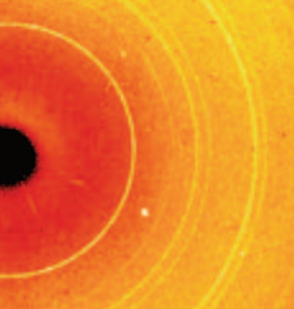


Synchrotron Radiation, Neutron, and Mass Spectrometry Techniques at User Facilities

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X-ray diffraction pattern of stishovite (SiO₂) in a diamond anvil cell at 40 GPa. From Prakapenka et al. (2004), *Journal of Physics and Chemistry of Solids* 65: 1537–1545

User research facilities around the world offer tremendous opportunities for scientific experimentation by members of the Earth science community. Synchrotron radiation sources, neutron sources, mass spectrometers, and others represent a powerful force in tackling complex scientific problems. In these techniques, Earth materials are bombarded with beams of ions, subatomic particles and/or photons to learn the secrets of their properties and histories. Some of these methods can be applied to nanoscale materials with “desktop” instruments while others require macroscopic samples and utilize large-scale devices residing in multiple buildings; and there is everything in between.

KEYWORDS: Synchrotron radiation, neutrons, mass spectrometry, user facilities, analytical techniques

INTRODUCTION

Analytical methods available at user facilities are remarkable in their scope, and their capabilities are highly complementary. Some methods require samples to be exquisitely prepared while others can be applied to “as-is” specimens. Some methods involve the coordination of large, multibuilding apparatus while others are carried out in a small room. Although the instruments are highly variable in their make-up, the techniques they offer represent a powerful force in tackling complex scientific problems. From chemical analyses of components in nanogram specimens from the interplanetary medium, to chronological studies of the earliest rocks from the Earth’s crust, to the properties of the mineral phases in the deep Earth, the scientific potential is huge and limited only by the imagination and innovation of Earth scientists.

Here, we highlight some current capabilities to give a flavor of the information that can be obtained at user facilities. Our focus is on techniques using synchrotron radiation, neutrons, and mass spectrometry. Each provides a different yet complementary view into the complex nature and histories of Earth materials and geological processes. Synchrotron radiation is well-suited for experiments that define the arrangement of atoms and their electronic structures. Neutrons can probe the structures and dynamics of light elements. Mass spectrometry yields information on isotopic composition valuable for radiometric dating. Although the

operation of these instruments is complex at the lowest level, they are designed, constructed, and operated with novice users in mind. User-friendly software interfaces and skilled technical assistance are available.

SYNCHROTRON RADIATION

Synchrotrons generate intense radiation in the infrared to X-ray regime. The unique properties of this radiation (high brilliance, polarization, continuous energy spectrum, temporal structure) allow a wide variety of analytical techniques. The application of these techniques can provide crucial information about the nature of minerals and other Earth materials, including crystalline structure, chemical composition, chemical speciation, surface and interface structure, electronic structure, and porosity (e.g. Fenter et al. 2002). One of the major advantages to using synchrotron light for investigating Earth materials is that the penetrating power of the radiation permits studies in near-natural conditions, for example, in the presence of water. Synchrotron experiments are conducted at a “beamline” consisting of optical equipment to condition the X-ray beam and a shielded experiment room containing a sample manipulator and X-ray detectors (FIG. 1).

Earth materials are often heterogeneous, and X-ray *microbeam* studies are valuable in unraveling this complexity. Spatial resolutions down to 100 nm are achievable using zone plates, mirrors, and refractive optics. Most X-ray-based methods can be applied with high spatial resolution, including X-ray fluorescence (XRF), X-ray absorption fine structure (XAFS), X-ray diffraction (XRD), and computed microtomography (CMT). By applying these techniques in a nearly simultaneous fashion, it is possible to produce elemental maps with sub-part-per-million sensitivity and determine the speciation and mineralogy at selected locations in the material. An example is a study of Ni- and Zn-contaminated soils from the Morvan region of France, which resulted in a quantitative assessment of the forms of these two elements (Manceau et al. 2003). Toxic and radioactive elements are also amenable to this approach. In a plutonium sorption experiment on Yucca Mountain (Nevada, USA) tuff, Pu was found to be strongly associated with Mn-rich smectite phases and all but absent in the zeolite and iron-oxide grains that dominate the rock (Duff et al. 1999).

