Sr isotope ratios and Rb-Sr ages by LA-ICPMS with isobar separation by online electrothermal vaporization

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HALE CEREN YILMAZ

MSc Chemistry, ETH Zurich

born on 08.01.1990

citizen of Nidau, BE

accepted on the recommendation of

Prof. Dr. Detlef Günther (examiner)

Prof. Dr. Maria Schönbächler (co-examiner)

Dr. Bodo Hattendorf (co-examiner)

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Abstract

Laser ablation (LA) is an established solid sample introduction technique for inductively coupled plasma mass spectrometry (ICPMS), which offers various advantages compared to solution-based techniques. Spatially resolved information about the trace elemental composition of solids can be assessed and contamination can be minimized due to virtually no sample preparation. Additionally, limits of detection (LOD) close to those of solution-based techniques are attainable. The online determination of Sr isotope ratios of solids by laser ablation ICPMS (LA-ICPMS), in particular with multi-collector MS, finds application in the field of forensics, food authentication, migration studies, provenance studies and geology, where geologic processes or the age of minerals are of particular interest. One major disadvantage of LA-ICPMS, however, is the occurrence of spectral interferences. In contrast to solution-based sample introduction techniques, where the separation of interfering elements is often feasible, LA does not provide this possibility. In the case of Sr isotope ratios measurements, the accuracy and precision are limited by the isobaric interference of $^{87}$Rb on $^{87}$Sr, which can only be accounted for by mathematical correction and for samples with [Rb]/[Sr] concentration ratios typically $<< 0.14$. It was shown in a previous study that a reduction in signal intensities of various metals can be achieved when a laser-generated aerosol is heated up to $2^\circ$700$^\circ$C in the furnace of an electrothermal vaporization (ETV) unit in a LA-ETV-ICPMS setup. The magnitude of this signal suppression and the respective onset temperatures were found to correlate with the boiling points of the studied metals. It is thus likely that changes in the chemical composition of the aerosol result from vaporization in the furnace and subsequent condensation at cooler parts downstream. It was shown for the first time that an element-specific removal can be initiated by thermal treatment of a laser-generated aerosols. In another study, the dependence of the signal suppression, particle size distribution (PSD) and aerosol morphology on the ETV temperature by LA-ETV-ICPMS was studied for a variety of samples. It was shown that for Rb and Sr containing solids, a partial suppression of the Rb signal can be achieved, while the Sr signals does not undergo suppression. With the selective elimination of Rb, Sr isotope ratios could be analysed with precisions of $\sim 100$ ppm for samples with [Rb]/[Sr] $\leq 0.28$.

In this work, fundamental processes that take place during the thermal treatment of laser-generated aerosols in an ETV unit were investigated by LA-ETV-ICPMS to determine changes in aerosol composition and morphology. SEM images of filter-collected aerosols and optical particle sizing have furthermore shown that metallic femtosecond (fs-)aerosols consisted of a larger fraction of individual particles with broader size distribution than nanosecond (ns-)aerosol, which consisted of a larger fraction of nanoparticle (NP) agglomerates and splashed droplets, reaching diameters in the $\mu$m-range. Due to these differences in morphology, ns- and fs-aerosols showed element specific suppression to a different extent under heating and, for the same ETV temperature setting, different ICPMS signal suppression factors were obtained. Furthermore, the heating had a different effect on the PSD and aerosol morphology for ns- and fs-LA. In this work it was demonstrated for the first time that NP agglomerates collapse to form homogeneous droplets when heated to the melting point of the material. Element-specific removal is considered to occur initially by surface melting and evaporation because elements were also found to be removed from the aerosol when the ETV temperature setting was below the boiling point of the material. Different particle sizes that were formed either in the ablation process or
during the collapse of the agglomerates would then show a size-dependency of the fraction of material that is evaporated and removed from the aerosol stream before the ICPMS. The fs-aerosol was found to become vaporized more efficiently, which was reflected in a stronger signal suppression and more pronounced Cu-Zn separation for brass. No dependence of the suppression efficiency for Cu and Zn was observed for brass samples with moderately different Cu and Zn compositions. The suppression in pure Cu or Zn vs. the alloy however appeared to differ, and the onset of suppression was shifted to higher temperatures for Zn and to lower temperatures for Cu in brass. Also, the Cu-Zn separation efficiency of two graphite furnace ETVs (GF-ETV), the HGA-600MS and ETV-4000, were compared. The ETV-4000 achieved a significantly higher separation of the two elements, which was attributed to its longer graphite tube compared to the HGA-600MS.

