Iron Distribution in Size-Resolved Aerosols Generated by UV-Femtosecond Laser Ablation: Influence of Cell Geometry and Implications for In Situ Isotopic Determination by LA-MC-ICP-MS

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The influence of ablation cell geometry (Frames single- and HelEx two-volume cells) and laser wavelength (198 and 266 nm) on aerosols produced by femtosecond laser ablation (fs-LA) were evaluated. Morphologies, iron mass distribution (IMD) and $^{56}$Fe/$^{54}$Fe ratios of particles generated from magnetite, pyrite, haematite and siderite were studied. The following two morphologies were identified: spherules (10–200 nm) and agglomerates (5–10 nm). Similarity in IMD and ablation rate at 198 and 266 nm indicates similar ablation mechanisms. $^{56}$Fe/$^{54}$Fe ratios increased with aerodynamic particle size as a result of kinetic fractionation during laser plasma plume expansion, cooling and aerosol condensation. The HelEx cell produces smaller particles with a larger range of $^{56}$Fe/$^{54}$Fe ratios (1.85%) than particles from the Frames cell (1.16%), but the bulk aerosol matches the bulk substrate for both cells, demonstrating stoichiometric fs-LA sampling. IMD differences are the result of faster wash out of the HelEx cell allowing less time for agglomeration of small, low-δ $^{56}$Fe particles with larger, high-δ $^{56}$Fe particles in the cell. Even with a shorter ablation time, half the total Fe ion intensity, and half the ablation volume, the HelEx cell produced Fe isotope determinations for magnetite that were as precise as the Frames cell, even when the latter included an aerosol-homogenising mixing chamber. The HelEx cell delivered a more constant stream of small particles to the ICP, producing a more stable Fe ion signal (0.7% vs. 1.5% RSE for $^{56}$Fe in a forty-cycle single analysis), constant instrumental mass bias and thus a more precise measurement.

Les influences de la géométrie de la cellule d’ablation (cellule «Frames» et deux volume «HelEx») et de la longueur d’onde laser (198 et 266 nm) sur les aérosols produits par ablation laser femtoseconde (fs-LA) ont été évaluées. La morphologie, la distribution en masse de fer (IMD) et les rapports $^{56}$Fe/$^{54}$Fe des particules générées à partir de magnétite, pyrite, hématite et sidérite ont été étudiées. Deux morphologies sont identifiées : sphères (10–200 nm) et agglomérats (5–10 nm). Les similarités entre IMD et taux d’ablation à 198 et 266 nm suggèrent des mécanismes d’ablation inchangés. Le rapport $^{56}$Fe/$^{54}$Fe augmente avec le diamètre aérodynamique des particules en réponse à un fractionnement cinétique au cours de l’expansion du plasma induit, du refroidissement et de la condensation de l’aérosol. La cellule HelEx produit des particules fines qui montrent une plus grande variation du rapport $^{56}$Fe/$^{54}$Fe (1.85%) que les particules formées à partir de la cellule Frames (1.16%), mais la composition totale est identique à celle du substrat pour les deux cellules, démontrant un échantillonnage stoïchiométrique. Les différences d’IMD résultent d’une extraction plus rapide avec la cellule HelEx, laissant moins de temps pour l’agglomération de petits particules ($^{56}$Fe faible) avec de plus larges (δ$^{56}$Fe haut) dans la cellule. Même avec une durée d’ablation plus courte, une intensité de signal moindre, et un volume ablaté deux fois plus petit, la cellule HelEx produit des analyses isotopiques du fer dans la magnétite aussi précises qu’avec la cellule Frames, même si cette dernière est équipée d’un système d’homogénéisation des aérosols. La cellule HelEx produit un flux plus constant de particules plus petites vers l’ICP, induisant un signal plus stable sur le fer (0.7% contre 1.5% RSE sur $^{56}$Fe au cours...
Keywords: femtosecond laser ablation, aerosols, isotopes, agglomeration, residence time.

Received 18 Aug 13 – Accepted 26 Apr 14

Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) has been an in situ analytical technique used successfully for the analysis of geological specimens for more than three decades (Gray 1985, Arrowsmith 1987, Niemax 2001, Günther and Hattendorf 2005, Koch and Günther 2011). Increasingly, LA-ICP-MS is being utilised for isotope ratio determination (Hirata and Ohno 2001, Woodhead et al. 2004, Horn et al. 2006a,b, Chmeleff et al. 2008, Shaheen and Fryer 2010, Yang et al. 2010, Fisher et al. 2011, Pettke et al. 2012). Although high-precision isotope ratio determinations can be achieved for nanosecond (ns) lasers (Fisher et al. 2011, Pettke et al. 2012 Beltran-Trivino et al. 2013), overall head-to-head comparisons of ns and fs LA systems show that fs-LA produces more stable ion signals (Poitrasson et al. 2003, Mozana et al. 2006, Gonzalez et al. 2007a, b, Perdian et al. 2008, Shaheen et al. 2013), and much less dependency on optical and thermal absorption for all types of substrates compared with ps/ns-LA (Gonzalez et al. 2002, Laville et al. 2002, Guillong et al. 2003, Beke et al. 2010). These differences are a result of distinct laser/matter interactions and ablation mechanisms with the incident photon beam. These interactions are thermally driven in the nanosecond regime, whereas femtosecond pulses are shorter than any thermal or physical response from the target (Lorazo et al. 2003), leading to photo mechanical ablation that is free of thermal effects for the substrate (von der Linde and Sokolowski-Tinten 2000, Seydoux-Guillaume et al. 2010). These properties result in negligible residual thermal traces (Perez and Lewis 2003, Ben-Yakar et al. 2007, Seydoux-Guillaume et al. 2010, d’Abzac et al. 2012a, b, Shaheen et al. 2013). This interpretation is confirmed by consistency in morphologies and particle size distributions of the aerosol particles over a wide range of materials when using femtosecond pulses. In contrast, nanosecond ablation tends to produce generally larger particles, including a substantial amount of melt ejection product, especially if the substrate is a semiconductor or conductor (Koch et al. 2004, Liu et al. 2004, Gonzalez et al. 2007a, b, Shaheen et al. 2013).

