Geochemical and Cosmochemical Materials

Michael E. Lipschutz,*,[†] **Stephen F. Wolf,**[‡] **John M. Hanchar,**[§] **and F. Bartow Culp**[†]

Department of Chemistry, Wetherill Laboratory, 560 Oval Drive, Purdue University, West Lafayette, Indiana 47907-2038, Department of Chemistry, Indiana State University, Terre Haute, Indiana 47809-5901, and Department of Earth and Environmental Sciences, The George Washington University, 2029 G Street N.W., Washington, D.C. 20006

Review Contents

This review surveys the literature on the chemical analysis of terrestrial and extraterrestrial solids for the two-year period October 2000 through September 2002. We continue to include extraterrestrial materials as we did for the 1998−2000 period (*A1*) because analyses of these samples on Earth continue to present new challenges to the analytical geochemist. We focused upon rocks and minerals and did not include gaseous species. We included aqueous solutions in our survey only where these bore upon geologic processes, but not environmental problems. We carried out comprehensive online searches of the pertinent chemistry and geoscience literature to support the reviewers' individual reading and subject expertise. We searched the following databases:

(1) GEOREF, established by the American Geological Institute in 1966, is the online complement of the printed *Bibliography and Index of Geology*. It is the most comprehensive database in the geosciences, containing over 2.27 million references to journal articles, books, conference proceedings, reports, and theses. The particular format used for these searches was the online version of the database covering 2000−2002.

(2) CAPLUS, produced by the Chemical Abstracts Service (CAS) of the American Chemical Society, is the most current version of *Chemical Abstracts Online*; it includes the entire *Chemical Abstracts* file from 1907 with additional new and unindexed entries. It covers the world's chemical literature comprehensively, with specific sections on geochemistry and cosmo-

chemistry. We used SciFinder Scholar, the search engine developed by CAS, to search these database.

In searching each database, we followed two strategies. First, we very broadly searched over the period (2000−2002) combining the concept terms for "geochemistry" and "chemical analysis". These searches resulted in large numbers of records—over 450 from each database. These records were scanned by the reviewers to check for their relevance to the scope of the review. Accordingly, we compiled a list of key terms for specific analytical procedures and carried out follow-up searches using these terms in the context of geochemistry. In addition, we manually searched *The Analyst, Analytica Chimica Acta, Analytical Chemistry, Chemical Geology, Critical Reviews in Analytical Chemistry, Earth and Planetary Science Letters, Fresenius Journal of Analytical Chemistry, Geochimica et Cosmochimica Acta, Geostandards Newsletter, Journal of Chromatography, Journal of Geophysical Research E, Meteoritics and Planetary Science, Nature, Science,* and *Talanta* for bulk elemental and isotopic analysis of geochemical and cosmochemical materials during the period of interest.

As with many other fields of endeavor, geochemistry and cosmochemistry are well represented on the Internet. The following selective list of Web sites contains numerous links to further resources:

(1) Elsevier Publishing Co. is now maintaining a website <http://earth.elsevier.com>, covering 70 scientific journals, online articles, books, etc., for the earth and planetary sciences. This new site contains an enormous amount of information and we recommend it in searching for very specific topics.

(2) The Geology section of the U.S. Geological Survey Web site <http://geology.usgs.gov/index.shtml> is particularly useful for its numerous publications in geochemistry.

(3) The Chemical Institute of Canada's Hamilton Section has compiled a useful site http://www.netaccess.on.ca/~*dbc/ci*c_hamilton/geo.html containing links to research groups, societies, and several software programs of geochemical interest.

A number of educational institutions have also assembled useful Web sites for cosmochemistry and/or geochemistry:

(1) Cornell University maintains the most complete site, http://www.geo.cornell.edu/geology/classes/Geochemweblinks. HTML, with links to organizations, journals, online geochemical data, standards information, and government laboratories.

(2) The International Association of Geochemistry and Cosmochemistry at Michigan State University maintains a Web site <http://www.cevl.msu.edu/~*long/IAGC/*> with numerous links. Its stated objective is to "foster cooperation in, and advancement of, geochemistry and cosmochemistry".

* Corresponding author. E-mail: rnaapuml@purdue.edu.

[†] Purdue University.

[‡] Indiana State University.

[§] The George Washington University.

(3) The University of Hawaii maintains a web site <http://www.psrd.edu> for Planetary Science Research Discoveries, which usually have a strong chemical component.

We continued to focus on a limited number of exciting areas and to highlight trends in trace analysis, particularly of smaller samples. In fact, this continues to follow analytical trends in geochemical and cosmochemical research that involve getting ever more compositional information from ever smaller samples. As in our previous review (*A1*), inductively coupled plasma mass spectrometry (ICPMS) with all of its hyphenated permutations continues to be the analytical method used most widely. Other trace analysis techniques are of lesser import, particularly for noteworthy studies. In our search, we tried not to be myopic, so that we could identify important studies outside of our focus areas.

A second trend in geochemical research that continued to broaden during the past two years is the application of two or more advanced techniques to characterize a terrestrial sample or suite of samples. This "consortium approach" has long been a staple in cosmochemistry, where samples are rare and usually small and where bulk host material is not generally plentiful. In geochemical studies where bulk material is usually plentiful, the major appeal of the multitechnique approach is that data sets generally prove synergistic. Even in such materials, it may be only rare grains that are of interest (for example, a single zircon that is to be dated.) Also, as techniques improve so that more and more information can be obtained from lesser quantities of sample, compositional heterogeneity becomes a potentially more serious problem. Whether this problem is serious can be determined by gathering several sorts of data, to establish whether sample heterogeneity can be affecting the conclusions of the primary study.

Finally, chemometrics is starting to assume a recognizable role in geochemistry and cosmochemistry, as it has in less applied areas.

GEOSTANDARDS

In his 21st and penultimate review of the geostandards literature, Roelandts (*A2*) commented on the continuing trends in this area of the geochemical literature: the prevalence of multielement analyses; the key role of ICP-AES (atomic emission spectroscopy) and ICPMS; and the increasing interest in isotopic analysis. By his count, the most popular journals for reporting geochemical reference standards work are *Geostandards Newsletter: The Journal of Geostandards and Geoanalysis*, *Journal of Radioanalytical Chemistry*, and *Fresenius' Journal of Analytical Chemistry* (Note: the last journal, after 140 years of continuous publication under the editorship of a Fresenius family member, just underwent an ownership and name change in 2003 to *Analytical and Bioanalytical Chemistry*.) Other recent trends in the area of geostandards are an interest in methodology of geostandards measurements and new advances in isotopic analysis and in establishing standards for the lighter elements.

A new and useful feature in the *Geostandards Newsletter* is the appearance of the "Back to Basics" reviews, commissioned by the editors to keep its readers abreast of fields related to their research. Several of these were published during the period covered by this review: indeed, the first one to appear (*A3*) was in the form of a tutorial on the use of geochemical reference materials or GRM. It reviews the literature with a specific focus

on best practices as outlined by the International Organization for Standards (ISO) guidelines. One of the criteria stated in ISO Guide 33 (1989) stipulates that uncertainty in reference material (RM) values must be small relative to the uncertainty in the pertinent analytical data. This has promoted the concept of fitness for purpose in the application of GRM used as calibration and quality control materials. Kane (*A4*) reviewed the fitness for purpose of RM values, using three popular standards, USGS BCR-1, NIST SRM 610, and IAEA NBS28, as examples. Kane and Potts (*A5*) also reviewed traceability, another concept that has assumed greater importance as a result of ISO guidelines. It refers to the requirement that every analytical measurement be traceable back to national or international standards through an unbroken chain of comparisons, each with a stated uncertainty.

The effort toward the international coordination of performance testing by analytical geochemistry laboratories that began with the GeoPT rounds 1−5, as reviewed earlier (*A1*), has continued with rounds 6−10. The results of these rounds have not yet been published. However, the results of G-Probe-1, the first round of a new series of proficiency testing for laboratories, has appeared (*A6*), using a variety of analytical techniques for trace analysis, including laser ablation (LA) ICPMS and instrumental neutron activation analysis (INAA).

Several papers have reexamined earlier measurements of GRM values; Weyer et al. [see details in MC-ICPMS section (*E16*)] presented more precise concentration data for Zr, Hf, Nb, and Ta in GRM BHVO-2, BCR-2, BE-N, BIR-1, and the ultradepleted, natural, whole-rock standards PCC-1 and DTS-1. Jochum et al. (*A7*) used multiple-ion counting spark-source mass spectrometry (MIC-SSMS) and a newly developed autospark beam stabilization system to measure Zr, Nb, and Y abundances in seven international RMs and other geological samples. They found that the isotope ratio measurements so obtained were more precise by a factor of 3 than in conventional SSMS. The extensive collection of GRM data for trace elements compiled in 1994 has been extensively updated by Dulski (*A8*). New values were obtained from a large number of samples using ICPMS, and the compiled data sets were critically discussed. Employing a scheme that uses 14 statistical tests rather than the usual 2 standard deviation method, Velasco-Tapia et al. (*A9*) reexamined elemental concentration data for five USGS GRM. They found that, although 53% of the recalculated mean data agree with previous values, 32% show differences of 1−5%, and the remaining values show larger differences of up to 50%. The geochemical behavior of the Lu−Hf isotope system has been reviewed by Blichert-Toft (*A10*). In an appendix to the work, the author (*A10*) outlined an improved protocol to his previous method for the analysis of Lu−Hf in Mg-rich samples and compiled old and new isotope compositions of international rock RM

Responding to the growing need for reference materials for in situ isotopic geochemical analyses, Woodhead and Hergt (*A11*) used isotope dilution thermal ionization mass spectrometry (ID-TIMS) to study NIST certified standard RM (SRM) 610, 612, and 614 for isotopic analysis. They found large intersample differences in their determinations of the Pb, Sr, and Nd isotopic compositions in these glasses and suggested the cause as significant trace element content in the initial starting material. This indicates that isotopic compositions for one SRM cannot be transferred to

another and that each must be independently calibrated. Kurosawa et al. (*A12*) used LA-ICPMS to determine the concentrations of 50 trace elements in NIST SRM 614 and 616 glass reference materials. The values reported for NIST SRM 614 agree well (e.g., within 3.6%) with the NIST certified values except for B, Sc, and Sb. The values for NIST SRM 616 agree within 1.5% of the NIST certified values except for B, Sc, and Ga. At the 80-μm sampling scale, both glasses were found to be homogeneous.

SAMPLE PREPARATION

Many techniques for bulk trace elemental and isotopic analysis of geochemical and cosmochemical materials have reached a maturity level sufficient for routine application. Thus, most of the bulk analytical application development focused on chemical procedures for preparation of analyte elements from particular sample types for the analytical technique of interest. Improvements in procedures used for sample dissolution and chemical separation of different analyte elements were aimed at producing a liquid sample in a known matrix to minimize sample preparation blank and spectroscopic interferences. These continue to improve the sensitivity, precision, and accuracy of analytical methods and allow determination of lower elemental concentrations in smaller samples.

Accurate determination of elemental concentrations in geological matrixes typically requires complete dissolution of the sample without analyte volatilization and loss or the formation of insoluble species. Many dissolution procedures have been developed based on mineral acids because they can be obtained in high purity and the resulting solutions have low total dissolved solids (TDS). For example, Nakai et al. (*B1*) described chemical procedures for determination of Th isotopes in silicate rock samples by multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS). Samples were dissolved in Savillex screw-top containers with $HF-HClO_4$, and Th was isolated via anion exchange. The method allowed determination of $^{230}Th/^{232}Th$ ratios in samples containing only 10 ng of Th. Axelsson et al. (*B2*) developed two acid digestion procedures (microwave-assisted and room temperature) for $Mn-Fe$ nodules. When combined with high-resolution, inductively coupled plasma mass spectrometry (HR-ICPMS), these techniques provided quantitative data for >60 elements with an accuracy of $\pm10\%$ in samples of ≥1 mg. Reagent volumes were optimized to minimize method blank. Yu et al. (*B3*) evaluated low-pressure acid digestion using HF/HNO_3 in Savillex Teflon vials, digestion using $HF/HClO_4$ in a high-pressure digestion system, low-pressure $Li_2B_4O_7$ fusion$-HF/HNO_3$ dissolution, and Na_2O_2 sintering for a variety of geological materials prior to ICPMS analysis. While fusion and sintering demonstrate the most complete sample dissolutions, trace impurities in these reagents can potentially increase method detection limits (MDLs) for some elements.