The separation of Rb from Sr in laser-generated aerosols was then studied in detail using two commercial GF-ETVs and a custom-made tungsten-wire based ETV. Most likely because of its longest vaporization zone, the ETV-4000 achieved the highest Rb-Sr separation for all investigated samples. A comparison of two different UV laser wavelengths did not reveal a significant influence on the Rb-Sr separation efficiencies when using fs-LA. Matrix dependencies of the Rb-Sr separation efficiency between silicate glass and fused tetraborate pellets were found, while different [Rb]/[Sr] concentration ratios did not influence the suppression of Rb significantly. When analyzing natural biotite samples, the efficient removal of Rb was however found to be more challenging. The heterogeneity of the minerals caused stronger variabilities in [Rb]/[Sr] concentration ratios during the laser ablation analyses and required a careful selection of the corresponding signal integration periods. Furthermore, matrix effects in between different mineral types and between the mineral samples were observed with respect to onset and magnitude of the suppression of Rb from Sr. It was also found that the natural samples showed a distinctly less efficient Rb elimination when the aerosol flux in the ETV was increased > 10 times. Still, a $^{85}\text{Rb}^+$ signal suppression by four orders of magnitude could be achieved for these materials.

Again, no dependency of the Rb-Sr separation efficiency on the sample composition was observed. Under operating conditions that yielded the highest possible Rb suppression and highest Sr sensitivity for the individual minerals, a complete suppression of the $^{85}\text{Rb}^+$ signal was achieved for samples with Rb < 1'000 ppm and [Rb]/[Sr] ≤ 25, while the $^{88}\text{Sr}^+$ ion signal suppression was in the order of 0.1 – 1.

$^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio measurements performed with a pressed pellet of NIST SRM 987 SrCO$_3$ embedded in NaCl revealed a systematic offset to an isotopically lighter composition at temperatures, where no substantial evaporation of Sr had occurred. This offset shifted towards a heavier composition as the Sr was gradually suppressed. The origin of the offset could not be isolated during this work. It shows however that fractionated isotope evaporation occurs in the ETV. This is particularly critical as isotope fractionation also needs to be expected during the evaporation of Rb. The mathematical correction of the contribution of $^{85}\text{Rb}^+$ to the ion signal of $^{87}\text{Sr}^+$ by assuming similar mass discrimination of Rb and Sr is therefore even more constrained in this case. Thus, a reasonable agreement between measured and reference values for the Sr isotopes could only be attained when the Rb could be completely eliminated from the sample aerosol while Sr can still be detected on all isotopes with sufficient sensitivity. This could be achieved for NIST SRM 610 in most cases, while mineral samples with [Rb]/[Sr] concentration ratios > 10 were still affected by large systematic errors.

Overall, this work provides a broader view into fundamental processes taking place under thermal treatment for ns- and fs-aerosols and the efficiency for Rb-Sr and Cu-Zn separations as model systems. The huge potential of a fs-LA-ETV-ICPMS setup for spatially resolved $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio measurements was demonstrated. However, the fact that a sequential ICPMS instrument was used and
the yet unsolved mass discrimination effects are the still limiting factors in the performance of the current configuration. Future work would aim at using a split-flow setup (fs-LA multi-collector ICPMS (fs-LA-MCICPMS) and quadrupole-based ICPMS (Q-ICPMS)) for age determinations of minerals in particular.
Zusammenfassung


Die Bestimmung von $^{87}\text{Sr}/^{86}\text{Sr}$ Isotopenverhältnissen in einem synthetischen NIST SRM 987 SrCO$_3$ - NaCl Pellet zeigten, dass auch bei Bedingungen, bei denen keine Unterdrückung des Sr-Signals zu beobachten war, eine systematische Abweichung des Verhältnisses zu leichteren Isotopenverhältnissen auftrat. Bei stärkerer Unterdrückung des Sr wurde diese Abweichung zu schwereren Zusammensetzungen verschoben. Der Ursprung der Abweichung konnte im Rahmen dieser Arbeit nicht eruiert werden. Dies bedeutet jedoch, dass beim Verdampfen des Sr eine messbare Isotopenfraktionierung stattfindet. Das
ist insbesondere kritisch, da eine solche Fraktionierung auch während der Eliminierung von Rb erwartet werden muss. Die mathematische Korrektur der Interferenz von $^{87}\text{Rb}^+$ an den Intensitäten des $^{87}\text{Sr}^+$, bei der eine ähnliche Massendiskriminierung der zwei Elemente angenommen wird, ist daher in diesem Fall sogar noch stärker fehlerbehaftet. Es konnte deshalb nur dann eine Übereinstimmung zwischen gemessenen und Referenzwerten für die Sr-Isotopen erreicht werden, wenn das Rb komplett aus dem Proben aerosol eliminiert werden konnte und wenn alle Sr-Isotopen mit einer genügend hohen Sensitivität gemessen werden konnten. Das wurde in den meisten Fällen für NIST SRM 610 erreicht, während die Mineralienproben mit $\frac{[\text{Rb}]}{[\text{Sr}]}$ Konzentrationsverhältnissen > 10 noch von den erheblichen systematischen Fehlern beeinflusst waren.