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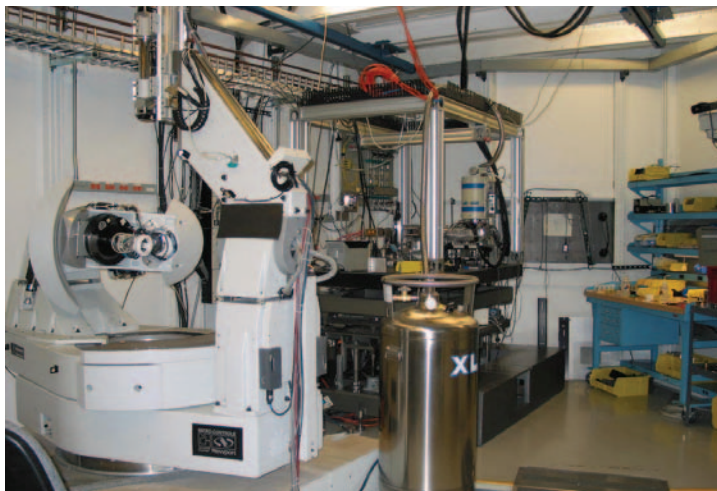


FIGURE 1 Photograph of the GeoSoilEnviroCARS undulator experimental station at the Advanced Photon Source (Argonne, Illinois, USA) showing the surface and interface diffractometer (left) and X-ray microprobe (back center). COURTESY OF GEOSOLENVIROCARS, UNIVERSITY OF CHICAGO

X-ray absorption fine-structure spectroscopy (XAFS) provides detailed information regarding the average electronic and molecular energy levels associated with a specific element. This information permits determinations of oxidation state, coordination number, identity of nearest neighbors and bond lengths (e.g. Koningsberger and Prins 1988). Such data are crucial for understanding the structure of complex minerals, geochemical properties of Earth materials, and transport mechanisms for ore-forming metals, for example. Speciation measurements can be obtained for trace elements down to about 10 parts per million and with or without spatial resolution. The XAFS measurement consists of collecting absorption intensity (or some product of the absorption, such as X-ray fluorescence) as the energy of the exciting X-ray beam is scanned with high-energy resolution (<1 eV) through the X-ray absorption edge of the element of interest. The resulting absorption spectra can then be interpreted in terms of the molecular environment of that atom (e.g. Stern and Heald 1983). The method is applicable to virtually all elements in the periodic table, and samples in all forms (liquid, solid, gas) can be analyzed in this way.

XAFS is extremely valuable in low-temperature geochemical studies, such as for establishing the speciation of contaminants in sediments (See Brown et al. 2006). For example, Zachara et al. (2004) showed that toxic hexavalent chromium from Hanford waste tanks was only partially reduced to trivalent chromium in the underlying sediments. It is also possible to determine the speciation of cations in glasses (e.g. Galois and Calas 1993) and in situ melts under controlled oxygen fugacity (Berry et al. 2003).

Synchrotron radiation also permits crystallography experiments in *high-pressure devices*, such as the large-volume press (LVP) and the diamond anvil cell (DAC), both of which can also be heated to high temperature. An advantage of in situ observations is that complications due to quench effects can be avoided. In this way, the extreme conditions deep in the Earth can be simulated, and determinations can be made of equations of state, crystal structures, and phase relations of mantle and core materials, for example. The DAC consists of two gem-quality diamonds with small facets opposed to compress a hole-bearing gasket (the sample chamber). Nanogram quantities of material (powder or single crystal) can be compressed to ~200 GPa and laser heated (FIG. 2) to several thousand degrees (i.e. to

outer core conditions). Pressure determinations are made in situ, using ruby fluorescence or diffraction from included materials of known lattice parameters. Temperature is determined from the color of the sample's incandescence. A recent flurry of DAC research activity has focused on the discovery of a post-perovskite phase transition in MgSiO_3 near 125 GPa (e.g. Murakami et al. 2004); this discovery is relevant to improving our understanding of the structure and dynamics of the lowermost portion of the mantle (<300 km from the core-mantle boundary).

The LVP is a floor-standing hydraulic ram with external heating and a larger (mm^3) sample chamber than the DAC. Pressure and temperature (<30 GPa, <3000K, i.e. mantle conditions) are determined by load and thermocouple, respectively. For both the DAC and LVP, conventional X-ray diffraction experiments are conducted to characterize the sample under these extreme conditions. A recent advance has been the development of deformation tooling for the LVP that allows samples to be deformed under high P-T conditions with well-controlled strain rates. By analyzing the distortion of the Debye rings in powder diffraction patterns, elastic lattice strain can be determined, which is related to stress through elastic constants (Singh 1993). This approach has been used to determine the pressure and strain dependence of the strength of Mg_2SiO_4 ringwoodite (Nishiyama et al. 2005).