Investigators have also paid greater attention to the determination of lighter elements; Makashima and Nakamura (*B4*) reported a new procedure for the determination of total S at microgram per gram levels. They used in situ-generated Br_2 to oxidize all S to SO_4, followed by isotope dilution (ID) and analysis by HR-ICPMS with a flow injection system. The ability of this procedure to remove sulfides and chromite from materials allowed it to be extended to the determination of Cr, Ni, Cu, and Zn in

silicates (*B5*). The authors emphasized the suitability of this method for analyzing small or precious samples, or both. Another approach to the detection of total S employed by Okai et al. (*B6*) used ICP-AES fitted with a semiconductor photodiode detector. The samples were decomposed using HF/aqua regia or $NaCO_3/H_3BO_3$ fusion.

Because dissolution procedures utilizing mineral acids at low to moderate temperatures and pressures may not completely dissolve certain refractory phases in geological and cosmochemical materials, alternative methodologies continue to be explored. Meisel et al. (*B7*) developed a high-pressure, acid digestion method for determination of platinum group elements (PGEs) with an apparatus similar to the Carius tube method but operating at higher temperatures. This method used direct sparging of OsO_4 for Os determination and preconcentration of remaining PGEs by anion-exchange chromatography. When used in combination with ID-ICPMS, this method achieved MDLs (3σ) of 0.012 ng for Re and Os and 0.77 ng for Pt. Hattori and Hirata (*B8*) developed an atmospheric pressure sample decomposition apparatus for sample decomposition and determination of Os in iron meteorites by ID-ICPMS. An advantage to this method is that it allows digestion of samples with masses >10 times larger than can be processed in Carius tubes, and Os recovery was monitored via a ^{190}Os tracer. Total method blank is <20 pg per 1-g sample. Similarly, Diegor et al. (*B9*) fabricated high-pressure digestion vessels and compared ICPMS results for digested SRM with those using standard, low-pressure PTFE screw-top vessels. The high-pressure vessels were more effective for dissolution of refractory minerals, such as zircons. Gros et al. (*B10*) investigated a NiS fire assay Te coprecipitation separation method to minimize volatile PGE losses (Os, Pd) prior to ICPMS analysis. The authors used 20.2% HCl to dissolve the NiS bead in an open system, permitting escape of H_2S without HCl loss.

While decomposition of even the most refractory phases is possible via fusion with a variety of flux materials, the resulting solutions can be difficult to analyze directly due to high TDS. Because of this, many authors are developing chemical separation methods to quickly and quantitatively separate analyte elements from the more abundant flux products. Pin and LeFévre (*B11*) reviewed current methodologies for high-precision, high-accuracy determination of trace elements in geological materials by ICPMS and concluded that the best approach is one that involves dissolution via fusion, chemical separation of analyte from flux and sample matrix constituents, and ID for quantitation. They (*B12*) described a method for Zr, Hf, Th, and U determination by MC-ID-ICPMS following $LiBO_2$ fusion and analyte separation via column extraction chromatography. Hf and Zr are isolated from flux and rock-forming constituents (Al, P, Ti, Cr, Fe, Mo) in a single step allowing >90% recoveries with blank levels of ~55 pg of Hf. This method was used for the analysis of four international SRMs spanning a range of silicate rock bulk compositions (*B13*). Kleinhanns et al. (*B14*) described a multistep procedure for separating Lu, Hf, Sm, Nd, and other REE from a single geological sample digest solution. After sample decomposition via sintering with Na_2O_2, a combination of anion-exchange, cation-exchange, and reversed-phase ion chromatography provide separated and purified fractions of Hf and the individual REEs. MC-ICPMS was then used to determine $Sm-Nd$ and $Lu-Hf$ isotopic compositions.

Because accuracy and precision of ICPMS determinations can be significantly affected by sample matrix, efforts continue to develop chemical separation methods yielding samples optimized for this instrument. Determination by ICPMS of the isotopic composition of light elements, such as Li and B, benefits from matrix−element separation, which lowers matrix-induced mass bias. Košler et al. (*B15*) demonstrated that ICPMS can be used to determine the Li isotopic composition in samples containing only 5−10 ng of Li with a within-run precision better than 0.05%. Lécuyer et al. (*B16*) developed a protocol to separate B using ion-exchange resins and determine its isotopic composition in natural waters, carbonates, phosphates, and silicates by MC-ICPMS. The technique requires 2 μg of B for adequate external reproducibility.

Most MC-ICPMS studies to be reviewed later in the relevant section were carried out using sample solutions purified by standard ion-exchange techniques. However, Se separation using Thio Cotton Fiber proved ideal for the work of Rouxel et al. (*E19*).

Accurate determination of trace heavy REE (HREE) by ICPMS can be complicated by the presence of polyatomic interferences from light REE (LREE) oxide. Baker et al. (*B17*) developed an ingenious approach to minimize these interferences at masses used for determination of HREEs by ID-MC-ICPMS. Sample are digested and spiked with a LREE (La−Gd) and a HREE (Dy−Lu) isotopic spike. The method (*B17*) involves a chemical separation procedure in which bulk REE are separated from sample matrix by cation exchange and the REEs are collected in three separate fractions. This approach separates LREEs from HREEs and renders oxide interferences negligible.

Lee et al. (*B18*) used acid digestion, matrix separation, and cation-exchange pretreatment to determine the REE content in two Geological Survey of Japan samples. Matrix separation was said to give more reliable analyses and greater reproducibility. Ion-exchange separation using Dowex minicolumns was also used to remove interfering elements from 11 rare earth elements for ICP-AES analysis (*B19*). The procedure was said to provide fast and inexpensive REE determinations. A preconcentration method for the XRF determination of REE used Thorin [*o*-(3,6-disulfo-2-hydroxy-1-naphthylazo)benzenearsonic acid] as a complexing agent retained on a polyamide film (*B20*). The advantage of this method is that the concentrated REE complex is distributed only on the surface of the film, making it possible to use large sample volumes to enhance sample enrichment. Olive et al. (*B21*) described a protocol for ICPMS determination of REE without employing the usual preconcentration step. Their approach involved the application of external correction procedures based on analyses of reference materials with compositions closely matching those of the unknown samples. Interferences and variations of instrument sensitivity can thus be corrected.

Increasing interest in Os−Re dating by ICPMS has led to the development of chemical procedures optimized for it. Malinovsky et al. (*B22*) developed a method for Os−Re dating of molybdenite using a two-stage, autoclave-based dissolution procedure, single-stage distillation of OsO_4, and anion exchange of Re from excess Mo in the remaining solution. Os and Re concentrations were determined via ID-HR-ICPMS. Brauns (*B23*) developed a rapid, low-blank method for Os extraction from geological materials prior to mass spectrometric analysis. This method relies on oxidation of Os to OsO_4, which is caught in a sulfuric acid-coated cold trap, subsequently extracted with HBr, and purified via microdistillation.

Of all analytical techniques used for bulk elemental and isotopic analysis of geochemical and cosmochemical materials, TIMS typically requires the highest degree of analyte purification from interfering matrix constituents. Kuritani and Nakamura (*B24*) developed a simplified sample preparation procedure for determination of Pb isotopic composition by TIMS at nanogram of Pb levels using two-stage ion exchange. The high chemical purity achieved by this method allows employment of a zero-time correction for mass bias correction and, thus, no need for a $^{207}Pb-^{204}Pb$ double spike. Paquette and Pin (*B25*) described a new separation of Pb and U in zircons for radiometric dating by TIMS. It uses a blend of extraction chromatography materials originally developed for radioisotope separation in nuclear wastes. A new silicic acid/phosphoric acid solution ionization activator has been used in the TIMS analysis of $^{234}U/^{238}U$ ratios (*F1*). The advantages to this procedure include a strong and stable UO_2^+ ion beam and a minimization of mass fractionation during measurement.

A new chromatographic procedure for Nd separation from other REEs has been described, allowing measurement of NdO^+ isotopes by TIMS (*B26*). This method utilizes a high-pressure liquid chromatographic (HPLC) separation with Aminex resin (Bio-Rad) and a methanol/acetic acid/nitric acid eluant. The method effectively separates Nd from potential Ce and Pr interferences. Quitté et al. (*B27*) described a two-stage anion-exchange procedure and an improved negative TIMS (N-TIMS) methodology for W determination along with a simplified method for Hf separation and determination. The approach can reliably be used on samples containing as little W as a few nanograms per gram.

While laborious compared to microprobe-based analytical techniques, chemical and physical separation methods can be used to assist traditional bulk analysis in providing compositional information with surface- or mineral-phase specificity. Stepwise acid leaching of two Apollo 17 trench soils, 78481,16 and 78241,16 were performed to delineate volume- and surface-correlated ^{10}Be components (*B28*). Leachates were analyzed for cosmogenic ^{10}Be (half-life, 1.5 Ma), ^{26}Al (710 ka), and ^{36}Cl (301 ka) by accelerator mass spectrometry. Excess ^{10}Be from that expected by in situ cosmic ray spallation was found in surface soil 78481,16. These results suggest incorporation of ^{10}Be produced on the Sun and transported to the lunar surface as solar wind. The difficult task of identifying in situ-produced cosmogenic ^{14}C in rock has been addressed; building on previous findings that contaminant ^{14}C is released below 500 °C, Lifton et al. (*B29*) developed a technique for extracting in situ ^{14}C from quartz by resistance heating of samples in the presence of $LiBO_2$ flux and collection of the evolved CO_2 at 500−1200 °C. This technique yields more reliable results than previous methods. Maas et al. (*B30*) used physical and colloidal separation techniques to prepare a purified sample of interstellar nanodiamonds from the Allende carbonaceous chondrite. After combustion of the diamonds in an oxygen plasma, the elemental and isotopic abundances of Te and Pd were determined by TIMS. Small isotopic anomalies were found for ^{128}Te, ^{130}Te, and ^{110}Pd, consistent with the neutron burst and rapid separation, r-process models of nucleosynthesis.

MULTITECHNIQUE SYMPOSIA AND REVIEWS

Nanoscience is a very popular focus area in chemical research, and Hochella (*C1*) provided a personal perspective and selective review of its applications in geochemistry.

Cosmochemical samples are often complex and available only in limited quantity so consortium study of well-curated samples by a number of investigators, each having a specific area of expertise, is not rare. This optimizes information return at the cost of minimal sample consumption. The fall of the Tagish Lake meteorite on 18 January 2000 provided a unique, new kind of carbonaceous chondrite perfectly suited for such a study. The consortium lead paper (*C2*) and accompanying nine papers reported its mineralogic, chemical (both organic and inorganic), isotopic, and spectral characteristics, demonstrating Tagish Lake's unique nature (and parent body).

Normally, we would not include a planetary flight mission in this review, but the amount of mineralogic and compositional information on 433 Eros by the NEAR−Shoemaker mission (*C3*) was very impressive. The accompanying seven papers were able to compare remote spectral observations with limited ground truth, obtained after a soft landing on the minor planet. Asphaug (*C4*) introduced a three-paper series on impact-cratering and regolith formational deduced from imagery of Eros by NEAR−Shoemaker.

In the leadoff paper (*C5*) of three published *seriatim*, Mars Odyssey's mapping by γ-ray (GRS) and neutron spectrometers, and a high-energy neutron detector of thermal, epithermal, and fast neutron fluxes, was reported. The flux of epithermal neutrons varies inversely with the hydrogen concentration in the Martian surface. While H_2O ice was identified near the surface wherever it was expected, a major reservoir was found near each of the Martian poles. In each of these reservoirs H_2O (ice) contents were $35 \pm 15\%$ (by weight), sited in a subsurface layer, each overlain by a hydrogen-poor (1−2%) layer.

The origin of life on earth and its existence elsewhere in the universe are problems taking on new life as "astrobiology", the successor to exobiology. In introducing a series of seven papers on this topic, Gee (*C6*) expects that astrobiology will deepen our understanding of humanity's place in the Universe, unique or not.

The Mineralogical Association of Canada sponsored a Short Course on LA-ICPMS principles and applications in the Earth Sciences in May 2001. A very useful volume, including 14 chapters written by presenters in the course, has been published (*C7*) and is very modestly priced. It covers a spectrum of topics from buying a new ICPMS, data reduction software, through trace element analysis of whole rocks, fluid inclusions and minerals, age dating, and chemometrics, all of which were written by internationally recognized experts in the different fields.

In this connection, Scarsi (*C8*) compiled a critical review of the crushing techniques used for gas extraction from magmatic crystals and inclusions in them, focusing on the accuracy and validity of He concentrations and the $^3He/^4He$ isotopic ratio.

Moser and Scott (*C9*) introduced a group of 10 papers from a GSA symposium, "What are we dating? Understanding the crystallogenesis of U−Pb geochronometers". The papers are arranged in order of decreasing closure temperature, amusingly also resulting in a mineral order from zircon to apatite. A variety of analytical techniques are employed in these 10 studies, which distinguish between the dating of crystallogenic effects and thermal conditions.

