



TECHVIEW: ISOTOPE GEOCHEMISTRY

New Tools for Isotopic Analysis

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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 ap-

proaches 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

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,

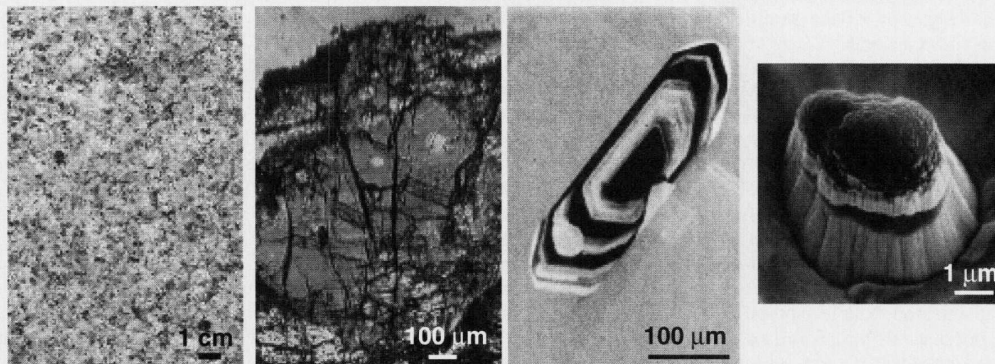


Fig. 1. What's in a grain? The scale of isotopic analysis is dictated both by the questions being asked and the nature of the sample. Bulk isotopic analysis of granite (A) requires destruction of the rock and homogenization of all phases, or mineral separation by hand picking. For such samples, conventional 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.

try (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

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

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