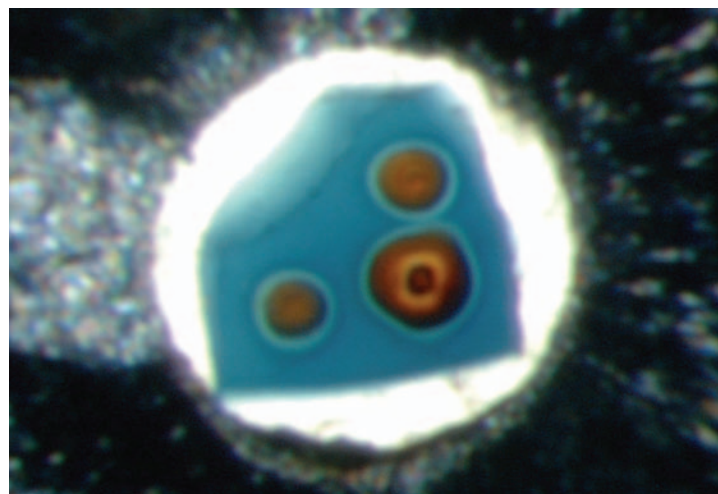


FIGURE 2 Laser-heated hydrous ringwoodite $[\gamma\text{-(Mg,Fe)}_2\text{SiO}_4]$ single crystal (~100 μm) at 30 GPa in a diamond anvil cell. A silicate perovskite plus magnesiowüstite assemblage formed at three different temperatures is present within each of the round heated areas. PHOTO COURTESY OF S.D. JACOBSEN (CARNEGIE INSTITUTION OF WASHINGTON) AND J.-F. LIN (LAWRENCE LIVERMORE NATIONAL LABORATORY)

Microtomography is the extension to finer spatial resolution of tomographic imaging techniques used in medicine (CAT scanning). By using high-brightness synchrotron radiation beams, spatial resolutions in the μm range can be achieved at the expense of maximum sample size (typically no sample larger than mm to cm size range). The internal microstructure of valuable or fragile objects can be examined. In addition, element-specific tomography is possible either by collecting transmission tomograms above and below an absorption edge or by using fluorescence techniques. An attractive aspect of microtomography is that virtually no sample preparation is required and essentially any object can be imaged. Microtomographic images can be used to determine the microdistribution of contaminants in plants, locate mineral inclusions in mantle-derived diamonds, visualize the inundation of soils by oil and water, determine

grain-size distributions in volcanic rocks, and observe the morphologies of vapor bubbles in melts (e.g. Rivers et al. 2004).

Mineral surface reactivity depends on the identity and arrangement of surface functional groups. *Interface scattering*—the angular distribution of X-radiation scattered from highly polished, atomically flat crystals—is one of the few approaches that can be used to determine the arrangement of atoms at truncated surfaces and at mineral–water interfaces. Such studies utilize high-precision diffractometers (Fig. 1) and are valuable in developing a detailed understanding of the chemical reactions at these surfaces and interfaces. In addition, in conjunction with spectroscopic methods, sorption experiments can reveal the bonding behavior of solute species, particularly those of interest from a geochemical transport standpoint. Recent work has focused on reactivity and sorption of hydrated metal oxide surfaces, such as hematite (Trainor et al. 2004) and orthoclase (Fenter et al. 2000). This work demonstrates that the arrangement of atoms at the mineral–water interface can have a dramatic control on reactivity (See Brown et al. 2006).

The discussion above, focusing on high-energy techniques, is far from an exhaustive description of methods used at synchrotron user facilities to investigate Earth materials. In particular, soft X-ray and vacuum ultraviolet (VUV) synchrotron sources offer methods optimal for studies of light elements. For example, scanning transmission microscopy is valuable for high-resolution (sub-50 nm) imaging and light-element speciation mapping (e.g. carbon compounds). Synchrotrons are also attractive sources of infrared radiation allowing Fourier transform infrared (FTIR) analyses with 100-fold intensity enhancement over laboratory sources plus spatially resolved capabilities at the ~10 μm scale.