QUADRUPOLE-BASED INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

Solution. ID quantitation provides the highest accuracy level achievable by ICPMS. Its primary drawback is increased time for preparation and analysis of each sample. To address this, Packer et al. (*D1*) designed a microflow system for online addition of isotopic spikes prior to Cd determination by ICPMS. The system utilizes a low-flow microconcentric nebulizer for low sample consumption and demonstrates a capacity of ∼30 ID determinations/h.

The determination of Hg by ICPMS has always been problematic due to high elemental volatility, relatively low ionization efficiency, Hg impurities in Ar gas used in the plasma, and large memory effects when pneumatic nebulization is used. Cold vapor (CV) sample introduction solves these problems. Long and Kelly (*D2*) developed a method based on ID-CV-ICPMS for determination of Hg in coal. Coal samples are digested in Carius tubes and equilibrated with ^{201}Hg spikes. This approach demonstrated an instrumental detection limit of 1 pg/g, with an average instrumental blank of 30 pg for Hg.

Postanalysis calculations correct for the presence of polyatomic interferences that complicate ICPMS determination of many elements. Aries et al. (*D3*) corrected for oxide and hydroxide interferences in 32 nuclides (mostly REE) using raw data generated from the analysis of each sample and an invariant database of oxide and hydroxide production ratios. Similarly, Jain et al. (*D4*) used postanalysis calculations to correct for ZrF_3 interferences for REE determinations in gem-quality zircons that had been dissolved by using HF.

A relatively new technique for elimination of polyatomic interferences has been introduced for ICPMS. In this, ion−molecule reactions with low-pressure gases in collision cells are used to break bonds in polyatomic ions, in particular, in the elimination of metalargide ($M-Ar^+$) species. Hattendorf et al. (*D5*) used this approach to quantify ultratrace levels of Zr and Nb in samples containing high Cr levels. Improvements in the ability to accurately determine Nd/Zr ratios will result in more precise results by the recently developed $^{92}Nb-^{92}Zr$ chronometer (*A1*).

In a series of 25 papers in the 6th International Silicate Melt Workshop, one paper studying dissolution kinetics from weathering of many elements is noteworthy for the samples taken as prototypical for natural glasses, i.e., stained glass from French and German cathedrals, some from the 9th century (*D6*). This study included 14 in situ samples from 5 13th-14th century cathedrals and 13 additional ones recovered in digs at 3 other sites. The techniques used involved ICP-AES and electron microprobe analysis (EMPA) for 10 major and minor elements and ICPMS for 38 trace elements. Scanning electron microscopy (SEM) was also used to examine weathered surfaces in the glass.

Laser Ablation. Several recent studies have used quadrupole ICPMS in combination with laser sampling for U/Pb geochronology. Košler et al. (*D7*), in the first direct comparison between secondary ion mass spectrometry (SIMS) and LA-ICPMS for in situ U/Pb dating, showed that results of the two methods for dating detrital zircon crystals correlate very strongly, with only a slightly poorer analytical precision for the LA-ICPMS (and slightly

larger sample volume). True real-time, mass bias fractionation was achieved by aspirating a Tl/U tracer into the ICPMS at the same time as the laser-ablated material. One advantage of LA-ICPMS over SIMS is the increased sample throughput. Fernández-Suárez et al. (*D8*) used LA-ICPMS to date detrital zircon crystals from Neoproterozoic rocks from Iberia and Brittany. As opposed to Košler et al. (*D7*), who used a 266-nm Nd:YAG laser, Fernández-Suárez et al. (*D8*) chose a 213-nm laser because of its slower and more stable ablation rate and the production of more consistently sized ablated particles. The results agree well with ages of zircon crystals previously dated by ID-TIMS and analyses of the standard zircon 91500. Li et al. (*D9*) used a linear-scan, laser ablation method to minimize the Pb/U fractionation during the ablation process. For zircon crystals older than 1000 Ma, they obtained an analytical precision of 1% or better.

There have been numerous LA-ICPMS studies in which trace elements were analyzed in geological samples. Using mineral separates of garnet, Prince et al. (*D10*) compared REE concentrations determined using both LA-ICPMS (in situ) and ID-TIMS (bulk sample). This study shows that results of these two techniques agree well, that the garnets analyzed are generally free of LREE-rich inclusions, and that even very small amounts of LREE-rich inclusions can produce anomalous concentrations for those elements in garnet.

Halter et al. (*D11*) discussed results of analyzing heterogeneous melt inclusions in plagioclase feldspar from a rhyodacitic intrusion using an excimer laser ablation (ELA)-ICPMS system. They concluded that melt inclusions in glass and devitrified samples can be directly analyzed without thermally processing to make the inclusion homogeneous as must be done for other techniques such as SIMS, EMPA, or PIXE. Halter et al. (*D12*) used ELA-ICPMS to determine major and trace element concentrations in sulfide and melt inclusions in mineral phenocrysts from porphyry-type ore deposits. The link between a magmatic sulfide liquid and composition of porphyry-type ore deposits was quantified, and it was determined that Cu, Au, and Fe are first concentrated in sulfide melt and then later released into an ore-forming hydrothermal fluid. De Hoog et al. (*D13*) used LA-ICPMS to determine the contents of chalcophiles and other trace elements in mafic melt inclusions in olivine from the Galunggung volcano in Indonesia. Their results suggest that sulfur in the mantle beneath this volcano is enriched relative to midocean ridge basalts and that large-scale processes introducing sulfur into the mantle wedge may occur during slab dehydration.

Ballard et al. (*D14*) used ELA-ICPMS to determine major and trace element contents of barren and ore-bearing calc-alkaline intrusive rocks and zircon crystals extracted from rocks from the Chuquicamata copper deposit in northern Chile. Using these data, they attempted to constrain the oxidation state of the magma based on the Ce^{4+}/Ce^{3+} ratio. In a related study, Ballard et al. (*D15*) used ELA-ICPMS (and verified by SIMS) to determine the ages of the Chuquicamata copper deposit. Two discrete ages were found, leading the authors to conclude that the emplacement was a protracted event resulting in at least two temporally distinct magmatic-hydrothermal events. In a geochemical study of highly siderophile trace elements in sulfides from abyssyl peridotites from the mid-Atlantic and southwest Indian Ridges, Luguet et al. (*D16*) used LA-ICPMS. They found that the anomalously high whole-rock concentrations of the siderophiles reflected high levels in C−Ni-rich magmatic sulfides precipitated at a late stage from incompletely extracted partial melts.

Rubatto (*D17*) used ELA-ICPMS and SIMS to determine the trace element composition of zircons from eclogite and granulite facies metamorphic rocks from the Alps. The metamorphic outer regions in the zircon crystals analyzed from both rock types vary widely in trace element contents. Metamorphic zircons from the granulites are similar to magmatic zircons in terms of high Y, Hf, and P contents but are distinguished from magmatic zircon by their low Th/U ratio. In eclogite-facies rocks, the HREE are depleted and exhibit a slightly negative Eu anomaly.

SECTOR-BASED HIGH-RESOLUTION AND MULTICOLLECTOR ICPMS

Solution. When compared with quadrupole-based ICPMS, sector-based instruments exhibit higher sensitivities and are capable, therefore, of achieving better MDLs. Thus, the number of studies using HR-ICPMS to quantify ultratrace elements/isotopes in terrestrial and extraterrestrial samples are increasing rapidly. This attribute of HR-ICPMS was demonstrated by Yu et al. (*E1*) in quantifying high-field-strength elements (Zr, Nb, Hf, Ta, Th, U, Rb, Sr, Mo, Sb, Cs, Tl, Bi) at low levels in GRM, e.g., BIR-1, DTS-1, DNC-1, PCC-1, UB-N, and TAFAHI. Detection at nanogram per gram levels required no preconcentration. The high sensitivity of HR-ICPMS is making possible the determination of minor actinide isotopes ^{234}U and ^{230}Th in many geological samples. Shen et al. (*E2*) developed a method for $^{238}U−^{234}U−^{230}Th−^{232}Th$ dating of speleothems and $^{230}Th−^{232}Th$ in ocean particulates by HR-ICPMS. HR-ICPMS measurements on reference materials demonstrate analytical precisions comparable to those from counting, and routine measurement times are 20 min for U and 10 min for Th. Samples containing <40 ng of ^{238}U can be measured with a precision of 0.1−0.2% (2σ). In a collaborative study, Jain et al. (*E3*) used both ultrasonic nebulization-ICPMS and microconcentric nebulization-HR-ICPMS to accurately determine REE in GRM DTS-1 and PCC-1. The demonstrated precision and accuracy of this study suggest new best estimates of REE concentrations in these standard materials. Undoubtedly, HR-ICPMS use to determine ultratrace elements in geochemical and cosmochemical studies will continue to increase as these instruments multiply in number.

When configured with multiple detectors, sector-based multicollector ICPMS instruments can perform isotopic analyses with precisions that match or, in many cases, exceed those achievable by TIMS. Rehkämper et al. (*E4*) reviewed the performance characteristics, analytical strategies, and applications of MC-ICPMS. While TIMS has traditionally been the method of choice for precise geochronology for systems such as Rb−Sr, Nd−Sm, and Pb−Pb, recent work has favored MC-ICPMS because the solution sample introduction system allows easier operation and increases sample throughput. Snyder et al. (*E5*) reported Hf−W data and the first Rb−Sr and Sm−Nd isotopic compositional results in individual silicate inclusions in four IIE iron meteorites: all three systems were measured by MC-ICPMS. Results indicate that the silicate proportion of these meteorites underwent a long processing history that continued until 700 Ma before the present (bp). Vance and Thirlwall (*E6*) evaluated an extensive $^{146}Nd/^{144}Nd$ database from MC-ICPMS instruments to obtain

systematic information on MC-ICPMS mass bias. They found increased accuracy and precision when an isotope pair close in mass to the ratio to be normalized is used for mass bias correction. Additionally, they (*E6*) used postnormalization linear correlations between isotope ratios to do secondary mass bias corrections.

The multielemental capabilities of MC-ICPMS allow great flexibility in making mass bias corrections using an element different from the isotopic system of interest. For example, mass bias correction for Rb isotopic analysis by TIMS is precluded because Rb has only two long-lived/stable isotopes. Waight et al. (*E7*) developed a new IC-MC-ICPMS technique in which Rb mass fractionation is corrected for by measuring the fractionation of admixed Zr. The analysis takes 1 min, consumes 20 ng of Rb, and has an internal precision of ~0.02%. Lead isotopic analyses by MC-ICPMS can be corrected for mass bias using Tl isotopes as an internal standard, but Thirlwall (*E8*) demonstrated with a $^{207}Pb-^{204}Pb$ double spike that Tl normalizations may underestimate mass bias corrections due to element-dependent bias during sample introduction. Anbar et al. (*E9*) employed natural Zr or Ru spikes to correct for mass bias in determining the Mo isotopic composition by MC-ICPMS. They found mass-dependent differences in the isotopic composition between reference standards and geological samples and observed a 0.015%/amu fractionation during ion-exchange chromatographic separation (E9).

Using MC-ICPMS, several groups (*E10–E13*) working independently obtained high-precision W isotopic data for numerous meteorites (including undifferentiated chondrites of various types, and eucrites, Martian meteorites and irons) and terrestrial (including Early Archaean) rocks. The overall conclusions of the three independent groups were essentially the same. Chondritic $^{182}W/^{183}W$ ratios are $\sim-2\epsilon$ below the previously accepted bulk Solar System ratios (*E10–E13*). This, in turn, requires substantial revision of planetary (including core) formation ages relative to our Solar System's beginnings as determined in chondrites (including Allende CAI) using data for now-extinct, 9-Ma ^{182}Hf. The new relative core formation ages are as follows: 3–4 Ma (*E12, E13*) for the eucrite parent body (~Vesta); 13 ± 2 Ma for Mars (*E12*); ~30 (26–34) Ma for the Moon (*E12, E13*); ~30 (30–34) Ma for the Earth (*E10–E13*). Assuming a magma ocean model, the Earth formed 11 ± 1 Ma after the beginning of the Solar System (*E12*). In view of these results, the most important conclusion reached is that the planets of our Solar System accreted rapidly (within a few tens of Ma) and formed their cores (which incorporated siderophiles, such as W) by metal/silicate fractionation while ^{182}Hf was still present. This is a surprisingly short time but well within times estimated by astrophysical models.