The differences in the response of substrates that are conductors or semiconductors to ns- and fs-pulsewidth lasers has made fs-LA a natural choice for Fe isotope determinations in iron oxides, iron sulfides, iron carbonates and metals (Hirata and Ohno 2001, Horn et al. 2006a, b, Steinhoefel et al. 2009, Nishizawa et al. 2010, Yoshiya et al. 2012, Czaja et al. 2013, Dzirny et al. 2013, Li et al. 2013); attainment of comparable data using ns-LA has proven to be analytically challenging (Kosler et al. 2005a, b, Kosler et al. 2006, Horn et al. 2006a, b). To better address how to produce the most precise and accurate Fe isotope determination by fs-LA at the highest spatial resolution we report LA-generated aerosol properties, including their morphology, aerodynamic size and the Fe isotope composition of size-sorted particles. These parameters directly affect ion signal stability (d’Abzac et al. 2011), where poor control of these parameters can result in poor precision, a decrease in spatial resolution and induce issues in transport of the aerosol from the ablation cell to the ICP torch that compromise precision and accuracy.

Several approaches have been proposed for optimisation of aerosol generation and transport. Shortening transport distances is the simplest solution to reduce losses and gain signal intensity (d’Abzac et al. 2011). Using He as the carrier gas helps to produce finer aerosols and less thermal residue on the sample surface, due to its low viscosity and high thermal conductivity, compared with Ar (Horn and Günther 2003). Overall, investigations of the transport of the ablated material from the cell to the ICP torch show that the aerosol transport is generally efficient to over 80% (Garcia et al. 2007) unless the overall tubing length is greater than 4 m (d’Abzac et al. 2011). However, heterogeneous aerosol fluxes can be produced by creation of complex aerosol flow patterns within the transport tubing if gas velocities are not optimised (Koch et al. 2008), if tubing of multiple diameters is used, or if additional tube connections are used (Auteque et al. 2008).

In contrast, numerous studies have shown that ablation cell design is a critical parameter that directly influences the wash-out time of a cell (Garcia et al. 2007, Gurevich and Hergenröder 2007, Lindner et al. 2009). A cell wash-out time is generally defined as the time it takes for the ion signal to drop to ~ 99% of the ion intensity after the laser has stopped firing (Asogan et al. 2011). Common cell designs include cylindrical-, hexagonal- or droplet-shaped cells. These shapes are used because of their simple geometry,
which makes them easy to build, and their often large volume allows one to load several samples at a time. The wash-out time in these cells is usually longer than 1 s. It can be shortened by using a smaller cell but this limits sample capacity. In addition to cell shape, numerical simulations have shown that gas flow patterns within a cell can change as a function of gas velocity entering the ablation cell. For example, if the gas flow is insufficient in a cylindrical cell, aerosol flux can form vortices, whereas at higher gas velocities the aerosol stream may be more homogenised, but undesirable effects such as unstable signals, high gas consumption and cell overpressure can be produced (Koch et al. 2008). Recognition of these issues in the extraction of the aerosol from the cell highlights that establishing the best gas flow conditions in the cell is an important tuning parameter for LA analyses and has lead to a number of proposed designs to make aerosol extraction from the cell as efficient as possible (Pisonero et al. 2006, Hirata 2007, Autrique et al. 2008, Muller et al. 2009, Fricker et al. 2011). Among these, the two-volume geometry (Eggins et al. 2005, Muller et al. 2009) provides a large volume that houses several samples, and a smaller inner cell wherein LA-generated particles are confined. Gas flows from the top and the bottom of the inner cell allow for efficient and fast extraction of particles. Wash-out times are in this case shorter than 1 s.

The present study characterises the aerosol produced by fs-LA using two different laser wavelengths (198 nm and 266 nm) and two cells of different design: a single volume and a two-volume cell, in order to better understand the impact of short ultraviolet wavelength and cell geometry on precision of Fe isotope ratio analyses that preserve naturally occurring, mass-dependent variations. For this purpose, we collected the aerosols produced by fs-LA of Fe-bearing minerals to determine their iron mass distribution, to evaluate whether the ablation mechanism is isotopically stoichiometric, and if there is a correlation between Fe isotope composition and the aerodynamic size of the aerosols. We use these fundamental studies of the aerosols extracted from the two different ablation cells to evaluate our observation that it is possible to determine Fe isotope ratios by the ablation of magnetite to the same precision, in less time and consuming half of the volume of material if the HelEx cell is used (Li et al. 2013), compared with the Frames cell (Czaja et al. 2013) using the same laser and mass spectrometer.

**Experimental methods**

**Laser systems and ablation cells**

Two laser configurations were used, both distributed by Photon Machines (San Diego, CA, USA). The first system used a flash lamp-based Nd:YAG pumped Ti:sapphire femtosecond source and a chirped pulse amplification device with a fourth harmonic generator to produce a UV beam with \( \lambda = 198 \) nm and a pulse width of \( \approx 1.50 \) fs, where the repetition rate was adjustable from 1 to 10 Hz. The second system used a diode-based Nd:YLF-pumped Ti:sapphire femtosecond source and a chirped pulse amplification device with a third harmonic generator to produce a UV beam with \( \lambda = 266 \) nm and a pulse width of \( \approx 150 \) fs, with a repetition rate adjustable between 1 to 250 Hz. The laser beam delivery system from the harmonic generator to the sample for both lasers was the same (see Appendix S1). Two laser ablation cells manufactured by Photon Machines were studied. The ‘Frames’ cell, used for tests at \( \lambda = 198 \) nm and 266 nm, is a droplet-shaped, single-volume design (~ 20 cm\(^3\)) that is intended to provide laminar-flow conditions over the entire sample substrate and has a characteristic aerosol wash-out time of 2 s (1% of ion intensity). The ‘HelEx’ cell was used with the 266 nm laser and is a two-volume cell, wherein samples are contained in a large volume (~ 900 cm\(^3\)) under Helium atmosphere at \( \approx 10^{-2} \) Pa, and ablation takes place within a small inner volume cell (~ 7 cm\(^3\); Shuttleworth 2012) that has a secondary He gas flow directed in a spiral downward onto the substrate. The dual He flow from the bottom and top of the inner volume rapidly extracts the aerosol from the small inner volume. The HelEx has a characteristic wash-out time of < 0.7 s (1% of ion intensity).

