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Instruments of Cosmochemistry

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ICP-MS and Planetary Geosciences



(MITERAC ICP-MS photo by Jesse Davenport.)

--- ICP-MS techniques provide acurrate and rapid elemental analyses.

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In this series of articles, "Instruments of Cosmochemistry," **PSRD** highlights the essential tools and amazing technology used by talented scientists seeking to unravel how the Solar System formed. You will find information on how the instruments work as well as how they are helping new discoveries come to light.

What is ICP-MS?

ICP-MS (inductively coupled plasma mass spectrometry) techniques have been widely used in a number of various disciplines since the 1980s but more recently have especially found a home in the Earth and Planetary Sciences. The accuracy, precision, and ease of use have pushed ICP-MS analysis to be superior over previously widely used techniques. Here I explain how ICP-MS works and give two examples of its great utility in cosmochemistry. Useful summaries of the technique are available in Short Course volumes edited by Paul Sylvester (Memorial University, St. John's, Newfoundland, Canada), see **additional resources** at the end of the article.

Developed for commercial use in the early 1980s, ICP-MS is used as an analytical technique for the determination of elemental concentrations. Geologists were quick to adopt this technology for geochemical analysis because of superior detection limits (i.e. its ability to detect small amounts of certain elements in rocks with parts-per-billion sensitivity), particularly for trace elements. ICP-MS analysis took the lead over other techniques such as atomic absorption spectroscopy (AAS) and ICP-Atomic Emission Spectroscopy (ICP-AES) because of these superior detection limits, capability to analyze more complex samples, and capacity to obtain isotopic data.



A typical ICP-MS setup is shown with the main machine in the background, parts labeled A and B are shown in more detail below. The laser ablation system appears in the rightforeground. Click the image for more information about this setup from MITERAC, the Midwest Isotope and Trace Element Research Analytical Center.

It is easiest to think of the ICP-MS process in four steps: 1) sample introduction/aerosol production, 2) ionization by **plasma**, 3) separation by mass, and 4) detection and reporting. Combining a plasma source (ICP) with a mass spectrometer (detector and analyzer), the ICP-MS ionizes atoms of the elements in the samples being analyzed. The ions are then separated by their atomic weights and their abundances are measured by the mass spectrometer. An ICP-MS device accepts samples in both solution and solid form.

Sample Introduction Method: Solution Mode



If samples are liquid solutions or can be easily dissolved in nitric, hydrofluoric perchloric, or hydrochloric acid (or any combination thereof) the preferred method of sample introduction is by a nebulizer/spray chamber. Rocks are usually dissolved with concoctions that involve hydrofluoric acid, but this strong acid tends to eat away at the equipment used to spray the dissolved sample into the ICP system. The liquid is delivered via a pump to the nebulizer. The nebulizer creates a fine aerosol that is carried to the plasma by the argon nebulizer gas. The plasma rapidly separates the

elements from solution, atomizes, and ionizes the sample, creating a beam of singly charged positive ions. Photo of a common nebulizer used to introduce liquid as an aerosol into the ICP-MS when conducting analyses by solution mode.

Sample Introduction Method: Laser Ablation on Solids



LA (laser ablation)-ICP-MS is a useful analytical technique to derive spatial compositions from solid sample surfaces. Photomicrographs of solid samples of a calibrationstandard glass showing a pit and a side view of a line scan ablated by a pulsed laser beam prior to ICP-MS analysis.

Cameras display an image on a computer screen of the sample area to be ablated. Using the laser ablation software, the user can find specific points of interest to

ablate. Spots or line scans are typically analysed. The laser essentially acts as a high precision photon jackhammer, which generates a stream of particles that is carried to the sample introduction system of the ICP-MS. Laser ablation energy is concentrated at a specific distance, thus samples appropriate for LA-ICP-MS should have a flat uniform surface. Thin sections and polished slabs work very well and the laser cells are designed to hold such samples. Laser ablation is advantageous over solution introduction due to the limited amount of sample preparation required. It does, however, decorate the sample with tiny, laser-made craters or furrows, so it is not advantageous for precious samples that might be analyzed by other techniques.

Ionization, Separation by Mass, Detection, and Reporting

Once the sample has been introduced with an argon carrier gas to the plasma generator, the elements from the sample are turned into a gas and completely ionized. The ionization process involves heating an atomized sample by electromagnetic induction, which involves varying the magnetic field surrounding the gaseous sample using a radio-frequency generator. The torch area of the system sparks the argon-rich gas, producing an ionized gas. The ionization affects the sample materials, not just the argon carrier gas. Once the elements from the sample are ionized they are directed toward the mass spectrometer via an interface region consisting of skimmer and sampler cones. These cones, which are small metal plates with tiny holes in the center, sample the center of the ion beam coming from the torch area of the ICP.



