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Investigation on elemental and isotopic fractionation during 196 nm femtosecond laser ablation multiple collector inductively coupled plasma mass spectrometry

Ingo Horn *, Friedhelm von Blanckenburg

Institut für Mineralogie, Leibniz Universität Hannover, Callinstr. 3, D-30167 Hannover, Germany

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Abstract

Despite the large number of successful applications of laser ablation, elemental and isotopic fractionation coupled to inductively coupled plasma mass spectrometry (ICP-MS) remain as the main limitations for many applications of this technique in the fields of analytical chemistry and Earth Sciences. A substantial effort has been made to control such fractionations, which are well-established features of nanosecond laser ablation systems. Technological advancements made over the past decade now allow the ablation of solids by femtosecond laser pulses in the deep ultraviolet (UV) region at wavelengths less than 200 nm. Here the use of femtosecond laser ablation and its effects on elemental and isotopic fractionation is investigated. The Pb/U system is used to illustrate elemental fractionation and stable Fe isotopes are used to illustrate isotopic fractionation. No elemental fractionation is observed beyond the precision of the multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) measurements. Without a matrix match between standard and sample, elemental fractionation is absent even when using different laser ablation protocols for standardization and samples (spot versus raster). Furthermore, we found that laser ablation-induced isotope ratio drifts, commonly observed during nanosecond laser ablation, are undetectable during ultraviolet femtosecond laser ablation. So far the precision obtained for Fe isotope ratio determinations is 0.1‰ (2 standard deviation) for the $^{56}Fe/^{54}Fe$ ratio. This is close to that obtainable by solution multiple-collector inductively coupled plasma mass spectrometry. The accuracy of the results appears to be independent of the matrix used for standardization. The resulting smaller particle sizes reduce fractionation processes. Femtosecond laser ablation carries the potential to solve some of the difficulties encountered during the two prior decades since the introduction of laser ablation.

Keywords: Femtosecond laser ablation; Elemental fractionation; Laser induced isotopic fractionation; Fe isotopes; Geochronology

1. Introduction

Laser ablation coupled to inductively coupled plasma mass spectrometry (ICP-MS) or ICP-optical emission spectroscopy (ICP-OES) traditionally employs a variety of systems such as Nd:YAG or Excimer lasers with a wavelength ranging from the infrared (IR) to the vacuum ultraviolet (UV) region [1–6]. These types of lasers produce pulses with a pulse width of between 3 and 20 nanoseconds (ns). Three types of laser-induced fractionation, which are superimposed onto the instrumental mass discrimination of the ICP-MS biasing the measurement, have been described for nanosecond laser ablation:

1) Fractionation through the preferential evaporation of volatile elements in the carrier gas. This type of fractionation mainly affects siderophile elements, such as Zn, Pb, Au, Tl, while the refractory elements, i.e. elements with high condensation temperatures, are less strongly affected. Elements with high condensation temperatures include the rare earth elements (REE), high field strength elements (HFSE), Ca, Th, and U [7–10]. With increasing crater depth, the ratio of a volatile element to a refractory element evolves during spot ablation from its real ratio to significantly higher values. For example, the increase in the Pb/U ratio is in the order of 100% during the course of a spot analysis of 100 s (with a wavelength of

* Corresponding author.
E-mail addresses: horn@mineralogie.uni-hannover.de (I. Horn), fvb@mineralogie.uni-hannover.de (F. von Blanckenburg).

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193 nm) when using a crater diameter of 35 μm [9]. The measured ratio increases even further with decreasing crater diameter, or increasing ablation- or laser repetition rate, all of which is influencing the crater depth. Applying femtosecond (fs) pulses, first experiments have been carried out by Russo et al. [11] using 100 fs pulse at a wavelength of 800 nm. The results obtained for single spot analysis of SRM NIST 610 under different fluence conditions show that the Pb/U ratio changes with depth in the opposite direction to that observed during ns-LA. Further investigations by Poitrasson et al. [12] using 100 fs pulses at a wavelength of 266 nm showed that at the level of the internal precision of 10% no significant fractionation between Pb and U could be observed. In contrast, ns LA-(MC)-ICP-MS is capable of achieving a precision of ~ 1% [9,13,14].

2) Particle-size-related elemental fractionation. This fractionation has been characterized for the Th/U ratio. Although both elements have similar first ionization potentials, significant fractionation has been observed that correlates strongly with the particle size distribution of the aerosol injected into the inductively coupled plasma (ICP) [15–20]. During the course of a spot ablation, the particle size distribution evolves from an initially wide spectrum including particle sizes of up to 2 μm to a more confined distribution with significantly smaller particle sizes. As shown by ablation studies of SRM NIST 600 series glasses the generated particle size distribution is strongly dependent on the wavelength used for ablation [15,16]. As a result of this the Th/U ratio measured shows an offset from the real ratio of about 200% at the beginning of the ablation process, evolving slowly towards the "real" ratio. This is opposite to the behavior observed for "Type 1" fractionation. For UV-fs-laser ablation at 200 and 266 nm Koch et al. [21] illustrated that this type of fractionation is within error of the determination. The particle size distribution determined in that study shows that particle size larger than 500 nm are absent and that most of the material transported has particle sizes of less than 100 nm which compares well with earlier measurements [22].