**Aerosol collection**

Aerosol collection methods for the two cells were done to make the collection as similar as possible to allow one to evaluate the physical characteristics of the aerosols as a function of ablation cell properties. The tubing length from the cell outlet to the aerosol collection apparatus was the same (~ 0.5 m). Additionally, the He gas flow conditions into the cell for aerosol extraction are based on values that are typically used for producing stable ion signal by ICP analysis. Aerosol particles generated by fs-LA of natural magnetite, haematite, siderite and pyrite were aerodynamically size sorted using a Micro Orifice Uniform Diameter Impactor (MOUDI; Marple et al. 1991). The MOUDI consists of twelve juxtaposed stages mounted together as a hermetically closed cylinder: the ‘inlet’, ten consecutive plates, and the ‘after filter’ stage. The size sorting is passively achieved by pressure differences between the successive stages, from the top to the bottom of the column, which affect the velocities of particles, where impacts on each stage occur according to particle kinetic energy. Consequently, the particles with the largest aerodynamic diameters are impacted on the first (top) stages, and the smallest aerodynamic diameters on the
between Ar and N2. Pressure differences between the stages in apparatus settings or observed results were noticed before the impactor inlet. No difference either filtered through a 0.2-
m HEPA filter and added using a 1“ connector before the impactor inlet. No difference either in apparatus settings or observed results were noticed between Ar and N2. Pressure differences between the stages were continuously monitored using a magnetelic gauge to ensure that the cascade impactor operated with the correct (30 l min⁻¹) total gas flow.

Aerosols were impacted on filters to determine the relative size distribution and Fe isotopic composition of different sized particles (Teflon filter collection) and to evaluate their morphology and size by scanning electron microscopy (SEM; Polycarbonate filter collection). A total of nineteen experiments were conducted (Table 1). Some of these experiments, marked with an asterisk in Table 1, are also used in d’Abzac et al. (2013) to discuss Fe isotopic fractionation during particle generation. Particles were generated by ablating rectangular areas of several 10⁴ mm² (raster mode) using a laser beam with a diameter of 12 µm on the sample surface, with a maximum of four passes in order to collect enough iron with a constant aerosol flux. Rastering was accomplished by using a computer-controlled stage to move substrate mineral grains embedded in epoxy and polished to within 0.05 µm. Parameters such as laser fluence and repetition rate were varied during the first seven experiments (Table 1) in order to evaluate how these parameters affected the aerodynamic size of the fs-LA-generated aerosols. We also evaluated the influence of laser wavelength using similar fluence and laser repetition rates. The bulk of the aerosol collection was done using a 25 Hz repetition rate, a raster speed of 2 µm s⁻¹, and a fluence of ~ 0.9 J cm⁻² which is the fluence used for fs-LA Fe isotope determination. These same parameters were used to evaluate how the mineral substrate may affect the produced aerosol.

**Scanning electron microscopy**

The morphology of particles produced by fs-LA has been evaluated using microscopic methods by a number of workers using a wide variety of lasers, ablation cells and collection methods (Liu et al. 2004, Gonzalez et al. 2007a, b, Glaus et al. 2010, d’Abzac et al. 2012a, b). These workers all report similar findings: particles generated by fs-LA consist of small (< 1 µm diameter) spherules and complex-shaped agglomerates composed of spheres that are ~ 5–10 nm in diameter. Thus, we have limited our impactor studies to using aerosols collected from ablation experiments done in the HelEx cell. Particles collected on polycarbonate substrates from ablation of siderite, pyrite and magnetite were studied at the Material Sciences Center at the University of Wisconsin, Madison. We used a Scanning Electron Microscope (LEO 1530; Zeiss-Leica, Switzerland/Germany) equipped with a field-emission gun (FEG) operated at 3 keV with a resolution of ~ 3 nm.

**Iron mass distribution analysis**

The iron mass distribution (IMD) as a function of aerodynamic size was determined by measuring the Fe content on each MOUDI filter stage. For short-duration experiments, in which less than ~ 10 µg of Fe were collected, the Fe content of each MOUDI stage was measured using isotope dilution mass spectrometry (IDMS) using an enriched ⁵⁷Fe tracer (see Appendix S1). In contrast, for longer duration experiments, in which the goal was to also measure the Fe isotopic composition of the different sized aerosols, the Fe content was determined colorimetrically using the Ferrazine method (Stockey 1970). For both methods, the Fe from each Teflon filter was dissolved by placing the filter in a 60 ml Savillex jar, followed by addition of mineral acid and then capping and heating the jar on a hot plate at ~ 175 °C for 12 hr. For IDMS, 7 mol l⁻¹ HNO₃ with a dissolved ⁵⁷Fe tracer it was used. For the Ferrazine analysis, 7 mol l⁻¹ HCl was used to dissolve the Fe particles.
Table 1.
Compilation of aerosol size sorting experiments conducted during this study