NEUTRON METHODS

Beams of neutrons provide an extremely versatile set of tools for mineral sciences, yet for a number of reasons the mineralogical and Earth sciences communities are a long way from fully exploiting the potential of neutron scattering (Rinaldi 2002; Dove 2002).

The power of neutron scattering arises from two factors: first, neutrons have a mass that is similar to the masses of atoms and second, neutrons interact with matter via short-range interactions with atomic nuclei or via dipolar magnetic interactions with any magnetized ions. The point about the mass of the neutron means that beams of neutrons can be tuned to have wavelengths comparable to typical interatomic spacings while simultaneously having energies that are comparable to the energies of thermal vibrations. Thus neutrons can uniquely give information about both the structure and dynamics of matter, and experiments can be designed to optimize one or the other, or both at the same time.

The second point is important because the interaction between neutrons and atomic nuclei is nucleus specific, which means, for example, that Mg^{2+} , Al^{3+} , and Si^{4+} have distinctly different neutron scattering cross sections, unlike scattering by X-rays. Thus neutrons are able to provide direct information about $Mg^{2+}/Al^{3+}/Si^{4+}$ ordering in minerals; for example, Welch and Knight (1999) studied cation ordering of these species in an amphibole. Hydrogen, an important component of many minerals, is a particularly special case. The scattering from the 1H nucleus when the spins of the neutron and proton are along the same direction is significantly different from the case where the spin vectors are aligned in opposite directions. On the other hand, the deuterium nucleus, 2H , has no spin, and its interaction with neutrons is different again. The significance of



FIGURE 3 Interior of the ISIS Neutron Facility Experimental Hall (Chilton, UK). COURTESY OF THE COUNCIL FOR THE CENTRAL LABORATORY OF THE RESEARCH COUNCILS (CCLRC)

all this is two-fold: first, neutrons can see hydrogen in diffraction experiments (typically deuterated samples are preferred in such experiments), and second, the strong spin-dependence of the scattering of neutrons from 1H means that part of the scattering is sensitive to the positions and dynamics of individual 1H atoms (Dove 2002; Bée 1988).

The strength of the interaction between neutrons and matter is usually relatively weak, both for scattering and absorption (there are some notable exceptions that can be exploited). There are two positive consequences. One is that it is possible to develop sample environment equipment, such as high-pressure equipment, without having to worry too much about beam attenuation (Zhao et al. 1999; Le Godec et al. 2001). The other is that a measurement is not dominated by scattering from the surface, as it is in X-ray diffraction. Thus neutrons provide a true probe of bulk properties. The downside of the weak interaction with matter, and the fact that neutrons are not usually produced in copious quantities, is that samples need to be quite large (cm^3 scale) and experimental stations are built to a larger scale than in other techniques.

Two methods are used to produce beams of neutrons (Winkler 2002). The traditional method exploits the fact that nuclear fission reactors produce neutrons, and designs of reactor cores can be optimized to reflect neutrons into beam tubes leading to experimental stations (e.g. ILL, Grenoble, France). This typically results in a continuous beam of neutrons containing a range of neutron wavelengths. Monochromator crystals are used to select the desired wavelength of the beam incident on the sample. The second method generates beams of neutrons by directing a beam of protons onto a metal target—the so-called “spallation” method in which neutrons are knocked out of the nuclei of the target atoms (e.g. ISIS, Oxfordshire, UK; Fig. 3). The spallation method lends itself to producing pulsed bursts of neutrons, and by measuring the time taken for the neutrons to travel from the target to the detector, it