Insgesamt konnte in dieser Arbeit anhand der Trennungseffizienz für Rb-Sr und Cu-Zn als Modellsysteme ein breiterer Einblick in grundlegende Prozesse, die bei thermischer Behandlung von ns- und fs-Aerosolen stattfinden, erarbeitet werden. Das grosse Potential von fs-LA-ETV-ICPMS für ortsaufgelöste $^{87}\text{Sr}/^{86}\text{Sr}$ Isotopenmessungen wurde gezeigt. Im momentanen Aufbau limitieren jedoch die Verwendung eines sequentiellen ICPMS und eine noch ungelöste Massendiskriminierung die Leistungsfähigkeit merklich. Zukünftige Studien zielen darauf ab, den Split-Flow Aufbau (fs-LA Multi-Kollektor ICPMS (fs-LA-MCICPMS) und Quadrupol-basierten ICPMS (-Q-ICPMS)) für Altersbestimmungen in Mineralien zu benutzen.
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1. Introduction

1.1. $^{87}\text{Sr}/^{86}\text{Sr}$ Isotope Ratio Measurements in Solids: Relevance, Problems and State of the Art

Small-scale variations of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio within solid samples are an important source of information for applications ranging from provenance studies, migration studies, food authentication, forensics and geological processes. When investigating the migration behavior of fish, for example, variations in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio within growth rings of a fish’s otoliths are reflecting the composition of the water environment during the different periods of its life. By comparing the Sr isotope ratios of the growth rings with the ratios of water samples from its habitat, the migration path of the animals can be reconstructed. Figure 1 shows an example of how the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio data can be extracted from the sample at the spatial resolution required for such a study. A LA scan across the otolith was performed and the transient Sr ion signals are recorded by ICPMS. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is calculated after performing a mathematical correction protocol and a $^{87}\text{Sr}/^{86}\text{Sr}$ value is assigned to each position.

Figure 1 – Example of a spatially resolved Sr isotope analysis of a fish otolith. Each datum in the time-resolved plot represents a single 0.2 s integration. A slit of 147 x 3 µm in size was traversed across the sample with a scan rate of 2 µm/s, providing ~ 2'000 data points.
The strong Sr-concentration contrasts between carbonate forming the otolith in marine (core) and freshwater (edge) and the corresponding isotope ratios can be resolved and compared to the ratios of sea- and freshwater samples.

Another field of application for Sr-isotope ratio measurements is the Rb-Sr Geochronology, which can be used for determination of mineralization ages or events. The Rb-Sr geochronology is based on the radioactive β-decay of $^{87}\text{Rb}$ to $^{87}\text{Sr}$ ($\tau = 4.88 \times 10^{10} \text{yr}$):

\begin{equation}
^{87}\text{Rb} \rightarrow ^{87}\text{Sr} + ^{0}\beta^- + ^{0}\nu + Q
\end{equation}

where a β-particle and an anti-neutrino $\nu$ are emitted. The decay energy $Q$ is shared as kinetic energy by these particles. The present $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of a mineral depends on the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio ($^{87}\text{Sr}/^{86}\text{Sr})_0$, as well as the $^{87}\text{Rb}/^{86}\text{Sr}$ ratio and its age. The decay constant is $1/\tau = \lambda = 1.42 \times 10^{-11} \text{yr}^{-1}$.

\begin{equation}
\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right) = \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_0 + \left(\frac{^{87}\text{Rb}}{^{86}\text{Sr}}\right)(e^{-\lambda t} - 1)
\end{equation}