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<th>Experiment</th>
<th>11/03/08</th>
<th>11/02/25</th>
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<th>11/04/18</th>
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<th>12/06/08</th>
<th>12/06/25*</th>
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<td>Min (mM)</td>
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<td>Wavelength (mm)</td>
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<td>Fluence (J cm⁻²)</td>
<td>2.0 2.0 1.9 1.0 1.0 1.7 0.9 0.9 0.9 0.9 0.9 0.9 0.9 0.9 0.9 0.9</td>
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<td>Fe normalised (pg per shot)</td>
<td>68 53 54 24 24 97 20 26 17 12 13 17 23 13 – – 14 7</td>
<td>68 53 54 24 24 97 20 26 17 12 13 17 23 13 – – 14 7</td>
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<td>Duration (s)</td>
<td>31 7.5 125 19.5 46 4.5 3 3 3 3 3 3 3 3 3 27 34</td>
<td>31 7.5 125 19.5 46 4.5 3 3 3 3 3 3 3 3 3 27 34</td>
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<td>Impactor</td>
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Impactor stage | Size class (μm) | Fe mass (μg) |
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<td>Alk</td>
<td>&lt; 0.056</td>
<td>425 0.20 0.92 0.52 1.78 0.00 0.33 0.08 0.39 1.01 1.48 6.64 13.50 7.24</td>
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<td>10</td>
<td>0.056–0.1</td>
<td>244 0.29 0.85 0.68 1.36 0.20 0.14 0.14 0.17 0.36 1.15 2.42 5.29 2.27</td>
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<td>9</td>
<td>0.1–0.18</td>
<td>1481 1.84 66.2 4.34 12.92 2.06 1.28 1.29 1.37 3.79 12.15 16.47 18.69 10.08</td>
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<td>8</td>
<td>0.18–0.32</td>
<td>1273 2.66 770 5.52 13.15 3.02 1.84 1.61 1.22 6.82 6.07 3.07 6.17 5.07</td>
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<tr>
<td>7</td>
<td>0.32–0.56</td>
<td>561 1.20 3.45 2.00 5.94 1.17 0.81 0.52 0.45 1.62 1.97 1.18 2.80 2.87</td>
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<td>6</td>
<td>0.56–1</td>
<td>193 0.40 1.35 0.65 1.84 0.53 0.23 0.24 0.10 0.76 0.45 0.53 1.65 0.60</td>
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<td>5</td>
<td>1–1.8</td>
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<td>1.8–3.2</td>
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<td>3.2–5.6</td>
<td>0.25 0.06 0.21 0.11 0.26 0.06 0.05 0.04 0.08 0.10 0.82 0.32 0.71 0.24</td>
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<td>2</td>
<td>5.6–10</td>
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<td>1</td>
<td>10–18</td>
<td>0.14 0.03 0.08 0.11 0.09 0.06 0.10 0.05 0.12 1.09 0.00 0.00 0.00 0.00</td>
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<td>Vent</td>
<td>&gt; 18</td>
<td>0.14 0.00 0.08 0.11 0.09 0.07 0.27 0.07 0.27 0.19 0.19 0.00 0.00 0.00 0.00</td>
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<tr>
<td>Total (μg)</td>
<td>4411 7.09 24.38 16.57 40.04 7.83 5.30 4.64 4.61 17.95 24.54 32.01 51.43 30.34 23.90 21.35</td>
<td>23.90 21.35</td>
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because these samples were also purified by ion-exchange chromatography for Fe isotope determination (see below).

**Iron isotopes ratio determination by solution nebulisation**

Size-sorted aerosol samples for complete Fe isotope determination were dissolved in 7 mol L\(^{-1}\) HCl. Following dissolution, each sample was evaporated on a hot plate, and re-dissolved in 0.5 mol L\(^{-1}\) HCl, from which a small aliquot was taken for the determination of total Fe content using Ferrozine and hydroxylamine hydrochloride. The remainder of the fraction was loaded onto AG 1X4 anion-exchange resin to separate Fe from other cations using conventional wet-chemistry methods, following those reported in Beard et al. (2003). The accuracy of Fe isotopes analyses for these low-level samples was evaluated by preparing test solutions that contained between 0.5 to 10 \(\mu\)g of Fe from a standard solution that had been previously measured for its Fe isotope composition by conventional methods; this solution was spiked with other elements to mimic the elemental composition of the mineral substrates. These test solutions were processed through the entire wet chemistry analytical procedure in the same fashion as unknown samples to evaluate possible matrix effects (see Appendix S1). Following anion exchange purification, samples and test solutions were analysed using conventional solution nebulisation techniques on a Micromass Isoprobe at the University of Wisconsin, Madison, following the methods of Beard et al. (2003), at a concentration of 0.6 \(\mu\)g ml\(^{-1}\) using a self-aspirating, concentric-flow nebuliser with an uptake rate of 50 \(\mu\)l min\(^{-1}\) and a desolvation unit (Cetac Andus II). Acquisitions included one minute integration for blank acid subtraction, followed by forty integrations of 10 s cycles of the analyte. Iron isotope compositions are expressed as \(\delta\) values in units of per mil (‰):

\[
\delta^{56}\text{Fe} = \frac{^{56}\text{Fe} / ^{54}\text{Fe}_{\text{sample}}}{^{56}\text{Fe} / ^{54}\text{Fe}_{\text{IgRxs}}} - 1 \times 10^3 \tag{1}
\]

\[
\delta^{57}\text{Fe} = \frac{^{57}\text{Fe} / ^{54}\text{Fe}_{\text{sample}}}{^{57}\text{Fe} / ^{54}\text{Fe}_{\text{IgRxs}}} - 1 \times 10^3 \tag{2}
\]

\[
\delta^{57/56}\text{Fe} = \frac{^{57}\text{Fe} / ^{56}\text{Fe}_{\text{sample}}}{^{57}\text{Fe} / ^{56}\text{Fe}_{\text{IgRxs}}} - 1 \times 10^3 \tag{3}
\]

During the course of this study, the IRMM-014 reference material yielded an average \(\delta^{56}\text{Fe} = -0.08 \pm 0.10\%\) (2\(s\), \(n = 36\)) relative to igneous rocks (Beard and Johnson 1999), a value that has remained unchanged since our initial report in Beard et al. (2003). Replicate analyses of our in-house reference materials J-M Fe and HPS Fe yielded \(\delta^{56}\text{Fe} = 0.25 \pm 0.10\%\) (2\(s\), \(n = 48\)) and \(\delta^{56}\text{Fe} = 0.48 \pm 0.10\%\) (2\(s\), \(n = 69\)), respectively. The test solutions made of pure Fe with no other matrix elements yielded results accurate to 0.16\% (2\(s\)). In contrast, Fe solutions that mimicked the chemical composition of the natural minerals or the dissolved minerals themselves were accurate if 2 \(\mu\)g or more Fe were processed through the ion-exchange columns (Figure SA1). Smaller aliquots were inaccurate by up to 0.48\% (Figure SA1). We suspect that inaccuracies for Fe masses < 2 \(\mu\)g are a result of matrix effects caused by the presence of trace quantities of other cations (e.g., Albarède and Beard 2004), because the pure Fe solutions do not display accuracy issues (Figure SA1).