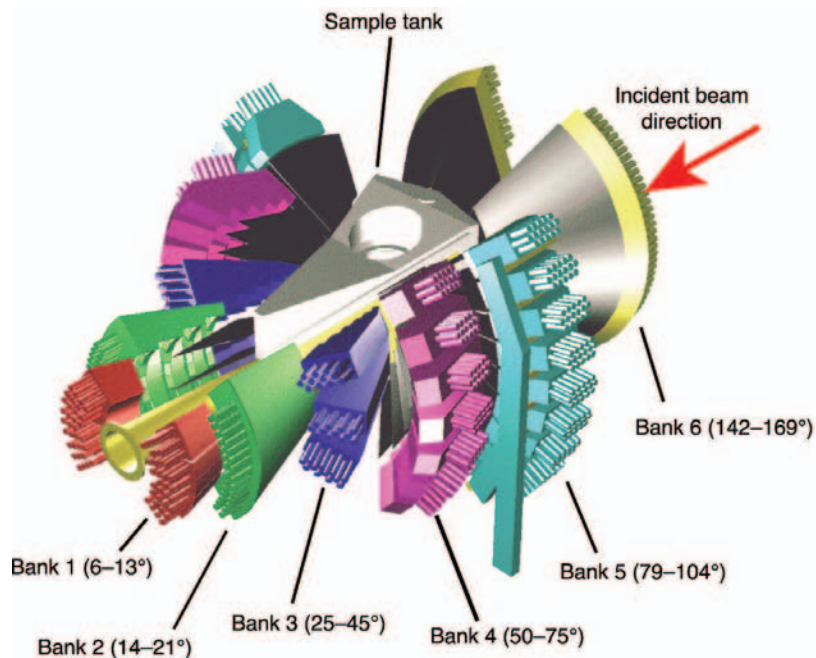


FIGURE 4 Schematic representation (left) and photograph (right) of the General Materials (GEM) diffractometer at the ISIS Neutron Facility (Chilton, UK). The instrument is stacked with banks of detectors covering all scattering angles, with the highest resolution obtained with the back-scattering detectors. This instrument is designed for both diffraction and total scattering measurements. COURTESY OF THE COUNCIL FOR THE CENTRAL LABORATORY OF THE RESEARCH COUNCILS (CCLRC)

is possible to determine the wavelength. These two sources often give rise to complementary experiment instrumentation. For example, a powder diffractometer on a reactor source will use a fixed wavelength and will have detectors in a plane covering a wide range of scattering angles, whereas with a spallation source the full range of wavelengths will be used, and detectors will be positioned around the Debye-Scherrer rings for a range of scattering angles.

We will describe two types of instruments, namely diffractometers and spectrometers. Both measure the intensity of the scattered neutron beam as a function of scattering vector \mathbf{Q} (or $Q = |\mathbf{Q}|$), but the two types of instruments are differentiated by the fact that spectrometers also measure as a function of energy change, E , at the same time. In many cases E can be related to the frequency, ν , of a quantum of excitation, $E = h\nu$.

Diffractometers can be designed to perform traditional measurements for both *powder* and *single-crystal diffraction*, and can be optimized for high resolution or high intensity (Fig. 4). The best high-resolution neutron powder diffractometers give as high a resolution as one could want, with measurements being limited by natural line broadening processes. Diffractometers can also be optimized for measurements with sample environment equipment, including high-pressure apparatus. Of note is the fact that high-pressure work can be performed with spallation sources with measurements taken for scattering angles of 90° , enabling nearly complete elimination of scattering from the equipment (Zhao et al. 1999; Le Godec et al. 2001). It is now also possible to measure sample temperature at simultaneous high pressures and temperatures using *neutron radiography* rather than thermocouples (Le Godec et al. 2001). Examples

of recent applications of diffraction measurements from minerals are given in Dove (2002), Pavese (2002), and Redfern (2002).

Other diffraction methods that are becoming increasingly popular in mineral sciences are techniques focusing on larger-scale structures. These include *small-angle scattering* (e.g. to measure the sizes of precipitates within solid solution), measurements of *texture maps*, and measurements of *strain distributions* within mineral assemblages (Schäfer 2002). Another application that has yet to be used in earnest in mineral sciences is *diffraction or reflection from surfaces*; this application has been greatly used by chemists.

The diffraction measurements described so far focus on measurements of Bragg peaks. Other instruments can be optimized to measure weaker, diffuse scattering. In the case of powder diffraction, measurements of diffuse and Bragg scattering, called “total scattering,” can provide information about pair distribution functions. This is particularly useful for studies of disordered crystalline materials, glasses, and melts, and is a diffraction technique that has a lot of untapped potential for research in mineral sciences (Dove et al. 2002).

Spectrometers are designed to measure the dynamics of atoms within matter. *Dynamical processes* include coherent excitations such as harmonic lattice vibrations (phonons) and spin waves (including sound waves and high-frequency bond-bending vibrations such as the O–H stretching vibration), low-frequency tumbling of water molecules, and even lower frequency diffusion motions. The frequency range spans several orders of magnitude, and spectrometers can be designed for different frequency ranges. The traditional instrument at reactor sources is the “triple-axis spectrometer,” which is designed to measure phonon dispersion curves point by point. This instrument has two monochromator crystals, one to set the incoming wavelength, and the other to reflect neutrons of different wavelengths into a single detector. It thus becomes possible to measure the intensity for specific changes in energy E and scattering vector \mathbf{Q} , and by mapping out measurements for a wide range of values of \mathbf{Q} and E it is possible to construct a nearly complete picture of the dispersion curves. There is no comparable instrument for spallation sources; instead spectrometers are designed using choppers and banks of detec-

tors, and give measurements for a whole range of Q and E values in a single setting. In addition to performing measurements of dispersion curves using single-crystal samples, by using polycrystalline samples and running experiments that will integrate over Q , it is possible to perform measurements of vibrational density of states. Chaplot et al. (2002) review the application of neutron spectroscopic methods to the study of the dynamic properties of minerals.

