fields. In the preaccretionary (nebular) environment, we wish to understand grain condensation, evaporation and recondensation, shock, radiation processing, solar energetic particle implantation, gas composition, the magnetic environment, and the evolution of organics. Finally, for solid bodies, we wish to examine accretion history, shock, brecciation, impact gardening, metamorphism, aqueous alteration, weathering, exposure history, volcanism, fumarolic activity, differentiation, the magnetic environment, atmosphere evolution, and the evolution of organics.

SAMPLING AND ANALYSIS MISSIONS

Missions In Preparation

There are several funded (*i.e.*, "real") missions at some stage of development that will return samples for analysis back on Earth over the next eight years. These are described here in the order of their delivery date to Earth.

Genesis–Genesis is a NASA Discovery mission to collect and return to Earth ~5 μg of solar wind atoms (for C through U, as the lighter atoms are of little interest here). Although the spacecraft is scheduled to lift off in 2001 and return to Earth in 2004, the launch period is very flexible, because the Sun is relatively fixed. The spacecraft will be inserted into a halo orbit about the L1 Lagrangean point (0.01 AU from Earth) where collector arrays will be exposed to the solar wind. During an approximately two year exposure period, solar wind atoms will impact and be implanted into ultrapure Si wafers, as well as a few other materials. Considerable efforts are being made to ensure low contamination levels both before and following solar wind collection. Following collection, the Si wafers will be stowed into a sample return capsule for return to Earth at the Utah Test and Training Range (UTTR). These samples will then be transported to a new curation facility located at NASA's Johnson Space Center (JSC) and will be handled, dissected, and curated in dry nitrogen.

This is not the first return to Earth of solar wind material, having been done on the surface of the Moon during the Apollo missions. However, the collection duration will be orders of magnitude longer for *Genesis*, and contamination concerns are (this time around) paramount. The highest priority measurement is stated to be the solar wind O-isotopic ratios, which will be measured to $\pm 1‰$ (Wiens *et al.*, 1999). Also, while collecting solar wind, the collection surfaces and surrounding structures will also be impacted by interplanetary dust particles (IDPs) and β-meteoroids. Efforts will be made to study the impact residues resulting from these impacting

asteroidal and cometary particles, although nothing has been done to mitigate the detrimental effects these particles suffer during impact.

Stardust–Another NASA Discovery mission, Stardust will be the first sample return from a comet. Grains from a comet's coma will be collected into high-purity silica aerogel. The mission was launched on 1999 February 7. Thus, it launched well before *Genesis*; however, it returns later. The *Stardust* spacecraft will perform two swing-by orbits of the Earth to gather sufficient speed to reach the comet under optimal encounter conditions. The spacecraft reaches Comet Wild II on 2004 January 10 (or more properly, the comet, being faster, passes the spacecraft at this time). During passage through the cometary coma, a tray of silica aerogel is exposed, and coma grains impact on it and are captured (Fig. 2). At the encounter velocity of 6 km/s, the grains will be decelerated as they pass into the aerogel and come to rest there in a reasonably intact state (Barrett *et al.*, 1992; Hörz *et al.*, 1998). It is anticipated that ~1000 grains measuring <100 μm will constitute the harvest. In fact, the majority of the sample will be under 10 μm, and no grains larger than a few hundred micrometers should be collected. The closest passage of the spacecraft will be engineered so that larger, potentially deadly grains are not encountered. Following the coma passage, the aerogel tray is closed for return to Earth.

There is also a dust impact mass spectrometer (CIDA, for cometary and interstellar dust analyzer) on board the *Stardust* spacecraft, provided by J. Kissel and the Max Planck Institute. This instrument is an improvement on the one that flew on the Giotto mission to comet Halley a decade ago (Kissel and Krueger, 1987), having a larger target area, better telemetry capabilities, and is calibrated for the lower dust impact velocities that it will experience (the instrument on board *Giotto* could never be calibrated at the actual, very high dust impact velocities). The CIDA spectrometer will be used to gather spectra of dust during the entire mission, including the coma passage. This instrument will be the best chance to obtain data on volatile grains, because the material collected in the aerogel will be heated and shocked significantly during the collection process. The CIDA instrument will also be used to study the composition of interstellar grains

There is also a third type of collection for *Stardust*. In the past five years, analysis of data from dust detectors aboard the *Ulysses* and *Galileo* spacecraft have revealed that there is a stream of interstellar dust flowing through our solar system (Grun *et al.*, 1993). These grains, of unknown mineralogy, generally measure <1 μm, and so are impossible to collect at Earth by current techniques. Approximately 100 of these grains will be captured during favorable periods of the cruise phase of the Stardust mission (*i.e.*, during the five years the spacecraft spends getting to the comet). Analysis of these particles will represent the most difficult challenge of the post-flight operations. The sample harvest from *Stardust* will thus consist of ~1000 cometary grains, measuring <100 μm each, and ~100 interstellar grains of mostly submicron size. The total mass of returned sample will be on the order of 1 mg. Previous robotic analysis of Halley dust, and experience with IDPs in the lab (some of which must be cometary) show that the grain size of cometary matter extends down to the nanogram-scale and may in fact be primarily at this level. Therefore, it appears that the types of analyses described in this paper will be very well suited for any returned cometary sample.

The sample return capsule will be open to air during atmospheric entry, which will occur in 2006 February, and will land at UTTR in western Utah. The capsule will be placed into a dry nitrogen environment immediately upon recovery on the Earth's surface and will be immediately flown to the curation lab at JSC. Approximately six months of preliminary investigation by a dedicated team will precede release of the sample to the general analysis community. This preliminary investigation period has the goal of documenting the initial state of the collected sample, identifying the range of samples present, and assessing the best way to proceed with general sample distribution and analysis. We have already demonstrated the ability to remove IDPs from aerogel, using collectors exposed on the MIR space station (Hörz *et al.*, 1998). We were successful in embedding, slicing, and analyzing grains as small as 0.5 μm; this is how we routinely prepare IDPs for transmission electron microscope (TEM) characterization, and we had previously developed these specific techniques for use with mineral grains captured in aerogel
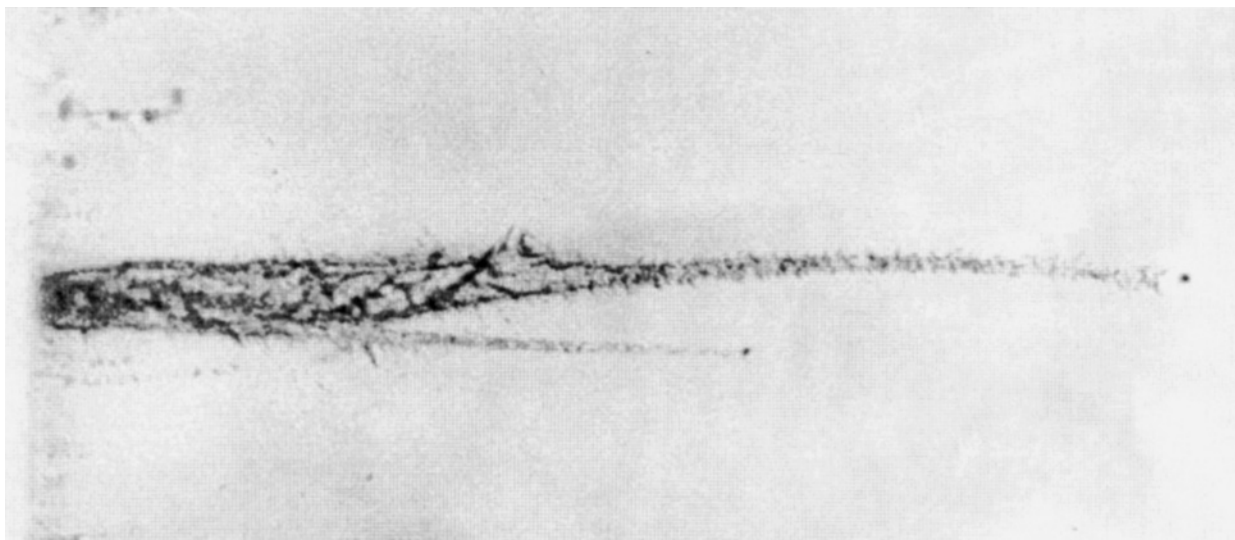

FIG. 2. Optical image of the penetration track made into silica aerogel (40 mg/cc) by a 50 μm diameter grain of the Pampa B ordinary chondrite traveling with a velocity of 6 km/s. The track length is ~2 mm. This image illustrates the expected state of the samples returned by the *Stardust* spacecraft from Comet Wild II in 2006. Image provided by Ron Bernhard and Fred Hörz.

in laboratory simulations using a light gas gun (Barrett *et al.*, 1992). A minor concern is the possible contamination of the captured samples by minute impurities within the silica aerogel; however, we have curated (at JSC) large quantities of flight-qualified aerogel to serve as contamination monitors and standards.

Muses-C–The Muses-C mission will be the first sample return mission by Japan's space science agency, the Institute of Space and Astronautical Science (ISAS). The goal of the mission is to return powdered or chipped samples from the surface (regolith?) of the small near-Earth asteroid 1989ML (ISAS, 1996). The spacecraft will leave Earth in 2002 and rendezvous with the near Earth-asteroid in 2004. Once in orbit, a rendezvous vehicle will separate from an orbiter. A "nano-rover" will drop from the former spacecraft and hop around on the asteroid's surface, making measurements and observing the collecting activities. The rendezvous vehicle itself will briefly touch down on the surface two or three times. During each of these touch-and-go landings, a 5g projectile will be fired at the surface at a velocity of a 300 m/s, which will blast a small quantity of material from the surface. This liberated sample could be powder if there is an asteroidal regolith, or chips if bed-rock is exposed. In any case, on the order of 1 g of material will be collected into a horn-shaped receptacle at each of three different sites. Following collection, the rendezvous vehicle re-mates with the orbiting spacecraft for Earth return. In 2006 June, the asteroid regolith sample is returned to Earth within a hermetically-sealed capsule and flown to the ISAS lab for one year of preliminary investigation in Japan. Following this period, the samples will be made widely available, with ~10% of the sample mass coming to NASA for curation and wide distribution.

These missions will all provide samples to the general science community for detailed analyses following a relatively brief period of initial assessment by the mission science teams. In the case of Stardust, the membership of the preliminary science investigation team will not be decided until just before sample recovery at Earth, in order to be as flexible as possible, and to make the best use of the labs and expertise available in 2006. In effect, this means that someone with an especially good idea can climb aboard the team at a fairly late date.

Mars Sample Return–A Mars sample return mission is a NASA goal for early in the next millenium. The current scenario calls for a first sample return mission to land on Mars in 2003, collect core samples (with multiple gram masses) from rocks and regolith, and then launch them into orbit within a small Martian assent vehicle (MAV). These will be regolith grab samples and tens of mini core rock samples. Two years later, a second mission would land elsewhere and repeat this collection scheme. A spacecraft orbiting Mars will attempt to retrieve both orbiting samples and return them to Earth in 2008.

Because the launch opportunities for Mars come along about every two years, slips of two-year steps could occur. Of the sample-return missions described here, this is the only one where larger sample mass and grain size could make analysis of microgram- to gram-sized samples possible. Absolute ages that require mineral separates would then be possible. It is envisioned that these sampling missions would be repeated into the future.

It is now apparent that a quarantine will be imposed on any Mars samples returned to Earth (Space Studies Board, 1998). Thus, the details of sample preliminary investigation, distribution, and curation are now being decided.

Proposed Mission

There is one sample return mission that is in the pre-approval stage. This means that the mission may or may not happen, and if it does, important details of the mission scenarios will undoubtedly change. Nevertheless, we introduce it briefly.

Aladdin–The proposed Aladdin Discovery mission will obtain samples from widely separated, carefully selected, well-characterized locations on the two martian satellites, Phobos and Deimos, with a single launch and without the need for soft landing (Pieters *et al.*, 1997). An innovative flyby "blast-and-grab" sample collection technique makes this possible. Targeted, unpowered projectiles are fired into the satellites' surfaces. Ejected particles are captured by the spacecraft as it flies by the surface. The low velocity of the flyby, ~1 km/s, allows capture of intact particles onto clean collector surfaces, preserving even organics and volatiles. High-resolution imaging and mapping spectrometry are used to map the moons' geology and to characterize the contexts of the samples, allowing global implications of sample science to be inferred. Radio science and imaging will provide measurements of mass and volume that allow density to be determined unambiguously; from this information, from stratigraphic relations of geologic units identified by imaging and from the samples' mineralogy, the interior structure of the moons may be inferred.

