Contrasting particle size distributions and Fe isotope fractionations during nanosecond and femtosecond laser ablation of Fe minerals: Implications for LA-MC-ICP-MS analysis of stable isotopes

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Abstract

Laser ablation coupled to a multi-collector inductively coupled mass spectrometer (LA-MC-ICP-MS) is a promising tool for in situ analysis of metal and metalloid stable isotope ratios. Potential isotopic fractionation associated with laser ablation may, however, cause biased sampling of the substrate, posing a major challenge for precise and accurate isotope ratio measurements. To better characterize the nature of laser ablation induced isotopic fractionation, this study compared particle morphologies, sizes, and size-dependent Fe isotope fractionations produced by ablation of a suite of semi-conductive samples, including natural Fe oxide, sulfide, and carbonate minerals, under various conditions using a 193 nm ArF nanosecond (ns) laser and a 266 nm Ti:sapphire femtosecond (fs) laser. Ablation-produced particles were sorted based on aerodynamic size using a cascade impactor, and Fe isotope compositions of size-sorted particles were then measured offline using conventional solution nebulization ICP-MS to quantify isotopic fractionation produced by the laser ablation. Particle morphology and size distributions produced by ns-laser ablation are more substrate and fluence dependent as compared to fs-laser ablation, resulting from the thermal nature of ns-laser ablation. Often, a higher proportion of the ablated Fe mass resides in particles with large aerodynamic sizes during ns-laser ablation as compared to fs-laser ablation, posing a potential difficulty for LA-ICP-MS analysis due to the increased possibility of incomplete ionization of large particles. Significant size-dependent Fe isotope fractionations of up to several per mil can occur during both ns- and fs-laser ablation, highlighting the importance of quantitative transport of particles to the ICP-MS for accurate Fe isotope analysis. Size-dependent Fe isotope fractionation observed for fs-laser ablation of all Fe minerals can be explained by particle formation through a condensation model, but multiple processes need to be considered to explain the observed Fe isotope fractionation during ns-laser ablation. Mass-balance calculations suggest that ns-laser ablation does not sample magnetite stoichiometrically for Fe isotope compositions at low fluence (1 J/cm²), but does at higher fluences for all minerals. In contrast, fs-laser ablation always provides stoichiometric sampling for Fe isotopes regardless of fluence. Results of this study demonstrate that ns-laser ablation is substrate- and fluence-dependent, resulting in variable particle size distributions and Fe isotope fractionations, and possible non-stoichiometric sampling of semi-conductive samples for Fe isotope analysis. Instead, fs-laser ablation largely minimizes the substrate and fluence dependence, providing more consistent ablation.

1. Introduction

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) allows for in situ analysis of chemical and isotopic compositions at a spatial resolution of several microns, providing a powerful tool for analyzing geological samples with small sizes (e.g., meteorites, mineral grains) or complex textures (e.g., zonation, micro-lamination). This method has been extensively used for U–Pb zircon geochronology (Gehrels et al., 2008; Jackson et al., 2004), for major- and trace-element analysis (Gao et al., 2002; Yuan et al., 2008), and for isotopic analysis of several radiogenic isotope systems (e.g., Hf and Sr isotopes) (Christensen et al., 1995; Woodhead et al., 2004). In addition to these well-established methods, there is a strong interest in developing LA-ICP-MS methods to analyze metal and metalloid stable isotopes, such as Si, Mg, Ca, Fe, and Cu (e.g., Kössler et al., 2005a; Lazarov and Horn, 2015; Oeser et al., 2014; Schuessler and von Blanckenburg, 2014; Tacail et al., 2016). This interest is driven by the fact that these elements show naturally occurring, mass-dependent fractionation up to several per mil, providing new insights into various geological processes. Stable isotope ratios of these elements can be analyzed with high precision and accuracy (±0.1‰, 2σ) by multi-collector ICP-MS (MC-ICP-MS).
Iron isotopes are of particular interest because of their ability to trace redox and microbial processes in the modern and early Earth (Beard et al., 2003; Johnson et al., 2008). In nature there is a ~5% range in $^{56}\text{Fe}/^{54}\text{Fe}$ ratios (Johnson et al., 2008), and experimental studies have shown that redox processes can produce fractionation between 1% and 3% at room temperature, where the ferric component has a higher $^{56}\text{Fe}/^{54}\text{Fe}$ ratio compared to the ferrous component (Johnson et al., 2002; Welch et al., 2003). In detail, Fe isotope fractionation is controlled by the type of ferric oxide produced (e.g., goethite or hematite) (e.g., Friedlich et al., 2014; Johnson et al., 2005; Skulan et al., 2002), the aqueous Fe speciation (e.g., Hill and Schauble, 2008; Johnson et al., 2002; Welch et al., 2003), and the temperature at which the redox process occurs (e.g., Welch et al., 2003). The limited natural variability in $^{56}\text{Fe}/^{54}\text{Fe}$ ratios demands an analytical accuracy and precision of a few tenths of permil for LA-MC-ICP-MS, which is an order or several orders of magnitude higher than the accuracy and precision typically achieved for major and trace element analysis by laser ablation.

For in situ analysis of Fe isotopes of certain minerals, it is recognized that LA-ICP-MS is typically superior to secondary ion mass spectrometry (SIMS). SIMS analysis of some high symmetry minerals results in an instrumental mass bias that is a function of the angle between the primary ion beam and the crystal lattice (Huberty et al., 2010; Kita et al., 2011; Lyon et al., 1998). For example, Fe isotopes can be fractionated by ~1% in $^{56}\text{Fe}/^{54}\text{Fe}$ as a function of the crystal orientation of magnetite ($\text{Fe}_3\text{O}_4$) with respect to the primary ion beam (Kita et al., 2011). Although crystal orientation effects can be reduced by adjusting the angle of primary beam relative to the sample surface and decreasing the impact energy, this still leads to loss in analytical precision (Huberty et al., 2010). Additional advantages of LA-ICP-MS include sample preparation, because the sample is at ground potential and is in an inert gas atmosphere. In contrast, SIMS analysis has strict requirements for sample coating and flatness, and analysis occurs under high vacuum and voltage. Despite these advantages, SIMS analysis offers higher spatial resolution than LA-ICP-MS, and this must be balanced with the analytical issues noted above.

Although LA-ICP-MS does not suffer from crystal orientation effects, there is potential for sampling bias during the laser ablation. For example, deviation of LA-ICP-MS measured elemental ratios from the true value, known as elemental fractionation, may occur due to different volatilization and condensation characteristics of elements during laser-material interaction and the formation of the laser ablation-induced aerosols, differential transport of chemically fractionated particles with different sizes, or incomplete ionization of large particles on the ICP-MS (reviewed by Zhang et al., 2016). The same processes, in principle, can fractionate isotope ratios, as reported for analysis of Fe and Cu isotopes by laser ablation (Hirata et al., 2003; Horn and von Blankenburg, 2007; Jackson and Günther, 2003; Kötler et al., 2005a).

Most previous studies have evaluated isotopic or elemental fractionation via online measurements, with the laser being directly coupled to the ICP-MS, which allow for estimates of the overall effect of isotopic or elemental fractionation. The measured stable isotope or elemental ratios are, however, affected by both laser ablation induced fractionation, as well as matrix effects that occur during ionization and ion-beam transport through the expansion chamber and lens stack of the ICP-MS (e.g., Guillong et al., 2003; Horn et al., 2006; Kötler et al., 2005a), it is, therefore, often difficult to determine the exact source of fractionation or quantify unambiguously the magnitude of fractionation using online approaches.