By measuring the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of different minerals of a sample specimen and plotting them against the $^{87}\text{Rb}/^{86}\text{Sr}$ ratio in an isochron diagram, as shown in Figure 2, the initial ($^{87}\text{Sr}/^{86}\text{Sr})_0$ ratio is the intersection point of the regression line with the y-axis. The age can then be calculated from the slope of the linear regression line with formula (3):

\begin{equation}
t = \frac{1}{\lambda} \left\{ 1 + \frac{^{86}\text{Sr}}{^{87}\text{Rb}} \left( \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right) - \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_0 \right) \right\}
\end{equation}

By magma cooling, igneous rocks are formed which can be sub-grouped to different minerals with different Rubidium/Strontium concentration ratios ([Rb]/[Sr]). For age calculations, the analysed samples must originate from the same magma pool. Figure 2 schematically shows the isochron diagram of different igneous minerals, which all have differing Rb concentrations. If a chemical process alters the Rb-Sr concentration of the affected sample, its point in the isochron diagram will not lie on the regression line. Leaching of certain elements, or an escape into the gas phase by sublimation are possible explanations for such an observation. The sample with altered elemental composition cannot be used for dating purposes.
$^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios are typically measured by thermal ionization mass spectrometry (TIMS) 6,16-17 or MCICPMS 10,18-19 from solutions. If a solid is analysed, in both cases, the sample has to be digested prior to analysis and subsequently, the Sr is separated from the sample aliquot prior to analysis, for example with chromatographic methods. In this way, an isotope ratio precision down to 0.0007 % can be achieved. The drawbacks of sample digestion are the extensive preparation time, contamination risk and sample destruction. Also, the spatial resolution attainable by micro-milling and subsequent digestion is practically limited to about 100 µm. In-situ analysis of $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios at high spatial resolution can for example be obtained with secondary ion mass spectrometry (SIMS). The achievable precisions with a single-collector SIMS are 0.01 – 1% and 0.002 - 0.1% with a multi-collector SIMS. SIMS is however not widely used due to the comparably complex operation and sample preparation requirements. A highly attractive method for this application is thus laser ablation sampling with ICPMS detection, which requires only little sample preparation and a relatively straightforward measurement protocol. It lacks however the possibility to isolate Sr from the sample matrix and thus spectral interferences are frequently the limiting factor with respect to accuracy and precision. 20 In this work an approach was investigated to allow for such a separation by means of on-line thermal treatment of the laser-generated aerosol.
1.2. Inductively Coupled Plasma Mass Spectrometry (ICPMS)

S. Houk et al. \(^{21}\) were the first to use an inductively coupled argon plasma as an ion source for elemental and isotope mass spectrometry. Over the last few decades, ICPMS was commercialized and can nowadays be found in many analytical chemistry laboratories. An ICPMS instrument can not only deliver qualitative, but also quantitative information about the major, minor and trace elemental composition of samples in a fast and reliable way. A relatively wide concentration range from mg/kg or mg/L (ppm) to pg/kg (ppt) is accessible due to the sensitivity and wide dynamic range of modern detection systems. Therefore, ICPMS has gained a wide user community.

1.2.1. Inductively Coupled Plasma (ICP)

The ion source of an ICPMS instrument, an inductively coupled argon plasma, can vaporize and ionize almost any sample which has been converted into a sufficiently fine aerosol. The ICP is generated in a so-called plasma torch, which usually consists of three concentric quartz glass tubes. Argon gas passes between the outer and middle tube at flow rates between 12 – 17 L/min and is used to cool the torch. A second argon gas flow, the auxiliary or intermediate gas, passes between the middle tube and sample injector and determines the position of the base of the plasma. Typical flow rates lie between 0.5 – 1.1 L/min. The sample is transported into the plasma with the nebulizer or carrier gas flow (~ 1 L/min) as an aerosol of droplets or particles, generated in the sample introduction system. Figure 3 shows a sketch of the plasma torch arrangement. \(^{22}\)

![Figure 3 – Plasma torch with RF-coil and three gas streams.](image)

For solution-based analyses, pneumatic nebulizers are used to generate an ultra-fine droplet aerosol. Spray chambers allow only the smallest fraction of those droplets to enter the plasma, since large droplets may be incompletely evaporated and can cause plasma instability. \(^{24}\) Direct solid sampling is an alternative sample introduction technique, where dry aerosols are generated by ablating solid samples with a focused laser beam.