3) Laser-induced isotopic fractionation is the third type of fractionation observed during spot ablation. This type has been described for the heavy stable isotope systems of Fe, Cu and Mg using MC-ICP-MS systems. A transient component of fractionation is superimposed on the mass discrimination of the ICP-MS system [23–25]. Here, the laser-induced effect of fractionation is of the order of a few ‰, similar to the natural stable isotope variations of these metals. Fig. 1 illustrates the transient behavior of laser-induced-fractionation, which is different to the constant mass discrimination observed during solution nebulisation. Such a matrix effects caused, for example, by differences in the acid concentration and are readily visible during solution nebulization [26–28]. These are therefore likely to exist during laser ablation, too. For example, $^{56}Fe/^{54}Fe$ raw ratios measured by MC-ICP-MS are similar for both solution nebulisation [28] and fs-laser ablation, suggesting that both introduction mechanisms result in a similar mass discrimination. Even so matrix

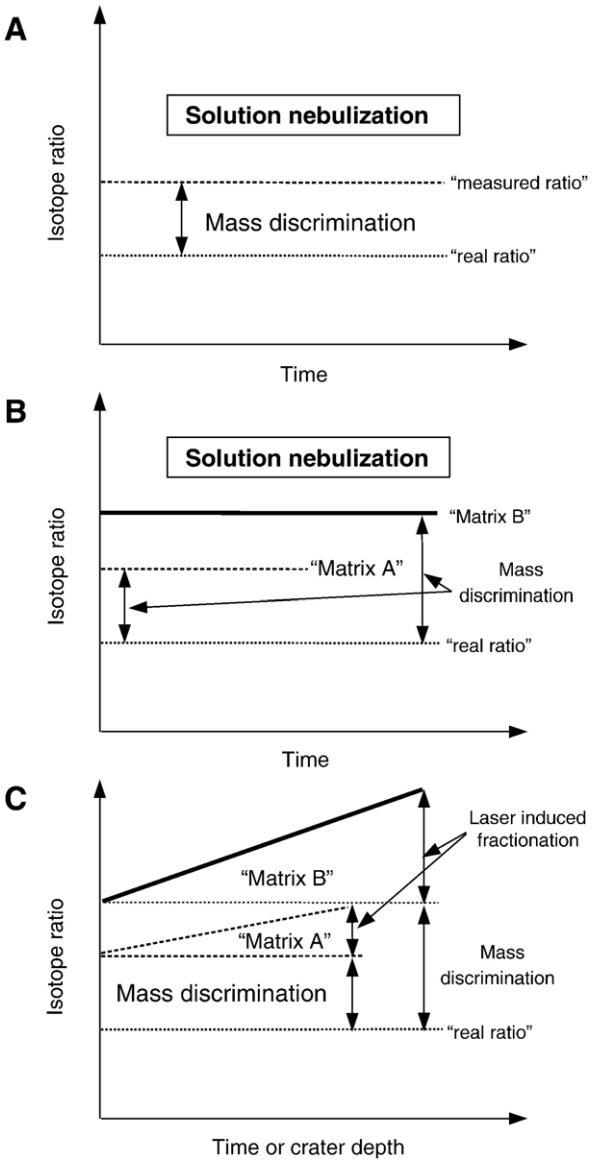

Fig. 1. Illustration of the varieties of isotope ratio bias introduced during ICP-MS measurements. A) The mass discrimination generated by the space charge effect in the interface during analysis by solution nebulisation is the offset from the measured to the "real ratio". B) The matrix effect on the mass discrimination for solution nebulisation, which can be caused by the presence of other elements or differences in the acid concentration which is usually kept constant. C) The transient behavior of laser-induced isotope fractionation is now superimposed onto the matrix effect (dashed), and the mass discrimination (solid). The transient behavior leads to a mass discrimination which is difficult to correct because it is not constant, and is difficult to separate from a matrix effect.

effects have been studied extensively by several authors [26,27,29–31] the occurrence of ‰ transient fractionation effects can only be resolved using MC-ICP-MS systems. This type of fractionation has been interpreted by Jackson and Guenther [24] and Kosler et al. [25] to be a particle size-related fractionation produced in the ICP by preferential evaporation of the light isotope during the course of a spot analysis, similar to that observed for the Th/U ratio. For Mg isotope ratios in olivine, Norman et al. [23] observed a systematic and transient isotope fractionation towards