TECHVIEW: ISOTOPE GEOCHEMISTRY

New Tools for Isotopic Analysis

Trevor Ireland

The isotopic compositions of natural materials are affected by a variety of processes. On Earth, radiogenic decay and physicochemical fractionation are the two dominant mechanisms. Radiogenic decay generally proceeds at a specific rate, allowing geochronologists to date rocks by measuring the ratio of parent to daughter atoms. Physicochemical fractionation results from the mass-dependence of certain chemical reaction rates and produces a systematic bias (with mass) in isotopic abundance. Extraterrestrial samples show effects of spallation, that is, the breakdown of nuclei from impacting cosmic rays, and may show large isotopic anomalies as a result of incorporation of nucleosynthetic material, whose isotopic composition differs substantially from terrestrial abundances.

Isotopic differences produced by these processes can vary widely in magnitude. More importantly, isotopic compositions can either be homogeneous over relatively large volumes or inhomogeneous on smaller scales. This has led to two fundamentally different approaches to isotopic measurement. So-called conventional analysis involves the chemical separation of an element, which is then mixed with material of known anomalous isotope composition (isotope dilution), followed by analysis to high precision. In contrast, in situ analysis by ion microprobe involves direct analysis of very small amounts of material; precision is typically limited by the number of ions counted in the analysis. These two approaches have often produced conflicting results because of the differences in the volume of the material analyzed and of questions concerning precision, accuracy, and reproducibility.

Recently, major advances have been made in laser ablation–inductively coupled mass spectrometry (LA-ICPMS), a technique that bridges the gap in sample size between isotope dilution mass spectrometry (IDMS) and ion microprobe analysis [secondary ion mass spectrometry (SIMS)]. As discussed below, these techniques are complementary in their analytical strengths. But it remains to be seen whether this arsenal of geochemical tools will be sufficient for the ambitious analytical goals of the near future.

The fundamentals of mass spectrometry have changed little since the pioneering work of Johnson and Nier (*1*), but what has changed is the way materials are sampled. The goal of ever higher precision competes with the goal of ever smaller sample size. The analyst must ultimately decide whether to measure a larger sample volume at the highest possible precision or to account for the possible presence of heterogeneities in that volume by choosing a technique that samples a smaller amount. The choice is dictated by the nature of the expected effect; a uniform but small variation is best measured on a large volume at high precision, whereas small, isotopically distinct objects require more selective analysis.

For problems requiring high-precision analysis (Fig. 1A), modern thermal ionization mass spectrometers can achieve extremely high levels of precision through sustained analysis and statistical reduction in the error of the mean. The internal statistics can be improved further through multiple collection, where individual ion beams are measured in separate detectors, thus maximizing efficiency and removing uncertainty associated with temporal variations in the total beam. However, at some level of uncertainty, systematic errors may arise that negate any gains achieved through the reduction of random errors. At these limits, the unequivocal partitioning between systematic and random errors is not straightforward and must rely on demonstrated reproducibility. Such measurements are not aimed at minimizing the amount of material consumed during analysis; rather, sufficient material is loaded to achieve the optimal running conditions for the analysis.