In contrast, offline studies that use an aerosol impactor to collect aerosol particles, followed by conventional solution nebulization analysis, allow one to isolate the fractionation that occurs during laser ablation processes relative to that occurred on the ICP-MS (e.g., d’Abzac et al., 2013; Koch et al., 2004). For example, d’Abzac et al. (2013, 2014) demonstrated that the total aerosol produced by femtosecond (fs) laser ablation of Fe oxides, sulfides, and carbonates is stoichiometric for Fe isotope compositions. Use of a cascade impactor by d’Abzac et al. (2013, 2014) to sort aerosol particles by their aerodynamic size showed that there is a general positive correlation between the $^{56}\text{Fe}/^{54}\text{Fe}$ ratio of the aerosol particle and its aerodynamic size, with up to a 2% range in $^{56}\text{Fe}/^{54}\text{Fe}$ from the smallest to largest particles. This significant size-dependent Fe isotope fractionation during laser ablation was not expected based on previous Fe isotope analysis by fs-laser ablation that used online approaches (Horn and von Blankenburg, 2007), and demands a comparison to isotopic fractionation associated with nanosecond (ns) laser ablation.

Such a comparison can offer a better understanding of the origin of isotopic fractionation produced by the fundamentally different mechanisms of ns- and fs-laser ablation (Chichkov et al., 1996; Russo et al., 2013a). For fs-laser ablation, the ablation process largely occurs without significant convective heating, because the pulse width of the fs-laser ($10^{-12}$ s) is shorter than the time required for electron–lattice heating, which occurs on the picosecond ($10^{-12}$ s) timescale. In contrast, ns-laser ablation tends to cause significant heating and melting, because the pulse width of the ns-laser ($10^{-9}$ s) is too long to prevent electron–lattice heat transfer. The comparison is also of practical significance. Two recent studies suggested that the performance of cost-intensive fs-laser is not superior to that of ns-laser on certain elemental and isotopic analyses for non-conductive or even conductive materials (Ohata et al., 2014, 2015), calling for reassessment of the long-standing view that fs-laser delivers better analytical performance than ns-laser.

To better understand the nature of isotopic fractionation associated with laser ablation, ns- and fs-laser ablation generated aerosols were collected by impactation to evaluate particle morphologies, size distributions, and Fe isotope compositions of size-sorted particles. This work represents the first comparison of size-sorted isotope fractionation induced by ns- and fs-laser ablation, and is also complimentary to previous studies that have compared morphology and sizes of particles produced by ns- and fs-laser ablation of conductive metals (e.g., Glaus et al., 2010; Gonzalez et al., 2007a; Koch et al., 2004; Liu et al., 2004; Perdian et al., 2008), and insulating substrates, such as silicates (e.g., Glaus et al., 2010; Gonzalez et al., 2007b; Perdian et al., 2008). The aerosol characterization for this study was performed on semi-conductive samples of significant geological interest for in situ Fe isotope analysis, including Fe oxides, sulfides, and carbonates. Different thermal properties of these phases allow us to assess the potential problem associated with melting during ns-laser ablation, and compare to fs-laser ablation, which is not associated with significant heating.

2. Experimental methods

2.1. Notation

Iron isotopes in this study are expressed by the $\delta^{56}\text{Fe}$ notation relative to igneous rocks (IgRcs) (Beard et al., 2003):

$$\delta^{56}\text{Fe} = \left(\frac{^{56}\text{Fe}_{\text{sample}}}{^{56}\text{Fe}_{\text{IgRcs}}} - 1\right) \times 1000$$

Another commonly used Fe isotope standard, IRMM-014, has a $\delta^{56}\text{Fe}$ value of ~0.05‰ under this scale.

The difference between two $\delta^{56}\text{Fe}$ values, A and B, is expressed by the $\Delta^{56}\text{Fe}_{A-B}$ notation in this study, where $\Delta^{56}\text{Fe}_{A-B} = \delta^{56}\text{Fe}_A - \delta^{56}\text{Fe}_B$.

2.2. Ablation substrates

Four different natural Fe minerals, including magnetite ($\text{Fe}_3\text{O}_4$), siderite ($\text{FeCO}_3$), pyrrhotite ($\text{Fe}_4\text{S}_5$), and pyrite ($\text{FeS}_2$), were ablated in this study. The same set of samples was used previously in d’Abzac et al. (2013, 2014). Large grains (>500 µm) of each mineral were mounted...
in epoxy and electron microprobe analysis indicates that all minerals are nearly chemically pure end members, except for siderite, which contains ~16% (wt) of cation impurities (Mn, Mg, and Ca) (d’Abzac et al., 2013). Iron isotope homogeneity of each mineral was confirmed by multiple single-grain analyses using conventional solution nebulization MC-ICP-MS after chromatographic purification. The results yielded a bulk δ56Fe value of 0.32 ± 0.05‰ (2σ) for magnetite, −0.40 ± 0.07‰ for siderite, −0.25 ± 0.05‰ for pyrrhotite, and −1.39 ± 0.06‰ for pyrite. No Fe isotope heterogeneity was observed within a grain based on multiple analyses done previously by fs-LA-ICP-MS at an external precision of ±0.2‰ (2σ) (Czaja et al., 2013).

2.3. Laser ablation systems

Two laser ablation systems were used in this study. One is the Excite.193 argon fluoride (ArF) excimer laser ablation system (Teledyne-Photon Machines), which produces a wavelength 193 nm laser with a pulse width of ~4 ns. The system permits a control of repetition rate between 1 and 300 Hz. Laser beam diameter on the sample (i.e., spot size) is controlled using a set of selectable apertures with predefined sizes. The system is equipped with a beam homogenizer, providing a uniform beam profile. The other system used is the Analyte fs system (Teledyne-Photon Machines)—a diode-pumped Ti:sapphire laser equipped with a chirped pulse amplifier and a third harmonic generator, which produces a 266 nm ultraviolet wavelength laser with a pulse width of ~150 fs. The repetition rate is adjustable between 1 and 250 Hz. Laser spot size can be controlled by image aperture or by focus mode. In the image aperture mode, a selectable sized aperture is imaged onto the sample, where the laser focus is set tens of μm below the sample. Alternatively, in focus mode, the spot size is controlled by focusing the laser onto the sample for the smallest size or focusing the laser below the sample for larger sizes. Additionally, the spot size can be changed by adjusting an iris located in front of the objective. In previous work by d’Abzac et al. (2013, 2014), the image aperture mode was used. In this study the focus mode was used, primarily because the focus mode bypasses a number of mirrors required in the image aperture mode, thereby allowing for higher pulse energy to be delivered to the sample. The output laser beam has a Gaussian energy profile.

Because the ablation cell geometry has major influence on particle size distribution and δ56Fe compositions of size-sorted particles (d’Abzac et al., 2014), both laser ablation systems were equipped with the same type of two-volume HelEx ablation cell (CETAC) to ensure that any difference in the results from the two laser systems was not caused by ablation cell parameters. Mass-flow controllers were used in both ablation cells to maintain a steady delivery of helium (He) gas.

2.4. Laser operating conditions and collection of laser induced particles

Detailed laser operating conditions used during particle collection experiments are provided in Table S1 (Supplementary Material). Briefly, laser ablation induced particle collection experiments were conducted using a raster mode with repetition rates of ~12-17 Hz and scan speed of ~1–2 μm/s. For the ns-laser, a fluence of ~2 J/cm² was used to ablate all four Fe minerals, and additional fluences ranging between ~1–4 J/cm² were also chosen to ablate magnetite and pyrite to evaluate the influence of energy density on particle sizes and Fe isotope fractionation. Changing fluence was achieved by adjusting the built-in attenuator in the system, and a constant laser spot size of 25 μm was used in all ns-laser ablation experiments. For the fs-laser, we augmented the previous work of d’Abzac et al. (2013, 2014) with new experiments on magnetite using different fluences. Changing fluence for the fs-laser was achieved by adjusting the attenuator to control laser pulse energy and by adjusting the z-axis of the laser objective to be closer to the sample to produce a larger spot size. Following the approach of Schuessler and von Blanckenburg (2014), we define the fluence for the fs-laser using a simple division of laser pulse energy at the sample surface by the crater size. This definition is nominal due to a Gaussian energy profile of the fs-laser beam used in our study. Direct comparison of ablation fluence between the ns- and fs-laser used in this study is difficult because of the different beam profiles.