Carlson and Hauri (*E14*) described a new MC-ICPMS technique to measure the Ag isotopic composition with a $^{107}Ag/^{109}Ag$ external precision of $\pm1.3\epsilon$. This precision allows resolution of Ag isotopic ratios in low-Pd/Ag samples such as pallasites, IA irons, chondrites, and the Earth. The correlation between Ag isotopic ratio variations and Pd/Ag suggests contributions of now-extinct, 6.5-Ma ^{107}Pd to some. Pd–Ag closure in the Brenham pallasite was 3.5 ± 0.3 Ma after Canyon Diablo, a IA iron: Grant (IIIB iron) has highly radiogenic Ag $(+36\epsilon)$ compared with Canyon Diablo, indicative of evolution in a parent with high Pd/Ag. Canyon Diablo sulfide has the lowest Ag isotopic ratio of any extraterrestrial material $(-11\epsilon$ relative to terrestrial standard) and

an initial $^{107}Pd/^{109}Pd$ ratio of $(2.39 \pm 0.26) \times 10^{-5}$ compared with a Solar System ratio of $(39 \pm 19) \times 10^{-5}$ from Allende. The high Allende ratio might reflect mass fractionation or a nuclear anomaly in its Ag.

The low sensitivity of the thermal ionization source has made determination of the Zr isotopic composition by TIMS difficult, if not impossible. One advantage of MC-ICPMS over TIMS is provided by the high efficiency of ICP sources. As noted in our last review (*A1*), evidence for Zr isotopic anomalies signals the presence of live 36-Ma ^{92}Nb in the early Solar System and early Zr/Nb fractionation. ^{92}Nb decays into ^{92}Zr and is produced only by the p-process during nucleosynthesis. Thus, this system can place constraints on genetic processes in the timing of early Solar System events.

Advances in ICPMS are now allowing instrument-based minimization of polyatomic interferences, thus eliminating the need for elaborate chemical separations. Schönbächler et al. (*E15*) developed a dynamic reaction cell (DRC) method based on MC-ICPMS (IC-DRCMS), for determining Nb/Zr ratios without chemical separations. [This technique was described in more detail elsewhere (*E16*). Reference *E16* also includes an isotope dilution method for determining Ta using ^{180}Ta tracer.] Their measurements (*E15*) require ≥50 ng of Zr, yielding a ^{92}Zr value with an external precision (2σ) of $\pm0.3\epsilon$ unit. Internal isochrons $(^{92}Zr/^{90}Zr$ vs $^{93}Nb/^{90}Zr)$ for whole rock and four mineral separates from Estacado (H6) and five mineral separates from a eucrite clast in the Vaca Muerta mesosiderite yielded initial $^{92}Nb/^{93}Nb$ ratios of $\sim10^{-5}$. Such low ratios had previously been reported for differentiated meteorites such as Vaca Muerta, but Allende CAI yielded ratios of $\sim10^{-3}$ (see references in *A1*), which should be among the earliest Solar System objects. Sanloup et al. (*E17*) used MC-ICPMS to determine the Zr isotopic composition of a suite of SNC meteorites as well as carbonaceous, enstatite, and ordinary chondrites and concluded that at least some part of the observed ^{92}Zr excess must result from the decay of the now extinct ^{92}Nb.

To confirm that the low internal isochron $(^{92}Zr/^{90}Zr$ vs $^{93}Nb/^{90}Zr)$ value for Estacado and the Vaca Muerta clast does not reflect late mineral equilibration, Schönbächler et al. (*E15*) determined Hf/W isochrons (based on 9-Ma ^{182}Hf) for the same Estacado and Vaca Muerta clast mineral separates in which they studied Nb/Zr systematics. They found that the last internal W isotope equilibration took place in those two meteorites 14.8 ± 1.3 Ma (even with possible corrections, certainly <20 Ma) after the Solar System formed. They note that prior studies cited previously (*A1*), proposing initial Solar System $^{92}Nb/^{93}Nb$ values of $\sim10^{-3}$, implied a protracted period for the Earth's initial differentiation. This, they argued, is inconsistent with the ratio of $\sim10^{-5}$ found by them and others for $^{92}Nb/^{93}Nb$ ratios in all Solar System materials on Earth but CAIs, which could conceivably have a presolar Zr isotopic signature. Undoubtedly, more will be heard in the future regarding this topic.

The advantage of the high sensitivity of MC-ICPMS compared to N-TIMS for precise determination of Ru isotopic measurements is offset by relatively large mass bias and plasma instabilities in the former. The use of MC-ICPMS for determination of Ru isotopes in meteorites was evaluated by Becker et al. (*E18*). They concluded that an extremely efficient Mo–Ru chemical separation scheme would be required to minimize isobaric interferences of

Mo on Ru isotopes. Because of these interferences, Ru isotopic results by MC-ICPMS are currently less precise than those of N-TIMS.

Rouxel et al. (*E19*) developed an MC-ICPMS method to determine the Se isotopic composition in geologic samples that requires ≥1 ng of Se, a tenth of that needed for N-TIMS. Thus far, Se isotopic data for terrestrial igneous samples and iron meteorites vary by <0.5‰: but in terrestrial sedimentary and hydrothermal materials, variations are up to 8‰. The mass-dependent kinetic fractionation of Se in aqueous environments may prove useful to distinguish biotic from abiotic processes.

MC-ICPMS was used to investigate whether transition elements can be isotopically fractionated by chemical processes in nature. Maréchal and Albarède (*E20*) observed that the $^{63}Cu/^{65}Cu$ ratio of Cu solutions eluted from anion-exchange resin is isotopically fractionated compared to nonchemically separated Cu standard. The stable Zn isotopes, ^{66}Zn and ^{68}Zn, also fractionate isotopically to a lesser extent. Batch experiments confirm that Zn fractionation is not kinetically determined (*E20*). These results suggest that Fe isotopic fractionation recently observed in nature and in laboratory experiments may involve low-spin Fe tetrahedral complexes.

Rehkämper et al. (*E21*) used MC-ICPMS for the first, in-depth investigation of Tl isotopic compositions in marine materials. They observed that the Tl isotopic composition is 40 times more variable than analytical reproducibility, consistent with fractionation of Tl during chemical adsorption processes.

Laser Ablation. Young et al. (*E22*) described a new LA-MC-ICPMS technique for in situ measurement (pit sizes of 100-μm diameter and ~30-μm depth) of Mg isotopic compositions in constituent minerals in four Allende chondrules (4−30 mg each) and in a 2 × 0.5 cm type B CAI. These remarkable measurements yield $\delta^{25}Mg$ and $\delta^{26}Mg$ values with a precision (2σ) of 0.2‰: oxygen isotopic data were obtained in conjunction with those of Mg. The $\delta^{25}Mg$ and $\delta^{26}Mg$ mass-dependent variations were up to 1.5‰/amu in chondrules and 0.3‰/amu in the CAI and were associated with alteration. The isotopic data for chondrules indicate incorporation of preexisting forsterite grains with discrete Mg and O isotopic compositions and postaccretion alteration so that high ^{25}Mg and low Δ ^{17}O correlate. The CAI data for $\delta^{25}Mg$ and $\delta^{26}Mg$ are sufficiently precise to deconvolute chronologic effects in the $^{26}Al-^{26}Mg$ system from elemental mobilization effects: the half-life of ^{26}Al is 730 ka.

Humayun and Campbell (*E23*) used W geochemistry and $^{182}Hf-^{182}W$ chronometric data to infer metamorphic times in ordinary chondrite parent bodies. Using LA-HR-ICPMS, they found that W/Ir and Re/Ir ratios in metal grains of equilibrated ordinary chondrites (H4−6) are precise and correlate positively. However, in unequilibrated ordinary chondrites (UOC or H3, L3, LL3), the W/Ir ratio in metal is very variable, 0.003−0.6, and uncorrelated with Re/Ir or any other siderophilic element. Since matrix metal in UOC contains less W than does matrix metal in EOC, Humayun and Campbell (*E23*) argued that W must enter metal during metamorphism of UOC to EOC. Hence, they suggested that the nominal time difference given by the $^{182}Hf-^{182}W$ and $^{207}Pb-^{206}Pb$ methods is real and reflects the metamorphic duration in the H chondrite parent(s), 2−12 Ma. Since $^{187}Re-^{187}Os$ and $^{182}Hf-^{182}W$ ages are set by the same metamorphic event(s), the authors argued that this establishes a link between an absolute chronometer and one based on a long-extinct radionuclide that measures a formation interval.

Campbell et al. (*E24*) used LA-MC-ICPMS to quantify siderophile element contents in the metal-rich chondrites Bencubbin, Weatherford, and Gujba. An attempt was made to measure these elements in the metal grains to constrain the origin of large metal aggregates in bencubbinites. Campbell et al. (*E24*) found that a strong, volatility-controlled signature is observed among the metal grains. Also, they found that refractory siderophile elements (e.g., Ru, Re, Os, Ir, and Pt) are unfractionated from one another and are present in approximately chondritic abundances. Less refractory siderophiles (e.g., Fe, Co, Ni, Pd, and Au) are fractionated from the more refractory ones, and moderately volatile elements (e.g., Ga, Ge, As, Sn, and Sb) are depleted in the metal grains.

In a study of siderophile element distribution in zoned metal grains in the QUE 94411 chondrite, Campbell et al. (*E25*) used LA-MC-ICPMS to determine the concentrations of P, V, Cr. Fe, Co, Ni, Mo, Ru, Rh, Pd, W, Re, Os, Ir, and Pt. The PGEs, excluding Pd, exhibit radial zoning in these grains as previously found for Ni and Co, with the concentration of these elements decreasing from grain centers to rims. The PGE distribution in these metal grains supports a condensation origin for the metal grains, arguing against an origin by redox-controlled processes.

Hirata (*E26*) determined the Zr isotopic composition and the U/Pb ages of selected zircon and baddeleyite crystals using LA-MC-ICPMS. The resulting precisions for the $^{92}Zr/^{90}Zr$, $^{94}Zr/^{90}Zr$, and $^{96}Zr/^{90}Zr$ isotopic ratios for zircon and baddeleyite are 0.01−0.02, 0.02−0.03, and 0.03−0.04% (2σ), respectively. The combination of these Zr isotopic data and the U/Pb age information allowed the authors to estimate the initial $^{92}Nb/^{93}Nb$ abundance at formation of the Solar System.

Flem et al. (*E27*) used LA sector field ICPMS to characterize the trace element composition of quartz to identify high-purity quartz resources, for geochemical modeling, and to constrain the petrogenetic history of quartz including its provenance in sediments and sedimentary rocks. Most elements in the periodic table were measured at the nanogram per gram level with an analytical precision of better than 10% for elements above the MDL.

Alard et al. (*E28*) used LA-MC-ICPMS to constrain the Re−Os isotopic systematics of sulfides in spinel peridotite xenoliths from the subcontinental lithospheric mantle. The results of this study indicate that the whole-rock Os isotopic signature reflects the mixing of multiple sulfide populations. Restite sulfide samples after melt extraction have nonradiogenic Os isotopic signatures that reflect ancient melt extraction and sulfide grains that were introduced by later metasomatic events contain more radiogenic Os.

Two recent studies used LA-MC-ICPMS to date accessory minerals. Willigers et al. (*E29*) presented results of a Pb−Pb dating study of apatite, monazite, and titanite (sphene) from Paleoproterozoic rocks from West Greenland. Pb isotopes were also measured in the NIST SRM 610 glass to monitor Pb isotopic fractionation and were corrected for mass fractionation by reference to the measured Tl isotopic ratio. The common Pb isotope ratios in the accessory minerals, which are required for age determinations, were either analyzed in coexisiting plagioclase or ignored. Apatite and monazite ages determined by LA-MC-ICPMS

were identical, within error, with ages determined using ID-TIMS on bulk mineral separates from the same samples. The titanite ages determined by LA-MC-ICPMS were ~1% younger than grains analyzed by ID-TIMS. The discrepancy may be due to yet unidentified isobaric interferences that interfere with the [207]Pb peak. Foster et al. (*E30*) used LA-MC-ICPMS, ID-TIMS, EMPA, and textural studies to understand the significance of Pb loss, inherited components, and continuous and episodic monazite growth in the generation of dispersed age data. Three monazite samples from the Canadian Cordillera and one from the Himalaya of Pakistan were studied. Each sample exhibited an age dispersion of between 1 and 12 Ma for single crystals and multigrain TIMS isotopic measurements. The LA-MC-ICPMS results indicate that the age dispersion may reflect an inherited component (<100 Ma older than the TIMS ages) in three of the four samples. Foster et al. (*E30*) also found that the majority of monazite crystals analyzed exhibited Y zoning, and the LA-MC-ICPMS ages determined within those crystals differed. Monazite that grew prior to garnet growth is relatively Y-rich while monazite that grew after garnet is relatively Y-poor.