Based on the results of the test solutions, only Fe isotope determinations by wet chemistry of samples that are greater than 2 \(\mu\)g of Fe in size are considered accurate. Thus, we combined a sequence of MOUDI stages to make composite samples that were greater than 2 \(\mu\)g of Fe to achieve accurate Fe isotope compositions. Based on replicate analyses of our test solutions, the precision of our wet chemistry Fe isotope analyses was estimated to be \(\pm 0.15\%\) (2\(s\)) for samples with 2–5 \(\mu\)g of Fe and \(\pm 0.10\%\) (2\(s\)) for samples with more than 5 \(\mu\)g of Fe, and these uncertainties are used for discussion of the Fe isotope compositions measured on the aerodynamic size-sorted particles.

**Magnetite Fe isotope determination by fs-LA**

Femtosecond-LA-MC-ICP-MS analyses of magnetite reference materials presented in this study were conducted during campaigns to measure the Fe isotope composition of magnetite from banded iron formations that were published recently by Czaja et al. (2013) and Li et al. (2013). These data sets are relevant to the present discussion because they represent a large number of Fe isotope analyses acquired over the course of several months, under routine conditions, and at the same time period during which the aerosol particle studies were performed. We emphasise that for the entire data set of Li et al. (2013), and a large portion of the data set of Czaja et al. (2013), the same 266 nm femtosecond pulse width laser was used. Moreover, for both studies, the same mass spectrometer was used (Micromass Isoprobe), and it was operated under the same conditions for both studies (Table SA1). For the purposes of this discussion, we only consider magnetite analyses reported by Czaja et al. (2013) that used the 266 nm laser with the analytical details reported in Table SA1, which represents sixty-one analyses of reference material mineral grains.
The major difference between these studies is that for that which used the Frames cell (Czaja et al. 2013), the analysis was longer (sixty integrations of 5 s) and was done at a higher $^{56}$Fe ion current ($15 \times 10^{-11} - 21 \times 10^{-11} \text{ A}$ using a $10^{10} \Omega$ resistor) compared with the study of Li et al. (2013), which used the HelEx cell (forty integrations of 5 s) with a $^{56}$Fe ion current of $7.3 \times 10^{-11} - 14.3 \times 10^{-11} \text{ A}$ (using the same resistor). Interestingly, both studies produced the same in-run statistics defined as the 2 standard error (2SE), which was calculated as the standard deviation (2s) from a single analysis normalised by the square root of the number of accepted ratios. The same error minimisation routine was used for all the analyses (Micromass IsoLynx software error minimisation algorithm, with rejection level set to 15% of the total number of cycles, based on one standard deviation of the mean for each analysis). The differences in ion intensity reflect the fact that for the Frames cell the laser repetition rate was 10 Hz whereas it was 5 Hz for the HelEx cell. The other significant difference between the data collected with the Frames cell from that of the HelEx was that a mixing chamber was placed before the ICP in order to homogenise the aerosol flux. Without the mixing chamber, it was difficult to obtain the same level of measurement repeatability for a Fe isotope ratio determination compared with an analysis performed without the mixing chamber. We also note that the reproducibility for both data sets was the same, where the reproducibility is defined as 2 standard deviation (2s) of the mean for multiple analyses of a reference material mineral grain that is considered isotopically homogeneous. Reference materials were considered to be isotopically homogeneous if conventional solution nebulisation Fe isotope determination (wet chemistry methods) of multiple single grains of the magnetite reference material yielded the same reproducibility as our analyses of Fe reference solutions such as IRMM-014.

Differences in the repetition rate and analysis time led to ablation of different volumes of material. For the HelEx cell, a total calculated volume of $\sim 8640 \mu\text{m}^3$ was ablated. For the Frames cell, a total volume of $\sim 18000 \mu\text{m}^3$ was ablated. These volumes are based on the areal extent of ablated material as measured using scanning electron microscopy. The depth was determined based on white-light interferometry imaging (see Appendix S1 for details).

**Results**

**Particle morphologies**

The size-sorted particles displayed only two morphological types for all the studied minerals (Figure 1): spherules that ranged in diameter from 10 nm (after filter impactor stage) up to 200 nm (impactor stage 6–7) and agglomerates that were composed of $\sim 5–10$ nm particles of variable shape and had long dimensions ranging from $\sim 50$ nm (after filter stage) to several micrometres (inlet through impactor stage 6).
The agglomerates sometimes contain spherules (Figure 1, see also d’Abzac et al. 2013), suggesting that agglomeration occurred before impact on the substrate. Agglomerate size is difficult to determine because most of the agglomerates are observed as accumulations of particles on the substrates (impactor stages 7 to after filter), making it difficult to evaluate whether some particles agglomerated or broke apart during impact. Sizes given here are estimated from isolated bodies that were imaged and do not contain evidence of breaking or accumulation.