Particles produced by laser ablation were extracted by He gas at a constant flow rate typical of that used during online LA-ICP-MS analysis of Fe isotopes (i.e., ~0.6 L/min) during all experiments. Ablation targets were always placed at the center of HelEx cell to ensure similar particle extraction conditions. For the experiments intended for examination of particle morphology, the flow of particle-bearing He gas was guided through a house-built trapping device that consisted of a modified 5-ml syringe with an SEM aluminum (Al) stub (diameter ≈ 12 mm) inside (d’Abzac et al., 2012a). Half of the Al stub surface was covered by carbon tape, and the other half was covered with three lacey carbon-coated TEM copper grids (diameter ≈ 3 mm). To ensure aerosol impaction onto the TEM grids and carbon tape, the He flow out of the ablation cell was augmented by addition of ~2 L/min nitrogen (N₂) flow through a T-connection just prior to the aerosol collection syringe.

For experiments intended for particle size distributions and offline size-sorted Fe isotope compositions by conventional solution nebulization analysis, ablation-induced particles were collected and sorted based on their aerodynamic diameters (Dₐ) using a microorifice uniform form deposit impactor (MOUDI) that comprises 12 impaction stages (including the inlet and after-filter). The upper 11 stages of the MOUDI sort and collect particles with Dₐ cut-sizes ranging from 0.056 to 18 μm (Marple et al., 1991) (Fig. 1). An additional stage, named as after-filter, is situated at the end of aerosol outlet of the MOUDI, and collects all particles with Dₐ < 0.056 μm. Before entering the MOUDI, the particle-carrying He gas was mixed with a flow of N₂ (~29.4 L/min) through a T-connector −0.7-m downstream from the HelEx cell outlet to reach a 30 L/min flow rate required by normal operation of MOUDI. Size-sorted particles were collected on PTFE membrane filters mounted on each of the 12 impaction stages. Aerosol collections lasted for ~6–7 h for the experiments intended solely for Fe mass distributions, and lasted for ~23–58 h for the experiments intended for size-sorted Fe isotope compositions. For some experiments, material left on the substrate surface after ablation was also collected and measured for Fe masses and isotope compositions. The gas flow rate was set to 30 L/min by using a calibrated orifice and manegaliche gauge prior to starting the aerosol collection, and was monitored throughout the collection by measuring the pressure differential between impaction stages via the built-in ports on the MOUDI and manegaliche gauges (Fig. 1).

2.5. Particle morphology and ablation depths

The particles collected on carbon tape were coated with iridium and then observed using a LEO 1530 field-emission scanning electron microscope (FE-SEM) operated at 3 KeV, and those collected on TEM grids were examined using a Philips CM200-UT transmission electron microscope (TEM) operated at 200 KeV. The TEM is equipped with an energy-dispersive X-ray (EDX) detector for analysis of chemical compositions. The depths of the ablated areas were measured using a Zygo white light interferometer (NewView 6200), which allows one to estimate the total volume removed during ablation. A series of spot ablations by ns-laser were conducted on each Fe mineral using different fluences ranging between 1 and 4 J/cm², and the crater depths were also measured by the white light interferometer.

2.6. Analysis of Fe masses and isotope compositions

Particles collected on each impaction stage were dissolved by leaching PTFE filters with distilled acids in 60-ml-sized Teflon beakers at ~110 °C for at least 12 h. Magnetite and siderite samples were dissolved by ~8 M HCl, and Fe sulfides (pyrrhotite and pyrite) were dissolved in mixed ~15 M HNO₃ and ~8 M HCl with a volume ratio of 1:3. For short collections intended only for particle size distribution, Fe mass collected on each
impaction stage was measured using isotope dilution (Fassett and Paulsen, 1989), where particles were spiked with a 57Fe-enriched tracer before dissolution, and then analyzed on an MC-ICP-MS for 54Fe/57Fe ratios without ion-exchange chromatography. For collections intended for both Fe contents and isotope compositions, dissolved particles from each impaction stage were not spiked. Iron contents were measured by the Ferrozine method (Stookey, 1970), and Fe isotopes were measured on an MC-ICP-MS using conventional solution nebulization after anion-exchange chromatography (Beard et al., 2003). Samples from adjacent stages were combined, where needed, before the chromatographic purification to ensure sufficient Fe (>2 μg) for accurate Fe isotope analysis.

Iron isotope ratios were measured on either a Micromass Isoprobe MC-ICP-MS following the method reported in Beard et al. (2003), or a Nu Plasma II MC-ICP-MS operating at the pseudo-high-resolution mode that resolves the Fe beams from polyatomic interfaces, notably 40Ar16O+ on 54Fe+ and 40Ar18O+ on 56Fe+. Instrumental mass bias was corrected by a sample-standard bracketing protocol, using an in-house HPS Fe standard as the bracketing standard. Repeated analyses of two in-house Fe standards (JM Fe and HPS Fe II) and IRMM-014, measured on the two MC-ICP-MS used in this study, yielded consistent δ56Fe values with an external precision <0.1‰ (2 SD). Aliquots of JM Fe and solutions dissolved from grains of the four Fe minerals ablated were routinely processed through the ion-exchange chemistry with varied Fe mass loading to check the accuracy and precision of Fe isotope analysis. The analytical precision of <0.1‰ (2 SD) can be achieved when Fe loaded mass on the ion-exchange resin ranges between ~10 and 100 μg, but the precision slightly worsened (~0.15‰, 2 SD) when total Fe loading was at the level of several μg. Iron mass loaded for ion-exchange column separation ranged from ~2 to ~70 μg in this study. Because inaccurate Fe isotope measurement can occur when total Fe loaded on the ion-exchange resin was <2 μg probably due to the decrease in Fe to matrix ratios (Supplementary Material Fig. S1), data with Fe mass loading <2 μg were not reported.

3. Results

3.1. Particle morphology and chemical compositions

The morphology of particles produced by fs-laser ablation of the same set of samples has been studied using SEM and TEM, and reported in a previous study (d’Abzac et al., 2013). Briefly, two morphologies, regardless of the substrate mineralogy, were always observed: spheres with diameters of ~20–200 nm, and agglomerates that are composed of components with individual sizes below ~10 nm. Agglomerates are mostly “soft-bonded”, meaning that there is no deformation of primary particles during agglomeration, and the rounded shape of primary particles is clearly observable (Gonzalez et al., 2007a).

Representative SEM and TEM images for ns-laser ablation are presented in Fig. 2. In general, the morphology of particles produced by ns-laser ablation is more variable depending on the substrate mineralogy and ablation fluence. For magnetite, spheres were rare for particles produced by ablation at a fluence of 1 J/cm², and agglomerates were the only morphology observed by electron microscopy (Fig. 2c). Spheres were observed in particles generated at higher fluences, but agglomerates were predominant (Fig. 2a,b). Large spheres with sizes of hundreds of nm to up to ~1 μm were observed in particles produced by ablation at a fluence of 4 J/cm² (Fig. 2b). For the ablation of pyrite, spheres are the dominant morphology regardless of the ablation fluence, and agglomeration of spheres is evident as viewed using both SEM and TEM (Fig. 2d,e). The observed spheres are mostly large in size (i.e., up to several μm), and large particles with irregular shapes are often observed (Fig. 2e). Particles generated by the laser ablation of pyrrhotite consist of spheres with sizes both smaller than ~100 nm and larger than ~500 nm, as well as agglomerates (Fig. 2g–i). Particles produced by ablation of siderite consist of small spheres and agglomerates (Fig. 2k,l), similar to those observed for fs-laser ablation. Large spheres are rare, but rhombohedral edged mineral debris particles with sizes of several μm were commonly observed using SEM (Fig. 2j). We note that mineral debris with sizes around ~1 μm were occasionally observed for magnetite, pyrite, and pyrrhotite under SEM (e.g., Fig. 2a), and melting features, such as rounded edges of these mineral chucks, are evident for all minerals. Distinct from soft-bonded agglomerates produced by fs-laser ablation, agglomerates produced by ns-laser ablation often lack discernible primary components under TEM (i.e., hard-bonded) for all Fe minerals ablated (Fig. 2c,f,i,l).