MASS SPECTROMETRY

Despite the fact that TIMS and N-TIMS are more time- and labor-intensive than MC-ICPMS, they are still widely used for several isotopic systems. The low thermal ionization efficiencies of the actinides can complicate determination of their isotopic compositions by TIMS. To address this, Yokoyama et al. (*F1*) developed a highly precise method for the TIMS determination of U isotopic composition utilizing a silicic acid-diluted phosphoric acid solution as an ionization activator to produce UO_2^+ ions. The method was demonstrated on 10−100 ng of U extracted from natural rhyolitic obsidian samples and demonstrated precisions ranging from 0.13 to 0.31% (2σ) for $^{234}U/^{238}U$ determinations. Rubin (*F2*) described an optimized technique for measuring Th isotopic compositions using a new single collector TIMS. The author performed unspiked determination of $^{232}Th/^{230}Th$ ratios in igneous rocks and concluded that the best results were obtained by single collector ion-counting analysis of 50-ng, single-filament, sample loads.

The applicability of time-of-flight secondary ion mass spectrometry (TOF-SIMS) to the analysis of extraterrestrial samples was reviewed by Stephan (*F3*). The advantages of this method, as compared to other ion microprobe techniques, include sufficient mass resolution for separation of major mass interferences and little sample destruction; in addition, the ability of TOF−SIMS to measure molecular and atomic ion species simultaneously extends its applicability to the investigation of indigenous extraterrestrial hydrocarbons.

The early history of the Solar System can be and is being studied using now-extinct radionuclides with half-lives of <100 Ma. These nuclides were produced during nucleosynthesis and were incorporated into primitive condensed matter where their decay products accumulated. One such system that essentially had not been studied is based upon 2.3-Ma ^{135}Cs, which decays into ^{135}Ba. Cesium-135, like 9-Ma^{182}Hf, is an r-process nuclide and Cs and Ba volatilities and solubilities differ so markedly that the ^{135}Cs−^{135}Ba system has substantial chronometric potential. Hidaka et al. (*F4*) investigated this system in some primitive extraterres-

trial materials [six Allende CAIs of 6−66 mg each and two chondrites, Beardsley (H5) and Zag (H3−6)] and found results of potential importance. After chemical separations by leaching and complete dissolution of the residues, the Ba isotopic composition was measured by TIMS, and Cs and Ba were quantified by ICPMS, using In as an internal standard. Excess ^{135}Ba was found in the CAIs, and after model-dependent correction for r-process contributions, an initial Solar System $^{135}Cs/^{133}Cs$ ratio of (4.8 ± 0.8) × 10^{-4} was calculated. From the correlation between ^{135}Ba and the Cs/Ba ratio in the two H chondrites, the data suggest that Beardsley and Zag parent material(s) experienced aqueous alteration at 8.2−11.9 and 13.9−17.6 Ma, respectively, after CAI formation. Since these ages are consistent with dates given by now-extinct chronometers, the ^{135}Cs−^{135}Ba system may well prove important for studying fractionation processes involving early Solar System bodies.

The other major sort of presolar grains are micrometer to submicrometer SiC present at 1−28 ppm levels in primitive chondrites. Daulton et al. (*F5*) applied a variety of techniques [selected area electron diffraction, TEM and HR-TEM, and SIMS and nano-SIMS (to obtain C and N isotopic compositions)] to characterize SiC polytypes present in the C2M chondrite Murchison). Essentially, only 2 of the >250 possible SiC polytypes were present: cubic 3c β-SiC and hexagonal 2H α-SiC and their intergrowths). The presolar origin of these grains is inferred from their clearly nonterrestrial $^{12}C/^{13}C$ and $^{14}N/^{15}N$ ratios. By kinetic and thermodynamic arguments, the formation of these grains seems to have occurred by direct nebular condensation at temperatures at or somewhat below 1700 K. In addition to providing clues to the (pre)history of the Solar System, this study also illustrates the detailed information that can be gleaned when several analytical techniques are applied to a single sample, even of minute size.

N-TIMS has been successfully applied to the ^{182}Hf−^{182}W chronometer to constrain magmatic process dates in the eucrite parent body. Quitté et al. (*F6*) developed a new technique to measure nanogram of W levels in small eucrite samples. After preparation of the sample using the method described in ref *B27*, the W fraction is loaded on an Ir filament, ionized as WO_3^-, and measured in static multicollector mode.

Isotope ratio mass spectrometry (IRMS) of the three stable O isotopes in extraterrestrial samples is an invaluable tool to classify meteorites or inclusions in them and even identify specific meteorite parent bodies. In one illustration of this approach, study of the northwest Africa meteorite find, NWA011, Yamaguchi et al. (*F7*) used optical microscopy, SEM, electron microprobe analysis of thin sections, INAA, prompt γ-ray analysis, IRMS, and ICPMS of bulk rock samples. While these techniques identify this meteorite as a eucrite, its δ^{17}O and δ^{18}O values differ from those of other eucrites, indicating that at least two different eucrite parents exist(ed) in the Solar System. Wiechert et al. (*F8*) used the high-precision laser fluorination technique to determine the O isotopic composition of lunar samples from Apollo missions 11, 12, 15, 16, and 17. The O isotopic compositions of all samples plot within ±0.016‰ (2σ) on a single mass-dependent fractionation line identical with the terrestrial fractionation line. While the existence of a single lunar−terrestrial fractionation line is not new, the precision of the data are, supporting the giant impact model

for the formation of the Earth−Moon system.

Improvements have been made in sample introduction methods for IRMS determination of O isotopic compositions. Despite the important role of liquid water in the evolution of carbonaceous chondrites and SNC meteorites from Mars, little work has been done on oxygen in water bound in hydrated minerals within such samples. Baker et al. (*F9*) developed a new technique in which solid CoF_3 is used to prepare O gas for IRMS measurements from aqueous solutions derived by direct injection of water or pyrolysis of solid geological materials. The technique was developed primarily for oxygen isotope determinations and is capable of determining O isotope ratios in small samples (1−50 mg). Wiechert et al. (*F10*) described a new technique for in situ oxygen isotopic analysis of silicates using isotope-ratio-monitoring gas chromatography/mass spectrometry and eximer laser fluorination. Only 10 min is required for a single analysis, and the precision for $\delta^{18}O$ is comparable to that obtained from dual-inlet systems.

IRMS can be used to provide information of the nature of ancient impacts on Earth. Mukhopadhyay et al. (*F11*) utilized mass spectrometric techniques to measure the $^3He/^4He$ ratios of marine carbonates through the 63.9−65.4-Ma interval and determined that the bolide associated with the Cretaceous−Tertiary (K−T) extinction event was not accompanied by an enhanced flux of extraterrestrial dust. Hence, the impactor was not part of a comet shower. Fullerenes have been associated with impact events of bolides with Earth. Becker et al. (*F12*) used laser desorption mass spectrometry to analyze toluene extracts from sediments at the Permian−Triassic (P−T) boundary, which occurred at 251.4 Ma. Fullerenes ($C_{60}-C_{200}$) were found to have trapped He and Ar, exhibiting isotopic ratios similar to those of the planetary component of carbonaceous chondrites. These data imply that an impact accompanied the P−T extinction, as in the K−T extinction, 65 Ma bp.

Several new sample introduction methods have been developed for IRMS. Hashizume et al. (*F13*) performed N and Ar isotopic analyses in a single 200-μm ilmenite grain from the lunar regolith via stepwise heating with a power-controlled CO_2 laser. The highly variable $\delta^{15}N$ values observed (*F13*) suggest substantial temporal variations of micrometeorite flux during the last 500 Ma. Grassineau et al. (*F14*) developed a continuous-flow method (CF-IRMS) for the rapid determination of S isotopic composition in sulfide and sulfate minerals. The technique yields high throughput (8 min/analysis) and has been used for more than 1000 analyses of geological samples with $\delta^{34}S$ ranging from −2 to +2‰.

Sharp et al. (*F15*) discussed a new method for online determination of δ^2H and $\delta^{18}O$ in water, hydrous minerals, and fluid inclusions. The method involves reduction of water or solid hydrous samples by reaction with glassy carbon at high temperatures. Gaseous H_2 and CO are produced by reaction with the carbon at 1450 °C in a He carrier gas. These gases are separated in a gas chromatograph and subsequently analyzed by MS. Samples as small as 1 μL of water (or equivalent amount of hydrous phases) could be analyzed successfully.

ELECTRON MICROBEAM TECHNIQUES

Presolar dust grains, preserved in meteorites of asteroidal origin, provide information regarding their formation around stars other than the Sun, and on early Solar System formation.

Meteoritic nanodiamonds are presumably the most abundant type of presolar grain known. TEM studies of carbon-rich, fragile interplanetary dust particles (IDP)−presumably of cometary origin−do not contain nanodiamonds (*G1*), while carbon-rich meteorites contain 750−1500 ppm of them. Either some/most nanodiamonds formed in the inner Solar System are not presolar or nanodiamonds are presolar but their abundance decreases with increasing heliocentric distance. In the latter event, large-scale material transport and circulation in the early Solar System is even less well understood than previously thought.

A TEM and SEM-EDS study (*G2*) of IDP recovered from aerogel exposed for 18 months on the Mir space station illustrates the current status of sample handling and gross characterization at the 10-μm sample level.

There is little doubt that CAIs were among the earliest, if not the earliest, materials condensed as the Solar System formed. Thus, their isotopic compositions are used as initial Solar System values, particularly for chronometers based upon early, long-extinct radionuclides. An implicit assumption is that all CAIs formed contemporaneously near or at the time of chondrule formation. However, one Allende CAI tested this: it consists of spinel-free islands (SFI) in a pyroxene-spinel-rich core (SRC) surrounded by a melilite mantle (MM) which petrographically appears to reflect three distinct, igneous crystallization stages. Hsu et al. (*G3*) made an ion probe study of various regions (identified by SEM) and found initial $^{26}Al/^{27}Al$ values of $(4.6-5.0) \times 10^{-5}$ for three separate SFI within the SRC, 4.3×10^{-5} for two SRC regions, and 3.3×10^{-5} for two MM regions. Assuming that the SFI are older CAI fragments or clasts later entrapped in a CAI liquid that crystallized around them, the $^{26}Al/^{27}Al$ values yield formation intervals as follows: SFI ≡ 0 years; SRC $\sim 10^5$ years; MM $\sim 4 \times 10^5$ years. The possibility that these age intervals of $\sim 10^5$ years reflect metamorphism of a single assemblage can be excluded, so that it appears that CAI crystallization from hot nebula region-(s) took place over a 0.4-Ma interval. Since CAI formation seems to have been an extended process, not a single-stage event, these results may affect the time resolution inferred using other short-lived radionuclides in the early Solar System.

Using an environmental scanning electron microscope (ESEM) with X-ray energy dispersive spectroscopy (EDS), Timofeeff et al. (*G4*) presented a new method for determining the major element composition of fluid inclusions in sedimentary and diagenetic minerals. These results can help better understand the composition of ancient surface and near-surface waters. This method permits analysis of fluid inclusions larger than 30 μm in diameter in a low-vacuum environment without the need for sample coating with conductive material such as carbon or gold. The method (*G4*) included the development of a new sample holder, a modification of fluid inclusion preparation to obtain homogeneous samples, and the preparation of flat, smooth, surfaces for analysis. The ESEM−EDS method yielded quantitative results for Ca, Mg, K, SO_4, and Cl at concentrations of >0.1 wt %, and for Na >0.5 wt %.

NUCLEAR TECHNIQUES

Information in a slim, 10-paper volume dealing with radionuclide geochemistry in soils (*H1*) may be of interest to some hard-rock types.

While nuclear-based methods are generally being replaced by ICP-based techniques for elemental analysis of geological/cosmochemical materials, instrumental neutron activation analysis (INAA), epithermal neutron activation analysis (ENAA), radiochemical neutron activation analysis (RNAA), and preconcentration neutron activation analysis (PCNAA) are still utilized in a few laboratories. The primary strength of the neutron activation techniques is the large number of elements that can be determined from a minimal amount (even 1 mg) of sample. INAA and RNAA were both used to determine the major, minor, and trace element composition of the recent, unique kind (*C2*) of carbonaceous chondrite fall, Tagish Lake (*H2*, *H3*).

The presence of elevated concentrations of PGEs in terrestrial materials can be a signature of an extraterrestrial component. Mao et al. (*H4*) used INAA, ENAA, RNAA, and PCNAA coupled with NiS fire assay to determine concentrations of Ru, Rh, Pd, Os, Ir, Pt, and 42 other elements in two candidate K−T boundary clay reference materials from Stevns Klint, Denmark. Giaveri et al. (*H5*) developed a procedure utilizing both pre- and postirradiation separation of Pt prior to its determination by RNAA in geological and environmental materials. The method ($\leq$0.1 ppm detection limit) utilizes a column chromatographic-based preirradiation where the Pt is separated from Au, Ca, Na, Br, and P followed by irradiation and separation of ^{199}Au for final determination of Pt. Dai et al. (*H6*) optimized an anion-exchange procedure for the analysis of trace PGEs in impact-associated rocks. The two-stage procedure involves chlorination and adsorption onto a small ion-exchange column. When combined with NAA and ICPMS, this method is suitable for determination of Ru, Pd, Os, Ir, Pt, Au, Ag, and Re in geological samples.