[Left, **A**] The interface region of the ICP-MS showing the sampler and skimmer cones. The ion stream passes through these cones into the rest of the machine for measurement. [Right, **B**] The main body of the ICP-MS where the magnet and other instrumentation for detection are located.

After the ion beam has traveled through the skimmer and sampler cones, the positive ion stream flows through a high-resolution magnet. The magnet is used to separate and focus ions based on mass and ion energy. After exiting the magnet, the ion beam then enters a set of electrostatic lenses. The beam is focused based on ion energy towards an exit slit, where the beam sprays a secondary electron multiplier. Here the ions are counted for the purpose of turning the number of ions hitting the detector into a concentration in the sample by comparison of counts on calibration standards.

Cosmochemical Applications Using LA-ICP-MS

New or improved analytical techniques almost always lead to new discoveries. Two are outlined below, with details given in previous **PSRD** articles.

Isotopic data obtained by ICP-MS have shed light on lunar origin by showing which elements have different isotopic compositions in the Moon compared to Earth. Considering titanium isotopes, for example, the ratio of ⁵⁰Ti to ⁴⁷Ti is identical in Earth and Moon to within four parts per million. In contrast, other solar system materials, such as carbonaceous chondrites, vary by considerably more than this—up to 150 times as much. On the other hand, the isotopes of the volatile element zinc in the Moon differs significantly from Earth in the abundances of zinc isotopes. This difference may have been caused by evaporation during formation of the Moon by a giant impact. The refractory elements, such as Ti, probably did not vaporize significantly during lunar formation, leaving their isotopic compositions unscathed by this significant event in Solar System history.





PSRD graphic based on published data.

Deviation in the ratios of ⁵³Cr/⁵²Cr, ⁵⁰Ti/⁴⁷Ti, ¹⁸²W/¹⁸⁴W, and ⁶⁶Zn/⁶⁴Zn in the Moon compared to Earth, in parts per ten thousand (epsilon units). For the whole story, see the PSRD article: Zinc Isotopes Provide Clues to Volatile Loss During Moon Formation.

ICP-MS data contribute to understanding the origin of our Solar System and, in fact, the history of the region of interstellar space where the Sun formed. For example, the variability of the amount of ⁶⁰Fe and ²⁶Al (both are short-lived, now extinct, isotopes) might conceivably mean that ⁶⁰Fe was added to our Solar System a million years after it formed, but when the solar nebula was still present. This could happen if the region of space where the Sun formed contained massive stars (perhaps 30 times the mass of the Sun). Such stars last only about 4 million years. They are extremely active, blowing away their outer layers in the last million years of existence. The dispersed material would have included ²⁶Al and might have caused collapse of interstellar gas and dust to cause formation of the Sun and its protoplanetary disk. A million years later the massive star exploded, ejecting ⁶⁰Fe from its interior. This huge event of destruction and creation is recorded in the meteorites and revealed by isotopic analyses done by ICP-MS.



NGC 2359 Nebula with Wolf-Rayet star

© P. Berlind and P. Challis Harvard-Smithsonian Center for Astrophysics 1.2-meter Telescope, Whipple Observatory Telescope image of stellar winds blowing from a massive Wolf-Rayet star (brightest star near center). Courtesy of P. Berlind & P. Challis, Harvard-Smithsonian Center for Astrophysics. For the whole story, see the PSRD article: The Sun's Crowded Delivery Room.

PSRD Articles Featuring ICP-MS

- A Complication in Determining the Precise Age of the Solar System
- Zinc Isotopes Provide Clues to Volatile Loss During Moon Formation
- Relicts from the Birth of the Solar System
- Titanium Isotopes Provide Clues to Lunar Origin
- The Sun's Crowded Delivery Room
- New Lunar Meteorite Provides its Lunar Address and Some Clues about Early Bombardment of the Moon
- A Younger Age for the Oldest Martian Meteorite

Additional Resources

Links open in a new window.

• Sylvester, P. editor (2001) Laser-Ablation-ICP-MS in the Earth Sciences (Principles and Investigations), *Mineralogical Association of Canada Short Course Series*, v. 29, 243 p., St. John's,

Newfoundland. Series Editor: Robert Raeside. [link]

 Sylvester, P. editor (2008) Laser-Ablation-ICP-MS in the Earth Sciences: Current Practices and Outstanding Issues, *Mineralogical Association of Canada Short Course Series*, v. 40, 356 p., Vancouver, B. C. Series Editor: Robert Raeside. [link] [table of contents]



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