An induction-coil, which typically consists of copper, is positioned around the top of the torch as indicated in Figure 3 (“RF-Coil”). For operation, the gas flow through the torch is enabled before applying an RF power (750 – 1500 W, 27 or 40 MHz) to the coil. A high-voltage spark is used to seed ions and electrons within the induction region. The electrons and ions are accelerated in the electromagnetic

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\(^{12}\)---

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\(^{21}\)---

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\(^{22}\)---

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\(^{23}\)---

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\(^{24}\)---

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field, collide with other argon atoms, eventually leading to a steady state of electron and ion density as the stable plasma discharge is formed. In the analytical zone of the plasma, temperatures between 6'000 – 7'000 K can be found, while the temperature can rise to values > 10'000 K in the core of the plasma. The ionization energy of Ar (15.76 eV) “buffers” the ionization of the ICP elements with ionization potentials near or above this value, which are then, as a consequence, less efficiently or barely ionized. Nonetheless most of the elements in the periodic table can be ionized to a degree of > 90%. Exceptions are fluoride, neon and helium, which have a first ionization potential higher than 15.76 eV. Several elements (e.g. the rare earth elements (REE)) have a second ionization potential below 15.76 eV and thus also doubly-charged ions can be generated. The conversion of a sample aerosol to atomic ions in an ICP consists of several steps. At first, the aerosol particle undergoes desolvation, in which the solvent is vaporized. The particle components are then vaporized and dissociated to atoms. Collisions with energetic electrons in the plasma strip off electrons from the atoms, creating positively charged ions. Variations in the degree of ionization of single elements, as caused by individual ionization potentials, can lead to substantial differences in detection sensitivity. The operating conditions of the ICP ion source are typically adjusted to maximize the sensitivity for the isotopes of interest, while minimizing molecular ion (dominated by oxide and argide compounds) and doubly-charged species abundances. The most critical parameters in this respect are the argon nebulizer gas flow rate and the RF-power. The sampling depth, which represents the distance of the torch from the vacuum interface, also affects the signal and molecular ion abundances substantially. Despite the high temperature in the source, molecular ions can still be observed. Prominent examples are N$_2^+$, NO$, O_2^+$, ArO$, Ar_2^+$, which are always present in the mass spectra. Molecular ions are however also formed from solvents or matrix elements, which are introduced into the plasma. Their presence can lead to additional spectral interferences (e.g. ArCl$^+$ on As$^+$ in presence of HCl). Oxide and hydroxide abundances in the mass spectra depend on many instrumental parameters, which can be adjusted specifically to minimize their contribution. A lower nebulizer gas flow rate usually leads to a reduction of oxide species. Another possibility is to diminish the solvent load in the plasma. Spectral overlaps can also occur between atomic ions, which are referred to as isobars.

1.2.2. The Vacuum Interface

From the plasma source, the ions are extracted into a so-called vacuum interface (Figure 4), which consists of two metal cones (Ni, Pt, Al) in a water-cooled housing. The first cone, the sampler cone, has an orifice diameter between 0.8 – 1.2 mm. The second cone, which is placed right after the sampler, is known as skimmer cone and has a smaller orifice (0.4 – 0.8 mm). A pressure of ~ 1 - 5 mbar is maintained with a mechanical roughing pump connected with the interface, while turbomolecular pumps are employed in the downstream ion optics and mass analyser regions to reach the operating pressure of ~ 10$^{-6}$ mbar.
In total, an ion loss of about 99% occurs in the interface region because the skimmer cone extracts only a small fraction of the expanding plasma. A particular characteristic of this vacuum interface is that all ions are extracted at approximately the same velocity, making their kinetic energies mass dependent.

1.2.3. The Ion Focusing System

The ion optics section, which consists of an arrangement of metal electrodes, is kept at a pressure of $\sim 1.3 \cdot 10^{-3} – 10^{-4}$ mbar with a turbomolecular pump. This rapid decrease in pressure compared to the interface region causes a transformation of the plasma expansion into a molecular flow, where electrostatic potentials of the ion lenses cause charge separation by removing the highly mobile electrons. Due to the electrostatic repulsion between the positively charged ions and the mass dependent kinetic energies, space-charge effects occur. Ions with high kinetic energy (high masses) remain closer to the expansion axis than ions with low energy (low masses). Therefore, the focusing of ions by the ion optics components is not equally efficient for all mass-to-charge ratios ($m/Q$).