The mission design allows sample return from both martian satellites with a *Delta II* launch. The spacecraft arrives at Mars within the year and eventually enters an elliptical orbit near Phobos' orbital plane and crossing both satellite orbits, such that the spacecraft makes a satellite flyby about once every nine days. Optical navigation images of the satellites are collected to refine knowledge of the spacecraft position relative to the satellites.

Aladdin has five independent, successive collector "carpet" areas of 1000 cm^2 each, separated by blank leader to prevent mixing of samples. Once a collector area has been exposed, it is retracted into the return capsule, and blank leader is exposed until the next sample collection. The first two collection areas are used for Phobos samples; the third and fourth for Deimos samples; and the fifth for a torus sample. To collect a Phobos or Deimos sample, the appropriate collection area need be exposed only a few minutes, during which time it sees a negligible fluence of torus particles. The torus collection area is exposed for more than a month. Each area has a control segment that is exposed to all ground and spacecraft environments but is shielded from the sample by designing the moderating baffle to divert incoming sample particles. The control strip validates sample science by measuring contamination levels.

The anticipated collected sample mass per moon is ~30 μg, or ~1100 particles each 10 μm in diameter. The return from the torus is poorly constrained, due to limited information on this phenomenon. The samples would probably be returned to Earth at UTTR.

Aladdin's miniature "regolith scoop samples" will provide information on the moons' mineralogic, elemental, and isotopic composition similar to that from the first Apollo 11 scoop sample of lunar regolith, which by itself provided the compositions of the maria and highlands and contained key evidence that led to the magma ocean hypothesis for lunar evolution which, in its essential form, remains accepted today. The impact and flyby speeds (1.0–1.4 km/s) are far lower than for *Stardust*; and the flybys are repetitive, allowing multiple sample acquisitions and providing the perfect test ground for evaluating and honing this new sample acquisition technique.

Even if *Aladdin* is never flown, the innovative sampling technique appears too useful to shelve and should see service on some future sampling missions to other small bodies. This sampling technique would be especially applicable to sampling of multiple bodies from the same spacecraft.

ANALYSIS OF NANOGRAM-SIZED ASTROMATERIALS

With advanced technology, small is beautiful. The capability of modern methods to characterize ultra-small samples is well established from analysis of IDPs (*e.g.*, McKeegan *et al.*, 1985; Clemett *et al.*, 1993; Zolensky *et al.*, 1994, Thomas *et al.*, 1995; Bradley *et al.*, 1996), interstellar grains recovered from meteorites (Zinner, 1997), and other materials requiring ultra-sensitive analytical capabilities. Powerful analytical techniques are available that require, under favorable circumstances, only nanogram- to microgram-sized single particles for entire suites of fairly comprehensive characterizations. Oxygen-isotope analyses, for example, can be applied to any O-bearing grain. Thus, a returned sample mass of just a few micrograms ($\sim$1000, 10 μm particles) permits comprehensive quantitative geochemical measurements that are impossible to carry out *in situ* with flight instruments.

On the other hand, for complex differentiated bodies, carefully-selected gram-sized quantities (and perhaps more) will clearly be required for the array of primary science issues related to the evolution of the body. Age dating requires recovery of specific, often trace mineral phases, which are unlikely to be present at the microgram scale. Petrographic relations between components (*e.g.*, cooling sequence, matrix–inclusion relations, *etc.*) cannot generally be directly addressed with individual particles, and many bulk physical properties (bulk density, porosity, *etc.*) are difficult to characterize with particulate samples. Furthermore, many organic compounds currently require a milligram or more for analysis (although advanced techniques are improving). However, even for these coarse-grained planetary bodies, the analysis of nanogram-sized samples will reveal fundamental information unobtainable *without a sample return, such as details of mineral paragenesis*; regolith processes; O-isotopic bulk composition; conditions of thermal and aqueous alteration (if any); relationships to planets, comets, meteorites; presence of water and hydrated material; presence and general nature of organics; history of volatile reservoirs; and the presence and origin of presolar and/or interstellar material that might remain.

The principal value of a returned sample (as opposed to remote sensing or robotic analysis) is that state-of-the-art instruments do not need to be flight qualified and flown. Instead, sample analyses can be performed in ground-based laboratories, checked by complementary techniques and labs, and questionable analyses be repeated. The purpose of this section is to describe the analytical techniques that are available today for characterization of nanogram-sized samples. We also briefly describe likely near-future advances for some of these techniques. Finally, we make recommendations for special development efforts for some critical analytical capabilities, where there are noticeable gaps in our analytical capabilities. Of course, another strength of having a sample on the Earth is that it can be safely stored until new analytical procedures become available at a later date. Still, it is desirable to minimize the time the samples must wait; because these sample analyses will not only answer critical questions about our distant history, they will also frame the important questions we will ask in the future and thereby shape the goals of the next generation of missions.

First-time visitors to the Cosmic Dust Lab at the Johnson Space Center are frequently surprised at the ease with which particles measuring only a few microns are manipulated, catalogued, stored, retrieved, and studied. Of course, nanotechnology is at the heart of our industrial civilization, although these skills are not particular to scientists. As documented by Weschler (1995), and displayed at the Museum of Jurassic Technology in Venice, California, a Soviet-Armenian immigrant to Los Angeles named Hagop Sandaldjian became adept at sculpting single human hairs into remarkable sculptures, which he then painted in many lifelike colors. He reportedly timed all sculpting actions to occur in between heartbeats, to minimize shaking. David Wilson reports that Mr. Sandaldjian must have been "a very calm man" (Weschler, 1995). In fact, the manipulation of submicron interstellar grains is the current state-of-the-art for planetary scientists.

We arbitrarily divide the analytical techniques below in the following groups: (1) imaging, (2) bulk and mineral compositional chemical analyses, (3) organic analyses, (4) noble gases and exposure history, (5) fluid inclusions, (6) age dating, (7) mineralogy and atomic structure, and (8) physical properties. This grouping is somewhat arbitrary (*e.g.*, isotopic analyses permeate the entire discipline of geochemistry). However, it does provide a convenient way to break up the next section and make it easier to digest in small portions. The following descriptions are summarized in Table 1, where we also identify such factors as ease of analyses (*in situ vs.* sample preparation required) and destructive *vs.* partially or non-destructive. We term many of the analyses as partially destructive because of complicated sample preparation. These samples are considered by us to be degraded but still remain in a state permitting significant subsequent analyses. Although the principal goal of this paper is to describe the analyses applicable to nanogram-sized samples, descriptions of some allied techniques requiring a bit more sample have crept in; these are clearly identified.

There are some common development requirements for all of these techniques. Blank levels must be decreased, as the necessary *developments in sample handling are accomplished. This is well* described by Miller and Pillinger (1997). Automation of the above techniques is necessary to permit rapid initial characterization of tremendous number of small grains, and to identify the subset of grains deserving of detailed characterization. The Washington University group has concentrated effort on this for x-ray and secondary ion mass spectrometry (SIMS) imaging, with a resulting tremendous harvest of data on interstellar phases preserved intact in meteorites (Zinner, 1997). Advances in image processing should go hand-in-hand in the automation development to yield the highest volume of information from the smallest possible samples.

Imaging

Scanning electron microscopy/energy dispersive spectrometry (SEM-EDX), in particular field emission gun instruments, provides fundamental, easily obtained information on sample morphology, and major and (some) minor elements, at spatial resolution down to a few nanometers (Flynn *et al.*, 1978). Though technically non-destructive, this technique generally requires that a conducting coating be applied to the sample, which may be unacceptable for some later analyses. Recently, workers have reported success in SEM microcharacterization of Antarctic micrometeorites and space-harvested IDPs *without conductive coatings using low-vacuum* SEM/EDX techniques (Yano *et al.*, 1998). This step renders SEM characterization truly nondestructive in most respects (there is still

TABLE 1. Summary of analytical techniques.

Technique	Required sample mass	Destructiveness
Imaging		
Light-optical techniques	ng	nondestructive
Scanning electron microscopy/energy dispersive spectrometry	ng	nondestructive
Transmission/analytical electron microscopy	ng	partially
Scanning transmission x-ray microscopy	ng	partially
Atomic force microscopy	ng	partially
Force spectroscopy	ng	partially
Holographic low-energy electron diffraction	ng	partially
Secondary ion mass spectrometry ion imaging	ng	destructive
Bulk and Mineral Compositional Analyses		
Microparticle instrumental neutron activation analysis	ng	nondestructive
Synchrotron x-ray fluorescence	ng	nondestructive
X-ray fluorescence tomography	ng	nondestructive
Electron microprobe analysis	ng–μg	partially
Protron-induced x-ray emission	ng	partially
X-ray spectroscopy	ng	partially
Secondary ion mass spectrometry	ng	destructive
Time-of-flight secondary ion mass spectrometry	ng	destructive
Laser ablation microprobe inductively-coupled plasma-mass spectrometry	ng	destructive
Double-focusing secondary ion mass spectrometry	ng–μg	destructive
Resonance ion mass spectrometry	ng	destructive
Thermal ionization mass spectrometry	ng–μg	destructive
Organic Analyses		
Micro Raman spectroscopy	ng–μg	nondestructive
Fluorescence	ng	nondestructive
Transmission and reflectance infrared–visible spectroscopy	ng	partially
Optically- and acoustically-excited phonon spectroscopy	ng	partially
Stepped combustion and static mass spectrometry	μg	destructive
Two-stage laser desorption/laser multiphoton ionization mass spectrometry	ng	destructive
Noble Gas and Exposure History		
Solar flare track analysis	ng	partially
Double-focusing mass spectrometer	ng–μg	destructive
Fluid Inclusions		
Raman microsampling spectrometry	μg–mg	nondestructive
Synchrotron x-ray fluorescence	μg–mg	nondestructive
Optical petrography/heating-freezing behavior	μg–mg	partially
Age Dating		
Laser ablation mass spectrometry	μg–mg	destructive
Secondary ion mass spectrometry	μg	destructive
Mineralogy and Atomic Structure		
Synchrotron x-ray diffraction	ng	nondestructive
X-ray absorption spectroscopy	ng	nondestructive
Transmission infrared–visible spectroscopy	ng	nondestructive
Transmission electron microscopy	ng	partially
Electron energy-loss near-edge structure	ng	partially
Atomic force microscopy	ng	partially
Electron energy loss spectroscopy	ng	partially
Extended x-ray absorption fine structure	ng	partially
X-ray absorption near-edge structure	ng	partially
Infrared–visible reflectance spectroscopy	ng	partially
Cathodoluminescence microscopy and spectroscopy	ng	partially
Physical Properties		
Magnetic force microscopy	ng–μg	partially
Force spectroscopy	ng	partially
Density measurements	ng	nondestructive to partially

limited beam damage and heating that can ruin a few later analyses such as ultra violet (UV) fluorescence; John Bradley, pers. comm., 1994). This problem can be overcome by use of a field emission SEM at a low accelerating voltage (Hua and Buseck, 1998); the gain in resolution more than overcomes the loss by use of uncoated samples.

Transmission electron microscopy (TEM) or **analytical electron microscopy** (AEM), in particular field-emission type, permits imaging of sample crystal growth and defects structures, and composition and mineralogy determination, all at the angstrom scale (Bradley et al., 1989; Bradley, 1994; Zolensky and Thomas, 1995; Greshake, 1997). Characterization of exsolution lamellae in pyroxene and spinel can be used to reveal paragenetic details of igneous melt compositions, and subsolidus processes including cooling and annealing conditions (Fig. 3). The fine scale of some lamellae requires TEM, whereas others are coarse enough to be characterized by standard microprobe analyses (Papike et al., 1971; Papike and Bence, 1972; El Goresy et al., 1972; Takeda et al., 1975, 1976; Harlow, 1979; Mori and Takeda, 1981; Tribaudino et al., 1997). Like pyroxene, plagioclase and olivine may also undergo subsolidus reactions (Petaev and Brearley, 1994), although the evidence supporting this process (in lunar rocks) is debated (Dixon and Papike, 1975). These electron microscopy techniques can hardly be improved for our purposes, because they already provide information at, or near, the atomic scale. A drawback is the severe sample preparation that must be performed. However, if ultra-microtomed slices are used, some slices can be used for many other analyses, as shown in Fig. 1. Also, allied analyses, such as EELS and ELNES (see below) can be used in concert with TEM.

