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Accurate determination of elements in silicate glass by nanosecond and femtosecond laser ablation ICP-MS at high spatial resolution

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ABSTRACT

Despite the large number of successful applications of LA-ICP-MS, elemental fractionation remains the main limitation for many of its applications in the Earth sciences. This limitation is particularly notable for high spatial resolution analysis. Elemental fractionation and mass-load effect in silicate glasses NIST SRM 610 and GSE-1G were investigated by using 193 nm ArF excimer nanosecond (ns) laser and 257 nm femtosecond (fs) laser ablation systems coupled to inductively coupled plasma mass spectrometry. Contrary to those observed in ns-LA-ICP-MS, the most elemental fractionation at the small spot sizes of 16–24 μm are lower than that at the large spot sizes of 44–60 μm in fs-LA-ICP-MS. The significantly different fractionation behaviors of Li, Na, Si, K, V, Cr, Mn, Fe, Co, Ni, Cu, Rb, Cs and U between silicate glass materials NIST SRM 610 and GSE-1G observed in 193 nm excimer LA-ICP-MS are eliminated by using 257 nm fs-LA-ICP-MS at high spatial resolution. In addition, the mass load effect and matrix dependent mass load effect are also found to be reduced by using fs-LA-ICP-MS in comparison with ns-LA-ICP-MS. Except for Sb, Pb and Bi, the elemental fractionation is independent on the laser fluence chosen, which is irrespective of ns- or fs-LA-ICP-MS. In this study, a spot size of 24 μm was used to test the capabilities of LA-ICP-MS analysis at high spatial resolution. The agreement between our data and the reference values is better than 10% for most of the elements in MPI-DING, USGS, and NIST glasses by using fs-LA-ICP-MS. For ns laser ablation analysis, the accuracy is highly dependent on the calibration strategies used (conventional external calibration method or 100% oxide normalization method) and the selected external reference materials (NIST SRM 610 or GSE-1G). The much less laser-induced elemental fractionation and matrix effect in fs-LA-ICP-MS in comparison with 193 nm excimer LA-ICP-MS make it more suitable for the analysis of silicate materials at high spatial resolution.

1. Introduction

Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) has become one of the most popular techniques for the in situ analysis of element and isotopic compositions for a wide variety of materials (Arrowsmith, 1987; Poitrasson et al., 2000; Jackson et al., 2004; Günther and Hattendorf, 2005; Košler, 2007; Sylvester, 2008; Russo et al., 2011; Orellana et al., 2013). Ever since the first feasibility studies were carried out during the 1980s (Gray, 1985; Arrowsmith, 1987), the performance characteristics of LA-ICP-MS have been strongly enhanced, principally with the use of ultraviolet (UV) wavelength LA systems (Günther and Hattendorf, 2005; Jochum et al., 2007). Among these different UV lasers, the 193 nm excimer laser was reported to be excellent for LA-ICP-MS because its laser pulse energy could be effectively absorbed by most materials and produce small-size particles that could be easily transported by the carrier gas and efficiently atomized and ionized in the ICP (Günther et al., 1997; Guillong et al., 2003; Hattendorf et al., 2003).

193 nm excimer LA-ICP-MS has been successfully applied for the analysis of minerals and silicate glasses with non-matrix matched calibration (Günther et al., 1997; Gao et al., 2002; Resano et al., 2003; Günther and Hattendorf, 2005). Most of these reported element determinations in minerals and silicate glasses were focused on using large spot sizes of 40 to 120 μm. This is also true for many other UV-LA-ICP-MS analyses (Kurosawa et al., 2006; Mertz-Kraus et al., 2009; Donohue et al., 2012). The major reason for large spot sizes is to improve sensitivity when the samples were analyzed.