At the other extreme of IDMS analysis, great efforts have been made to enable

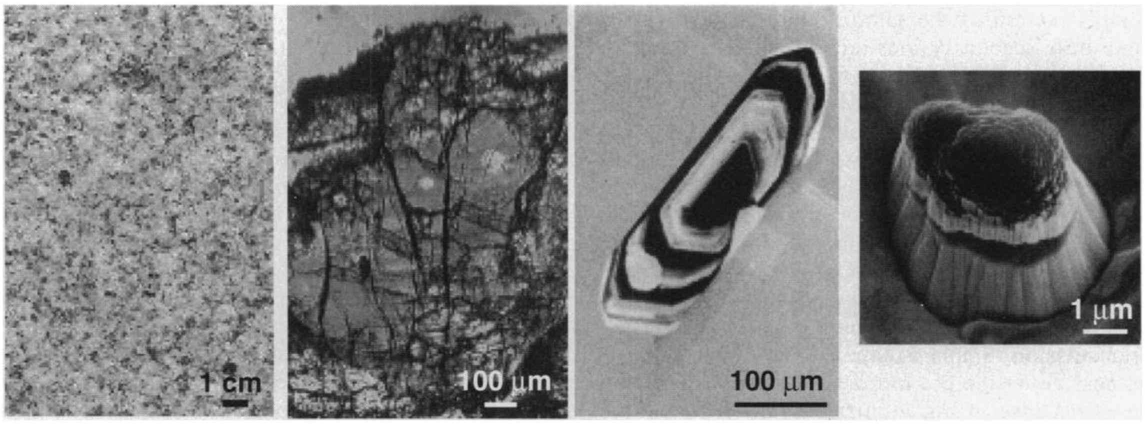

Fig. 1. What's in a grain? The scale of isotopic analysis is dictated both by the questions being asked and the nature of the sample. Bulk isotopic analysis of granite (**A**) requires destruction of the rock and homogenization of all phases, or mineral separation by hand picking. For such samples, conventional analysis involving isotope dilution can yield isotope ratios at 10 ppm. When samples are heterogeneous, however, in situ analysis is appropriate, so petrographic context can be related to the isotopic composition. In an Allende refractory inclusion (**B**), fractures and altered areas are to be avoided, but homogeneous mineral phases are present throughout the thin section. For isotopic analysis, vertical heterogeneity is not a problem, and LA-ICPMS will yield the most rapid and precise results because an analysis can average over 30 ng of material. Zircons (**C**) can be homogeneous on a grain-by-grain scale, or can show complex growth zones within a single crystal. The zircon shown here has coarse oscillatory zoning [from 370 million years ago (Ma)], which is overprinted by a later magmatic event (340 Ma) that embays the edge of the zircon and also creates an "island" of young zircon surrounded by the older magmatic phase. For precise dating of such complex grains, shallow sampling is necessary such as that with an ion microprobe, which consumes only 2 ng of zircon in an analysis. Interstellar grains (**D**) are a precious resource that require multiple element isotopic analysis of single grains. A single analysis by ion microprobe spectrometry might only consume 10 pg of material.

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The author is in the Department of Geological and Environmental Sciences, 253 Green Building, Stanford University, Stanford, CA 94305–2115, USA. E-mail: tri@pangea.stanford.edu

the analysis of small amounts of lead in U-bearing minerals (mainly zircons) for geochronology. This type of analysis requires great chemical control to avoid Pb contamination, which degrades the radiogenic signal. The U-Pb ratios of zircons can now be measured at the single-grain or even sub-grain level (Fig. 1C), but zircons can be highly complicated and it is difficult to reliably determine the age complexity of a zircon that is being analyzed by IDMS.

The limited selectivity at small scale for samples investigated by IDMS was one of the prime motivations for the development of in situ isotopic microanalysis tools such as ion microprobes (*2*). In these techniques, a focused ion beam is used to sputter the sample directly. A small fraction of the sample is ionized, and these secondary ions are accelerated into a mass spectrometer for analysis. Even for simple targets, SIMS is complicated by a plethora of atomic and molecular species, which might differ only slightly in mass. SIMS thus requires high-mass resolution for isobaric separation. Small Cameca ion microscopes (Cameca Instruments, Courbevoie, France) are capable of high-mass resolution measurements, but at the expense of transmission. Stable isotope analysis (*3*) is possible at the per mil or sub–per mil level because of high ionization yields. These instruments have been highly successful in the search for isotopic anomalies in meteorites where isotopic variations cover orders of magnitude (*4*). Also the slow sample consumption and high efficiency allows multiple analyses of even micrometer-sized dust grains.

The SHRIMP (sensitive high-resolution ion microprobe) was the first instrument to combine high-mass resolution with high transmission. This was achieved through a physically large mass analyzer and allowed U-Pb isotope analyses of zircon (*5*, *6*). Large-geometry ion microprobes such as SHRIMP and Cameca 1270 are available, but they are expensive and their availability has been limited.