EDX analysis confirms that the observed particles are Fe phases, rather than dust deposited on the TEM grids, and provides semi-quantitative information on elemental ratios of the particles, thereby an assessment of the laser ablation-induced elemental fractionation. EDX

Fig. 1. A schematic diagram showing the experimental setup for particle collection by MOUDI.
spectra for the particles produced by ns-laser ablation of sulfides (pyrite and pyrrhotite) are presented in Supplementary Material (Figs. S2 and S3). Following d’Abzac et al. (2013), we define an enrichment factor between agglomerates and spheres as \( \frac{\text{Fe}/\text{S}}{\text{agg}} / \frac{\text{Fe}/\text{S}}{\text{sph}} \), ns-laser ablation yielded a \( \frac{\text{Fe}/\text{S}}{\text{agg}} / \frac{\text{Fe}/\text{S}}{\text{sph}} \) ratio of ~1.2 for pyrite, and ~4.7 for pyrrhotite, showing ablation induced Fe–S fractionation between different particle morphology with varied extent between different sulfides studied. The enrichment factor for ns-laser ablation of pyrite is lower than that obtained previously by fs-laser ablation of the same mineral substrate (~2.2), but the enrichment factor for ns-laser ablation of pyrrhotite is significantly higher than that obtained by fs-laser ablation of the same mineral (~1.5) (d’Abzac et al., 2013), demonstrating that the degree of elemental fractionation for ns-laser is not always smaller than that of fs-laser ablation as suggested by Glaus et al. (2010). Results of Fe/O ratios for the particles produced by ns-laser ablation of magnetite are not considered, because possible oxidation of magnetite during ablation can overprint the laser ablation induced elemental fractionation. In addition, Fe/C ratios for the particles produced by ablation of siderite are not considered because of potential contamination or/and interference of C from the carbon film on the TEM grids used for particle collections.

3.2. Particle collection efficiency

Total volume of materials removed during laser ablation was estimated using the depths measured by the white light interferometer. Because particles produced by laser ablation may be too large to be transported, or lost during collection, comparison between total Fe
mass collected on the MOUDI and that estimated using the total removal volume and mineral density provides an assessment of potential particle loss (details in Supplementary Material). The results indicate that the collection efficiency, defined by Fe mass collected on the MOUDI divided by volume-estimated Fe mass, is >80% for all experiments in our study (Supplementary Material Table S2), suggesting insignificant particle loss during our collection experiments. These results are consistent with previous studies using a similar approach (d’Abzac et al., 2013, 2014), and is also consistent with the fact that Fe masses of materials left on the substrate surface after ablation always account for <20% of total Fe mass collected on the MOUDI in the experiments where the leftover materials were collected.

Fig. 3. Percentage of Fe mass (%Fe) collected on each impaction stage of MOUDI relative to total Fe collected as a function of aerodynamic size (Da). Green vertical bars indicate the two main Da ranges where Fe masses were dominant for fs-laser ablation: one at Da < 0.056 μm (10–30% of total Fe mass) and the other at 0.1 μm < Da < 0.32 μm (60–90% of total Fe mass). D13 denotes data reported in d’Abzac et al. (2013).
3.3. Particle size distribution

Particle size distributions from all experiments, reflected by the percentage of Fe mass collected on each impaction stage relative to the total Fe mass collected (%Fe) as a function of aerodynamic diameter Da, are illustrated in Fig. 3, and the data are reported in Table S1. Conversion from aerodynamic diameter to physical diameter is difficult, because Da is a function of particle density and shape (Marple et al., 1991). Because of the dynamic nature of particle formation and agglomeration during transport, several replicate experiments were conducted to assess the degree of reproducibility of particle size distribution. Results of replicate experiments, including one experiment on fs-laser ablation of magnetite using similar laser conditions described in d’Abzac et al. (2013), typically agree within 10% and, more importantly, show highly reproducible overall patterns (Fig. 3).

For ns-laser, ablation of magnetite under four different fluences ranging from 1 to 4 J/cm² produced similar bimodal patterns of particle size distribution, with 25–45% of the total Fe mass collected being found at Da < 0.056 μm, and 10–35% of the total Fe mass being found at Da = 0.1 μm. There is no obvious change in the pattern in response to fluence, although Fe collected at Da = 0.1 μm at a fluence of 1 J/cm² (%Fe = −12%) is slightly less than that collected at the same Da at higher fluences (%Fe = −20–30%). Agglomerates are the dominant morphology observed under microscopes for particles produced by ablation at 1–4 J/cm² (Fig. 2a,b,c). Spheres with sizes up to several hundreds of nm are only observed in particles produced by ablation at fluence N1 J/cm² (Fig. 2a,b), but are absent from particles produced by ablation at 1 J/cm² (Fig. 2c).

Fig. 4. Results of δ⁵⁶Fe values for size-sorted particles produced by ns- and fs-laser ablation of Fe minerals, together with percentage of Fe mass (%Fe) collected on each impaction stage of MOUDI. Particles from adjacent stages of low Fe masses were combined to ensure accurate δ⁵⁶Fe analysis, but the same δ⁵⁶Fe value was plotted individually for the impaction stages that were combined for magnetite (a) and pyrite (c) to maintain figure clarity. The combined stages were shaded in the same areas for siderite (b) and pyrrhotite (d). D13 denotes data reported in d’Abzac et al. (2013).

Nanosecond laser ablation of pyrite under three different fluences ranging between 1 and 4 J/cm² also yielded very similar bimodal patterns, with one peak at Da = 0.1 μm that contained ~15% of the total Fe collected, and a broad peak between 0.32 and 1 μm Da that contained >50% of the total Fe ablated. This Fe mass distribution is dramatically different from the one observed for magnetite, where the mass of Fe is small (%Fe = −5%) at Da < 0.056 μm as compared to those collected at the same Da for magnetite that contained 25–45% of the total Fe. Moreover, a significantly higher proportion of Fe mass was found at Da between 0.32 and 1 μm as compared to the same Da range for magnetite. Although it is not possible to directly convert Da to physical sizes, the significant presence of large spheres of up to several μm observed under microscopes for pyrite at all fluences (Fig. 2d,e) contrasts sharply with that observed for magnetite, and is consistent with size distributions where higher percentages of Fe mass were found at Da between 0.32 and 1 μm for pyrite.

For pyrrhotite, ns-laser ablation produced a bimodal pattern with 15–20% of the total Fe collected being found at Da < 0.056 μm, and 15–25% of the total Fe collected being found at Da = 0.1 μm. Additionally, a significant percentage of Fe (%Fe = ~8%) occurs around Da = 1 μm, and a cumulative percentage of Fe over the Da range from 0.1 to 1 μm accounted for ~70% of the total Fe collected.

Ablation of siderite by the ns-laser also produced a bimodal pattern, with 30–40% of the total Fe collected being found at Da < 0.056 μm, and 15–20% of the collected Fe being found at Da = 0.1 μm. Additionally, ~5% of the total Fe occurs on each impaction stage with a Da from 0.18 to 3.2 μm, totaling >30% of Fe mass collected within this size range. Mineral debris with physical sizes of up to several μm are commonly observed
for siderite using SEM (Fig. 2), and these large particles presumably account for significant percentages of Fe mass found at Da between 0.18 μm and 3.2 μm.

For fs-laser ablation, experiments were conducted on magnetite using three different fluences (0.3, 0.6 and 1 J/cm²). At a fluence of 1 J/cm², the pattern of Fe particle size distribution showed a bimodal shape with a peak at Da < 0.056 μm (15–25% of the total Fe mass collected) and the other one at Da = 0.1 μm (32% of the total Fe collected). This pattern is consistent with that reported using similar laser conditions in d’Abzac et al. (2013). For experiments done at lower fluences, however, the second peak at Da = 0.1 μm is shifted towards larger Da between 0.18 μm and 0.32 μm.

3.4. Iron isotope compositions of size-sorted particles

Results of δ⁵⁶Fe values for size-sorted particles are reported in Table S3 (Supplementary Material) and plotted in Fig. 4 as deviations of the measured δ⁵⁶Fe values of size-sorted particles from the true Fe isotope composition of the substrate (Δ⁵⁶Fe_particle–true = δ⁵⁶Fe_particle − δ⁵⁶Fe_true). For comparison, results from d’Abzac et al. (2013) that used the same mineral samples and experimental approaches as used here are shown for fs-laser ablation.