The technological progress in ICP-MS instrumentation has led to the possibility of analyzing craters of smaller diameter. In addition, spatially resolved analysis using a laser beam spot as small as possible is necessary for microanalysis applications, such as for the analysis of melt inclusions, dust aerosols and the zonations of minerals. Liu et al. (2010) reported simultaneous measurements of zircon U–Pb ages and trace elements by LA-ICP-MS at spot sizes of 16–32 μm by introducing N_2 into the ICP to increase sensitivity. The obtained U–Pb ages were consistent with the preferred values within about 1% uncertainty (2σ) by external calibration against 91500. Whereas, the most trace elements for 91500 and relatively homogenous GJ-1 showed a systematic deviation of 10%–30% calibrated against NIST glasses using Si as an internal

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standard. The systematic deviation of REEs in carbonate pellets was also as high as 20% when calibrated against NIST SRM 610 with the use of Ca as an internal standard at a spot size of 32 μm (Chen et al., 2011). Hu et al. (2011) showed the effect of spot sizes on the determined 24 element concentrations in zircon GJ-1, GSE-1G and NIST SRM 612 using NIST SRM 610 as an external reference material and Si as internal standard. By changing the spot sizes from 16 μm to 60 μm, the determined element concentrations in zircon GJ-1 and GSE-1G were increased by 30% (Pb in zircon GJ-1 is an exception), and they were almost not effected in NIST SRM 612. The determined Pb concentration in carbonate MACS-1 calibrated with NIST SRM 612 varied from approximately 170 to 130 ppm with spot sizes varying from 25 μm to 110 μm for 193 nm laser measurements (Jochum et al., 2012). These results implied that matrix dependent effects would significantly deteriorate the analysis results of LA-ICP-MS at high spatial resolution when matrix-matched calibration standards were not available. Therefore, how to reduce the matrix dependent fractionation is important for high spatial resolution analysis.

Many investigations suggest that a fs laser might be one of the best solutions to reduce the matrix effect and elemental fractionation in the ablation process (Russo et al., 2002; Fernández et al., 2007; Koch and Günther, 2007; Garcia et al., 2008; Shaheen et al., 2012). The LA process using a fs laser is significantly less thermal and leads to a shrinking of the heat-affected zone (Fernández et al., 2007). However, the applications of fs-lasers have mainly been concentrated on the fractionation behavior and the analysis of a few elements in conductors and semiconductors (González et al., 2004; Liu et al., 2004; Koch et al., 2005; Bian et al., 2006; Garcia et al., 2008; Wiltsche and Günther, 2011). For example, Koch et al. (2005) studied the composition and fractionation properties of dielectric aerosols generated by near infrared (NIR) fs-LA of silicate glass. It had been found that for fluences larger than 5 J cm^{-2}, the total Zn-, Ca-, Sr-, Ba-, and Pb-specific composition of these aerosols corresponded to that of the bulk material even though the composition of different aerosols was size-dependent. Bian et al. (2006) measured the major and minor concentrations of Zn and Cu in brass, aluminum, and silicate glass using NIR-fs-LA-ICP-MS. Their results indicated the possibility of non matrix-matched calibration if the fluence, depending on the matrix, was appropriately adjusted. Garcia et al. (2008) observed that the fractionation of a few elements in binary metallic and semiconductor samples as well as multi-component glass samples occurred in the first laser shots particularly if the laser fluence was near the ablation threshold of the sample. The fractionation could be reduced by applying many low-fluence laser shots or one high-fluence laser shot only. In most cases, the fractionation could most likely be correlated with the respective ionization energies of the elements. There are only a few publications on multi-element analyses of silicate materials by using fs-LA, especially for an UV-fs-LA (Jochum et al., 2014; Ohata et al., 2014). Jochum et al. (2014) reported the less matrix-dependent fractionation for volatile and siderophile/chalcophile elements such as Pb and Zn with 200 nm fs laser compared to the 193 nm excimer laser and 213 Nd:YAG laser. The concentrations of 47 elements in twenty-two international synthetic silicate glass, geological glass, silicate mineral, phosphate and carbonate reference materials were successfully determined by using NIST SRM 610 as an external reference material at the spot size of 40–65 μm with spot analysis and line scan analysis. Ohata et al. (2014) demonstrated that middle ultraviolet (MUV) fs- and far ultraviolet (FUV) ns-LA-ICP-MS applying either Ca or Si as an internal standard resulted in only minor discrepancies of element concentrations at spot sizes of 60–90 μm. Glaus et al. (2010) observed the similar morphologies of silicate glass aerosols generated by ns- and fs-LA. They considered that fs-LA of silicate with non-matrix matched calibration would be limited because of a pronounced element separation into different particle size fractions.