As noted above, the spin dependence of the scattering of neutrons from ^1H means that a strong component of the scattering from hydrogen provides information about individual atoms in a process called “*incoherent scattering*.” This has been exploited in studies of the dynamics of hydrogen-containing molecules in solids and liquids (Bée 1988), and has been used in some early studies of the motions of hydrogen in minerals, including water in cordierite (Winkler 1996).

One mineral for which a range of neutron scattering measurements have been performed is cristobalite. Early high-resolution neutron powder diffraction measurements were used to characterize the disorder in the high-temperature β phase and to facilitate modeling of the thermodynamics of the low-temperature α phase (Schmahl et al. 1992). It was subsequently proposed that the phase transition would be accompanied by a large change in the low-frequency dynamics, and this was confirmed by neutron spectroscopy measurements (Swainson and Dove 1993). Total scattering studies have been used more recently to provide detailed information about the structure of the disordered β phase (Tucker et al. 2001).

At the time of writing, we are seeing a dramatic increase in neutron scattering research capabilities, which matches the pace of development of facilities such as synchrotron radiation sources. These developments are described by Parise and Brown (2006) in this issue.

MASS SPECTROMETRY

Mass spectrometry has become a vital technique for Earth scientists, allowing high sensitivity analyses of elemental abundance and isotopic composition. Such information is valuable in chronological studies over the entire age of our solar system, for example. Mass spectrometers range from relatively simple, bench-top instruments to complex apparatus that require dedicated facilities and are based on sophisticated technologies such as particle accelerators, focused ion beams, and lasers. The physical principle upon which these instruments are based is the mass separation of charged particles as they traverse a magnetic field. Many of these advanced mass spectrometry facilities are open to the scientific community as user facilities.

Most Earth and planetary materials are extremely heterogeneous assemblages. In many instances the constituents are less than a millionth of a meter in size, much smaller than a human hair. Detailed information regarding the evolutionary history of the constituents can only be obtained via a technically challenging, grain-by-grain analysis. The rigorous challenges of spatial resolution coupled with sufficient sensitivity to detect the masses of a few thousand atoms are being met by *secondary ion mass spectrometry (SIMS)*.

SIMS works by sputtering the surface of a grain with a primary beam of ionized cesium or oxygen. As atoms residing near the surface are liberated, some are ionized and collected into a spectrometer with high mass resolution. Virtually the entire periodic table is accessible, with detection limits of 10–100 ppb for many elements and precision of isotope ratios as good as 0.1 per mil. These secondary ions are mass analyzed by a combination of electrostatic and

magnetic components. Particle detection is achieved using a combination of electron multipliers, Faraday cups, and imaging detectors, such as microchannel plates. Most of these so-called *ion microprobes* (FIG. 5) have the capability to perform both momentum and energy mass analysis and are commonly available as user facilities. The mass resolving power ($m/\Delta m$) of SIMS instruments covers a large range, is adjustable on individual instruments, and typically extends from ~ 1000 to 50,000 (inverse of the smallest mass fraction that can be measured). Ion microprobe/SIMS instruments are capable of focusing the primary beam to spots as small as 50 nm for in situ analysis of thin sections or grain mounts. In addition to performing elemental and isotopic abundance ratio measurements, many SIMS instruments can also create an image of the microdistribution of isotopic ratios in a sample, effectively creating an isotopic map.

