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Laser ablation inductively coupled plasma mass spectrometry for direct isotope ratio measurements on solid samples

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Abstract

Isotope ratio measurements have been increasingly used in quite different application fields, e.g., for the investigation of isotope variation in nature, in geoscience (geochemistry and geochronology), in cosmochemistry and planetary science, in environmental science, e.g., in environmental monitoring, or by the application of the isotope dilution technique for quantification purposes using stable or radioactive high-enriched isotope tracers. Due to its high sensitivity, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is today a challenging mass spectrometric technique for the direct determination of precise and accurate isotope ratios in solid samples. In comparison to laser ablation quadrupole ICP-MS (LA-ICP-QMS), laser ablation coupled to a double-focusing sector field ICP-MS (LA-ICP-SFMS) with single ion detection offers a significant improvement of sensitivity at low mass resolution, whereby isotope ratios can be measured with a precision to 0.1% relative standard deviation (R.S.D.). In LA-ICP-SFMS, many disturbing isobaric interferences of analyte and molecular ions can be separated at the required mass resolution (e.g., $^{40}Ar^{16}O^{+}$ and $^{56}Fe^{+}$ for iron isotope ratio measurements). The precision on isotope ratio measurements was improved by one order of magnitude via the simultaneous detection of mass-separated ion currents of isotopes using multiple ion collectors in LA-ICP-MS (LA-MC-ICP-MS).

The paper discusses the state of the art, the challenges and limits in isotope ratio measurements by LA-ICP-MS using different instrumentations at the trace and ultratrace level in different fields of application as in environmental and biological research, geochemistry and geochronology with respect to their precision and accuracy.

Keywords: Geochronology; Isotope ratio measurements; Laser ablation inductively coupled plasma mass spectrometry; Mass bias correction

1. Introduction

The determination of isotope ratios is becoming increasingly important, e.g., in geological research (geochronology) [1–11], in biology and life sciences [12–15], for the characterization of radioactive waste [16] or environmental control [17–20]. Besides the different mass spectrometric techniques such as inductively coupled plasma mass spectrometry, ICP-MS; glow discharge mass spectrometry, GDMS; thermal ionization mass spectrometry, TIMS; secondary ion mass spectrometry, SIMS; sputtered neutral mass spectrometry, SNMS; spark source mass spectrometry, SSMS; laser ionization mass spectrometry, LIMS; resonance ionization mass spectrometry, RIMS, ICP-MS is the method most frequently employed for isotope ratio measurements due to its excellent sensitivity, good precision and accuracy. Isotope ratios were studied more often by ICP-MS than laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) [21]. However, laser ablation ICP-MS is becoming the method of choice for analysis of solid samples due to the advantage of direct solid sampling and its capability of providing micro-scale information. For a long time, TIMS was the most frequently used solid mass spectrometric technique for determining precise and accurate isotope ratios of metals with ionization potentials lower than 7 eV. Today TIMS is still used as a routine technique in many laboratories worldwide in geochemistry, geochronology,

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the nuclear industry and environmental research. Due to instrumental developments in LA-ICP-MS with single and multiple ion collectors and the advantages in comparison to TIMS, e.g., high sensitivity, comparable precision and accuracy, practically no restriction on the ionization potential of chemical elements, time-independent mass fractionation and the possibility of additional multi-element analysis at trace and ultratrace level, no complicate chemical sample preparation procedure, TIMS will be increasingly replaced in future by powerful LA-ICP-MS for direct isotope ratio measurements on solid samples without sample preparation.

Laser ablation ICP-MS, as a relatively new and powerful analytical mass spectrometric technique (introduced onto the commercial analytical market in 1990), was originally developed for direct multi-element analysis on solid samples at the trace and ultratrace level. The major limiting property for precise isotope ratio measurements has been observed in the instability of inductively coupled argon plasma and the laser ablation process itself. Instrumental developments therefore focused on improving the laser ablation regime, on increasing plasma stability, improving sample introduction of ablated material in the inductively coupled plasma and especially on developing multiple ion detection systems. With the introduction of the multiple ion collector (MC) instruments "Plasma 54" about 12 years ago, LA-ICP-MS has become an established method for high-precision isotope analysis with a performance comparable to MC-TIMS. The first work that demonstrates the potential of LA-MC-ICP-MS for very high-precision isotope ratio measurements performed directly on solid samples was done by Walder et al. [37] in case of lead isotope ratios measurements of NIST glass standard reference material 610. Already in this work it has been demonstrated that measured isotope ratios agree with those determined by TIMS and also the precision in LA-MC-ICP-MS is comparable to that obtained in TIMS.