Additionally, the ion focusing system is designed to reduce the fraction of neutrals, photons and particles, which can contribute to the instrumental background signals. Possible ways to prevent those species to enter the mass analyser are to bend the ion beam, to install a physical barrier or by positioning the mass analyser off axis.

1.2.4. The Mass Analyser

In the mass analyser, the ions are separated according to their $m/Q$ before they hit the detector. A pressure of $\sim 10^{-6}$ mbar is maintained in this part of the instrument by turbomolecular pump(s). The first commercial ICPMS were equipped with quadrupole mass filters exclusively. Nowadays three different mass analyser types are available: Q-ICPMS, double-focusing sector field magnetic sector systems (SFICPMS) and time of flight instruments (ICPTOFMS). Some instruments are equipped with additional collision/reaction cells to eliminate interferences. In this work, quadrupole-based and sector field instruments were used. Details about their characteristics will be discussed further in the following sections.
Two important performance specifications of a mass analyser are the mass resolving power \( R = \frac{m}{\Delta m} \) and the abundance sensitivity. Here, \( m \) is the nominal mass and \( \Delta m \) the difference between two resolved peaks of identical peak height. \(^{35}\) The \( \Delta m \) term can be determined in different ways. Since two neighboring peaks have rarely an identical height, \( \Delta m \) is often derived from the masses corresponding to 5% of the peak height (5% valley definition) of one single peak. \(^{36}\) A quadrupole-based instrument is usually operating with variable mass resolving power between \( = 10 \) and \( 300 \), while sector field ICPMS instruments operate at a fixed \( R \), which is adjustable between \( 300 \) ("low resolution") and \( > 10'000 \) ("high resolution"). The abundance sensitivity is defined as the contribution of the signal to the tail of an adjacent peak at one mass unit lower and higher, respectively. Typical abundance sensitivities for a quadrupole-based instruments are \(< 1.0 \times 10^{-6}\) on the low mass side and \(< 1.0 \times 10^{-7}\) at the high-mass side, while high-resolution instruments achieve abundance sensitivities \(< 5.0 \times 10^{-6}\) (\(10^9\) cps per ppm with pneumatic nebulization). Typical background levels of a sector field ICPMS instrument are \(0.1 – 0.2\) cps, while an instrumental background \(< 1\) cps is achievable with quadrupole-based instruments. \(^{22}\)

1.2.4.1. Quadrupole-Based ICPMS Instruments

Since their development in the 1980s, the availability of Q-ICPMS instruments has constantly grown. \(^{21}\) The quadrupole mass filter consists of 4 rods of round or hyperbolic cross section with identical length (15 – 20 cm) and diameter (1-2 cm).

![Figure 5 - Quadrupole mass analyser, which selects only one \( m/Q \) ratio. \(^{22}\)](image)

Typically, the alternating current (AC) of the quadrupole mass filter operates at a frequency of 2 – 3 MHz with opposite polarities applied to adjacent rods. An additional direct (DC) potential is applied to opposite rods. A specific mass-to-charge ratio is allowed to travel through the rods across stable trajectories towards the detector by choosing a specific AC/DC ratio. Ions with other \( m/Q \) ratios hit the rods or are ejected from the quadrupole between the rods. \(^{37-38}\) If more than one isotope must be measured in a multi-element analysis, different AC/DC ratios are applied on the quadrupoles sequentially to scan across the \( m/Q \) range of interest. Typically, a quadrupole mass analyser can scan \(2'500\) atomic masses units per seconds, which means, that the mass range relevant for ICPMS (6 – \(< 300\) amu) can be scanned in \(~ 0.1\) s. Practically however, measurements are carried out with integration times of several ms per isotope per mass scan in order to improve measurement statistics. The mass resolving power that can be achieved with a quadrupole is defined by the shape, diameter and length of the rods, the frequency of the power supply, the vacuum and the AC/DC voltage settings. The peak width of a quadrupole MS is normally kept between 0.7 and 0.8 amu, since higher mass resolving powers
deteriorate ion transmission. Parameters like the design of the rods, frequency of the power supply, and operating vacuum affect the abundance sensitivity. Even though quadrupole-based ICPMS instruments have a simple configuration and are thus a reasonable and cost-effective choice for a large number of applications, the mass resolving power and sensitivity are limited.