Iron mass distribution

Iron mass distribution (IMD) graphs of the relative masses of Fe as a function of aerodynamic size are plotted in Figure 2 and numerical data are available in Table 1. In Figure 2a, the IMD of particles from fs-LA of magnetite in the Frames cell under different fluences and repetition rates are shown. The IMD profile was the same over the explored range of settings. Figure 2b shows that there was no effect on IMD as a function of changes in laser wavelength (198 and 266 nm) or nature of the substrate (magnetite, pyrite or haematite). The IMD was bimodal, centred on \( d_v = 0.18 \) µm. The IMD of aerosols produced in the HelEx cell for magnetite, siderite and pyrite were similar to one another, although distinct compared with the IMD produced in the Frames cell. It was bimodal, with a main peak at \( d_v = 0.14 \) µm (35% of the Fe), and a secondary peak at \( d_v < 0.015 \) µm representing ~20% of the total mass of Fe collected. With the HelEx cell, more than 60% of the total mass of Fe was contained in particles smaller than \( d_v = 0.14 \) µm, whereas only ~30% lay in this size range with the Frames cell.

Fe isotope composition of size-sorted aerosols derived from magnetite

There was a positive correlation between aerodynamic size of impactor-sorted aerosols and their Fe isotope composition (Figure 3, Table 2). Experiments performed with the Frames cell showed that the correlation between aerodynamic size-sorted aerosols and their Fe isotope composition was similar for experiments done with a laser wavelength of 198 nm (exp 110408, Table 2) and an experiment done using 266 nm (exp 120508, Table 2). The total range in \( \delta^{56}\text{Fe} \) values within an experiment varied from 0.65‰ to 1.16‰ (Table 2). The Fe isotope composition of size-sorted aerosols collected using the HelEx cell showed the same trend of increasing \( ^{56}\text{Fe}/^{54}\text{Fe} \) ratios with aerodynamic size. The only significant difference is that the spread in \( \delta^{56}\text{Fe} \) values was larger for the HelEx cell (1.85‰; Table 2). Importantly, the calculated mass-balance \( \delta^{56}\text{Fe} \) value for the bulk aerosol, based on the mass-weighted aerosols sizes (Table 2), matched that of the ablated substrate as determined by conventional wet chemical analysis (\( \delta^{56}\text{Fe} = +0.32 \pm 0.05 \)%o; d’Abzac et al. 2013). This highlights the critical conclusion that although there are differences in the Fe isotope compositions of different aerodynamically size-sorted particles, the bulk aerosol matches the bulk substrate and thus demonstrates that fs-LA stoichiometrically samples the substrate (d’Abzac et al. 2013).
The precision of a single Fe isotope determination and the reproducibility of multiple analyses of magnetite reference material mineral grains attainable with both Frames and HelEx cells were comparable (Figure 4), but there are significant differences in the way this performance was achieved (Table SA1). Analysis of magnetite using the Frames cell required use of a mixing chamber on the transport line to produce a more stable Fe ion signal, and these analyses were conducted over 60 × 5 s on-peak integrations (i.e., 300 s of ablation), typically sampling a volume of ~18000 l m⁻³. These conditions routinely produced a 2SE of ±0.12‰ in δ⁵⁶Fe and a measurement reproducibility of ±0.24‰ in δ⁵⁶Fe (2σ), based on n = 61 analyses of magnetite reference material grains analysed during ten different analytical sessions over the course of 2 months (Czaja et al. 2013; Figure 4a). Experiments done using the Frames cell showed that if shorter integration times were used, or significantly smaller volumes were ablated (e.g., more than 30% smaller), the overall performance for Fe isotope ratio determination became poorer. In contrast, no mixing chamber was needed with the HelEx cell, and Fe isotope analyses were based on the average of forty 5 s on-peak integrations (i.e., 200 s of ablation), typically only sampling a volume of ~8640 l m⁻³. These conditions routinely produced a measurement repeatability value (2SE) of ±0.11‰ in δ⁵⁶Fe and a measurement reproducibility of ±0.20‰ in δ⁵⁶Fe (2σ), based on n = 115 analyses of magnetite reference material grains analysed during ten different analytical sessions over the course of 5 months (Li et al. 2013; Figure 4b). Overall stability of the two cells can be quantified based on the stability of the measured ⁵⁶Fe ion intensity. For example, the relative standard error (1 RSE) for the ⁵⁶Fe ion intensity for a single determination if forty cycles are included was typically 1.52% for the Frames cell equipped with a mixing chamber and 0.69% for the HelEx cell.

Figure 3. Iron isotope compositions of the size-sorted aerosols collected from ablation of magnetite using the Frames cell (a: experiment 110418 at 198 nm and b: experiment 120508 at 266 nm) and the HelEx cell (c: experiment 120726 at 266 nm), determined by conventional solution-nebulisation Fe isotope determination of collected aerosols to eliminate post-ablation mass biases. The δ⁵⁶Fe values are reported relative to the average of igneous rocks (Beard et al. 2003), and the bulk-sample Fe isotope composition is shown by the solid line (δ⁵⁶Fe = 0.32 ± 0.05‰, 2σ) determined using the average Fe isotope composition of eight analyses of individual magnetite grains analysed using conventional solution nebulisation. Note that there is a larger range of δ⁵⁶Fe values observed with the HelEx cell (~2‰) (c) compared with the Frames cell (~0.8‰) (a, b), which is interpreted to reflect agglomeration of particles with variable Fe isotope compositions in the Frames cell resulting in a muted range in size sorted Fe isotope compositions. Data from Table 2.