Paul (*H7*) used cold neutron, prompt γ-ray activation analysis for nondestructive determination of nitrogen in solid geologic samples, a technique that can replace the destructive, hoary Kjeldahl method. This new technique can nondestructively determine nitrogen in geological samples at a detection limit near 1‰.

Naturally occurring radionuclides ^{238}U, ^{235}U, ^{232}Th, and their progeny are unique in that they can be determined directly via radiometric techniques. Measurement of these radionuclides is used to study the chronology of a variety of geological processes via U-series disequilibria methods. Direct determination of ^{238}U via γ-spectrometric analysis in sedimentary samples is impossible due to very low emission probability of its most prominent emission line. El-Daoushy and Hernández (*H8*) evaluated analytical problems associated with γ-spectrometric determination of ^{238}U via its ^{234}Th daughter. The authors concluded that the 63-keV peak is the best option to minimize X-ray contributions from Th. Tanner et al. (*H9*) compared two analytical methodologies involving ^{210}Pb decay products for dating sediment cores using: γ-spectrometry for ^{210}Bi and α-spectrometry for ^{210}Po. While both techniques yielded coefficients of variation of 12%, the former technique involves much simpler sample preparation requirements than the α-spectrometric method.

CHEMOMETRICS
Chemometric data analysis techniques allows geoanalytical chemists to control the quality of results from routine analyses, discover trends within large multivariate data sets, and assess and even improve data quality. Howarth et al. (*I1*) proposed using multivariate quality control techniques to assess data quality in routine analyses by bulk analytical techniques such as ICPMS, XRF, and INAA. The authors suggested that that a combination of Hotelling's T^2 statistic and principal component analysis can provide tools for error recognition and diagnosis. Vendemiatto and Enzweiler (*I2*) used the modified Horwitz expression, which gives precision as a function of concentration, as a quality control measure for XRF results for silicate rock samples. Results indicate that the accuracy of XRF analysis is strongly dependent on instrumental settings and uncertainties in concentrations of certified materials used for calibration. Ely and Neal (*I3*) described a method for data reduction and uncertainty estimation for PGE data determined by ICPMS. Their method is applicable to any analytical technique where drift corrections or regression models are used for quantitation of concentrations

The term "nugget effect" has been coined to describe the geochemical fractionation of siderophiles, such as PGE and Au, into/as metal in geologic samples. Meisel et al. (*I4*) studied uncertainties created by such sample inhomogeneity as distinct from those caused by sample preparation and used chemometric methods to separate and estimate their respective contributions to the overall uncertainty of measurement. They demonstrated in two special cases that irreproducible results in the analysis of Os and Re were caused by the nugget effect, rather than by inadequacies of the analytical method.

Multivariate techniques can define structure in large multivariate data sets. Recent examples of this approach are given by Swanson et al. (*I5*) and Hannigan et al. (*I6*). Swanson et al. (*I5*) used two-way cluster analysis of geochemical data to identify and group groundwaters possessing distinct geochemical characteristics and constrain their origin. Hannigan et al. (*I6*) utilized multivariate chemometric analysis of concentrations of 21 trace elements in 51 basaltic glasses analyzed by ICPMS to identify four, statistically significant, end-member mantle components compositionally.

The accuracy of geochronological dating methods can be improved by application of chemometric techniques. Because the U−Pb isotopic system does not have a pair of daughter isotopes possessing an invariant ratio, the accuracy of isotopic analyses is limited by mass-fractionation uncertainties. Double spiking (for TIMS) and Tl normalization (for ICPMS) minimizes this limitation. Ludwig (*I7*) demonstrated a multivariate mathematically based method, the "total Pb/U isochron", that requires only a single-spiked mass spectrometric analysis and eliminates fractionation-related imprecision for rocks of any age. Powell et al. (*I8*) utilized robust statistical methods and the bootstrap technique to account for non-Gaussian distributions in typical isochron data.

Verma et al. (*I9*) have subjected a variety of REE determination methods to statistical evaluation in order to determine the most precise technique among interlaboratory performance results. After rejection of outlying values, it was shown that MS provides the most precise data.

MISCELLANEOUS
Modern ion microprobes are capable of precision that could only be dreamed of a few years ago. Using the PANURGE instrument (a modified Cameca IMS-3f), Amelin et al. (*J1*)

determined Pb–Pb isochron (^{207}Pb/^{206}Pb vs ^{204}Pb/^{206}Pb) ages for 21 chondrules (0.97–20 mg mass) from the CR chondrite, Acfer 059, and 19 samples (0.7–11 mg) from 2 CAIs in Efremovka, a CV chondrite. The mean ages for chondrules and CAIs were 4564.7 ± 0.6 and 4567.2 ± 0.6 Ma, respectively, the CAI– chondrule difference being 2.5 ± 1.2 Ma. Although a small difference between two large numbers, this value is consistent with the 2–3-Ma difference between CAIs in CR chondrites and chondrules inferred from initial ^{26}Al/^{27}Al ratios for them. This consistency, in turn, argues that ^{26}Al–^{26}Mg systematics have chronologic significance. An excellent summary of early Solar System chronometers and planetary formation by Alexander et al. (*J2*) gives illustrations of the precision levels attainable by modern geochemical/cosmochemical techniques.

Ultraviolet, visible, and infrared spectral reflectance can be used to provide evidence for a link between meteorites and their parent bodies. Hiroi et al. (*J3*) used bidirectional ultraviolet– visible–near-infrared reflectance spectrometry and biconical Fourier transform infrared to examine the unique fall, Tagish Lake (*C2*, *H2*, *H3*). The reflectance spectrum of this meteorite resembles those of D-type asteroids; previously, these asteroids had no known meteoritic analogue.

Remote compositional assessment of planetary surface materials by spectral techniques is complicated by the physical state of the rocks and their environment. To better understand the relationship between spectral features, particle size, and composition, Cooper et al. (*J4*) studied 35 terrestrial rock samples (acidic, intermediate, basic, and ultrabasic) by thermal infrared spectroscopy (7–13 μm). They found that the Christianson feature (a reflectance minimum or emission maximum) and the transparency feature (a reflectance maximum or emittance minimum) vary with the rocks' compositions and can be used to estimate those compositions. Additional environmental similation spectral data are needed to improve the accuracy of the fits.

While most methods reviewed in this paper are instrumentally based, wet chemical techniques are still the benchmark by which the accuracy of all analytical techniques are judged. In one of those examples of simultaneous inspiration, two chemical techniques for the determination of Fe^{2+} in rocks appeared in the geochemical literature within two weeks of each other. Both are based on a modified Wilson method involving quantitative oxidation of Fe^{2+} to Fe^{3+}, followed by back-titration. The first method (*F1*) uses V^{5+} to oxidize Fe^{2+} and the second (*J5*) uses K$_2$Cr$_2$O$_7$. The precisions of both methods were ∼0.5%.

Since microbial biota secrete organic extracellular polymeric substances (EPS), Westal et al. (*J6*) suggested that they have a strong likelihood of being preserved in the geologic record as fossilized polymeric substances (FPS). The EPS form biofilms, and they and FPS date back to the Early Archaean (3.5 Ga) and are distinguishable from prebiotic films. Since the EPS and biofilms are widespread on Earth and have a great preservation potential as FPS, they should constitute useful biogenic markers in extraterrestrial materials.

As noted earlier, a set of seven papers dealing with different aspects of astrobiology appeared in *Nature* (*C6*). A virtual National Astrobiology Institute has been created (J*7*) and a new International Journal of Astrobiology has been established by Cambridge University Press. Grady (*J8*) provided an excellent introductory overview in a slim volume of the current status of astrobiology.

Asteroids and comets have been assumed to be sources for deposition on Earth of amino acids and other organic compounds that may have led to biogenesis. Cooper et al. (*J9*) provided the first conclusive evidence for the presence of polyhydroxylated compounds or polyols (sugars, sugar alcohols, and sugar acids) in Murchison and Murray, both CM2 chondrites. These polyols seemingly formed preterrestrially and thus were present on the early Earth for incorporation into the first life forms.

Pizzarello et al. (*J10*) extracted organic material from the unique (*C2*) Tagish Lake carbonaceous chondrite: analysis of water and solvent extractions of interior powdered samples by gas chromatography-combustion-isotope ratio mass spectrometry and nuclear magnetic resonance show that this carbonaceous chondrite contains a suite of soluble organic compounds (∼100 ppm) that includes mono- and dicarboxylic acids, dicarboximides, pyridinecarboxylic acids, a sulfonic acid, and aliphatic and aromatic hydrocarbons. Insolubles exhibit aromatic character, deuterium enrichment, and fullerenes containing planetary-type He and Ar. Fluid inclusions in rocks represent relics of past hydrothermal geochemical activity, and a growing number of techniques have been designed to investigate them.

While XRF is a well-established analytical method for determination of major and minor elements in geological materials, it has not traditionally been utilized to study extraterrestrial samples due to the relatively large amount of material required for analysis. Wolf and Palme (*J11*) developed an XRF method for the analysis of small quantities (∼120 mg) of extraterrestrial materials. Use of this technique improves Solar System abundance determination of P and Ti from concentrations of these elements (and Si, Fe, Mg, Ca, Al, Mn, Cr) in Orgueil and 25 other carbonaceous chondrites.

In two related studies, Engi et al. (*J12*) and Scherrer et al. (J*13*) discussed the development and application of an in-house-built XRF microprobe to date young monazites from the central Alps. The former (*J12*) compared the XRF microprobe and ID-TIMS results, and the latter (*J13*) compared XRF microprobe and laser ablation plasma ionization multicollector mass spectrometry data. The precision achieved using the XRF microprobe is only slightly poorer than those of isotopic measurements. The XRF micropropbe can be used for precise chemical Th–U–Pb dating of individual monazite grains separated from Pb-free polished petrographic thin sections. Reference monazite FC-1 has an ID-TIMS age of 54.3 ± 1 Ma and a XRF microprobe age of 55.3 ± 2.6 Ma. The analytical precision achieved is dependent on the spatial resolution and the integration time. The XRF microprobe is nondestructive and easy to use and maintain.

Several recent studies have used synchrotron radiation in novel and innovative applications. Takahashi et al. (J*14*) used X-ray absorption, near-edge structure (XANES) to determine Ce^{III}/Ce^{IV} ratios in geological materials. Ce may be either trivalent or tetravalent in nature, and the ratio of the two states is useful in understanding redox conditions during mineral formation. This application has been limited in the past because few techniques can determine the oxidation state of Ce, and since, in many but not all minerals, Ce occurs at relatively low concentrations, precise measurements may thus be difficult. The XANES method (*J14*) permits determination of the oxidation state of Ce at concentra-

tions as low as 15 ppm. Differences in Ce^{III}/Ce^{IV} ratios in a variety of geological materials were discussed (*J14*) and, in combination with Ce anomalies in chondrite-normalized REE patterns, will help geochemists refine our understanding of geochemical processes.

Two recent studies used synchrotron radiation to determine trace elements in fluid inclusions in minerals. Philippot et al. (*J15*) used synchrotron XRF (SXRF) to quantify Cu, Zn, and As in individual fluid inclusions in quartz of a gold−quartz vein from the western Alps. The results agree well with determination by crush−leach analysis, demonstrating that this technique is applicable for concentrations down to tenths of ppm levels. Vanko et al. (*J16*) used SXRF and PIXE to compare the compositions of porphyry-type, ore-forming brines and two types of ocean crustal brines. The inclusions contained high salt concentrations and typically one or more daughter crystals. The trace element concentrations obtained by SXRF and PIXE generally agree well with published values and with each other.