Scanning transmission x-ray microscopy (STXM) is used to generate soft x-rays from suitably thinned samples, and these x-rays can be used to generate element maps with a spatial resolution of ~100 nm under favorable circumstances (Flynn et al., 1999). Flynn et al. (1999) describe the mapping of C and K in planetary materials by STXM, and other elements in terrestrial samples at a Brookhaven synchrotron beam line. They point out that this technique should be applicable to C, N, and O using K transition lines, and K through Ti using 1-α lines.

Atomic force microscopy (AFM) provides images of samples at atomic scales, answering fundamental questions about the properties of surfaces (Binnig and Rohrer, 1987; Burnham and Colton, 1993); there is now a wide variety of AFM instruments. All of these make use of a sharp tip scanning the surface of a sample and derive information from the electromagnetic interaction between the tip and sample. Using state-of-the-art piezo-electric motion systems, surface features can be resolved with atomic resolution yielding the topography of atoms, and some additional physical properties of the sample (e.g., magnetic domain properties). In AFM, a tip mounted in a flexible cantilever rasters across the sample surface. In the contact mode, at each point of the scan, the tip barely touches the sample surface (with a force of 10^{-7} to 10^{-6} N).

Atomic force microscope is also possible in a noncontact mode, where the tip and sample separation is typically kept between 5 and 10 nm. At this distance, the receptive electron orbits tend to interact, resulting in a weak attractive force that can be measured and used to calculate surface topography. Although the noncontact mode only subjects the sample to a force of $\sim 10^{-12}$ N, which is attractive for electric and soft samples, it is a significantly more demanding technique.
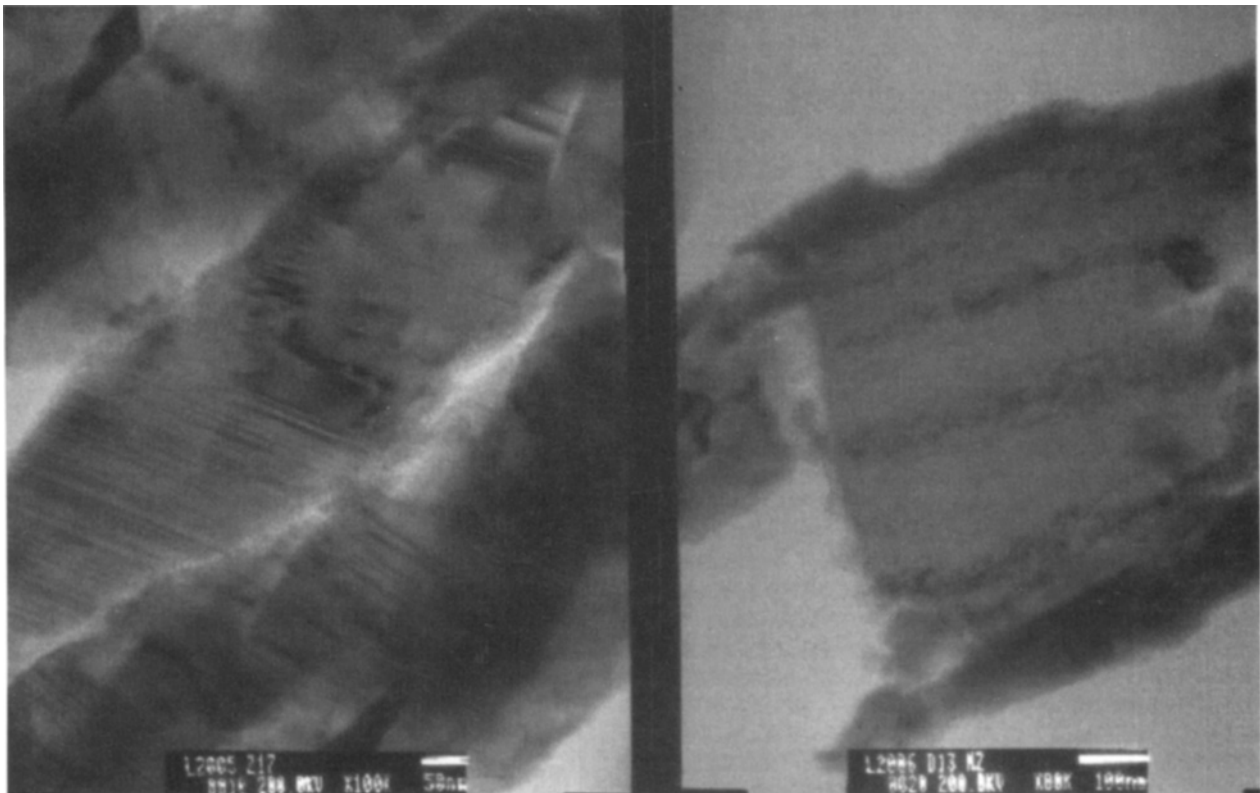

FIG. 3. Transmission electron microscope dark field images of exsolution phenomena in chondritic interplanetary dust particles (IDPs). (a) A clinopyroxene grains within IDP L2005 Z17. Scale bar measures 50 nm. (b) A Fe-Ni metal grain within IDP L2006 D13. In this grain, the diffuse horizontal bars reflect a higher Ni content, and the fine-scale vertical lines are crystal defects. Scale bar measures 100 nm.

The ability to image the atomic structure of a mineral surface can sometimes provide critical information not obtainable in any other way. For example, a recent study has suggested that the morphology of dislocations at the growing surface of calcite crystals can be controlled in a unique way by the presence of organics (Teng *et al.*, 1998). Growth spiral morphology for calcite from aspartic acid-bearing solutions exhibit distinctive asymmetric hillocks, unique terrace heights and widths, and highly rounded step corners. The ability to distinguish carbonates formed from organic compound-bearing solutions is clearly a topical item. It is also possible to image on mineral surfaces thin, discontinuous coatings of amorphous to crystalline materials resulting from incipient dissolution reactions (Nugent *et al.*, 1998). These could be the only resultant signs of limited aqueous activity on sparsely hydrated bodies such as comets; such coatings have been observed to result from the activity of "unfrozen water" at temperatures below the nominal freezing point. These are just two examples of the underutilized potential of AFM for planetary scientists (Zolensky and Paces, 1986).

Secondary ion mass spectrometry ion imaging is described under isotopic techniques.

Holographic low-energy electron diffraction (HLEED), is a recent advance on conventional LEED, whereby superstructure diffraction spot intensities are transformed into well-resolved atomic images by holographic inversion (Reuter *et al.*, 1997). This technique thus yields a three-dimensional image of the atoms at the surface of a crystal. It can only be used where the crystal's unit cell is large enough to provide a sufficiently high density of superstructure diffraction spots, and where there are occasional prominent atoms at the surface to serve as the holographic beam splitters. Such atoms can be attached to the crystal surface artificially before imaging. This procedure can be used to provide direct information on the nature of complex and unknown surfaces. Such interesting phases as pyrrhotites (common nebular and asteroidal minerals) and silicon carbide (SiC) (known to form in circumstellar, interstellar, and nebular environments; Zinner, 1997) both show a considerable polytypism related to environmental factors and could be expected to be amenable to this imaging technique. In fact, SiC was the first material to be imaged by this technique (Reuter *et al.*, 1997). This analysis requires flat cleaved sample surfaces, with undisturbed atoms. For some materials heavy atoms must be applied to the surface, which might interfere with later analyses.

Mineral and Bulk Compositional Analyses

Certain elemental ratios provide extremely useful information on sample origin, but one has to be careful to distinguish preaccretionary (nebular) from postaccretionary (asteroidal, planetary, *etc.*) processes. Depletions in some moderately volatile elements (*e.g.*, K, Mn) have apparently occurred in parent body environments, and therefore bulk K/U and Mn/Fe ratios have been used to tie meteorites to specific parent bodies (BVSP, 1981; Drake *et al.*, 1989). Igneous minerals formed on different parent bodies have also been shown to have distinct major and minor element compositions arising from differing melt conditions. Useful in this regard are the minor element substitutions for Al and Ca in plagioclase; Cr, Ca, Mn, and Al into olivine; and Mn substituting for Fe in pyroxene (Papike, 1998). Elemental ratios have also been used to reveal the extent of parent body differentiation (Newsom and Drake, 1982) and intrinsic O fugacity (Crozaz and McKay, 1989). Minor and trace element studies of zoning patterns in many rock-forming minerals reveal

essential details of paragenesis including whether reacting systems were open or closed and degree of melting and subsequent manner of crystallization (Bence and Papike, 1972; McSween *et al.*, 1996; Papike, 1996). For iron meteorites, plots of critical elements, such as Ge *vs.* Ni and Ir *vs.* Ni, have been used to discriminate between parent asteroids (Wasson, 1985; Mittlefehldt *et al.*, 1998).

In some instances, discrete olivine and pyroxene grains can be shown to have originated from disaggregated chondrules based upon bulk composition, zoning characteristics, and presence of melt inclusions (Jones, 1992; Jones and Danielson, 1997; Leshin *et al.*, 1997). This is critical for spacecraft sampling strategies that return only submillimeter-sized grains and where it is important to know whether chondrules may have been originally present, but not collected. The Stardust, Muses-C, and Aladdin missions all fit this description.

Microparticle **instrumental neutron activation analysis** (INAA) has been successfully applied to the major-to-trace element bulk composition of individual IDPs as small as 15 μm (Lindstrom *et al.*, 1990; Zolensky and Lindstrom, 1992). This work can only be performed in a buried facility made of very low-background materials specially constructed to shield the sensitive Ge gamma-ray detectors from as much background radiation as possible. The counting equipment must also be made from very low background materials. As such, this technique is not widely available. Though not an *in situ* type analysis, it is applicable to fine, separated grains and is nondestructive. Lindstrom made a special effort to demonstrate that fine-grained extraterrestrial materials can be compositionally homogeneous to the nanogram level (Lindstrom *et al.*, 1990), a necessary consideration for anyone contemplating the value of bulk analyses of such tiny samples. However, this property must be established for each new material. The reader is referred to the Lindstrom paper for a discussion of elemental detection limits; generally only 10–20 elements could be determined from IDPs with roughly chondritic composition.

Synchrotron x-ray fluorescence (SXRF), sometimes called **synchrotron radiation-induced x-ray emission** (SRIXE), is nondestructive, can analyze for all elements heavier than K (due to absorption of the emitted beam by air), has high sensitivity for most elements (<0.1–5 ppm), respectable spatial resolution (5–10 μm using conventional collimators), is an *in situ* analysis technique, and uses straightforward analysis reduction algorithms (Flynn and Sutton, 1990; Bassett and Brown, 1990) (see Fig. 4). These sources are now available but require focused beams available in only a few locations. This technique has recently been improved by use of a newer, still brighter photon source, the Advanced Photon Source (APS) (at Argonne National Laboratory) to increase sensitivity and spatial resolution (Sutton *et al.*, 1999). The APS instrument has a beamspot that is easily focused down to ~1 μm in diameter and has been focused even smaller. In addition, the APS microprobe has a flux density ~3 orders of magnitude greater than, say, the Brookhaven National Synchrotron Light Source (whose minimum beam size for x-ray microprobery is ~17 μm in diameter), and a total incident flux greater by more than one order of magnitude. The decrease in required analysis time coupled with the decreased analysis spot makes it practical to map the spatial distribution of elements, including minors, in nanogram-sized samples. Minor specimen heating occurs with these techniques; however, the extent of this potential problem has not been rigorously investigated.