The aim of this study is to evaluate the matrix effect and elemental fractionation in the analysis of silicates by using the UV 193 nm ArF excimer LA-ICP-MS and the advanced 257 nm fs-LA-ICP-MS at high spatial resolution. The widely used NIST SRM 610 and USGS new synthesis GSE-1G have been selected for studying the elemental fractionation and matrix effect. This is because they not only fulfill the need for different types of matrices due to different major element compositions, but also have sufficient levels of trace elements to provide adequate signals for calibrating the fractionation indexes. For the purposes of comparison, the MPI-DING, USGS and NIST reference glasses were also analyzed by ns- and fs-LA-ICP-MS with different calibration strategies at a high spatial resolution of 24 μm.

2. Experimental

2.1. Instrumentation

Experiments were conducted on an Agilent 7500a ICP-MS (Agilent Technology, Tokyo, Japan) in combination with a 193 nm ArF excimer LA system (GeoLas 2005, Lambda Physik, Göttingen, Germany) and a 257 nm Yb fs-LA system (NWR-Femto^{UC}, USA) owned by the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences (Wuhan). Details of the instrumental operating conditions and measurement parameters are summarized in Table 1. The excimer 193 nm laser is installed with an optical configuration producing a fairly flat-topped lateral energy distribution leading to pan-shaped ablation pits on the sample. The Yb fs-laser system has a Gaussian energy beam profile across its diameter. Helium was chosen as the ablation cell gas as it has been found to consistently enhance the signal 2- to 5-folds compared to argon gas with the 193 nm excimer laser (Eggins et al., 1998; Günther and Heinrich, 1999). The carrier and make-up gas flows were optimized by ablating NIST SRM 610 to obtain maximum signal intensity for La^+, while keeping the ThO/Th ratio <0.3% and the U/Th ratio close to 1. Except for spot analysis, we also performed line scan analysis at a 10 μm/s speed applying crater diameters of 16–120 μm (193 nm excimer) and 16–60 μm (257 nm fs) to investigate a possible

Table 1

Summary of the operating parameters for 193 nm excimer LA-ICP-MS and 257 nm fs-LA-ICP-MS.

Laser ablation system		
Laser type	ArF excimer laser	Yb:YAG femtosecond laser
Wavelength	193 nm	257 nm
Pulse length	15 ns	300 fs
Energy density	8.0 J/cm^2	3.14 J/cm^2
Spot size	16, 24, 32, 44, 60, 90 and 120 μm	16, 24, 32, 44 and 60 μm
Laser frequency	8 Hz	8, 20 Hz
Ablation cell gas	Helium	Helium
Makeup gas	Argon	Argon
ICP-MS	Agilent 7500a	
rf power	1380 W	
Plasma gas flow rate	14.0 l min^{-1}	
Auxiliary gas flow rate	1.0 l min^{-1}	
Ion optic settings	Typical	
Sampling depth	5.4 mm	
Isotopes measured	^{7}Li, ^{9}Be, ^{11}B, ^{23}Na, ^{25}Mg, ^{27}Al, ^{29}Si, ^{31}P, ^{39}K, ^{42}Ca, ^{45}Sc, ^{49}Ti, ^{51}V, ^{52}Cr, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{60}Ni, ^{65}Cu, ^{66}Zn, ^{71}Ga, ^{72}Ge, ^{75}As, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{93}Nb, ^{95}Mo, ^{107}Ag, ^{111}Cd, ^{118}Sn, ^{121}Sb, ^{133}Cs, ^{137}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{143}Nd, ^{147}Sm, ^{151}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{173}Yb, ^{175}Lu, ^{179}Hf, ^{181}Ta, ^{182}W, ^{208}Pb, ^{209}Bi, ^{232}Th, ^{238}U	
Dwell time per isotope	10 ms	
Detector mode	Dual	