ACKNOWLEDGMENT

Michael E. Lipschutz *is a Professor in the Chemistry Department at Purdue University. He received a B.S. degree in chemistry from the Pennsylvania State University in 1958 and his Ph.D. in physical chemistry from the University of Chicago in 1962 under the direction of Prof. Edward Anders. His research interests include chemometrics and neutron activation and inductively coupled plasma mass spectrometric analysis of trace and ultratrace elements, particularly thermally sensitive ones, in meteorites as thermometers for genesis and evolution of planetary bodies. He also studies cosmic ray irradiation histories of meteorites.*

Stephen F. Wolf *is an Assistant Professor in the Chemistry Department at Indiana State University. He received his B.S. degree in chemistry from Purdue University in 1987 and his Ph.D. in analytical chemistry from Purdue University in 1993 under the direction of Prof. Michael E. Lipschutz. From 1993 to 2001, he was a Staff Chemist at Argonne National Laboratory. His research interests include the application of trace element analytical techniques such as ICPMS, HR-ICPMS, and HPLC−ICPMS as well as chemometric data analysis methods for the study of the disposition of trace elements in cosmochemical, geochemical, and environmental materials.*

John M. Hanchar *is an Assistant Professor of geochemistry in the Department of Earth and Environmental Sciences at The George Washington University. He received his B.S. degree in geology from Memphis University (now University of Memphis) in 1985, his M.S. in geology from Vanderbilt University in 1990, and his Ph.D. in geochemistry from Rensselaer Polytechnic Institute in 1996 under the direction of Professor E. Bruce Watson. From 1996 to 1998, he was a Postdoctoral Appointee at Argonne National Laboratory and from 1998 to 1999 was a Visiting Assistant Professor at the University of Notre Dame. His research interests are in the chemical composition and physical properties of potential radioactive waste storage materials and the trace element and radiogenic isotopic composition of accessory minerals (e.g., zircon, monazite, apatite, and xenotime).*

F. Bartow Culp *is an Associate Professor of library science and the Chemistry Librarian at Purdue University. He received his B.S. in chemistry from the University of South Carolina in 1965, his Ph.D. in organic chemistry from the University of Delaware in 1971, and his M.L.S. from Indiana University in 1996. His research interests include chemical information instruction methods and the historical aspects of information science.*

LITERATURE CITED

GEOSTANDARDS

(A1) Lipschutz, M. E.; Wolf, S. F.; Hanchar, J. M.; Culp, F. B. *Anal. Chem.* **2001**, *73*, 2687−2700.
(A2) Roelandts, I. *Geostand. Newsl.* **2002**, *26*, 101−120.
(A3) Kane, J. S. *Geostand. Newsl.* **2001**, *25*, 7−22.
(A4) Kane, J. S. *Geostand. Newsl.* **2002**, *26*, 7−29.
(A5) Kane, J. S.; Potts, P. J. *Geostand. Newsl.* **2002**, *26*, 7−29.
(A6) Potts, P. J.; Thompson, M.; Wilson, S. *Geostand. Newsl.* **2002**, *2*, 197−235.
(A7) Jochum, K. P.; Stoll, B.; Pfänder, J. A.; Seufert, M.; Flanz, M.; Maissenbacher, P.; Hofmann, M.; Hofmann, A. W. *Fresenius J. Anal. Chem.* **2001**, *370*, 647−653.
(A8) Dulski, P. *Geostand. Newsl.* **2001**, *25*, 87−125.
(A9) Velasco-Tapia, F.; Guevara, M.; Verma, S. P. *Chem. Erde* **2001**, *61*, 69−91.
(A10) Blichert-Toft, J. *Geostand. Newsl.* **2001**, *25*, 41−56.
(A11) Woodhead, J. D.; Hergt, J. M. *Geostand. Newsl.* **2001**, *25*, 261−266.
(A12) Kurosawa, M.; Jackson, S. E.; Sueno, S. *Geostand. Newsl.* **2002**, *26*, 75−84.

SAMPLE PREPARATION

(B1) Nakai, S.; Fukuda, S.; Nakada, S. *Analyst* **2001**, *126*, 1707−1710.
(B2) Axelsson, M. D.; Rodushkin, I.; Ingri, J.; Öhlander, B. *Analyst* **2002**, *127*, 76−82.
(B3) Yu, Z.; Robinson, P.; McGoldrick, P. *Geostand. Newsl.* **2001**, *25*, 199−217.
(B4) Makishima, A.; Nakamura, E. *Anal. Chem.* **2001**, *73*, 2547−2553.
(B5) Makishima, K.; Kobayashi, K.; Nakamura, E. *Geostand. Newsl.* **2002**, *26*, 41−51.
(B6) Okai, S.; Terashima, S.; Imai, N. *Geostand. Newsl.* **2001**, *25*, 133−136.
(B7) Meisel, T.; Moser, J.; Fellner, N.; Wegscheider, W.; Schoenberg, R. *Analyst* **2001**, *126*, 322−328.
(B8) Hattori, M.; Hirata, T. *Analyst* **2001**, *126*, 846−851.
(B9) Diegor, W.; Longerich, H.; Abrajano, T.; Horn, I. *Anal. Chim. Acta* **2001**, *431*, 195−207.
(B10) Gros, M.; Lorand, J.-P.; Luguet, A. *Chem. Geol.* **2002**, *185*, 179−190.
(B11) Pin, C.; Le Fèvre, B. *Geostand. Newsl.* **2002**, *26*, 135−148.
(B12) Le Fèvre, B.; Pin, C. *Anal. Chem.* **2001**, *73*, 2453−2460.
(B13) Pin, C.; Le Fèvre, B. *Geostand. Newsl.* **2002**, *26*, 161−170.
(B14) Kleinhanns, I. C.; Kreissig, K.; Kamber, B. S.; Meisel, T.; Nägler, T. F.; Kramers, J. D. *Anal. Chem.* **2002**, *74*, 67−73.
(B15) Košler, J.; Kučera, M.; Sylvester, P. *Chem. Geol.* **2001**, *181*, 169−179.
(B16) Lécuyer, C.; Grandjean, P.; Reynard, B.; Albaréde, F.; Telouk, P. *Chem. Geol.* **2002**, *186*, 45−55.
(B17) Baker, J.; Waight, T.; Ulfbeck, D. *Geochim. Cosmochim. Acta* **2002**, *66*, 3635−3646.
(B18) Lee, K.; Shishido, S.; Motomizu, S. *Geochem. J.* **2000**, *34*, 383−393.
(B19) Boaventura, G.; De Oliveira, R.; Santelli, R. *Geostand. Newsl.* **2002**, *26*, 63−69.
(B20) De Vito, I. E.; Olsina, R. A.; Masi, A. N. *Fresenius J. Anal. Chem.* **2000**, *368*, 392−396.
(B21) Olive, V.; Ellam, M.; Wilson, L. *Geostand. Newsl.* **2001**, *25*, 219−22.
(B22) Malinovsky, D.; Rodushkin, I.; Baxter, D.; Öhlander, B. *Anal. Chim. Acta* **2002**, *463*, 111−124.
(B23) Brauns, C. M. *Chem. Geol.* **2001**, *176*, 379−384.
(B24) Kuritani, T.; Nakamura, E. *Chem. Geol.* **2002**, *186*, 31−43.
(B25) Paquette, J.; Pin, C. *Chem. Geol.* **2001**, *176*, 311−319.
(B26) Griselin, M.; van Belle, J. C.; Pomies, C.; Vroon, P. Z.; van Soest, M. C.; Davies, G. R. *Chem. Geol.* **2001**, *172*, 347−359.
(B27) Quittè, G.; Birck, J.-L.; Capmas, F.; Allègre, C. J. *Geostand. Newsl.* **2002**, *26*, 149−160.
(B28) Nishiizumi, K.; Caffee, M. W. *Science* **2001**, *294*, 352−354.
(B29) Lifton, N. A.; Jull, A. J. T.; Quade, J. *Geochim. Cosmochim. Acta.* **2001**, *65*, 1953−1969.
(B30) Maas, R.; Loss, R. D.; Rosman, K. J. R.; De Laeter, J. R.; Lewis, R. S.; Huss, G. R.; Lugmair, G. W. *Meteorit. Planet. Sci.* **2001**, *36*, 849−858.

MULTITECHNIQUE SYMPOSIA AND REVIEWS

(C1) Hochella, M. F., Jr. *Geochim. Cosmochim. Acta* **2002**, *66*, 735−743
(C2) Brown, P. G.; Hildebrand, A. B.; Zolensky, M. E. *Meteorit. Planet. Sci.* **2002**, *37*, 619−621.
(C3) Trombka, J. I.; Nittler, L. R.; Starr, R. D.; Evans, L. G.; McCoy, T. J.; Boynton, W. V.; Burbine, T. H.; Brückner, J.; Gorenstein, P.; Squyres, S. W.; Reedy, R. C.; Goldsten, J. O.; Lim, L.; Hurley, K.; Clark, P. E.; Floyd, S. R.; McClanahan, T. P.; McCartney, E.; Branscomb, J.; Bhangoo, J. S.; Mikheeva, I.; Murphy, M. E. *Meteorit. Planet. Sci.* **2001**, *36*, 1605−1616.
(C4) Asphaug, E. *Nature* **2001**, *413*, 369−370.
(C5) Feldman, W. C.; Boynton, W. V.; Tokar, R. L.; Prettyman, T. H.; Gasnault, O.; Squyres, S. W.; Elphic, R. C.; Lawrence, D. J.; Lawson, S. L.; Maurice, S.; McKinney, G. W.; Moore, K. R.; Reedy, R. C. *Science* **2002**, *297*, 75−58.
(C6) Gee, H. *Nature* **2001**, *409*, 1079.
(C7) Sylvester, P., Ed. *Laser-Ablation-ICPMS in the Earth Sciences, Principles and Applications*; Mineralogical Association of Canada: Ottawa, ON, Canada, 2001; pp 1−243.
(C8) Scarsi, P. *Geochim. Cosmochim. Acta* **2000**, *64*, 3751−3762.

(C9) Moser, D. E.; Scott, D. J. *Chem. Geol.* **2001**, *172*, 1−3.

QUADRUPOLE-BASED INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

(D1) Packer, A. P.; Giné, M. F.; dos Reis, B. F.; Menegário, A. A. *Anal. Chim. Acta* **2001**, *438*, 267−272.
(D2) Long, S. E.; Kelly, W. R. *Anal. Chem.* **2002**, *74*, 1477−1483.
(D3) Aries, S.; Valladon, M.; Polvé, M.; Dupré, B. *Geostand. Newsl.* **2000**, *24*, 19−31.
(D4) Jain, J. C.; Neal, C. R.; Hanchar, J. M. *Geostand. Newsl.* **2001**, *25*, 229−237.
(D5) Hattendorf, B.; Günther, D.; Schönbächler, M.; Halliday, A. N. *Anal. Chem.* **2001**, *73*, 5494−5498.
(D6) Sterpenich, J.; Libourel, G. *Chem. Geol.* **2001**, *174*, 181−193.
(D7) Košler, J.; Fonneland, H.; Sylvester, P.; Tubrett, M.; Pedersen, R.-B. *Chem. Geol.* **2002**, *182*, 605−618.
(D8) Fernández-Suárez, J.; Gutiérrez Alonzo, G.; Jeffries, T. E. *Earth Planet. Sci. Lett.* **2002**, *204*, 75−88.
(D9) Li, X.-h.; Liang, X.-r.; Sun, M.; Guan, H.; Malpas, J. G. *Chem. Geol.* **2001**, *175*, 209−219.
(D10) Prince, C. I.; Košler, J.; Vance, D.; Günther, D. *Chem. Geol.* **2000**, *168*, 255−274.
(D11) Halter, W. E.; Pettke, T.; Heinrich, C. A.; Rothen-Rutishauser, B. *Chem. Geol.* **2002**, *183*, 63−86.
(D12) Halter, W. E.; Pettke, T.; Heinrich, C. A. *Science* **2002**, *296*, 1844−1846.
(D13) de Hoog, J. C. M.; Mason, P. R. D.; van Bergen, M. J. *Geochim. Cosmochim. Acta* **2001**, *65*, 3147−3164.
(D14) Ballard, J. R.; Palin, J. M.; Campbell, I. H. *Contrib. Mineral. Petrol.* **2002**, *144*, 347−364.
(D15) Ballard, J. R.; Palin, J. M.; Williams, I. S.; Campbell, I. H.; Faunes, A. *Geol.* **2001**, *29*, 383−386.
(D16) Luguet, A.; Alard, O.; Lorand, J. P.; Pearson, N. J.; Ryan, C.; O'Reilly, S. Y. *Earth Planet. Sci. Lett.* **2001**, *189*, 285−294.
(D17) Rubatto, D. *Chem. Geol.* **2002**, *184*, 123−138.