Discussion

The study of particle characteristics and their dependency on laser wavelength and ablation cell geometry requires a careful comparison that must be validated by discarding any influence of secondary parameters. The data reported for the Frames cell with various fluences, repetition rates, and using different mineral substrates allow this validation, where, for example, the IMD was unchanged over a large range of fluences (~1–4 J cm⁻²), repetition rates of 5 and 10 Hz (Figure 2a), and different minerals, including magnetite, pyrite and haematite (Figure 2b). The
Table 2. Iron isotope composition of aerodynamically size-sorted particles formed from ablation of magnetite

<table>
<thead>
<tr>
<th>Impactor stage</th>
<th>Size class (µm)</th>
<th>Experiment</th>
<th>Frames cell (198 nm)</th>
<th>Frames cell (266 nm)</th>
<th>HelEx cell (266 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>110308</td>
<td>110412</td>
<td>110414</td>
<td>110418&lt;sup&gt;1&lt;/sup&gt;</td>
</tr>
<tr>
<td>After filter</td>
<td>&lt; 0.056</td>
<td>0.26</td>
<td>0.38</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>10</td>
<td>0.056-0.1</td>
<td>0.23</td>
<td>0.10</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>9</td>
<td>0.1-0.18</td>
<td>0.19</td>
<td>0.06</td>
<td>0.00</td>
<td>0.02</td>
</tr>
<tr>
<td>8</td>
<td>0.18-0.32</td>
<td>0.68</td>
<td>0.02</td>
<td>0.57</td>
<td>0.02</td>
</tr>
<tr>
<td>7</td>
<td>0.32-0.56</td>
<td>0.48</td>
<td>0.12</td>
<td>0.69</td>
<td>0.11</td>
</tr>
<tr>
<td>6</td>
<td>0.56-1</td>
<td>0.49</td>
<td>0.15</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>5</td>
<td>1-1.6</td>
<td>–</td>
<td>–</td>
<td>0.41</td>
<td>0.26</td>
</tr>
<tr>
<td>4</td>
<td>1.8-3.2</td>
<td>–</td>
<td>–</td>
<td>0.39</td>
<td>0.10</td>
</tr>
<tr>
<td>3</td>
<td>3.2-5.6</td>
<td>–</td>
<td>–</td>
<td>0.99</td>
<td>0.03</td>
</tr>
<tr>
<td>2</td>
<td>5.6-10</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.31</td>
</tr>
<tr>
<td>1</td>
<td>10-18</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.29</td>
</tr>
<tr>
<td>Inlet</td>
<td>&gt; 18</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.33</td>
</tr>
<tr>
<td>Aerosol mass balance&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.36</td>
<td>0.08</td>
<td>0.42</td>
<td>0.05</td>
<td>0.22</td>
</tr>
</tbody>
</table>

For some experiments, multiple MOUDI stages were combined to have enough Fe for isotopic determination (larger cells in the table, bold type; see text for details). Blank cells indicate size fractions for which no Fe was collected. The mass balance of the collected aerosol was calculated from the measured δ<sup>56</sup>Fe values and mass fraction of the combined MOUDI stages. The uncertainty is the weighted average of the 2σ value of every measured sample. The substrate had a δ<sup>56</sup>Fe = 0.32±0.05‰. The laser conditions and mass fraction of each size class are reported in Table 1.

<sup>a</sup> Designation from Marple et al. (1991).

<sup>b</sup> Given as aerodynamic diameter.

<sup>c</sup> Calculated as the weighted average of δ<sup>56</sup>Fe based on IMDS reported in this Table.

<sup>d</sup> Relative to igneous rocks.

<sup>e</sup> Uncertainties are 2σ of test solutions made from High Purity Standard (see Appendix S1) and containing similar amount of Fe as that of the measured sample, given by the IMD (see Table 1). Uncertainty on the mass balance is the sum of the 2σ values weighted by the Fe mass fraction for the collected stages.

<sup>f</sup> Data reported in Figure 3.

<sup>g</sup> Experiment also used in d’Alazac et al. (2013).
reason for the consistent IMD is thought to result from the short pulse width of fs laser. For example, fs-LA induces only minor thermal ablation (Perez and Lewis 2003, Ben-Yakar et al. 2007, Seydoux-Guillaume et al. 2010, d’Abzac et al. 2012a, b), which avoids production of large particles (> 1 μm) through ejection of melt (Koch et al. 2004, Hergenröder 2006b, Shaheen et al. 2013). Second, particles produced by fs-LA are generated within the laser plasma plume induced by matter breakdown (von der Linde and Schüler 1996), following a pattern of condensation, coalescence, and agglomeration (Hergenröder 2006a, Gonzalez et al. 2007a, b, d’Abzac et al. 2012a, b) that is independent of the ablated substrate and produces systematic morphologies of spheres and agglomerates (Figure 1; Gonzalez et al. 2007a, b, Glaus et al. 2010, d’Abzac et al. 2012a, b, 2013). In contrast, it has been shown that ns pulse width lasers produce variable particle size distributions depending on whether the substrate is a conductor and thus prone to significant thermal heating during lasing or an insulator, which is much more resistant to ablation heating (Gonzalez et al. 2007a, b).

A second unique feature of fs-LA is that there are no apparent differences in the ablation of substrates as a function of wavelength. For example, the IMD of magnetite shows that results obtained at 198 and 266 nm are the same (Figure 2, Table 1). Moreover, the ablation rate, defined as total mass of Fe collected with the MOUDI, divided by the total number of laser shots, is the same at 198 nm and 266 nm for a given fluence. For example,
experiment 110414 was conducted with the 198 nm fs laser where the ablation rate was 16 pg of Fe per laser shot at a fluence of ~ 1 J cm$^{-2}$; whereas experiment 110603 was done with the 266 nm fs laser, using an ablation rate of 19 pg of Fe per laser shot at a fluence of ~ 1 J cm$^{-2}$ (Table 1). The similarity in IMD and ablation rate at 198 and 266 nm indicates similar ablation mechanisms, which is a result of the fact that the laser energy lost via optical transmission through the sample (wavelength dependent) is negligible with femtosecond pulses; this reflects the very high photon flux that saturates the irradiated surface and induces multi-photon absorption and avalanche ionisation processes (Du et al. 1994, von der Linde and Schuler 1996). An extreme case was studied by Courtieu et al. (2011), who performed fs-LA of quartz at 800 nm and reported an ablation rate similar to that observed with opaque minerals. Hence, the ablation process does not change with wavelength and aerosols are always produced in the same fashion, and this is confirmed by the similar range in Fe isotope composition of the size-sorted particles produced in the Frames cell using the two different wavelengths (Figure 3, Table 2).