These techniques have become common for analysis of the bulk composition of individual IDPs, and it is anticipated that it will

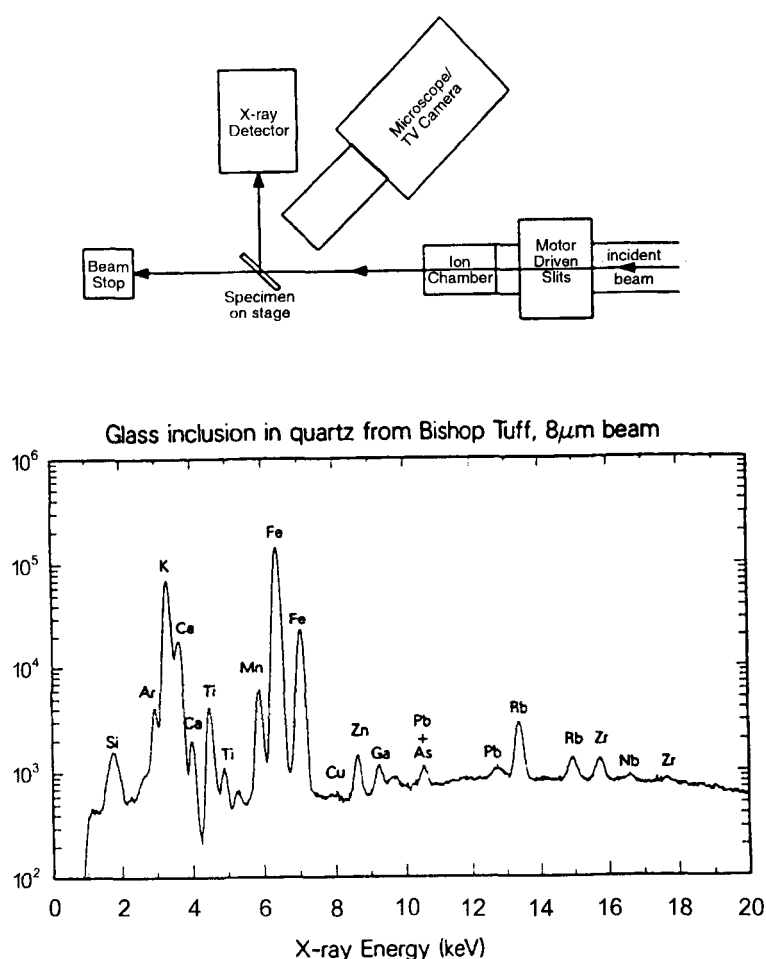Glass inclusion in quartz from Bishop Tuff, 8μm beam

FIG. 4. (a) Schematic of the x-ray microprobe using collimated synchrotron radiation as the excitation source, and (b) synchrotron XRF spectrum of a glass inclusion within quartz, demonstrating that *in situ* analyses can be performed at the ~10 μm scale. Adapted from Bassett and Brown (1990).

similarly serve for the preliminary survey of *Stardust* comet coma samples, because these analyses can probably be performed *in situ*, without removing the samples from the enclosing aerogel. Elements lighter than K could be determined using SXRF if the experiment were enclosed in a vacuum or He atmosphere.

Use of new ellipsoidally-shaped lead glass capillaries to focus polychromatic synchrotron radiation can reduce incident beam size to 4 μm with a total flux increase of an order of magnitude over conventional collimated beams (up to 10^{10} photons μm^{-2}) (Janssens *et al.*, 1998). Such highly energetic, micron-sized beams permit two-dimensional mapping of the distribution of elements including rare earth elements (REE) (Rindby *et al.*, 1997). It is also possible to obtain three-dimensional mapping of elements in particles by synchrotron **x-ray fluorescence tomography** (XRFT). In XRFT, the sample is mounted onto a goniometer head; and during data collection, the sample is translated stepwise through the beam, after which the sample is rotated (~3°), and translation is repeated. This continues until the sample has been completely rotated with respect to the beam. Reconstruction algorithms are then used to provide three-dimensional elemental maps of the sample (Janssens *et al.*, 1998).

Protron-induced x-ray emission (PIXE) provides major and minor element compositions, at a spatial scale of 1–2 μm, and has been profitably applied to the characterization of individual IDPs

(Jessberger and Wallenwein, 1986; Arndt *et al.*, 1996). However, with typical Si(Li) detectors, there are unresolved or marginally resolved overlaps between the heavy trace element L lines and the major element K lines (Burnett and Woolum, 1983). The result is that this technique is not widely used for analysis of fine-grained extraterrestrial materials, despite the fact that it is relatively non-destructive.

The **electron microprobe analyzer** (EMPA), the workhorse of the modern mineralogy lab, can be successfully used for composition work on nanogram-sized samples, provided that they are suitably prepared. One technique developed for use with individual IDPs has been to embed the sample in low-viscosity epoxy and microtome a little off the top, leaving a "polished" mineral surface exposed (measuring only a few micrometers across) suitable for EMPA (Zolensky and Lindstrom, 1992; Zolensky and Barrett, 1994). Although this instrument is generally used to provide mineral compositions, it can be used for bulk analysis of nanophase mineral mixtures. However, elemental fractionations can be severe (*e.g.*, Na is severely vaporized from glasses during analysis if proper care is not taken).

Although generally used to provide high-quality major and minor element compositions of suitably-polished mineral grains, EMPA is also used for determination of trace elements (McKay, 1989) in extraterrestrial samples. Fialin *et al.* (1999) provide a recent review of methods for doing this, and the pitfalls. With their preferred technique, they report detection limits as low as 1–6 ppm for some elements and corresponding analytical precision (±2σ) below 50%. Their electron beam diameter was defocussed to 10 μm across, yielding an excitation diameter on the order of 11–12 μm. However, these results were obtained using long counting times (~15 min) that accumulated results of shorter counts on multiple samples for beam-sensitive materials. Such work might not be possible for individual, one-of-a-kind nanogram-sized grains.

There are techniques for determining the oxidation state of transition elements by **x-ray spectroscopy** with the EMPA. The most important of these elements is Fe, and Höfer *et al.* (1996) have reported success with a method of determining the Fe^{3+}/Fe^{2+} ratio in simple oxides and garnets, by observing the change in the $L\beta/L\alpha$ intensity ratios measured on the high-energy wing of the $L\alpha$ peak and on the low-energy wing of the $L\beta$ peak. Precision and accuracy of the $Fe^{3+}/\Sigma Fe$ determination for the simple iron oxides is reportedly as good as 0.02 (1σ), although the technique has to be evaluated for each EMPA instrument. In addition, the determination must be calibrated for each different mineral to correct for the effects of composition and Fe coordination (Höfer *et al.*, 1996). It would be very desirable to extend this technique to other Fe-bearing minerals important in extraterrestrial materials, which include the ferromagnesian silicates and phyllosilicates. However, Sobolev *et al.* (1999) provide a good example of the significant errors that can result in use of EMPA for $Fe^{3+}/\Sigma Fe$ determination in common rock-forming minerals. As we discuss below, EELS appears to be a more promising technique for obtaining this information at the nanoscale.

X-ray absorption near-edge structure (XANES) analysis can also be used to determine Fe oxidation states, as described by Bajt *et*

al. (1995). These authors examined the oxidation state of Fe in chondritic IDPs and chondrite matrix, using the National Synchrotron Light Source (NSLS) Brookhaven x-ray beam line.

The mass spectroscopy of secondary ions by a time-of-flight instrument offers attractive advantages over conventional ion microprobes using double-focusing magnetic mass spectrometers (Stephan *et al.*, 1994). New generation **time-of-flight secondary ion mass spectrometry** (TOF-SIMS) instruments have a primary beam only ~0.1 μm in diameter; and when ionization is made by laser, this technique can provide almost complete elemental and isotopic analyses using only 10^8 atoms (assuming chondritic composition) (Jessberger, 1991a). It has also been applied to the elucidation of the surface chemistry of chondritic IDPs to provide information on the degree of contamination and nature of surface reactions (Rost *et al.*, 1999). The TOF-SIMS technique has significant sample preparation requirements and is considered destructive.

Time-of-flight secondary ion mass spectrometry permits simultaneous detection of all ions with the same charge sign and is characterized by high transmission through the spectrometer (20–80%), by high mass resolution (m/Δm $\leq 20\,000$ at low and m/Δm $\leq 6\,000$ at high lateral resolution), and by low sample consumption (just monolayers in favorable situations). Quantification problems persist with this as for all SIMS analyses. Also, because negative ions must be analyzed separately from positive ions, and each analysis consumes some sample, it can be difficult to properly register the negative and positive ion images. However, in general, it is possible to study elemental correlations in samples on a submicron scale and, if combined with TEM or other mineralogic analyses, with sample mineralogy. This technique has been applied to the analyses of individual chondritic IDPs for some years now, and a good review of the results are given by Jessberger (1991a).

Laser microprobes have been used for some time for mass spectrometry of geological materials. For example, Alonso-Azarate *et al.* (1999) have recently described application of this technique to determination of S isotopes in sample volumes 100 μm in diameter. This technique will no doubt be applied to planetary materials in quick order.

A promising new technique for *in situ* trace element analysis of 10–50 μm diameter spots is **laser ablation microprobe-inductively coupled plasma-mass spectrometry** (LAM-ICP-MS). With the very low detection limits characteristic of ICP-MS, coupled with the *in situ* analytical capabilities of laser ablation, this technique is particularly appropriate for high-precision analysis of elements such as Y, REE, Zr, Hf, Nb, Ta, and other lithophile elements that characteristically show no fractionation during laser ablation (Taylor *et al.*, 1997). The laser ablation microprobe uses a focused YAG laser to ablate a tiny sample in a closed cell, with the ablated material being carried by Ar into an inductively-coupled plasma-mass spectrometer. The use of frequency quadrupling hardware has reduced the ablated pit to a minimum of 10 μm in recent work on silicates (Taylor *et al.*, 1997). Current detection limits for this instrument for elements with atomic mass >85 are typically <1 ppm for 10 μm sampling resolution, and subparts-per-billion for 30 μm sampling resolution, and subparts-per-million detection limits for many lithophile elements (Gunther *et al.*, 1995).

Addition of a multiple collector to the ICP technique is the latest advance (Halliday *et al.*, 1998). In this technique, superior peak shapes are obtained due to the ion optical focal plane of a large dispersion magnetic sector mass spectrometer, permitting multiple collection of elements, particularly for elements with a high first-ionization potential. Although still new, the multiple collector–ICP-MS technique, especially when combined with laser ablation, has already been applied to Lu-Hf systematics, ^{182}Hf-^{182}W dating, and the first high-sensitivity measurements of isotopes of In, Cd, Te, Cu, Zn, U, Th, and Pt-group elements. Enthusiasts for this technique predict that it will quickly supplant now standard trace element analytical techniques, including spark source mass spectrometry, x-ray fluorescence, neutron activation analysis, and conventional ICP emission spectroscopy.

Isotopic studies are among the most powerful tools available to the planetary scientist. For example, many meteorite groups plot in unique positions on the three-isotope plot for O, although these trends are smeared out for separated minerals as opposed to bulk samples (Clayton, 1993). Similarly, oxidation state shows a huge variation according to meteorite type, owing to differences established both during pre- and postaccretionary periods (Brearley and Jones, 1998). Thus, it is in principle possible to tie specific grains to specific known meteorite types, although ambiguities are reduced if bulk or, at least, polymineralic grains are used.

Recent improvements in sensitivity and spatial resolution are available for **double-focusing secondary ion mass spectrometry** (SIMS). In SIMS, a primary ion beam, such as ^{3}He$^+$, ^{16}O$^+$, or ^{40}Ar$^+$, is accelerated and focused onto the surface of a sample and sputters material into the gas phase. Approximately 1% of the sputtered material comes off as ions, which can then be analyzed by a mass spectrometer. Secondary ion mass spectrometry has the advantage that material can be continually sputtered from a surface to determine analyte concentrations as a function of distance from the original surface (depth profiling). Also, *in situ* analyses are available in the newest generation of instruments (*i.e.*, analyses can be done on grains within thin sections). Secondary ion mass spectrometry provides information on H, C, N, O, Mg, Ca, Ti, S, and Si isotopes, as well as some trace elements, including the REE (Papike, 1996), at a minimum spatial scale of 2–3 μm (Fig. 5) (though often up to 100 μm in reality), with a maximum precision on the order of 1–10 ppm or, when presented on an isotopic ratio diagram, much less than 1‰. However, precision is more typically 4–10× these values (Zinner *et al.*, 1983; McKeegan *et al.*, 1985; McKeegan, 1987; Stadermann *et al.*, 1990; Paterson *et al.*, 1997; Leshin *et al.*, 1998; Goswami *et al.*, 1998). The discussion of inter-instrument analysis comparisons for two SIMS techniques (for analysis of S) given by Paterson *et al.* (1997) is particularly valuable and points out the need for rigorous interlaboratory calibration, particularly for SIMS where instrumental factors are so important. This critical activity should be performed before the return of the Stardust and Muses-C samples in 2006, in order to provide maximum utility and minimum confusion.