Nowhere have comparisons between SIMS and IDMS been more factional than in the field of U-Pb geochronology. The goal of IDMS is to obtain high precision, whereas SIMS aims to derive a relatively low-precision age of one or several petrographically distinct zones within a single mineral grain. The greatest differences arise when complicated zircons are analyzed (Fig. 1C); conventional single-grain analysis can usually determine only that multiple age components are present, whereas individual spot analyses can identify the specific age components. This is indeed the strength of SIMS analysis, especially when coupled with electron imaging techniques such as cathodoluminescence, which allow for better targeting. For uncomplicated zircons, the comparisons between SIMS and IDMS are remarkably good (*7*). However, because individual SIMS data have relatively low age precision, there is some concern that distinct age components, whose ages cannot be individually resolved, may be grouped together. In this case, the mean becomes an average of components, which may be geologically meaningless.

The chosen technique for a particular problem must be capable of age analysis of single domains of zircon and must have sufficient resolution to describe those age components individually. If single grains of zircon that contain only one age component are present, then there is no question that IDMS analysis will be the most precise and the most accurate. If multiple domains are present in a single grain, SIMS will yield the most accurate estimate of the ages of those components. Therefore, combined SIMS and IDMS analysis would generally give the best results.

ICPMS, the relative newcomer to the arsenal of tools, uses an argon plasma to ionize most elements. The sample can be introduced either from solution (hence ICPMS is capable of IDMS) or through laser ablation. LA-ICPMS has microsampling and high-precision capability and will bridge some of the analytical abilities of IDMS and SIMS (Fig. 1B) as well as open new ones (*8*). Both quadrupole and magnetic sector mass spectrometers are used. The high ablation rate and ionization levels allow fractionation-corrected isotopic analyses at 0.1 per mil to be achieved. But a large number of ions must be counted to achieve high precision, and the ablated spot can consume as much material as an IDMS analysis. The advantage of LA-ICPMS, though, is its ease of analysis of highly refractory elements and its minimal sample preparation.

It could be argued that LA-ICPMS U-Pb dating will supersede ion microprobe analysis because of its greater precision, but it is somewhat unlikely that it will overtake all other types of analysis. Difficulties still remain in achieving high precision U-Pb ratios and in measuring ^{204}Pb (*9*, *10*). The superior depth resolution of SIMS facilitates analysis of complicated samples where domain sizes are limited, and IDMS cannot be surpassed for the precision requirements of time scale calibration. In U-Pb analysis, LA-ICPMS will fill a niche where domain sizes are large and rapid analysis of zircon is required, such as in detrital zircon profiles and documentation of simple magmatic systems.

LA-ICPMS promises to revolutionize terrestrial geochemistry both in elemental analysis and in isotopic analysis of suitable materials. Of the various instruments available, the quadrupole mass spectrometer is adequate for trace element analysis, whereas multiple collection ICPMS will be required for isotopic analysis. Applications already include Hf isotopic analysis of zircon (*11*) and trace element geochemistry of materials (*12*). But in situ analysis by LA-ICPMS or by SIMS will never be able to resolve most atomic isobars, and applications such as Rb-Sr isotopic analysis can therefore never be achieved. For this work, chemical separation and analysis by IDMS are required.

Probably the most exciting areas for isotope geochemistry in the next 20 years will be extraterrestrial materials from Mars, asteroids, comets, and the solar wind. Will the techniques now available allow characterization of this material to the fullest extent possible? The requirement is for the highest analytical return per gram, or fraction thereof, that is possible. Martian and asteroidal material will be characterized in bulk by IDMS and ICPMS. However, the particulate nature of cometary dust is compatible only with microscale techniques. Time of Flight–SIMS will be an advantageous technique in cometary dust analysis because isotopic analysis of all ions can be achieved, thereby minimizing waste. Analysis of samples exposed to solar wind, which causes atom-by-atom implantation into a substrate, requires high sensitivity. How can the solar-wind implanted targets be analyzed efficiently to yield the precision required to test current solar nebula models? Concentrations of target elements will be low, and contamination is a major concern. Availability of these materials, and the technical demands they impose, will fuel an era of analytical development similar to that seen for the lunar return missions.

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