1.2.4.2. Collision/Reaction Cell Technology

As mentioned earlier, for some elements, the detection capability is limited due to polyatomic species generated with solvent-, argon- or matrix-based ions. Rowan and Houk were the first to use Xe and CH₄ to reduce ⁴⁰Ar⁻¹⁶O⁺ on ⁵⁶Fe⁺ and ⁴⁰Ar⁺ on ⁸⁰Se⁺. The collision/reaction cells, which contain a multipole ion guide (hexa- or octapole) operated in RF-only mode, are positioned in front of the quadrupole mass analyser. Dynamic reaction cells (DRC) are equipped with a quadrupole ion guide and make use of the mass discrimination to allow for some control of the secondary ions generated inside the cell. Collision (He) or reaction (H₂, O₂, NH₃, CH₄) gases are introduced into the cell and the ions entering the cell from the interface are focused by the RF-field to achieve a high collision rate with the gas molecules. If a reaction gas is used for interference separation, either the interfering ions react with the molecules and form new species or the analyte ion itself reacts with the gas. In either way, the m/Q of the interfering polyatomic species or the analyte is shifted to a different m/Q and ideally separated from the interference. The ⁴⁰Ar⁺ interference on ⁴⁰Ca⁺ can for example be resolved with H₂ as reaction gas and the ⁴⁰Ca⁺ ion can then be measured interference-free. Other approaches include collision induced dissociation of weakly bound molecular ions (e.g. ⁴⁰Ar¹⁶O⁺) and collisional retardation or kinetic energy discrimination (KED). The latter makes use of the greater loss of kinetic energy of the polyatomic ion because of its larger collision cross-section. The higher number of collisions compared to the atomic ions slows them down more effectively and due to a lower electrostatic potential inside the collision cell relative to the mass filter, these species are rejected by the potential barrier at the exit of the cell.

1.2.4.3. Double-Focusing Sector Field ICPMS Instruments

As the name already suggests, the mass analyser of a double-focusing ICPMS instrument consists of two sections, a magnetic and an electrostatic analyser (ESA). Throughout the last century, different geometries have been discussed. Most common in single-collector instruments is a reverse Nier-Johnson arrangement (Figure 6), where the magnet is located in front of the ESA, while multi-collector instruments typically employ the opposite configuration (Nier-Johnson or Mattauch-Herzog arrangements) to allow for a wider range of m/Q to be focused on a common focal plane.
Figure 6 – Reverse Nier-Johnson geometry of the mass analyser in a double-focusing sector field ICPMS instrument. \(^45\)

The magnetic field of the sector field instruments is the mass-dispersive element. In the magnetic sector, the Lorentz force and the centripetal force allow for ions of selected \(m/Q\) to travel on exactly the radius of the flight tube and reach the exit slit. The \(m/Q\) transmitted is then depending on the magnetic flux density \(B\), the ion velocity \(v\), as well as the radius \(r_m\) of the trajectory. This means, that the ions are spatially separated according to their \(m/Q\) ratio.

Even though ions with the same \(m/Q\) ratio enter from the source slit with different angles, the magnet focusses them onto the same focal point. Ions with different \(m/Q\) ratios fly different paths with different radii \(r_m\). \(B\) is the magnet field and \(U\) the acceleration potential:

\[
\frac{m}{Q} = \frac{r_m^2 B^2}{2U}
\]
The ESA is the energy-dispersive system and in reverse Nier Johnson geometry, it focuses the ions of slightly different energies to the exit slit of the MS. It consists of two curved metal plates with a more negative voltage applied to the inner electrode. For given operating conditions, the radius \( r_e \) of the circular path of an ion is determined by

\[
(5) \quad r_e = \frac{dmv^2}{Ee}
\]

\( E \) is the differential voltage of the ESA, \( d \) the gap between the inner and outer plate, \( m \) the mass, \( v \) the velocity and \( Q \) the charge of the ion. This means that the radius \( r_e \) is determined by the kinetic energy of the ion. Therefore, at the end of the ESA, ions with the same kinetic energy are focused at the same point at the collector or energy slit.

Figure 8 – Electrostatic analyser (ESA) of the double-focusing mass analyser. ⁴⁵

One major advantage of sector-field instruments is that they can achieve resolving powers up to 10'000 in the case of ICPMS instruments. A high number of spectral interferences can be resolved. A popular example is the polyatomic \(^{40}\)Ar\(^{16}\)O\(^+\) interference on \(^{56}\)Fe\(^+\), which can be separated by operating a sector-field instrument with a mass resolving power near 3'000 m/\( \Delta m \). The width of two mechanical slits in the instrument placed at the entrance and exit of the mass spectrometer, respectively, determines the resolution. High resolution is achieved by using narrow slits, while wide slits are used for low resolution, which leads to a decrease in ion transmission with increasing resolution.