With these data, it is indeed possible to discriminate between material formed in the nebula and presolar grains (Zinner, 1991; Nittler *et al.*, 1998) (Fig. 6). In interstellar grains recovered from unequilibrated chondrites, isotopic compositions of H, C, N, Mg, Si, Ca, Ti, and Zr have been measured by SIMS (Anders and Zinner, 1993; Hoppe *et al.*, 1993, 1996a,b), and noble gases by sensitive mass spectrometry, and these analyses have proved sufficient to tie specific grains to various carbon stars, Type II supernovae, O-rich red giant stars, and (possibly) Wolf-Rayet stars. All this from diamond, carbide, nitride, oxide, and graphite grains individually measuring no more than 20 μm, and usually a good deal smaller.
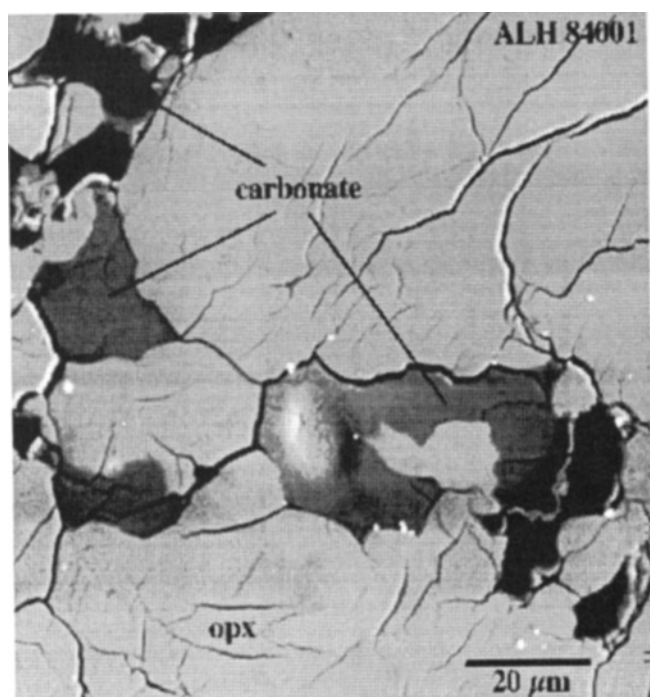
FIG. 5. Scanning electron backscattered image of a carbonate occurrence in ALH84001, showing an ion microprobe pit (center) resulting from analysis of O isotopes. The image shows the small (15 μm) size of the analyzed area. Figure provided by Laurie Leshin.
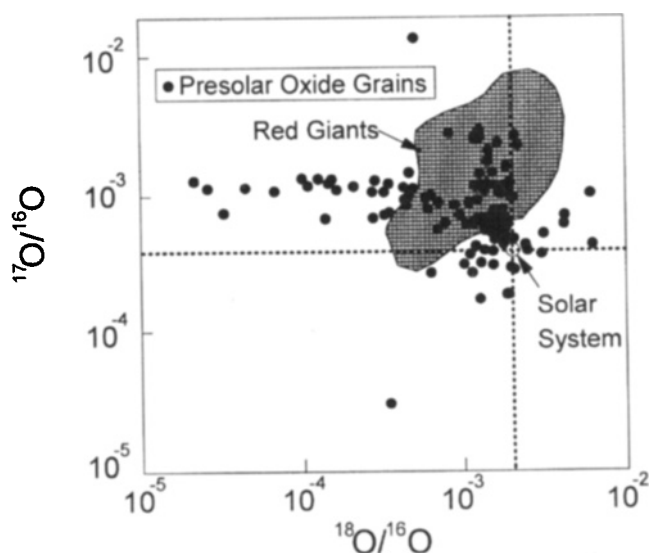

FIG. 6. Three-isotope plot of O, showing values obtained from micron-sized and smaller interstellar grains separated from chondrites. This diagram shows the precision possible from such analyses and also demonstrates that material from different sources (red giants, solar system, type II supernovae) can be distinguished. Figure provided by Larry Nittler.

Just on the horizon is a new generation SIMS, called the nano-SIMS (Stadermann et al., 1999). The first of these instruments will find a home at Washington University in the coming year. Its unique design features a normal incidence primary beam, and a reduced working distance, resulting in a substantially smaller primary beam spot and high secondary ion collection efficiency. The prototype instrument has achieved a beam diameter as small as 30 nm, with significantly higher ion yields that the ims3F and ims1270 SIMS instruments at mass resolutions up to 6000. The applications of such an instrument are obvious.

The best current analytical precision of in situ O-isotopic analyses (1‰) just permits resolution of martian from terrestrial or asteroidal materials (Clayton, 1993; Leshin et al., 1998), a fundamental goal of the proposed Aladdin mission to the martian moons (Pieters et al., 1997).

Secondary negative ion images can be made with a resolution of 1 μm, permitting location of grains with unusual isotopic compositions from within a fine-grained mineral assemblage or from among a large collection of separate grains (McKeegan et al., 1985).

Young and Russell (1998) have recently reported success with a new UV laser ablation and fluorination method for in situ analysis of $^{18}O/^{16}O$ and $^{17}O/^{16}O$ ratios in meteoritic components. The increase in sensitivity is achieved by preconcentrating O from a fluorination line for analysis by isotope ratio monitoring gas chromatography mass spectrometry (irm-GCMS). This technique requires 10–20 nmol of O (~1 μg of a typical silicate) to be successful but then produces data with an accuracy of ±0.2‰ or better, and precision between ±0.1 and ±0.3. The technique has been applied to in situ analysis of CAI and should find more general application (Young et al., 1998). However, these authors note that laser ablation in a fluorinating environment relies on the presence and distribution of

crystalline defects in the mineral surface and is complicated by dynamical interactions between the plasma plume and ambient reagent gas. This means that results will vary depending on composition as well as the structural state of the sample. Although the O mass requirement of this techniques are order of magnitude smaller than for other fluorination methods yielding similar analytical precision and accuracy, the sample mass requirements of this technique are still greater than those of SIMS (which, however, has less accuracy and precision). Thus, one can obtain very high-quality O-isotopic data for submicrogram samples, but SIMS is still required for masses of a few nanograms.

Resonance ion mass spectrometry (RIMS) uses a laser beam focused to ~1 μm to promote an atom or molecule above its ionization potential to create an ion. Ablated atoms are then resonantly ionized with two or three tuned lasers. This ionizes only the element of interest, which is then accelerated and mass analyzed in a time-of-flight mass spectrometer. Because each element has a unique energy level structure, RIMS provides a selective ionization method. Resonance ion mass spectrometry is useful for studying the electronic structure of atoms or molecules and to make quantitative measurements of analyte concentrations. The sensitivity is excellent—one can count a few percent of the atoms removed from the sample, compared with ~1% for SIMS. The selectivity is also excellent—for example, one can easily ionize Mo without ionizing Zr (which overlaps Mo isotopes at three masses). Meteoriticists are currently using RIMS to analyze presolar grains, where the isotopic anomalies are huge and very interesting. Thus far, isotopes of Ca, Sr, Zr, and Mo have been variously determined in SiC and graphite (Nicolussi et al., 1997a,b, 1998).

Thermal ionization mass spectrometry (TIMS) has been used to determine Mg isotopes in some IDPs, with a spatial resolution of ~10 μm (Esat and Taylor, 1987). However, this technique does not appear to be as versatile as some of the other MS techniques, because entire grains must be placed onto filaments and destroyed to be analyzed.

Organic Analyses

Reviews of organic chemistry of meteorites and IDPs show that more than 400 different compounds have been definitively identified—many thousands undoubtedly await detection by the more sensitive techniques that will be available in the future (Hayatsu and Anders, 1981; Mullie and Reisse, 1987; Cronin *et al.*, 1988; Anders, 1991). Mixing and secondary processing of the original interstellar and proto-solar organics is expected to make analysis and interpretation of results from any analyses very messy. The mass spectrometric results from the Giotto and Vega missions to comet Halley have been interpreted to indicate that at least half of the organics there are interstellar in origin (Kissel and Krueger, 1987; Anders, 1991). Important questions to be answered during further analysis of cometary or primitive asteroidal organics include (1) for the interstellar organics, what was the relative contributions from ion–molecule reactions, grain surface reactions, UV photolysis of ices, circumstellar condensation, and shock chemistry (Peterson *et al.*, 1997); and (2) what was the origin of the remaining 50% of the organics? (Anders, 1991). A severe limitation of the existing techniques is the need for analysis of polymers, which are destroyed during most current analyses. We need information particularly regarding polymers on the graphite–kerogen–PAH continuum, including information on morphology; structure; bonding of C, H, O, and N; molecular weights; structural subunits; and reactivities. We will also need to check for the effects of secondary alteration processes, including radiation, heat, and aqueous alteration (Anders, 1991).

Because of the enormous complexity of organic matter in comets and asteroids, that probably consist of thousands of molecules which cannot be separated and analyzed individually, it may be more fruitful to obtain an elemental composition of the bulk organics and then use **optically- and acoustically-excited phonon spectroscopy** to provide an overall view of the material (Jessberger, 1991b).

The D/H ratio is the marker for ion–molecule reactions and needs to be determined in all organic materials. Also, the carrier of the D needs to be determined in all cases. If possible, the carriers of the interstellar D should be separated from the proto-solar D, and the two samples analyzed separately, because the interstellar cloud environment should have produced different populations of organic compounds than the proto-solar nebular cloud (Jessberger, 1991b). This effort should be facilitated by the Genesis mission, which will provide a much improved D/H determination for the solar wind.

Micro Raman spectroscopy provides the molecular structure of a limited number of important inorganics and organics for samples measuring 1–2 μm and has been applied to the characterization of individual IDPs (Wopenka, 1988; Munro *et al.*, 1996). However, this technique needs multi-channel capability to lessen sample damage from the intense, focused laser beam (Jessberger, 1991b). It should be more appropriate for refractory organic species and inorganics.

Stepped combustion and **static mass spectrometry** are the most commonly employed techniques for isotopic analysis of organics and associated stable isotope species. However, the large sample sizes generally required for these bulk techniques (*e.g.*, 6–100 μg for C and 2 μg for N; Carr *et al.*, 1986; Wright and Pillinger, 1989; Wright *et al.*, 1997) highlight the increases in sensitivity required for the future of this technique. At present, only individual chondritic grains measuring 50–100 μm in diameter can be analyzed by these techniques.

Two-stage laser desorption/laser multiphoton ionization mass spectrometry (μL2MS) is a relatively new technique enabling

direct *in situ* analysis with a spatial resolution of about 10–100 μm for selected organic molecules in complex mixtures. In the first step of this technique, neutral molecules from the sample surface are desorbed intact with a pulsed, focused infrared (IR) laser. These desorbed molecules are then ionized with a pulsed, tunable ultraviolet (UV) laser, by resonance-enhanced two-photon ionization of the desorbed species; this soft ionization scheme prevents fragmentation. The resulting ions are swept into a reflection time-of-flight mass spectrometer (Zenobi *et al.*, 1989; Kovalenko *et al.*, 1991). In the first step, desorption occurs without decomposition; whereas in the next step, the desorbed molecules are ionized "softly," resulting in mass spectra consisting mainly of parent ion peaks. The mass spectra are dominated by intact parent ions of those mixture components that strongly absorb the selected ionization laser wavelength. Under some instrument configurations, only molecules with an excited state in resonance with the photon energy are ionized, enabling selective detection of a chosen class of compounds for analysis. Thus far the PAHs have been best analyzed by this technique in IDPs (Fig. 7) and meteorites (Hahn *et al.*, 1988; Clemett *et al.*, 1993). Although nowhere near as precise as SIMS, μL2MS is also capable of providing information on D/H and $^{13}C/^{12}C$ ratios (Scott Sandford, pers. comm., 1998).

Two-stage laser desorption/laser multiphoton ionization mass spectrometry offers several advantages over conventional methods for analysis of organic in diminutive samples. Little or no sample preparation is necessary, and the direct analysis of complex environmental samples is possible. Furthermore, a measurement is performed within a few minutes. The detection limit is only ~1 attomole (500 000 molecules), a million times lower than for most conventional methods.