Size-dependent Fe isotope fractionation occurs in most experiments for both ns- and fs-laser ablation. For ns-laser ablation of magnetite at a fluence of 1 J/cm², δ⁵⁶Fe values of particles are considerably lower than that of the substrate (Δ⁵⁶Fe_particle–true = −0.7 to −1.3‰) at Da < 1 μm, and become slightly higher than that of the substrate (Δ⁵⁶Fe_particle–true = 0.17‰) with Da > 1 μm. Under higher fluences (2–4 J/cm²), particles with Da > 0.056 μm tend to have δ⁵⁶Fe values slightly or moderately lower than that the substrate (Δ⁵⁶Fe_particle–true = −0.01 to −0.7‰, but the smallest particles (Da < 0.056 μm), which account for 25–45% of the total Fe mass collected, have δ⁵⁶Fe values slightly higher than that of the substrate (Δ⁵⁶Fe_particle–true = −0.1–0.3‰). Ablated material that was not extracted from the ablation cell and left on the substrate surface was collected for the experiments using ablation fluences of 3 and 4 J/cm², and this so-called “ejecta blanket” has δ⁵⁶Fe values similar to the substrate.

For ns-laser ablation of pyrite, particles with Da < 0.1 μm have δ⁵⁶Fe values that are −0.3‰ to 1.9‰ higher than that of the substrate at fluences between 1 and 4 J/cm². Particles with Da > 0.1 μm have Fe isotope compositions that are similar to the substrate (Δ⁵⁶Fe_particle–true = ±0.2‰) at fluences of 1 and 4 J/cm². In contrast, at a fluence of 2 J/cm², particles with Da > 0.18 μm have δ⁵⁶Fe values that are −0.3‰ lower than that of the substrate, and at Da > 3.2 μm the δ⁵⁶Fe values are −0.6‰ higher than the substrate. Like magnetite, the ejecta blanket from ns-laser ablation at a fluence of 4 J/cm² for pyrite also has a δ⁵⁶Fe value similar to the substrate.

The ns-laser ablation experiments conducted on pyrrhotite and siderite were only done at a fluence of 2 J/cm². For pyrrhotite, the δ⁵⁶Fe values of particles are 0.94‰ higher than that of the substrate at Da < 0.056 μm, and are −0.6‰ lower that the substrate at Da of 0.18 μm. At larger Da, the particles have δ⁵⁶Fe values that are similar to the substrate (Δ⁵⁶Fe_particle–true = ±0.2‰). For siderite, the δ⁵⁶Fe values of particles are 0.5‰ to 0.7‰ lower than that of the substrate at Da < 0.1 μm, and are 0.3‰ to 1.6‰ higher at Da of 0.18 and 0.56 μm. At Da > 0.56 μm, the particles have δ⁵⁶Fe values that are similar to the substrate.

For fs-laser ablation on magnetite at fluences of 0.3 and 0.6 J/cm², there is an overall positive correlation between δ⁵⁶Fe values and particle size. For example, at Da = 0.1 μm the particles have Δ⁵⁶FeParticle–true between −1.6‰ and −0.6‰, and at Da between 0.18 and 0.32 μm the particles have Δ⁵⁶FeParticle–true between −1.0‰ and 1.7‰. As in the ns-laser ablation experiments, the largest particles tend to have δ⁵⁶Fe values that are similar to that of the substrate (Δ⁵⁶Fe_particle–true = −0.3‰). The ejecta blanket has a δ⁵⁶Fe value −1‰ lower than the substrate at a fluence of 0.3 J/cm², but has a δ⁵⁶Fe value −1.4‰ higher than the substrate at a fluence of 0.6 J/cm².

4. Discussion

4.1. Ablation mechanisms for ns- and fs-lasers

There are differences in particle morphology, size distribution, and size-dependent isotope fractionation produced by ns- versus fs-laser ablation. These differences ultimately result from different laser–matter interactions that remove material from the substrate. A variety of mechanisms, such as vaporization, explosive boiling, exfoliation and spallation, have been proposed to explain removal of materials from the substrate, and laser ablation often involves multiple mechanisms (e.g., Bogart et al., 2003; Chichkov et al., 1996; Paltauf and Dyer, 2003; Yoo et al., 2000). For ns-laser ablation, thermal mechanisms are considered important for material removal (Cristoforetti et al., 2008; Mao et al., 1996). Vaporization occurs when absorption of laser photon energy by electrons raises the temperature of the substrate surface to several thousand Kelvin. Because the pulse width of ns-laser is longer than the duration required for thermal equilibrium between electron and lattice phonons, energy propagates from surface electrons into the interior of the substrate through heating of the lattice, creating a molten layer on the substrate. The presence of a molten layer can lead to mass removal through hydrodynamic spattering, where ejection of materials from the molten layer takes place when the recoil pressure, resulting from expansion of laser induced plasma plume and shockwave, overcomes surface tension and gravity of the melt (Hergenröder, 2006a).

Non-thermal mechanisms, such as explosive boiling and spinodal decomposition (i.e., critical temperature phase separation), are important pathways for material removal during fs-laser ablation (Cheng and Xu, 2005; Lorazo et al., 2003; Vidal et al., 2001). Because deposition of laser energy on the substrate by fs-laser irradiation is too fast to allow for the electron–lattice thermal equilibrium, superheating occurs and drives the thermodynamic state of the substrate away from equilibrium vaporization binodal into a non-equilibrium region. When substrate temperature reaches or exceeds the critical temperature, the system undergoes a transition from a metastable to unstable state, leading to explosive boiling or spinodal decomposition processes that remove mass as a mixture of vapor and fluid droplets. Compared to ns-laser ablation, the heat-affected zone generated by fs-laser ablation is largely minimized due to a lack of conventional heat transfer in the substrate (d’Abzac et al., 2012b; Russo et al., 2013b).

Explosive boiling has also been reported during ns-laser ablation of silicon crystals and metals at high fluences (e.g., ~5 J/cm² for a pure nickel target) (Pornea and Willis, 2006; Song and Xu, 1998; Yoo et al., 2000), and was inferred by a dramatic increase in ablation depth at a threshold fluence, deviating from the linear fluence–depth trend observed at lower fluences. This phenomenon was attributed to more intensive mass removal due to the explosive nature of the mechanism as compared to normal evaporation. Our results, however, show an opposite trend where ablation depth per laser shot at higher fluences is shallower than that expected by a linear increase with fluence (Fig. 5). This demonstrated decrease in laser ablation efficiency with increasing fluence probably reflects increased absorption of laser energy by the expanding plasma plume above the substrate (i.e., plasma shielding). Nonetheless, no anomalous increase in ablation depth was observed within the range of 1–4 J/cm², precluding explosive boiling as a major ablation mechanism in our ns-laser ablation experiments.

Mechanical breakdown of the substrate can also occur when tensile stress, mainly resulting from the impaction associated propagation of the shockwave and plasma plume, exceeds tensile strength of the substrate during both ns- and fs-laser ablation. These photomechanical mechanisms (e.g., exfoliation or spallation) are only of secondary significance during ns-laser ablation of magnetite and Fe sulfides, as demonstrated by sporadic occurrence of μm-size mineral debris for these minerals observed by electron microscopy, but are more important for siderite, as supported by frequent occurrence of mineral debris observed by SEM (Fig. 2), probably due to well-developed cleavage of...
the siderite mineral as compared to other minerals. In all cases, melting features on mineral debris reflect the thermal nature of ns-laser ablation, as well as longer interaction time between the ns-laser beam and laser-induced plasma plume. For fs-laser, mechanical breakage may also have occurred during ablation of siderite, as suggested by the occurrence of a relatively high percentage of the ablated Fe mass (12%) in particles with \( D_a > 18 \mu m \) (d’Abzac et al., 2013).