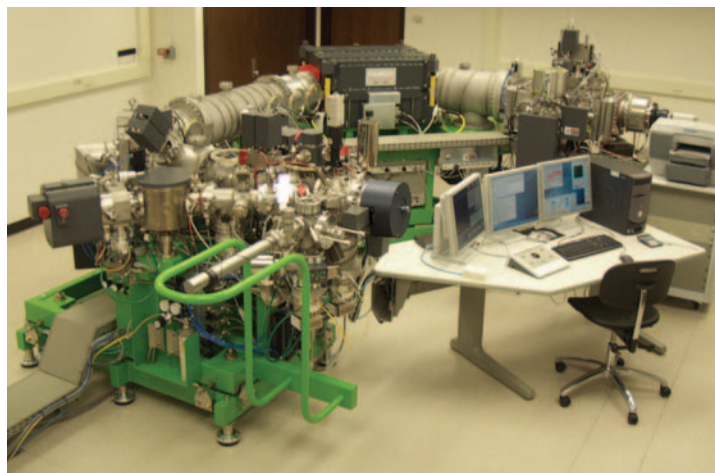


FIGURE 5 CAMECA IMS-1280 large radius multicollector ion microprobe optimized for analysis of stable isotope ratios at the University of Wisconsin–Madison WiscSIMS Laboratory. PHOTO COURTESY J. VALLEY

An exciting research direction in single-grain mass spectrometry is the search for grains produced prior to the formation of our solar system. These “presolar grains” from meteorites have isotopic compositions distinct from those of typical solar system material, so the precise isotopic abundances can shed light on the type of star that produced them. Presolar silicon carbide grains (e.g. Bernatowicz et al. 2003) range in diameter from 0.1 to 10 microns and have an abundance in meteorites of ~ 10 parts per million. Their distinctive isotopic signatures are large variations in $^{12}\text{C}/^{13}\text{C}$ and $^{14}\text{N}/^{15}\text{N}$, which are comparable to the ranges observed in the atmospheres of carbon-rich giant stars. The discovery of rare presolar silicate grains (e.g. Anders and Zinner 1993) was made possible by the imaging capability of SIMS techniques (FIG. 6). Currently, mass spectrometric methods are being developed for “dating” these grains and using them to characterize the chemical evolution of our galaxy (e.g. Clayton 1997). The extent to which these studies will be successful may well hinge on further advances in mass spectrometric techniques and the availability of these advances to the general scientific community.

The ages of solar system materials are based on a number of isotopic chronometers. These isotopic ratios are determined using a variety of mass spectrometers, including a new generation of instruments collectively referred to as *inductively-coupled plasma mass spectrometers (ICP-MS)*. These instru-

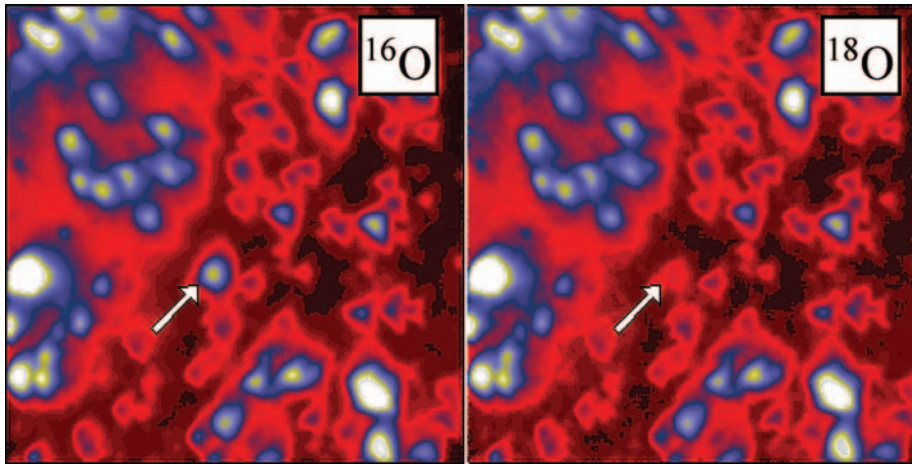


FIGURE 6 SIMS maps (~30 μm wide) of oxygen isotopic microdistributions (^{16}O left; ^{18}O right) in oxide grains separated from the Tieschitz meteorite. The arrows show the presence of a grain of anomalous (presolar) isotopic composition. PHOTO COURTESY OF L. NITTLER, CARNEGIE INSTITUTION OF WASHINGTON, DEPARTMENT OF TERRESTRIAL MAGNETISM

ments measure isotopes of Cr, Fe, Ca, Sr, Pd, Ag, Mn, Ni, Hf, W, Nd, Sm, U, Cm, Pb, Li, B, Be, Cu, Zn, Hg, Mo, and others. ICP-MS utilizes several sample introduction techniques, including laser ablation and direct introduction of a solution into the ionization region. Laser ablation enables the in situ analysis of isotopic structures of mineral grains. Ionization is achieved by argon plasma at atmospheric pressure. The ions are then introduced into the mass spectrometer through a differentially pumped region. The mass spectrometer itself may consist of magnetic and/or electrostatic sectors followed by one or more detectors. The power of high-resolution ICP-MS is in its ability to distinguish between molecules of very similar masses.