Two remaining problems have prevented μL2MS from finding broader application in analytical chemistry until now: mass isomers could not be separated in a satisfactory way and quantitative analysis in complex mixtures was difficult or impossible. However, recent work has concentrated on overcoming these impediments (Haefliger and Zenobi, 1998).

Transmission and reflectance infrared–visible spectroscopy techniques are described below under the section concerning Mineralogy and Atomic Structure.
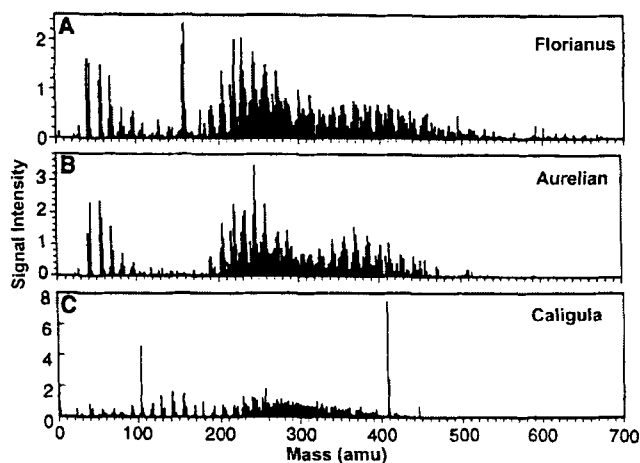

Fig. 7. The micro-L²MS organic analysis of three individual chondritic IDPs, named Florianus, Aurelian, and Caligula. The peak groupings have been identified as including the polycyclic aromatic hydrocarbons napthalene (128 amu), phenanthrene (178 amu), pyrene (202 amu), chrysene (228 amu), benzopyrene (252 amu), and pentacene (278 amu), and their alkylated series. Figure provided by Simon Clemett.

Fluorescence behavior of organic molecules can be used as a gross identification technique (*i.e.*, that fluorescence can reveal the presence of organics but cannot permit characterization). Briggs and Mamikunian (1963) and Murae (1997) have used the fluorescence behavior of some organics to suggest the presence of PAHs and related heavier organics in CM2 carbonaceous chondrites. Obviously, this is a simple, nondestructive technique that can be applied to nanogram-sized samples. However, the reported results suggest that specific organic characterization is not possible by this technique. In addition, interference by inorganic fluorescing minerals (some carbonates, phosphates, Fe-poor silicates being common examples) would be a severe impediment to the useful application of this technique for organic characterization.

Carbon has been mapped within chondritic IDPs using **XANES** by Flynn *et al.* (1998a,b), with a spatial resolution of a few hundred nanometers. This technique can be useful in distinguishing organic from amorphous C, because the former exhibits several pre-edge peaks from C–C, C–H, and C–O bonds; whereas most forms of elemental C have only a single pre-edge peak.

Noble Gases and Exposure History

Noble gases display differences between chondrite, planetary, and solar wind origins. Origin on specific planets can be distinguished owing to differences in the atmospheric evolution for each body (Ott and Begeman, 1985).

Sensitive step-heating measurements of He and Ne isotopes using a high-performance **double-focusing mass spectrometer** have been made for individual chondritic IDPs by Nier and Schlutter (1992, 1993). This information can also be used to gauge heating in a regolith environment, because the quantity of gas released at each temperature step can be used to infer the degree of preanalysis heating, as elegantly shown by Nier and Schlutter (1993). Allowance has also to be made for the possible effects of noble gas loss due to shock (Nakamura *et al.*, 1997). Recently, newer mass spectrometers are being constructed that will permit measurement of isotopes of all noble gases in nanogram-sized samples (Tomoki Nakamura, pers. comm., 1998), and these instruments are slated to be available before the turn of the century.

Solar flare tracks, imaged by TEM, can be used to constrain grain origins. Track densities are indicative of the exposure duration to solar wind, either as a free floating object or during residence in a parent body regolith (Bradley *et al.*, 1984; Sandford, 1986). Sandford (1986) further used track densities in IDPs to constrain the heliocentric distance during exposure and used this information to distinguish, on a statistical basis, between asteroidal and cometary grains. This technique requires the presence of competent silicates, like olivine and pyroxene, in crystals large enough to preserve the tracks. This requires crystals on the order of 0.1 μm; the grains have to be larger than the tracks they are recording.

Fluid Inclusions

Because so many meteorites show pervasive effects of aqueous fluid processing, it is reasonable to expect to find fluid inclusions in extraterrestrial samples. In fact, these have recently been recognized in the ordinary chondrite Monahans (1998) and are receiving attention at this moment (Zolensky *et al.*, 1999). The failure to find these inclusions more frequently may be due to decrepitation of these inclusions during the shock events that launched meteorites from their parent asteroids. If fluid inclusions are present in recovered samples, it will present us with opportunities to directly analyze extraterrestrial mineralizing solutions.

Upon recognizing inclusions, one would want to perform the conventional heating/freezing work using a petrographic microscope in order to learn trapping temperatures and possibly solution salinities (Roedder, 1984).

It can be expected that the gas and liquid compositions of such inclusions will be analyzable by Raman and mass spectrometry (Miller and Pillinger, 1997) and that any solid daughter crystals would also be suitable for characterization by Raman microsampling spectrometry (Pasteris and Chou, 1998), analytical electron microscopy, and microparticle x-ray diffraction techniques (Zolensky and Bodnar, 1982; Ohsumi and Zolensky, 1998). It may also be possible to measure the isotopic composition of O in the fluid (assuming it is water) by a sensitive laser ablation technique.

Raman microsampling spectrometry deserves additional comment here, because it is a nondestructive, *in situ* technique not normally applied to meteorites (for an exception, see Wopenka, 1988). The technique is easy to use and involves laboratory-scale equipment. This vibrational spectroscopic technique examines the inelastic scattering of monochromatic visible light as it interacts with covalent bonds in minerals, liquids, and gases. Thus although applicable to three of the four states of matter, it is limited to materials containing covalent bonds. For these materials, Raman spectrometry can be used to identify compounds, characterize composition and degree of crystallinity, and study bonding modes (Wopenka, 1988; Pasteris and Chou, 1998). In addition, careful analysis of the Raman scattered line shape can give insight into the dynamics of displasive phase changes (McMillan, 1989).

The monochromatic laser can be focused to 1 μm diameter and can be used to study materials embedded as far as 100 μm deep into transparent materials. It is possible that thermal effects are produced in the sample during such fine focusing—this effect has yet to be adequately addressed. In the past, the structures of such materials as graphite and PAHs have been profitably studied. The technique has been successfully applied to qualitative and quantitative analysis of molecular species (including CO, CO_2, CH_4 and other hydrocarbons, N_2, H_2, O_2, and H_2S) in liquid and glass inclusions down to only a few micrometers in diameter (McMillan, 1989). Clathrates can also be studied by Raman spectroscopy (Dubessy *et al.*, 1982; Seitz *et al.*, 1987).

It is possible to complement the Raman analyses of gases and daughter minerals with *in situ* SXRF analyses of the fluid-inclusion solution composition. This nondestructive technique can be applied immediately following the Raman work and leaves the inclusion available for later isotopic characterization.

Age Dating

It seems likely that some components of both comets and asteroids predate the formation of the solar system. Detection of extinct radionuclides would provide an important picture of the pre-accretion and accretion stage of the nebula. Cosmic-ray exposure clocks could also be used to distinguish between mineralogic processes occurring during irradiation within a comet as opposed to that occurring before this stage. It should ultimately be possible to distinguish between irradiation occurring before the nebula in interstellar space. This is not currently possible.

The most commonly used radionuclide clocks are based on lithophile elements such as K, Rb, Sm, Th, U, and Pb. For iron meteorites derived from asteroidal cores, the high concentration of noble metals makes it possible to use the β-decay of [187]Re to [187]Os, although the uncertain half life of this reaction renders results

ambiguous (Mittlefehldt *et al.*, 1998). Chronological information can also be obtained from extinct radionuclide systems, if the isotopic signature of the early radioactive decay has been preserved. These systems include ^{107}Pd, ^{182}Hf, ^{205}Pb, ^{244}Pu, ^{146}Sm, ^{53}Mn, and ^{129}I, and can be used to measure the time after accretion when the important geologic processes of magmatism, core formation, and metamorphism occurred (Rowe *et al.*, 1970; Mittlefehldt *et al.*, 1998).

A severe limitation on analysis of the required elements for age dating is the availability of reliable blanks at the subpicogram level. For example, at CI abundance, in order to determine the concentrations of the critical elements Rb, Sr, Sm, Nd, U, and Pb, 1–10 μg of sample are required just to equal the elemental concentrations present in the best available blanks (Turner, 1991). It is clear that heroic work is required in the essential, though unexciting, effort to improve the quality of blanks.

The brightest candidate in this otherwise dim picture is ^{39}Ar-^{40}Ar dating by **laser ablation mass spectrometry**, due principally to the relatively high abundance of K in chondritic samples (566 ppm), and also to the small required mass for analysis (1 μg). Metamorphism and impact ages are probably best determined by the $^{39}Ar/^{40}Ar$ method (Bogard and Garrison, 1995). This technique uses ^{39}Ar produced by ^{39}K by (n, p) reactions by fast neutrons from a nuclear reactor to establish the amount of parent ^{40}K in the sample. A major technical advantage of this technique over conventional K-Ar dating is that only one aliquot of sample needs to be analyzed, therefore reducing problems of sample heterogeneity (Reddy *et al.*, 1997). The current limitation by interference from absorbed atmospheric ^{40}Ar could be circumvented by returning the sample to Earth in a pressurized canister (as is planned for Muses-C), but another interference by organic matter at mass 39 will continue to be a problem. A serious impediment to ^{39}Ar-^{40}Ar dating sensitivity improvement is ^{39}Ar recoil (Villa, 1997), which should be a serious problem for submicron masses or aggregates of smaller grains (Turner, 1991). However, a technique has recently been developed to vacuum encapsulate the ultra-small sample during analysis, preventing loss of ^{39}Ar gas (Foland *et al.*, 1992; Smith *et al.*, 1993). This technique has been modified and applied to *in situ* dating of illite grains of microgram mass within thin sections (Dong *et al.*, 1997). This mass corresponds to volumes on the order of 60 μm on a side. There is promise that the analytical sensitivity can be further reduced to permit *in situ* dating of nanogram-sized samples in the foreseeable future. Nevertheless, it must be borne in mind that, to be successfully dated, a mineral must contain essential K and have remained competent (no degassing) for its lifetime; these are not simple limitations. Few minerals will be found to satisfy these requirements; however, the recent discovery of sylvite (KCl) within an ordinary chondrite by one author (M. E. Z.) demonstrates that these K-bearing phases can be found.

The greatest spatial resolution for ^{39}Ar-^{40}Ar dating is possible when an IR or UV laser is used to release the Ar. The advantages of this approach include (1) low blank levels, because only the area impinged by the laser is heated, and (2) high spatial resolution, permitting minerals of different generations or with varying textural or petrographic relationships to be analyzed separately (Kelley, 1995).

Ion probe techniques promise solutions to the age dating problem but so far have only been applied to U-Pb studies of relatively U-rich mineral grains. Such grains will be extremely rare in anticipated cometary or asteroidal samples (Turner, 1991).

Mineralogy and Atomic Structure

Transmission electron microscopy has already been discussed. The combination of TEM with **electron energy loss spectroscopy** (EELS) has proven to be a powerful tool for qualitative to quantitative chemical analyses at the nanometer scale. With EELS one studies the primary processes of electron excitation, in which an electron looses a characteristic amount of energy (Garvie *et al.*, 1994; Egerton, 1996). The apparatus for this analysis is attached to a TEM and is used in conjunction with imaging of ultra-thin slices of a sample. Electron energy loss spectroscopy is particularly sensitive to the presence of molecular species in minerals, such as CO_3^{2-} and BO_3^{3-}. This is because molecular units show characteristic spectral peaks due to excitation of oxygen K-shell electrons (called O-K near edge structure) (Wirth, 1997). In fact, Wirth (1997) has shown that a small peak at ~528 eV in EELS spectra is correlated with water and/or OH content. This observation promises to permit water determination in some minerals at the nanometer scale, which is several orders of magnitude higher spatial resolution than possible with optical spectroscopy.