### 4.2. Particle morphology produced by ns- and fs-laser ablation

Significant differences exist in particle morphology observed for fs- and ns-laser ablation (Fig. 2). Femtosecond laser-produced particles are always dominated by two morphologies: spheres of \( \sim 20–200 \) nm in diameter and agglomerates that are composed of soft-bonded components with individual sizes below \( \sim 10 \) nm (d’Abzac et al., 2013; Glaus et al., 2010). In contrast, particles produced by ns-laser ablation show more variability in morphology. Firstly, although spherical particles with sizes similar to those observed for fs-laser ablation were produced by ns-laser ablation, large spheres with sizes \( \geq 500 \) nm can be found in most of our experiments (Fig. 2b,e,h), except for ablation of siderite and low-fluence ablation of magnetite. In particular, large spheres are abundant in particles produced by ns-laser ablation of pyrite (Fig. 2e). Large spheres with diameters of hundreds of nm to several \( \mu m \) have also been observed previously during ns-laser ablation of silicates and metals (Glaus et al., 2010; Köser et al., 2005b). Secondly, the particle morphology of ns-laser ablation varies with the substrate mineralogy and laser fluence. In contrast to the dominance of spheres in particles produced by ablation of pyrite at laser fluences ranging between 1 and 4 J/cm\(^2\), spheres were essentially absent from particles produced by ns-laser ablation of magnetite at fluence of 1 J/cm\(^2\) (Fig. 2c), and only appeared during ablation at higher fluences. The dominance of spheres during ns-laser ablation of pyrite is contrary to a previous study that suggested predominant production of agglomerates during ablation of pyrite using a similar 193 nm ArF laser (Glaus et al., 2010), perhaps reflecting different laser conditions (e.g., fluence, spot size) in the two studies. Thirdly, distinct from soft-bonded agglomerates produced by fs-laser ablation, agglomerates produced by ns-laser ablation are typically hard-bonded (Fig. 2c,f,i,l), reflecting protracted heating during ns-laser ablation.

Different mechanisms have been proposed to account for particle formation during laser ablation (reviewed by Hergenröder, 2006b). For fs-laser ablation, a gas-to-particle conversion, followed by coalescence-collision processes, has been attributed to formation of the majority of spheres and agglomerates (d’Abzac et al., 2012a; Hergenröder, 2006c). This chain of processes starts with condensation of atoms through homogenous or heterogeneous nucleation when the cloud of ablation induced plume becomes oversaturated due to cooling of the system after laser irradiation. Further condensation and coalescence of initial clusters of atoms lead to the growth of small particles into bigger ones. Agglomerates are formed by collision of small particles. Because of the soft-bonded nature of agglomerates, it can be inferred that agglomeration occurs after solidification of primary particles. The two morphologies for fs-laser ablation appear largely independent of substrate thermal properties, because similar features were observed previously in particles produced by fs-laser ablation of metals, semi- and non-conductive samples (d’Abzac et al., 2012a; Glaus et al., 2010; Gonzalez et al., 2007a). This can be explained by the non-thermal ablation mechanisms associated with fs-laser ablation, where strong superheating and subsequent removal of materials by non-equilibrium processes override the differences in substrate thermal properties, providing a similar starting state for particle formation.

A condensation–collision model that is similar to the one proposed for fs-laser ablation may explain some small particles (\( \leq 100–200 \) nm) produced by ns-laser ablation, although it is important to recognize that the initial vapor should largely form through normal evaporation during ns-laser ablation. The model, however, is not able to explain the occurrence of larger particles. Previous calculations have suggested that formation of particles with sizes \( \geq 100 \) nm requires unrealistically high numbers of collision of small particles during expansion of plasma plume induced by laser ablation. Instead, mechanical ejection of liquids from the molten layer (i.e., hydrodynamic sputtering) is a more probable mechanism responsible for generating large particles observed for ns-laser ablation (Hergenröder, 2006a). The relative contribution of condensation and hydrodynamic sputtering in forming particles depends on the competition between surface evaporation and the extent of molten layer formation, which is critically controlled by thermal properties of the substrate (e.g., thermal conductivity, thermal capacity) (Rogaerts et al., 2003). Thus, it is not surprising that particle morphology for ns-laser ablation shows a higher degree of dependence on fluence and substrate as compared to fs-laser ablation.

### 4.3. Particle size distribution produced by ns- and fs-laser ablation

Particle size has a major impact on precise and accurate LA-ICP-MS analysis, because it affects particle transport and ionization on the ICP-MS (Bleiner et al., 2005; Garcia et al., 2009; Guillon and Günther, 2002; Horn and von Blanckenburg, 2007; Jeong et al., 1999; Koch et al., 2004; Moses and Farnsworth, 2015). For example, large particles are thought to produce elemental and isotopic fractionation during LA-ICP-MS analysis because they are more likely to be lost during transport of the aerosol to the ICP source due to gravitational settling and inertial deposition, and are more likely to undergo incomplete ionization on the ICP-MS. It should be noted, however, that particles with very small sizes also have lower transport efficiency because of diffusion losses (Garcia et al., 2009). Large particles are often defined as sizes larger than several hundreds of nm, and very small particles generally refer to sizes of a few nm. The exact sizes for the two categories, however, are system specific because the transportability of particles depends on many parameters, such as the carrier gas flow and diameter and length of sample tubing (e.g., Garcia et al., 2009; Jeong et al., 1999). The shapes of particle size distributions for specific minerals produced by ns-laser ablation do not change significantly with fluences, inferred from the experiments that ablated magnetite and pyrite, although size distributions can vary dramatically with substrate mineralogy (Fig. 3). In contrast, fs-laser ablation produced largely similar patterns of particle size distributions for different minerals, with the first peak at \( D_a < 0.056 \) \( \mu m \) and the second peak at \( D_a = 0.1 \) \( \mu m \). There are small differences in the second peak, which can shift towards slightly
larger Da between 0.18 and 0.32 μm, probably in response to fluence during ablation of magnetite as compared to other minerals. When comparing ns- and fs-laser ablation, a higher percentage of the ablated Fe mass tends to reside in particles with larger Da for all Fe minerals ablated by ns-laser, except for magnetite, which yielded similar size distribution patterns to those produced by fs-laser ablation.

The differences in overall patterns of particle size distributions appear to correspond well with particle morphology observed by electron microscopy, although a direct comparison of aerodynamic size, Da, with physical size is difficult. For magnetite, large spheres produced by hydrodynamic sputtering were either absent at low fluence (1 J/cm²) or relatively sparse at higher fluences during ns-laser ablation, so ablation of magnetite yielded very similar patterns in particle size distributions for both ns- and fs-laser ablation. Ablation of pyrrhotite by ns-laser shows more large spheres than those seen for magnetite, indicating more extensive melting associated with ablation of pyrrhotite. Melting of pyrrhotite during ablation by a 193 nm laser has been observed previously (Gilbert et al., 2014). Large particles produced by hydrodynamic sputtering, and potentially higher degree of agglomeration due to longer laser–plume interactions, during ns-laser ablation may have contributed to the significant percentage of Fe mass observed at larger Da (-1 μm) as compared to fs-laser ablation of pyrrhotite. For pyrite, a significant amount of large particles were formed during ns-laser ablation as compared to ablation of other Fe minerals by ns-laser, or to ablation of pyrite by fs-laser, and these large particles may have contributed to the dramatic increase in proportion of Fe mass observed at the Da range between 0.32 and 1 μm for ns-laser ablation. For siderite, ns-laser ablation produced particle sizes and morphologies largely similar to those seen for fs-laser ablation, but considerable production of μm-sized mineral debris, probably through mechanical breakage, may have contributed to the higher proportions of Fe mass observed within the Da range between 0.56 and 3.2 μm (i.e., >20% of the total Fe) as compared to fs-laser ablation (<10% of the total Fe).