SECTOR-BASED HIGH-RESOLUTION AND MULTICOLLECTOR ICPMS

(E1) Yu, Z.; Robinson, P.; Townsend, A. T.; Münker, C.; Crawford, A. J. *Geostand. Newsl.* **2000**, *24*, 39−50.
(E2) Shen, C.-C.; Edwards, R. L.; Cheng, H.; Dorale, J. A.; Thomas, R. B.; Moran, S. B.; Weinstein, S. E.; Edmonds, H. N. *Chem. Geol.* **2002**, *185*, 165−178.
(E3) Jain, J. C.; Field, M. P.; Neal, C. R.; Ely, J. C.; Sherrel, R. M. *Geostand. Newsl.* **2000**, *24*, 65−72.
(E4) Rehkämper, M.; Schönbächler, M.; Stirling, C. H. *Geostand. Newsl.* **2001**, *25*, 23−40.
(E5) Snyder, G. A.; Lee, D.-C.; Ruzicka, A. M.; Prinz, M.; Taylor, L. A.; Halliday, A. N. *Earth Planet. Sci. Lett.* **2001**, *186*, 311−324.
(E6) Vance, D.; Thirlwall, M. *Chem. Geol.* **2002**, *185*, 227−240.
(E7) Waight, T.; Baker, J.; Willigers, B. *Chem. Geol.* **2002**, *186*, 99−116.
(E8) Thirlwall, M. F. *Chem. Geol.* **2002**, *184*, 255−279.
(E9) Anbar, A. D.; Knab, K. A.; Barling, J. *Anal. Chem.* **2001**, *73*, 1425−1431.
(E10) Schoenberg, R.; Kamber, B. S.; Collerson, K. D.; Eugster, O. *Geochim. Cosmochim. Acta* **2001**, *65*, 1839−1848.
(E11) Schoenberg, R.; Kamber, B. S.; Collerson, K. D.; Moorbath, S. *Nature* **2002**, *418*, 403−405.
(E12) Kleine, T.; Münker, C.; Mezger, K.; Palme, H. *Nature* **2002**, *418*, 952−955.
(E13) Yin, Q.; Jacobsen, S. B.; Yamashita, K.; Blichert-Toft, J.; Telouk, P.; Albarede, F.. *Nature* **2002**, *418*, 949−952.
(E14) Carlson, R. W.; Hauri, E. H.. *Geochim. Cosmochim. Acta* **2001**, *65*, 1839−1848.
(E15) Schönbächler, M.; Rehkämper, M.; Halliday, A. N.; Lee, D.-C.; Bourot-Denise, M.; Zander, B.; Hatterndorf, B.; Günther, D. *Science* **2002**, *295*, 1705−1708.
(E16) Weyer, S.; Münker, C.; Rehkämper, M.; Mezger, K. *Chem. Geol.* **2002**, *187*, 295−313.
(E17) Sanloup, C.; Blichert-Toft, J.; Télouk, P.; Gillet, P.; Albarède, F. *Earth Planet. Sci. Lett.* **2000**, *184*, 75−81.
(E18) Becker, H.; Dalpe, C.; Walker, R. J. *Analyst* **2002**, *127*, 775−780.
(E19) Rouxel, O.; Ludden, J.; Carignan, J.; Marin, L.; Fouquet, Y. *Geochim. Cosmochim. Acta* **2002**, *66*, 3191−3199.
(E20) Maréchal, C.; Albarède, F. *Geochim. Cosmochim. Acta* **2002**, *66*, 1499−1509.
(E21) Rehkämper, M.; Frank, M.; Hein, J. R.; Porcelli, D.; Halliday, A. N.; Ingri, J.; Liebetrau, V. *Earth Planet. Sci. Lett.* **2002**, *197*, 65−81.
(E22) Young, E. D.; Ash, R. D.; Galy, A.; Belshaw, N. S. *Geochim. Cosmochim. Acta* **2002**, *66*, 683−698.
(E23) Humayun, M.; Campbell, A. J. *Earth Planet. Sci. Lett.* **2002**, *198*, 225−243.
(E24) Campbell, A. J.; Humayun, M.; Weisberg, M. K. *Geochim. Cosmochim. Acta* **2002**, *66*, 647−660.
(E25) Campbell, A. J.; Humayun, M.; Meibom, A.; Krot, A. N.; Keil, K. *Geochim. Cosmochim. Acta* **2001**, *65*, 163−180.
(E26) Hirata, T. *Chem. Geol.* **2001**, *176*, 323−342.
(E27) Flem, B.; Larsen, R. B.; Grimstvedt, A.; Mansfeld, J. *Chem. Geol.* **2002**, *182*, 237−247.
(E28) Alard, O.; Griffin, W. L.; Pearson, N. J.; Lorand, J.-P.; O'Reilly, S. Y. *Earth Planet. Sci. Lett.* **2002**, *203*, 651−663.
(E29) Willigers, B. J. A.; Baker, J. A.; Krogstad, E. J.; Peate, D. W. *Geochim. Cosmochim. Acta* **2002**, *66*, 1051−1066.
(E30) Foster, G.; Gibson, H. D.; Parrish, R.; Horstwood, M.; Fraser, J.; Tindle, A. *Chem. Geol.* **2002**, *191*, 183−207.

MASS SPECTROMETRY

(F1) Yokoyama, T.; Makishima, A.; Nakamura, E. *Chem. Geol.* **2001**, *181*, 1−12.
(F2) Rubin, K. H. *Chem. Geol.* **2001**, *175*, 723−750.
(F3) Stephan, T. *Planet. Space Sci.* **2001**, *49*, 859−906.
(F4) Hidaka, H.; Ohta, Y.; Yoneda, S.; DeLaeter, J. R. *Earth Planet. Sci. Lett.* **2001**, *193*, 459−466.
(F5) Daulton, T. L.; Bernatowicz, T. J.; Lewis, R. S.; Messenger, S.; Stadermann, F. J.; Amari, S. *Science* **2002**, *296*, 1852−1855.
(F6) Quitté, G.; Birck, J.-L.; Allègre, C. J. *Earth Planet. Sci. Lett.* **2000**, *184*, 83−94.
(F7) Yamaguchi, A.; Clayton, R. N.; Mayeda, T. K.; Ebihara, M.; Oura, Y.; Miura, Y. N.; Haramura, H.; Misawa, K.; Kojima, H.; Nagao, K. *Science* **2002**, *296*, 334−336.
(F8) Wiechert, U.; Halliday, A. N.; Lee, D,-C.; Snyder, G. A.; Taylor, L. A.; Rumble, D. *Science* **2001**, *294*, 345−348.
(F9) Baker, L.; Franchi, I. A.; Maynard, J.; Wright, I. P.; Pillinger, C. T. *Anal. Chem.* **2002**, *74*, 1665−1673.
(F10) Wiechert, U.; Fiebig, J.; Przybilla, R.; Xiao, Y.; Hoefs, J. *Chem. Geol.* **2002**, *182*, 179−194.
(F11) Mukhopadhyay, S.; Farley, K. A.; Montanari, A. *Science* **2001**, *291*, 1952−1955.
(F12) Becker, L.; Poreda, R. J.; Hunt, A. G.; Bunch, T. E.; Rampino, M. *Science* **2001**, *291*, 1530−1533.
(F13) Hashizume, K.; Marty, B.; Wieler, R. *Earth Planet. Sci. Lett.* **2002**, *202*, 201−216.
(F14) Grassineau, N. V.; Mattey, D. P.; Lowry, D. *Anal. Chem.* **2001**, *73*, 220−225.
(F15) Sharp, Z. D.; Atudorei, V.; Durakiewicz, T. *Chem. Geol.* **2001**, *178*, 197−210.

ELECTRON MICROBEAM TECHNIQUES

(G1) Dai, Z. R.; Bradley, J. P.; Joswiak, D. J.; Brownlee, D. E.; Hill, H. J. M.; Genge, M. J. *Nature* **2002**, *418*, 157−159.
(G2) Hörz, F.; Zolensky, M. E.; Bernhard, R. P.; See, T. H.; Warren, J. L. *Icarus* **2000**, *147*, 559−579.
(G3) Hsu, W.; Wasserburg, G. J.; Huss, G. R. *Earth Planet. Sci. Lett.* **2000**, *182*, 15−29.
(G4) Timofeeff, M. N.; Lowenstein, T. K.; Blackburn, W. H. *Chem. Geol.* **2000**, *164*, 171−181.

NUCLEAR TECHNIQUES

(H1) *Geochemistry of Soil Radionuclides*; Zhang, P.-C., Brady, P. V., Eds.; SSA Special Publication 59; Soil Science Society of America: Madison, WI, 2002; pp 1−252.
(H2) Mittlefehldt, D. W. *Meteorit. Planet. Sci.* **2002**, *37*, 703−712.
(H3) Friedrich, J. M.; Wang, M.-S.; Lipschutz, M. E. *Meteorit. Planet. Sci.* **2002**, *37*, 677−686.
(H4) Mao, X.; Hou, X.; Li, C.; Ouyang, H.; Chai, Z. *Geostand. Newsl.* **2001**, *25*, 167−171.
(H5) Giaveri, G.; Rizzio, E.; Gallorini, M. *Anal. Chem.* **2001**, *73*, 3488−3491.
(H6) Dai, X.; Koeberl, C.; Fröschl, H. *Anal. Chim. Acta* **2001**, *436*, 79−85.
(H7) Paul, R. P. *Analyst* **2001**, *126*, 217−221.
(H8) El-Daoushy, F.; Hernández, F. *Analyst* **2002**, *127*, 981−989.
(H9) Tanner, P. A.; Pan, S. M.; Mao, S. Y.; Yu, K. N. *Appl. Spectrosc.* **2000**, *54*, 1143−1146.

CHEMOMETRICS

(I1) Howarth, R. J.; Coles, B. J.; Ramsey, M. H. *Analyst* **2000**, *125*, 2032−2037.
(I2) Vendemiatto, M. A.; Enzweiler, J. *Geostand. Newsl.* **2001**, *25*, 283−291.
(I3) Ely, J. C.; Neal, C. R. *Geostand. Newsl.* **2002**, *26*, 31−39.
(I4) Meisel, T.; Moser, J.; Wegscheider, W. *Fresenius J. Anal. Chem.* **2001**, *370*, 566−572.
(I5) Swanson, S. K.; Bahr, J. M.; Schwar, M. T.; Potter, K. W. *Chem. Geol.* **2001**, *179*, 73−91.
(I6) Hannigan, R. E.; Basu, A. R.; Teichmann, F. *Chem. Geol.* **2001**, *175*, 397−428.
(I7) Ludwig, K. R. *Geochim. Cosmochim. Acta* **2001**, *65*, 3139−3145.
(I8) Powell, R.; Hergt, J.; Woodhead, J. *Chem. Geol.* **2002**, *185*, 191−204.

(I9) Verma, S. P.; Santoyo, E.; Velasco-Tapia, F. *Int. Geol. Rev.* **2002**, *44*, 287−335.

MISCELLANEOUS

(J1) Amelin, Y.; Krot, A. N.; Hutcheon, I. D.; Ulyanov, A. A. *Science* **2002**, *297*, 1678−1683.
(J2) Alexander, C. M. O'D.; Boss, A. P.; Carlson, R. W. *Science* **2001**, *293*, 64−68.
(J3) Hiroi, T.; Zolensky, M. E.; Pieters, C. M. *Science* **2001**, *293*, 2234−2236.
(J4) Cooper, B. L.; Salisbury, J. W.; Killen, R. M.; Potter, A. E. *J. Geophys. Res.* **2002**, *107* (E4), 1-1−1-18.
(J5) Andrade, S.; Hypolito, R.; Horstpeter, H.; Ulbrich, G. J.; Silva, M. L. *Chem. Geol.* **2002**, *182*, 85−89.
(J6) Westall, F.; Steele, A.; Toporski, J.; Walsh, M.; Allen, C.; Guidry, S.; McKay, D.; Gibson, E.; Chafetz, H. *J. Geophys. Res.* **2000**, *105*, 24511−24527.
(J7) NASA Astrobiology Institute. http://nai.arc.nasa.gov; accessed Feb 2003.

(J8) Grady, M. *Search for Life/Astrobiology*; Smithsonian Institution Press: Washington, DC; 2001; pp 1−96.
(J9) Cooper, G.; Kimmich, N.; Belisle, W.; Sarinana, J.; Brabham, K.; Garrel, L. *Nature* **2001**, *414*, 879−882.
(J10) Pizzarello, S.; Huang, Y.; Becker, L.; Poreda, R. J.; Nieman, R. A.; Cooper, G.; Williams, M. *Science* **2001**, *293*, 2236−2239.
(J11) Wolf, D.; Palme, H. *Meteorit. Planet. Sci.* **2001**, *36*, 559−571.
(J12) Engi, M.; Cheburkin, A. K.; Köppel, V. *Chem. Geol.* **2002**, *191*, 225−241.
(J13) Scherrer, N. C.; Engi, M.; Berger, A.; Parrish, R. R.; Cheburkin, A. *Chem. Geol.* **2002**, *191*, 243−255.
(J14) Takahashi, Y.; Shimizu, H.; Kagi, H.; Yoshida, H.; Usui, A.; Nomura, M. *Earth Planet. Sci. Lett.* **2000**, *182*, 201−207.
(J15) Philippot, P.; Menez, B.; Drakopoulos, M.; Simionovici, A.; Snigirev, A.; Snigireva, I. *Chem. Geol.* **2001**, *173*, 151−158.
(J16) Vanko, D. A.; Bonnin-Mosbah, M.; Philippot, P.; Roedder, E.; Sutton, S. R. *Chem. Geol.* **2001**, *173*, 227−238.