Recently, Garvie and Buseck (1998) have reported a procedure for determining $Fe^{3+}/\Sigma Fe$ in rock-forming minerals at nanomater-scale resolution using EELS. They find that spectra for particular minerals show Fe $L_{2,3}$ edges with constant shapes for given oxidation states, which permits calculation of $Fe^{3+}/\Sigma Fe$ for a mineral provided that suitable standards have been previously characterized. Apparently, this procedure will work also for noncrystalline materials. The results of this EELS study appear to be more precise than those for the EMPA techniques reported above (Höfer *et al.*, 1996; Sobolev *et al.*, 1999); certainly they are applicable to much smaller samples.

Electron energy-loss near edge structure (ELNES) analysis can be used to investigate the local solid-state environment of certain elements in crystalline and amorphous materials, including valency, coordination, and site symmetry of excited atoms (Garvie *et al.*, 1994). The apparatus for this analysis is also attached to a TEM. Bradley (1994) used ELNES in tandem with TEM imaging to characterize the structural and compositional state of amorphous materials within chondritic IDPs. Electron energy-loss near edge structure has also been applied to determination of the spectroscopy of mixed Si coordination in minerals, such as the silica polymorphs (Poe *et al.*, 1997). This would be very useful in characterization of silica phases formed during impact processes (*i.e.*, stishovite, coesite, and keatite), although silica is not a common phase away from the Earth. This technique should also be applicable to majorite and some garnets (Poe *et al.*, 1997).

Usual x-ray diffraction techniques cannot be applied to nanogram-sized mineral grains (measuring only few a few microns at most). However, the crystal structure of such diminutive samples can be fully characterized using **synchrotron x-ray diffraction** (SXRD) (Ohsumi and Zolensky, 1998). In this Laue technique, an extremely bright x-ray beam (~10 orders of magnitude brighter than conventional x-rays provided by a rotating anode instrument) is collimated down to ~3 μm, permitting collection of a full three-dimensional x-ray intensity data set for a grain measuring at least this size, in only 1–6 h. The procedure can be performed on separated crystals or on grains *in situ* and is nondestructive. Most recently, Ivanov *et al.* (2000) collected single-crystal Laue patterns of a new meteoritic mineral (FeTiP) present in only one thin section as three grains measuring a maximum of 10 μm in dimension (Fig. 8). The x-ray data set was used to perform a full three-dimensional
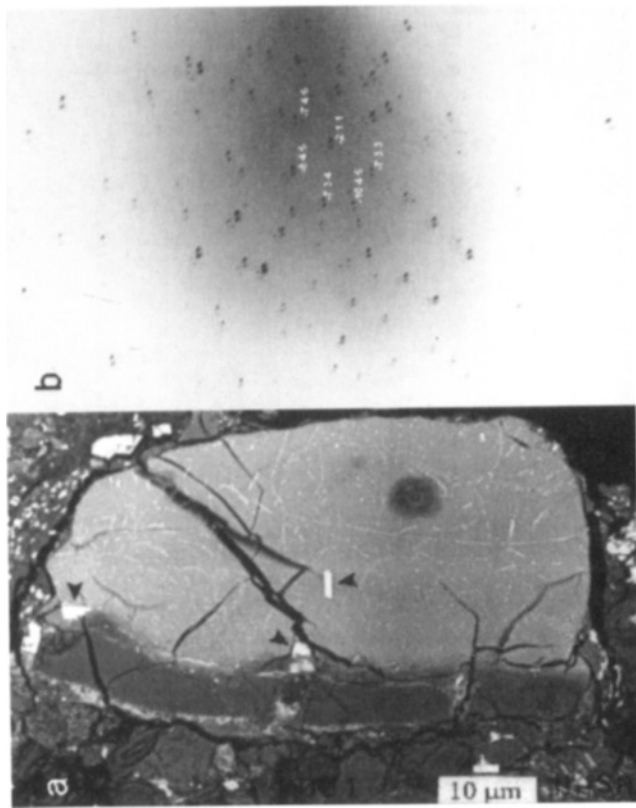
FIG. 8. (a) Backscattered electron image of a rounded grain of cronstedtite from the Kaidun chondrite, containing three small crystals of the new phase FeTiP (arrowed). Scale bar measures 10 μm. (b) Single-crystal Laue pattern obtained from the middle FeTiP crystal in (a) by synchrotron x-ray diffraction. A few of the reflections are labeled with miller indices. Each reflection consists of four separate spots, indicating that the crystal actually consists of four domains in nearly parallel growth. Even with this imperfection, the data set was sufficient to permit a full three-dimensional crystal structure analysis to be performed.

crystal structure refinement of the new mineral, yielding valuable clues regarding the genesis of the host meteorite. Because this analysis was performed *in situ*, the grains remain in the section, available for further study.

The short-range atomic structure of noncrystalline materials (phases lacking long-range order) can be investigated by non-Bragg scattering methods and spectroscopic methods using synchrotron x-rays. X-ray scattering from such materials is about two orders of magnitude less intense than normal Bragg scattering from crystalline materials, and thus difficult to observe without the intense synchrotron x-ray source (Basset and Brown, 1990). This technique might prove to be one of the most important for cometary and space-weathered samples, where we may encounter abundant amorphous phases.

A key element in understanding cosmochemical and physical processes to all size scales is the dependence of physical and chemical properties of extraterrestrial materials on molecular structure, chemical bonding, and composition. Spectroscopic studies of minerals can provide much of this information. However, because of the small sample volumes, low concentrations of some important trace elements, and eternal need for high signal-to-noise ratio data, extremely high photon fluxes are required for many of these studies. Synchrotron-based analytical techniques have recently permitted use

of these techniques to very small sample volumes, and ppb-level trace element concentrations. Probably, the most important of these are **x-ray absorption spectroscopy** (XAS) methods, including **extended x-ray absorption fine structure** (EXAFS) and XANES, which can provide information on the local structure (<5 Å radius around a selected atom) and bonding for atoms in all types of solids (Bassett and Brown, 1990). Again, using synchrotron light sources, these techniques are applicable to nanogram-sized sample volumes. The EXAFS spectra can yield the distance, number, and identity of first- and second-nearest neighbors surrounding an absorber atom in a sample, and can be applied to almost all elements. The XANES spectra can provide information on the absorber atom's local environment and its valence (oxidation state) (Bajt *et al.*, 1995). Thus, this technique would yield critical data on the valence and spin state of Fe, Ti, Co, Ni, Cu, or Mn in a mineral. X-ray absorption near-edge structure has recently been used to map the distribution of K and C within chondritic IDPs (Flynn *et al.*, 1998a,b). Sutton and Flynn report that the new APS beamline can be used to measure Fe-oxidation state on samples containing as little as 1 femtogram of Fe (Sutton and Flynn, 1999).

Thus, EXAFS and XANES complement x-ray diffraction studies by providing details of the local structure rather than the average structure. This is particularly important in studies of minerals where more than one element may occupy one type of crystallographic site, which is to say, practically all important rock-forming minerals. Examples of the use of these spectra are legion. For example, knowledge of the oxidation state of Fe in minerals provide information on the O fugacity of a planetary object's interior or its past atmosphere, and its degree of aqueous alteration (Browning *et al.*, 1996). The site geometry of Ti^{4+}, for example, cannot be studied by any other technique (Waychunas, 1987). The cation environments in silicate glasses can also be characterized, which can reveal critical details of their formation processes—radiation damage *vs.* igneous, for example.

Transmission IR-Vis spectra have been successfully made from individual nanogram-sized IDPs, over the range 2.5–25 μm, for grains >5 μm (Sandford and Walker, 1985; Bradley *et al.*, 1992). In addition, Bradley *et al.* (1996) have collected IR-Vis reflectance spectra of ~10 μm in diameter IDPs in the laboratory using a specially-fitted micro FTIR instrument, over the range 380 to 1100 nm (Fig. 9). The high-intensity IR beamline at the Brookhaven NSLS is well suited for characterization of subnanogram-sized objects, because it provides an IR beam spot >100× brighter than laboratory IR spectrometers and can cover the entire range from 2–25 μm in wavelength (Reffner *et al.*, 1994). Using IR-Vis spectroscopy, workers have identified similarities for some particles to reflectance spectra collected from asteroids. This work is of fundamental importance, because it ties together laboratory-collected data for samples with remote sensing information of probable parent bodies.

Atomic force microscopy (AFM) (discussed above) is currently being applied to interplanetary dust by Wolfgang Klöck, Jens Romstedt, and their collaborators in Europe as they prepare for the European Space Agency's Rosetta mission, which will include AFM on the payload. This instrument is also planned for the payload of the Mars 2001 mission. Although this technique is promising, the results from analyses of the dust have been somewhat disappointing (Klöck, pers. comm., 1998). This is probably due to the widely varying electrical properties making up these materials. It is clear that this technique will be applicable to some natural materials.
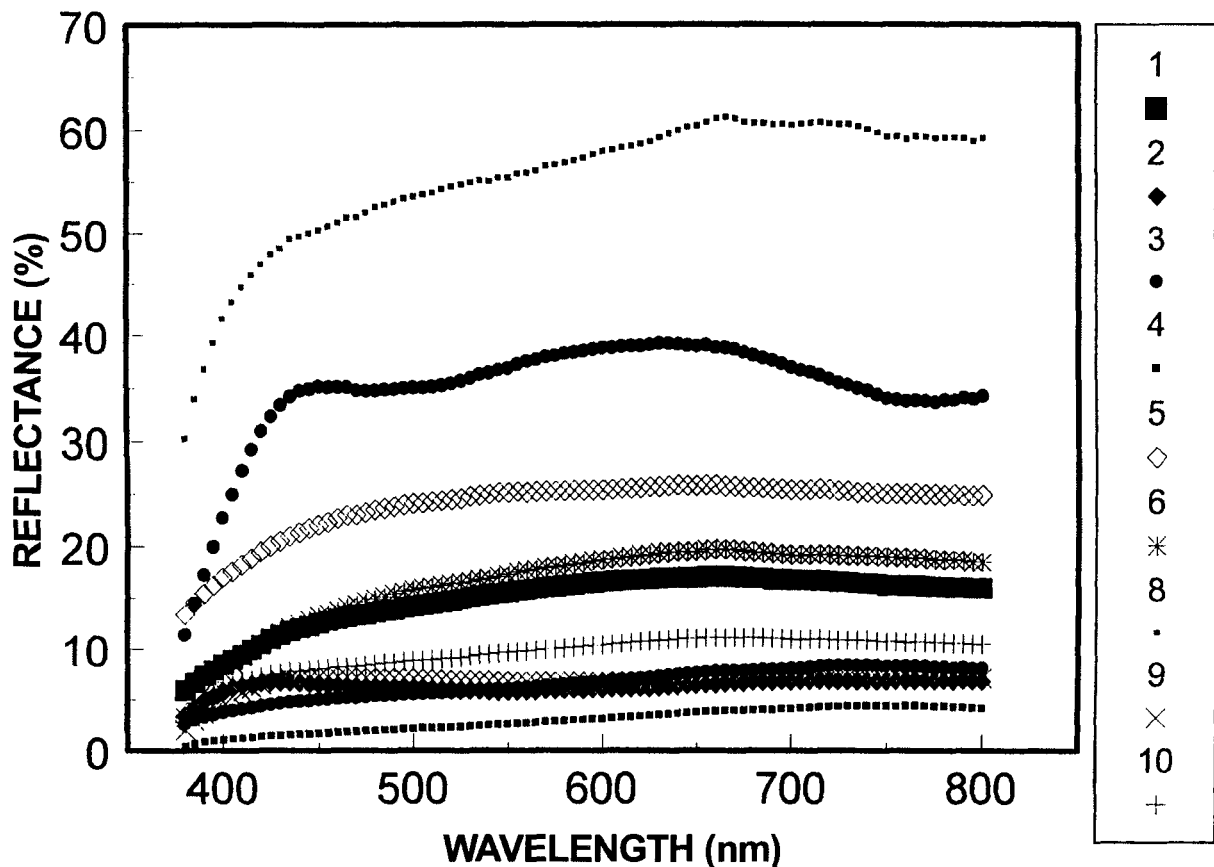
FIG. 9. Reflectance spectra of 10 individual chondritic IDPs. The spectrum at the top, with the steepest rise, resembles those for P and D-class asteroids, which are believed to be rich in organics. This particular IDP, L2006 cluster 4, has a bulk C content of ~50 wt%. Spectra collected by John Bradley and Lindsey Keller.