The aim of this work is to review the advantages, the limits and new applications in environmental and biological science, geology and geochemistry of laser ablation ICP-MS using quadrupole-based or sector field ICP-MS with single and multiple ion collectors.

2. LA-ICP-MS instrumentation and capability for isotope analysis

LA-ICP-MS uses the ablation of sample material by a focused laser beam in an inert gas atmosphere (e.g., Ar) under normal pressure and transferring ablated material into an inductively coupled plasma ion source of an ICP-MS. The experimental arrangement of LA-ICP-MS using several types of mass spectrometers – as used in the author's laboratory – is shown in Fig. 1. In LA-ICP-MS, different commercial laser ablation systems—mostly solid state Nd-YAG laser ablation systems, (e.g., CETAC LSX 200, LSX 500 and LSX 3000, Cetac Technologies, Omaha, NE, USA; Merchantek LUV 266 nm laser microprobe, UP 213, UP 266, UP 266 Macro from New Wave Research/Merchantek, Fremont, CA, USA; VG MicroProbe II, Thermo Finnigan, Bremen Germany; Ablascope 213 nm, Bioptic, Berlin, Germany) are coupled directly to several types of ICP-MS. Especially the new Nd-YAG laser ablation systems, which work at a wavelength of 213 nm at small laser spot and relatively high laser power density (e.g., Ablascope from Bioptic), as demonstrated in two other papers in this issue [12,50], are advantageous for a multitude of applications on isotope ratio measurements. Furthermore, a few commercial excimer laser ablation systems (e.g., UP 193H, New Wave Research/Merchantek; GeoLasArF, MicroLas, Göttingen, Germany) are available on the analytical market and several home-made laser ablations systems [2,22–24] are also in use in several laboratories. Application of excimer lasers in laser ablation ICP-MS is increasing because the shorter the wavelength, the less fractionation effects are in general observed [25]. Minimizing of fractionation effects is possible by performing laser ablation (independent of the laser ablation system used) with a laser power density of 10^9 W cm^{-2} and higher [26–28]. Elemental fractionation does not play an important role for the determination of inter-element isotope ratios, but in the case of geochronology where intra-element isotope ratios (e.g., $^{206}Pb/^{238}U$, $^{208}Pb/^{232}Th$, $^{187}Re/^{188}Os$) are measured elemental fractionation has to be considered and minimized. Fractionation effects of Pb and U isotopes caused by defocusing of the laser beam during ablation on a crater have been avoided by using the active focusing mode [29] or linear scan mode of laser ablation [9].

The most frequently used LA-ICP mass spectrometers worldwide are quadrupole-based instruments (LA-ICP-QMS) without collision cells (PQ II, VG-Elemental; Elan 6000, Perkin-Elmer; Agilent 7500, Agilent; X Series, Thermo Elemental; Ultramass, Varian). LA-ICP-QMS allows isotope ratio measurements with an internal precision for short-term isotope ratio measurements from 0.2 to 1% relative standard deviation (R.S.D.). The precision in isotope ratio measurements for elements at the trace concentration level using LA-ICP-QMS is limited, for example, by counting statistics, which can be improved by increasing the integration time (number of laser shots, repetition frequency). Instrumental progress in isotope ratio measurements by quadrupole ICP-MS with a single ion detector has been achieved by the introduction of the collision cell (CC) interface in order to neutralize plasma gas ions (Ar^+) and to dissociate disturbing argon-based molecular ions (ArX^+, X = O, N, C, H or Ar) by ion–molecule reactions if, for instance, He/H_2 was introduced into the cell as the collision gas mixture. The application of the collision cell in LA-ICP-MS (LA-ICP-CC-MS) results in higher ion transmission by reducing the kinetic energy of ions, and in an improvement of the sensitivity and precision of isotope ratio measurements compared to LA-ICP-MS without the collision cell. In spite of the advantages LA-ICP-MS with collision cell is difficult to handle (requires careful time-consuming optimization procedure, and new molecular ions are formed