4.4. Iron isotope compositions of size-resolved particles

Isotopic fractionation has been observed during LA-ICP-MS analysis of stable isotopes, but its origin remains ambiguous. Horn and von Blanckenburg (2007) precluded isotopic fractionation at the ablation site during fs-laser ablation of Fe sulfides and metal for Fe isotope analysis, and emphasized incomplete ionization of particles on the ICP as the source for isotopic fractionation. Norman et al. (2006), however, concluded that isotopic fractionation occurs at the ablation site rather than on the ICP-MS during ns-laser ablation of olivine for Mg isotope analysis. Jackson and Günther (2003), on the other hand, suggested that isotopic fractionation occurs at both ablation site and on the ICP during ns-laser ablation of copper metal and chalcopyrite for Cu isotope analysis.

Our measurements of Fe isotope compositions of size-sorted particles demonstrate that significant Fe isotope fractionation can occur before sample aerosols reach the ICP-MS during laser ablation by both ns- and fs-laser (Fig. 4). For fs-laser ablation, size-dependent Fe isotope fractionation, based on results using a similar impaction approach and the same suite of samples, has been explained by a condensation model, where Fe isotopes fractionate during condensation of Fe, in competition with other elements, into particles from the cooling plasma plume (d’Abzac et al., 2013). In this model, laser ablation induced Fe isotope fractionation primarily occurs during formation of particles. Light Fe isotopes are preferentially incorporated into small particles that form at an early condensation stage due to kinetic isotope effects, so small particles, including agglomerates of these early-formed particles, have δ56Fe values lower than that of the substrate. Because the plasma plume becomes isotopically heavier in Fe with time owning to formation of isotopically light small particles, the growth of early-formed small particles into larger ones through continued condensation of isotopically heavier Fe from the plume, or through coalescence with later-formed particles from the isotopically enriched plume, leads to a progressive increase in δ56Fe values of particles with increasing sizes. The magnitude of size-dependent Fe isotope fractionation is affected by the Fe condensation timescale, and competitive condensation of other elements that has a higher degree of supersaturation in the multi-element plasma may shorten Fe condensation timescale, resulting in smaller Fe isotope fractionation. This explains negligible size-dependent Fe isotope fractionation during fs-laser ablation of pyrite, where early condensation of sulfur (due to its high abundance) may have partially alleviated ion supersaturation of the plume, and hence delays and shortens Fe condensation. New Fe isotope results from this study also show that δ56Fe values are lower than the substrate in the smallest particles, and become higher than the substrate towards larger particles, a trend consistent with the model described above.

The proposed model predicts that small particles should have δ56Fe values lower than, or similar to, the substrate, and intermediate and large particles should have δ56Fe values higher than the substrate. This trend is consistent with the size-sorted δ56Fe values of siderite ablated by ns-laser, where δ56Fe values are lower than the substrate in small particles, and become higher towards larger ones. This indicates that Fe isotope fractionation during ns-laser ablation of siderite is probably caused by a condensation mechanism similar to that proposed for fs-laser ablation. This is supported by very similar morphologies of spheres and agglomerates observed for ablation of siderite by both ns- and fs-laser. Large particles from ns-laser ablation of siderite are probably produced by mechanical breakage from the substrate, so they show little Fe isotope fractionation and have δ56Fe values similar to the substrate.

The model, however, is inconsistent with the size-dependent Fe isotope fractionations observed during ns-laser ablation of Fe sulfides and magnetite. The smallest particles have δ56Fe values higher than that of the substrate for ns-laser ablation of sulfides and for ablation of magnetite at fluences between 2 and 4 J/cm². For ns-laser ablation of magnetite at 1 J/cm², δ56Fe values of particles are significantly lower than the substrate within the small and intermediate size ranges (Da < 1 μm), and only become slightly higher than the substrate at larger sizes.

Iron isotope fractionation, in principle, may occur through several kinetic processes, including (1) solid state diffusion of light Fe isotopes into the heat-affected areas of the substrate; (2) preferential diffusion of light Fe isotopes from the substrate into the molten layer during laser ablation induced melting; (3) preferential evaporation of light Fe isotopes from the molten layer; (4) preferential evaporation of light Fe isotopes directly from the solid substrate when the molten layer is not well developed; and (5) preferential condensation of light Fe isotopes from the vapor during formation of particles. The particles with Da around ~1 μm produced during ns-laser ablation of sulfides are attributed to hydrodynamic sputtering from the molten layer. The δ56Fe values of particles at this size range are similar to that of the substrate, and this is particularly evident in the case of pyrite, where most of particles within Da between 0.32 and 1 μm are probably produced from sputtering processes during ns-laser ablation. These results suggest that the molten layer largely retains Fe isotope compositions of the substrate either due to small kinetic fractionation factors associated with processes (2) and (3) mentioned above or mass balance of isotopically fractionated material is too small to alter the δ56Fe value of the melt inherited from the bulk substrate. This conclusion also applies to ns-laser ablation of magnetite at high fluences (2–4 J/cm²), where large particles (Da around ~1 μm and above) have δ56Fe values similar to the substrate. Further supporting evidence comes from δ56Fe values of materials collected on the substrate surface (“ejecta blanket”) after ns-laser ablation for several experiments. The ejecta blanket may represent particles with sizes too large to be transported, as well as fluid ejecta sourced directly from the molten layer, and δ56Fe values of these materials are almost identical to the substrate.

Iron isotope fractionations observed at small and intermediate size ranges during ns-laser ablation are probably also caused by condensation
During particle formation, the patterns of size-sorted Fe isotope compositions for ns-laser ablation, however, are distinct from fs-laser ablation. The smallest particles tend to have $\delta^{56}$Fe values lower than the substrate for fs-laser ablation, but particles with $\delta^{56}$Fe values lower than the substrate are found in larger size ranges for ns-laser ablation. This is interpreted to reflect longer laser-plume interaction for the ns-laser ablation, so that low $\delta^{56}$Fe, small particles formed during early nucleation have higher chance to grow into larger ones through coalescence and collision processes, or hard agglomeration. The smallest particles produced during ns-laser ablation may be formed near the end of condensation from the Fe isotopically heavier vapor, and do not have sufficient time to grow or agglomerate before the plasma plume cools. Consequently, these smallest particles have $\delta^{56}$Fe values higher than the substrate.

The only exception is ns-laser ablation of magnetite at 1 J/cm$^2$, where both the smallest and larger particles have $\delta^{56}$Fe values significantly lower than the substrate. Because the morphology was dominated by agglomerates, and large particles (hundreds of nm to several μm) were absent for ns-laser ablation of magnetite at 1 J/cm$^2$, it can be inferred that the molten layer was not well developed during laser ablation. Preferential diffusion of light Fe isotopes into the heat-affected areas of the substrate, which creates an isotopically light area at the site of ablation, or preferential evaporation of light Fe isotopes from the substrate, may have occurred at this low fluence ablation condition, and led to formation of a vapor with a $\delta^{56}$Fe value lower than the bulk substrate. This is supported by mass-balance calculation of size-sorted $\delta^{56}$Fe values that suggest a lower $\delta^{56}$Fe value of the bulk aerosol in this particular case (details in Section 4.5). Formation of particles from this pre-fractionated vapor, therefore, causes $\delta^{56}$Fe values of particles with small and intermediate sizes to be significantly lower than the substrate.

4.5. Sampling stoichiometry of Fe isotopes for ns- and fs-laser ablation

Whether laser ablation can provide stoichiometric aerosols that match chemical compositions of the substrate is a fundamental concern for accurate LA-ICP-MS analysis. Sampling stoichiometry has been assessed by the impaction method for elemental compositions for both ns- and fs-laser ablation (Koch et al., 2004; Kühn and Günther, 2004), and for Fe isotope compositions during fs-laser ablation of Fe minerals (d’Abzac et al., 2013, 2014), but an impactor method has never been used to rigorously evaluate sampling stoichiometry of stable isotope compositions for ns-laser ablation. Isotope mass balance can be calculated based on size-resolved data and Eq. (1):

$$\delta^{56}\text{Fe}_{\text{mass}} = \sum_{i} f_{i} \times \delta^{56}\text{Fe}_{i}$$

where $f_{i}$ represents the fraction of Fe collected by the MOUDI, and $\delta^{56}\text{Fe}_{i}$ represents Fe isotope composition of the corresponding Fe fraction, and $\delta^{56}\text{Fe}_{\text{mass}}$ represents the calculated bulk Fe isotope composition of total aerosols collected by the MOUDI.