Cathodoluminescence (CL) is the emission of light from a material following electron irradiation. **Cathodoluminescence microscopy and spectroscopy** in an SEM is a nondestructive technique for characterization of defect centers in materials with high sensitivity and spatial resolution (Yacobi and Hoyt, 1990). Although CL spectroscopy can be used to characterize the nature of impurity ions within materials, it is a point technique. Therefore, a quantitative correlation between CL integrated intensities and bulk trace element analyses by any other technique should not be expected. In addition, the observed CL spectra may be reduced by competitive nonradiative de-excitation processes in some samples, or when impurities are present in nonluminescent structural configurations. It is most effective to use a trace element analysis to assist in identification and interpretation of the CL spectra (Stevens Kalceff *et al.*, 1997).

Physical properties

Magnetic force microscopy (MFM) permits imaging of the magnetic structure of materials, using much of the same equipment as AFM (Cloete *et al.*, 1998, 1999). In this technique, the AFM tip interacts with the stray magnetic field emanating from the sample. Submicron-resolution imaging of the magnetic orientation and domain structure of the sample is obtained (Fig. 10). In fact, this technique is facilitated by small (submicron), single domain samples, because these are very efficient carriers of remnant magnetization signatures; larger crystals develop a multidomain character.

Another application of the AFM technique is the investigation of mechanical properties by **force spectroscopy** (Burnham and Colton, 1993). In this technique, the tip indents the sample surface. If the indentation force is periodically modulated, the amplitude of the tip position is a function of the material elasticity.

Density measurements may be made of individual nanogram-sized grains by three techniques, as shown by work on IDPs. Direct weighing of IDPs has been performed using a glass fiber balance (Fraundorf *et al.*, 1982). Flynn and Sutton (1991) have used the synchrotron x-ray excitation of some elements (*i.e.*, Fe) within chondritic IDPs, having calibrated this using standards of known mass and composition. Corrigan *et al.* (1997) performed image processing of carefully sliced IDPs, again with reference to a known density standard.

Sample Analysis Flow Charts

A major goal is to maximize the science return from the smallest possible sample mass. Analyses should be as nondestructive as possible. The analysis plan has to be flexible because of the still unknown nature of the samples, especially for the comets and interstellar grains. One can use Table 1 to construct analyses flow charts, taking full advantage of the nondestructive analyses before proceeding to the more destructive ones. The critical thing is to be aware of the full universe of applicable analyses before launching into the sample preliminary investigation, to ensure that maximum information is obtained from the precious returned sample.
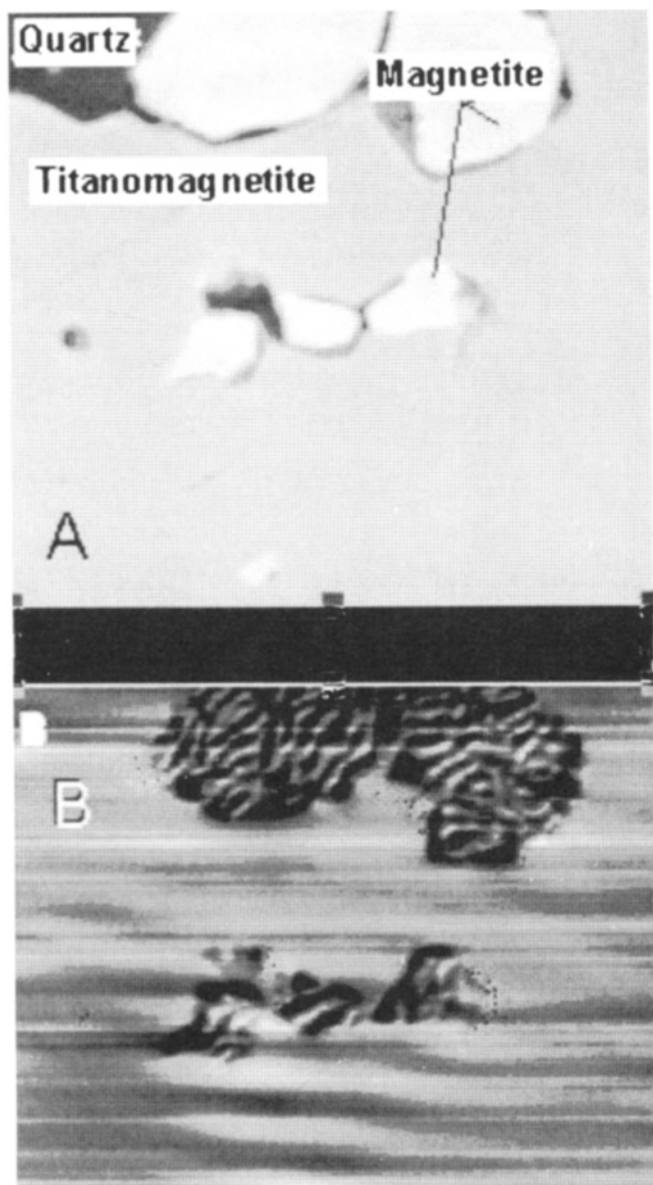
FIG. 10. (a) Backscattered electron image of titanomagnetite, magnetite, and quartz of a granite-gneiss, Vredefort, South Africa. (b) Magnetic force microscope image of the same area as in (a), showing the multidomain magnetic structure of the magnetite and the nonmagnetic nature of the titanomagnetite and quartz. The width of field of view is 20 μm. Image provided by Thinus Cloete.

HOW REPRESENTATIVE OF PRIMITIVE OR EVOLVED SOLAR SYSTEM OBJECTS ARE NANOGRAM-SIZED SAMPLES?

A key question to then ask is how representative are microscopic samples of bodies that measure a few to many kilometers across? A decade of work by persistent IDPs workers has demonstrated that carefully organized, sequential analyses permit a comprehensive series of measurements to be obtained even from individual nanogram-sized particles (~10 μm in diameter). From such analyses of a grand total of 0.5 μg of chondritic IDPs (~1500 particles), multiple compositional types have been identified, and their geochemistry has been determined sufficiently to infer key aspects

of their origins and histories. The gross similarities of these nanogram-sized chondritic IDPs reveal that their parent comets and primitive asteroids have exceedingly fine-grained regoliths (Lindstrom et al., 1990). Comets are certainly not homogeneous at the femtogram grain scale (Clark et al., 1987) but perhaps are homogeneous at the nanogram mass scale.

With the Galileo flybys of Gaspra and Ida, and Mars Global Surveyer's observations of Phobos, it is now recognized that small airless bodies have indeed developed a particulate regolith. Acquiring a sample of the bulk regolith, a simple sampling strategy, provides two critical pieces of information about the body. Regolith samples are excellent bulk samples because they normally contain all the key components of the local environment, albeit in particulate and somewhat processed form. Furthermore, because this fine fraction dominates remote measurements (Pieters et al., 1993), regolith samples also provide information about surface alteration processes and are a key link to remote sensing of other bodies.

Of course, regoliths are also the places where foreign materials (meteorites, micrometeorites) will reside, and one will have to be ever vigilant to recognize non-indigenous materials among regolith grains. The lunar experience tells us that this can be done, although the problem will be more acute with purely fine-grained sample returns. The lunar regolith was demonstrated to contain 1–4 wt% foreign (predominantly chondritic) material, which was recognized early on through a comparison of the siderophile composition of the lunar regolith vs. lunar basalts, and this posed no significant problems for characterization of the Moon (Wasson et al., 1975). If one wished to obtain a bulk composition of another regolith, one could make a similar correction, subtracting out 1–4 wt% chondritic composition materials, as a first approximation. For most elements, this should not introduce significant analytical uncertainty. However, if one is characterizing the mineralogy or more detailed nature of individual particles, one will probably have to measure the O-isotopic composition of suspect grains (or make some similar diagnostic measurement) in order to weed out interlopers, at least until one understands the sample well enough to recognize foreign material more readily.

Meteorite studies indicate that a statistically significant number of nanogram-sized particles should be able to characterize the regolith of a primitive asteroid. The carbonaceous chondrite Murchison, for example, contains both fine-grained matrix as well as larger components such as chondrules, CAIs, large crystal fragments, etc. An INAA study of grains from the carbonaceous chondrite Murchison found that the matrix component of this meteorite is homogenous to the nanogram scale (Lindstrom et al., 1990). However, the presence of larger components within Murchison (e.g., chondrules, CAIs, large crystal fragments, etc.) points out the limitations of using data obtained from nanogram-sized samples to characterize entire primitive asteroids. Analyses of Allende bulk material indicate that gram-sized quantities are required to yield bulk chemical analyses accurate to within 1%; for 100 mg, accuracy is degraded to 3% (Jarosewich et al., 1987). However, the most important asteroidal geological processes have left their mark on the matrix, becauce this is the finest-grained portion and therefore most sensitive to chemical and physical changes. Thus, the following information can be learned from this fine grain size fraction alone: (1) mineral paragenesis and igneous processes; (2) regolith processes; (3) bulk composition; (4) conditions of thermal and aqueous alteration (if any); (5) relationships to planets, comets, meteorites (via isotopic analyses, including O); (6) abundance of water;

(7) abundance of organics; (8) history of volatile mobility; and (9) presence and origin of presolar material.

CONTAMINATION CONCERNS

A significant constraint on any sample return is the absolute requirement for a contamination-free sample container. Calculations indicate that for a chondritic composition sample weighing 1 μg, the total permitted contamination levels for inorganic elements on the walls of the sample container vary from 10^{-9} to 10^{-16} g for instrumental and radiochemical neutron activation analyses (INAA and RNAA). For nanogram-sized grains, the requirements are significantly more stringent. Accordingly, smaller-scale techniques such as ion probery, PIXE, and RIMS require even more care in contamination control. For organic compounds, contamination control requirements are not only hard to achieve but currently often difficult to usefully define.

Blank levels must be decreased, as the necessary developments in sample handling are accomplished. This is well described by Miller and Pillinger (1997). The experiences of Al Nier are instructive in this regard. In his initial attempts to measure noble gas contents of individual chondritic IDPs, he discovered that the metal foils he was using for sample containment contained hitherto unrecognized, and rather high, amounts of these same noble gases (Al Nier, pers. comm., 1990). He was therefore led into a tedious side-investigation of the noble gas contents of many laboratory materials. Similar fates undoubtedly await other careful analysts.

In summary, current technology allows even the tiniest samples to provide major breakthroughs in understanding the origin and compositional evolution of the solar system. Fortunately, further advances in sensitivity and accuracy of laboratory analytical techniques can be expected to enhance the science value of nano- to microgram-sized samples further. This factor highlights a key advantage of sample returns—that the most advanced analysis techniques can always be applied in the laboratory and that a well-preserved sample is available for future investigations.

SAMPLE DEGRADATION

Although it would be most informative to have as returned samples undisturbed, pristine materials maintained at the exact environmental conditions as they existed on the parent body (temperature, atmosphere, *etc.*), this is not practical at this time. Even where great pains were taken to ensure this sampling fidelity, for the Apollo lunar samples, many samples were exposed to pure O and the humid environment of the lunar excursion module and return capsule (Freidman *et al.*, 1970; Epstein and Taylor, 1974). We have to understand how the returned samples will have been affected by heating, shock, disaggregation, and pulverization. Sometimes the samples will be flooded with terrestrial air (albeit clean air) upon reentry, as will happen for *Stardust*. For low-cost missions, it may not be practical to return samples without some degradation. By careful control of contamination sources and the judicious employment of thermal control, we generally can preserve samples such that a very large fraction of science objectives can be met.

CONCLUSIONS

Thus, the following information can be learned from this fine-grain size fraction alone: (1) mineral paragenesis; (2) regolith processes; (3) bulk composition; (4) conditions of thermal and aqueous alteration (if any); (5) relationships to planets, comets,

meteorites (*via* isotopic analyses, including O); (6) abundance of water; (7) abundance of organics; (8) history of volatile mobility; and (9) presence and origin of presolar and/or interstellar material.

Therefore, current technology allows even the tiniest samples to provide major breakthroughs in understanding the origin and compositional evolution of the solar system. Fortunately, further advances in sensitivity and accuracy of laboratory analytical techniques can be expected to enhance the science value of nano- to microgram-sized samples further. This factor highlights a key advantage of sample returns—that the most advanced analysis techniques can always be applied in the laboratory and that a well-preserved reservoir of samples remain available for future investigations.

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