In one example of ICP-MS work, measurements of Pb isotopes in meteoritic Ca-Al-rich inclusions give a chronological reference point of 4.566 ± 0.002 billion years for the first matter condensed in our solar system (Amelin et al. 2002). The measurement of W isotopes by high-resolution ICP-MS, in conjunction with the initial $^{182}\text{Hf}/^{183}\text{Hf}$, indicates that core formation in the iron meteorite parent bodies took place within 10 million years of the beginning of the solar system (Kleine et al. 2002). Other isotopic systems indicate that by ~40 million years, Earth itself had differentiated (e.g. Halliday and Lee 1999) and that by 200 million years melts had crystallized in the crust, forming zircons.

These zircons provide a wealth of information regarding the early evolution of Earth. Zircon simultaneously concentrates uranium and excludes lead, so it is a perfect mineral for U-Pb chronometry. Zircon grains are highly resistant to weathering and can survive multiple geologic events. They preserve isotopic records of events occurring over much of Earth history, most notably within several hundred million years after the formation of Earth. Their isotopic records can be deciphered using micro-analytical techniques, in particular SIMS. Measurements of $\delta^{18}\text{O}$ and trace element compositions can then be used to delineate geologic processes occurring in the early Earth (e.g. Wilde et al. 2001).

Mass spectrometric techniques have also shed considerable light on the collisional processes responsible for the transport of asteroidal objects to Earth by using cosmic ray exposure ages to date the collisional events. Noble gases are useful for determining cosmic-ray exposure ages in mete-

rites, principally ^3He , ^{21}Ne , ^{38}Ar , ^{81}Kr , and $^{124,126}\text{Xe}$. These measurements are performed using *noble gas mass spectrometers*, which typically have a mass resolving power of <1000 and an abundance sensitivity of $\sim 10^{-6}$. Radionuclides used to determine cosmic-ray exposure ages, pre-atmospheric sizes, and shielding depths include (with half-lives given in brackets) ^{10}Be (1.5 Myr), ^{26}Al (0.705 Myr), ^{36}Cl (0.301 Myr), ^{53}Mn (3.5 Myr), and ^{129}I (16 Myr). The development of *accelerator mass spectrometry (AMS)* increased the detection sensitivity of all these radionuclides by virtue of detecting atoms rather than decay products. The abundance sensitivity is realized by accelerating the ions to ≥ 1 MeV. Ions accelerated to this energy can

pass through a thin carbon foil or a stripper gas at the accelerator terminal, effectively disassociating molecular interferences. AMS facilities are commonly made available as user facilities, so that exposure age determinations are available to the general scientific community.

In a variant of this collisional dating method, cosmic-ray exposure ages on terrestrial rocks can be used to date collisional events on Earth. In the case of Meteor Crater in Arizona (USA), the explosive force of the Canyon Diablo iron meteorite excavated rock that, until that time, had been shielded from exposure to cosmic rays. AMS measurements have determined the subsequent accumulation of cosmogenic ^{14}C , ^{10}Be , ^{26}Al , and ^{36}Cl , thereby establishing the age of the crater at ~50,000 years (Nishiizumi et al. 1991; Phillips et al. 1991), consistent with the first absolute dating of the crater using thermoluminescence measurements of impact-heated sedimentary rocks (Sutton 1985).

Thus, mass spectrometry methods have provided pieces to the geologic puzzle stretching in time from before the formation of the solar system 4.566 billion years ago to recent meteorite collisions with Earth. Acquisition of this knowledge would not have been possible without the use of a variety of mass spectrometric techniques, many of which, notably those at AMS and SIMS facilities, have been developed and are operated as user facilities.

CONCLUDING REMARKS

We are currently in a very productive period for user facility-based research in the Earth sciences. A large number of facilities exist representing a wide spectrum of analytical capabilities. Each technique provides a unique window into the composition, structure, and history of Earth materials, the processes that produce these materials, and the processes they control. Equally significant, sufficient experience in the operation of user facilities has been gained to make them very effective in responding to and meeting the needs of the research community. Many Earth scientists are currently taking advantage of the frontier capabilities offered by user facilities, and their numbers are growing.

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