Results of mass balance calculations based on new data of size-sorted particles from fs-laser ablation experiments in this study, as well as those from previous studies (d’Abzac et al., 2013, 2014), demonstrate that fs-laser provides stoichiometric sampling for Fe isotopes analysis during ablation of Fe minerals under all conditions tested in these studies, regardless of the substrate mineralogy, laser fluence and wavelength (Fig. 6).

Mass-balance calculations from ns-laser ablation experiments show that the $\delta^{56}$Fe value of total particles collected agrees within analytical uncertainty (~0.2‰) with that of the substrate ablated in nearly all experiments (Fig. 6), suggesting stoichiometric sampling of substrate for Fe isotopes for the total aerosol produced by ns-laser ablation. Non-stoichiometric sampling, however, occurs during ns-laser ablation of magnetite at a low fluence of ~1 J/cm$^2$, where the calculated $\delta^{56}$Fe value of total particles was ~0.8‰ lower than that of the substrate. Significant isotopic fractionation has also been found previously during ns-laser ablation of chalcopyrite and Cu metal at low fluence for stable Cu isotope analysis (Jackson and Günther, 2003), consistent with our findings.

Loss of large particles, either through direct deposition on the substrate surface or transport loss during MOUDI collection, can hardly explain the observed non-stoichiometric sampling of Fe isotope compositions for magnetite at low fluence, although only large particles ($D_{p} > 1.8$ μm) have $\delta^{56}$Fe values higher than the substrate for the ns-laser ablation experiment on magnetite at 1 J/cm$^2$ (Fig. 4), and thus have the potential to balance the total aerosol that has a $\delta^{56}$Fe value significantly lower than the substrate. Firstly, assuming that the missing particles have the same $\delta^{56}$Fe value as that measured in particles with $D_{p} > 1.8$ μm, mass-balance calculations predict that the Fe mass of missing particles needs to be an unrealistic number, ~4.5 times of the Fe masses collected, to result in a stoichiometric sampling of Fe isotopes. Secondly, comparison between the total Fe mass collected on the MOUDI and that estimated by the removal volume (i.e., measured by white light interferometry) and mineral density suggests collection efficiency of 83%, which is comparable to the collection efficiency for other aerosol collection experiments conducted on magnetite using ns-laser ablation at higher fluences (Supplementary Material Table S2). This indicates that significant material that remained on the substrate surface or was not collected by the MOUDI is unlikely. Assuming that the missing material of 17% of the total Fe ablated was large particles that had the same $\delta^{56}$Fe value as the substrate (due to hydrodynamically sputtering), re-calculation of isotope mass balance for this experiment still shows an ~0.6% deviation in $\delta^{56}$Fe values from that of the substrate.

The exact origin of non-stoichiometric sampling of Fe isotope compositions of magnetite by ns-laser ablation at low fluence remains unclear, but, as discussed in the previous section, this non-stoichiometric effect is likely to be caused by diffusion of light Fe isotopes into the heat-affected zone of the substrate, creating areas with lower $\delta^{56}$Fe values for the ablation, or by preferential evaporation of light Fe isotope either directly from the solid substrate surface or from the underdeveloped molten layer.

Recent work has shown that low fluence does not always compromise precision and accuracy of stable isotope analysis by LA-ICP-MS. Analysis of Cu isotopes for a wide range of Cu metals and natural samples using fs-laser were achieved at low-fluence ablation (Lazarov and Horn, 2015), opposite to what can be expected based on our results from ns-laser ablation. This suggests that the optimization of laser conditions for in situ stable isotope analysis may follow dramatically different paths in practice for ns- and fs-laser. In addition, removal of large particles by filtration has been suggested in some previous studies to...
avoid isotopic fractionation caused by incomplete ionization of large particles on the ICP-MS (e.g., Jackson and Günther, 2003). Our results of Fe isotope compositions of size-sorted particles produced by ns- and fs-laser ablation, however, demonstrate that large particles may have fractionated $^{56}\text{Fe}$ values relative to the substrate, and removal of these large particles by filtration may result in non-stoichiometric sampling of the substrate.

5. Conclusions

Particle morphologies, sizes, and size-resolved Fe isotope compositions were compared for ns- and fs-laser ablation of different Fe minerals. Spheres and soft-bonded agglomerates are two primary morphologies observed in particles produced by fs-laser ablation, and are thought to be formed through a condensation–collision process. These features are largely independent of the substrate mineralogy, probably resulting from the non-thermal ablation mechanisms associated with fs-laser ablation. During ns-laser ablation, large spheres with diameters of several hundred nm to several μm are probably produced by hydrodynamic sputtering, and agglomerates are typically hard-bonded. Mechanical removal is important for ns-laser ablation of siderite, although it may also occur during fs-laser ablation of siderite. Compared to fs-laser ablation, the higher dependence of particle morphology on the substrate mineralogy and fluences for ns-laser may result from the thermal nature associated with ns-laser ablation. Particles produced by laser ablation were aerodynamically sorted by a cascade impactor–MOUDI. Particle size distributions of fs-laser ablation show largely similar patterns for all Fe minerals ablated, although minor changes were found during ablation of magnetite in response to different fluences. In contrast, particle size distributions vary dramatically with the substrate mineralogy during ns-laser ablation, and often a higher proportion of the ablated Fe mass resides in particles with larger Dm, as compared to fs-laser ablation (i.e., pyrite, pyrrhotite and siderite). Substrate-dependent particle size distributions and production of large particles that contain a significant proportion of ablated Fe mass during ns-laser ablation can be adverse for LA-ICP-MS analysis.

Variable extent of size-dependent Fe isotope fractionation was observed for both ns- and fs-laser ablation. The magnitude of Fe isotope fractionation is substrate- and fluence-dependent for both lasers. Iron isotope fractionation during fs-laser ablation has been explained by a condensation model that incorporates competitive Fe condensation from a multi-element system within a laser-induced plasma (d’Abzac et al., 2013). In contrast, isotopic fractionation during ns-laser ablation is more variable and difficult to explain by a single mechanism. Size-sorted Fe isotope data suggest that the molten layer formed during ns-laser ablation largely retains Fe isotope compositions of the substrate, and Fe isotope fractionation probably mostly occurs during particle formation processes.

Mass-balance calculations suggest that fs-laser ablation offers stoichiometric sampling of the substrate for Fe isotope analysis under all conditions tested in this study and previous studies (d’Abzac et al., 2013, 2014), regardless of mineralogy, laser fluence, and wavelength. In contrast, ns-laser ablation does not provide stoichiometric aerosols in some cases, particularly ablation of magnetite at low fluence ablation (1 J/cm²). Complications exist in ns-laser ablation with production of large particles that contain significant percentages of ablated Fe mass, variable particle size distributions, and laser ablation-induced isotopic fractionation. On the other hand, fs-laser provides more consistent ablation that is less dependent on substrate properties or laser conditions, resulting in largely similar particle-size distributions, relatively predictable size-dependent Fe isotope fractionations, and constant stoichiometric sampling of semi-conductive samples for Fe isotope analysis. Size-dependent Fe isotope fractionations observed for both ns- and fs-laser ablation highlight the importance of quantitative transport of laser-induced particles to the ICP-MS for accurate Fe isotope analysis by LA-ICP-MS.

In terms of general implications of this study for LA-MC-ICP-MS analysis of metal and metalloid stable isotopes in semi-conductive samples of geological importance, such as various Fe minerals studied here, this study demonstrates that fs-laser is superior to ns-laser, because fs-laser provides largely uniform particle size distributions, and stoichiometric sampling, regardless of sample properties and laser conditions. In contrast, ns-laser can provide stoichiometric sampling under appropriate conditions, validating the possibility of using ns-laser for in-situ stable isotope analysis. High accuracy and precision for such analysis, however, are inherently more challenging to achieve for ns-laser, because substrate- and fluence-dependent ns-laser ablation leads to variable particle size distributions for samples with different thermal properties, and possible non-stoichiometric sampling during ablation. Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.chemgeo.2016.12.038.

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References