**Cell geometry and aerosols properties**

All our data show that the cell geometry and, most probably, the wash-out time induced substantial changes in laser-induced aerosol properties (Figures 2 and 3). We note that for a subset of the experiments done with magnetite, the same laser (266 nm) was used and operated at the same fluence and repetition rate for both the Frames and HelEx cells (e.g. Experiments 120503, 120508, 120726; Table 1). Moreover, the path of the particles from the exit of the cell to the impactor was the same and thus we interpret differences in the IMD between the two cells to reflect processes that occurred in the ablation cell. We therefore conclude that the fact that the IMD from the Frames cell contains a smaller mass of small aerodynamic-sized particles is a result of particle agglomeration within the cell. Agglomeration depends on a particle’s probability of collision with other particles, and because the wash-out time is longer for the Frames cell the residence time a particle spends in the cell will be longer relative to the HelEx cell, and thus it is more likely to undergo more collisions with other particles.

The differences in the magnitude of Fe isotope compositions as a function of aerodynamic size, for experiments done using the HelEx and Frames cell, is consistent with this agglomeration hypothesis. The larger variations in $^{56}$Fe values for particles generated with the HelEx cell originate from kinetic fractionation during plasma expansion and fast cooling, as discussed in d’Abzac et al. (2013). Because particles in both cells are generated using the same laser, we expect these kinetic isotopic fractionations to be the same, thus, the smaller range of $^{56}$Fe values measured with the Frames cell (Figure 3a,b) is probably a result of mixing a larger range of isotopic compositions through agglomeration of the small, low-$^{56}$Fe particles with larger, high-$^{56}$Fe particles, resulting in a muted range of Fe isotope compositions. The corollary to this interpretation is that the IMD is relatively dependent on the wash-out time of the ablation cell. Here, the IMD measured with the HelEx cell might reflect the most ‘primitive’ size distribution, reflecting little agglomeration of the primary particles. The ‘original’ size distribution should reflect the following processes:

1. Growth inside the laser-induced plasma leads to formation of nanometre-size clusters that further coalesce at different levels (Hergenrötter 2006a);
2. Agglomeration is initially very limited, because the plasma expands rapidly, pushing particles away from one another;
3. Spherules are the result of a long coalescence process due to their early condensation (d’Abzac et al. 2012a, b), and maximum sizes reach ~ 200 nm; their size distribution does not evolve significantly after formation because they tend to become more isolated from agglomerates (Figure 1);
4. Micrometre-size particles are very rare in fs-LA, and likely reflect agglomeration after plasma cooling or ejection from the pit (Hergenrötter 2006b). The latter morphology has not been observed in the present study.

From our observations and the above constraints on the primary IMD, we can propose an interpretation of the evolution of the IMD as a function of the wash-out time of the ablation cell (Figure 5). The peak of very small particles ($d_\alpha < 20$ nm) that initially formed during plasma expansion (Figure 5, phase 1) is diminished in an ablation cell such as the HelEx, as this size fraction becomes agglomerated and creates a main peak around 0.1 < $d_\alpha$ < 0.18 μm (Figure 5, phase 2). If the wash-out time is longer, as in the Frames cell, the main peak broadens and shifts towards $d_\alpha$ = 0.32 μm (Figure 5, phase 3) because only agglomerates of $d_\alpha$ = 0.1 μm are available for collisions (Hergenrötter 2006a).

**Implications for stable isotope analysis by laser ablation MC-ICP-MS**

The precision of fs-La analyses of magnetite for a single Fe isotope determination and the reproducibility of multiple
Conclusions

The influence of cell geometry and laser wavelength on the size distribution and Fe isotope composition of size-sorted aerosol particles generated by fs-LA were investigated to better constrain the requirements for precise Fe isotope determinations on as little material as possible using fs-LA-MC-ICP-MS. The Fe mass distribution and the Fe isotope compositions of the size-sorted particles were independent at the laser wavelengths investigated (198 nm and 266 nm) and were not changed as a function of laser repetition rate (5–25 Hz) or fluence (~1 to ~4 J cm⁻²). We interpret these results to reflect fundamentally constant laser/matter interactions in the femtosecond regime, independent of the optical absorption properties of the substrate. We highlight that this consistency over a wide range of substrates is important for Fe isotope determination because the most likely phases to be analysed for Fe isotopes are iron oxides, sulfides, carbonates and metals. These materials are semiconductors and conductors and are substantially heated during ablation if longer pulse length lasers are used. We highlight that the consistency of laser/matter interaction for these different Fe-bearing substrates is well displayed by the fact that similar IMDS of aerosols are produced by fs-LA.

The ablation cell geometry had a significant influence on the IMD and on the Fe isotope composition of the size-sorted particles. This is interpreted to reflect variable agglomeration levels of generated particles. The two-volume HelEx cell minimised agglomeration of particles through fast aerosol extraction (<0.7 s), which reduced the amount of time that the particles could potentially collide with one another. The Frames cell had a longer wash-out time (~2 s) that
increased the amount of time that particles could collide with one another, which induced a more variable aerosol flux as shown by the greater ion signal instability compared with analyses done using the HelEx cell. Despite these differences, optimal conditions can be found for Fe isotope determination that produce similar performance in measurement repeatability and reproducibility (Czaja et al. 2013, Li et al. 2013). Nevertheless, the use of the Frames cell requires a mixing chamber and longer ion counting times at higher ion intensity compared with the HelEx cell. We interpret these differences to reflect subtle variations in instrumental mass bias caused by a more variable ion signal produced from the Frames cell compared with the HelEx cell. The larger ion instability for the Frames cell is inferred to be caused by non-steady-state aerosol delivery as a result of agglomeration processes within the Frames cell.

Acknowledgements

The authors gratefully acknowledge use of facilities and instrumentation supported by the NSF-funded University of Wisconsin Materials Research Science and Engineering Center (DMR-1121288). This study was funded by NSF and NASA grants to C.M.J. and B.L.B., including funding from the NASA Astrobiology Institute. The anonymous reviewers are thanked for their constructive comments.

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