It has to be noted, that the stabilization of the magnetic field (magnet settling) takes a relatively long time (several 10 ms) compared to fast electronic switching. Sequential isotope analyses thus require several 100 ms per mass scan, depending on the number of isotopes detected. Scanning across a small mass region (= 30% from the magnet’s rest mass), can be carried out by varying the ion acceleration voltage without need to adjust the magnetic field. This enables a higher correlation of time variable ion signals and is the preferred mode for isotope ratio analyses using single-collector (SC) instruments. By continuously ramping the magnetic field and specific deflection of the ion beam before the magnet, the entire atomic mass range can be scanned in about 200 ms (100 ms up + 100 ms down) ⁴⁶, but this method leaves less flexibility in isotope selection.

1.2.5. Ion Detectors

After passing through the mass separation device, the ion currents are registered by means of suitable detectors. In the following three subsections, three common types of analogue and digital detectors used in ICPMS are discussed.
1.2.5.1. Discrete Dynode Electron Multiplier

In dynode electron multipliers, the ions strike the first dynode and release secondary electrons, which are accelerated towards the following dynode where additional electrons are released. This electron cascade serves to amplify the initial current by about $10^6$ times and converts it to a readable signal. For ion currents $< 10^6$ ions/s the “pulse-counting mode” is used, where the incoming pulse signal is processed directly. Ion currents $> 10^6$ ions/s are registered using a so-called “analogue mode” where the electron current is usually registered at an intermediate dynode instead of the pulse signals. By proper cross-calibration of both modes, the linear dynamic range can be extended to 9 orders of magnitude. If the rate, with which the ions arrive at the detector gets too high, their individual pulses cannot be distinguished anymore. The minimum delay between distinguishable pulses is the so-called dead time which, up to a count rate of $10^6$ s$^{-1}$, is conventionally corrected for mathematically. Typical dead times of a discrete dynode multiplier are 20 - 30 ns.

![Figure 9 – Setup of a discrete dynode electron multiplier.](image)

1.2.5.2. Faraday Collector

In a Faraday cup, high ion currents can be registered directly. The lower working range of a Faraday cup corresponds to around $10^4$ cps ($10^{11}$ Ω-resistor) and the linear dynamic range is around $10^4$. If a higher resistance is used, the working range can be lowered $< 10^4$ cps, which however reduces the linear dynamic range in parallel. A general advantage of Faraday detectors is the excellent long term stability, which makes them ideally suited in multi-collector applications for isotope ratio measurements when sufficiently high ion currents can be obtained. They are also used in combination with discrete dynode detectors in double-focusing ICPMS instruments to extend the measurement range to about 12 orders of magnitude.

![Figure 10 – Setup of a Faraday collector.](image)
1.3. Laser Ablation ICPMS (LA-ICPMS)

1.3.1. Advantages and Drawbacks

Figure 11 shows a typical LA-ICPMS set-up. The sample surface and the ablation process can be observed with a CCD camera or microscope. The sample is placed in the ablation chamber, which is usually positioned on an x-y-z-positioning stage and flushed with the carrier gas. Nowadays, mostly helium is used, since it was shown to be advantageous over argon in terms of sensitivity, elemental fractionation and aerosol transport losses. \(^{50-51}\) Furthermore, a shift to a smaller mean particle size is observed when using helium instead of argon. \(^{52-53}\) By moving the stage under the ablation cell, the surface of the sample can be scanned to target the region of interest. The aerosol is transported with the carrier gas out of the cell towards the ICP. Argon make-up gas is admixed to the aerosol stream before the ICP to ensure stable plasma operation. \(^2\)

![Figure 11 – Scheme of a LA-ICPMS set-up.](image)

Solid sample introduction into an ICPMS instruments by LA offers several advantages over solution-based analyses. When using digestion protocols for solid samples, possible sample contaminations and loss of volatile elements must be considered. In some cases, hazardous dissolution agents like HF or H\(_2\)O\(_2\) must be used to achieve a complete dissolution of the sample. Furthermore, dissolution protocols can consist of numerous steps, which extend the required time for the sample preparation to hours or even days. The factor limiting the reliability and accuracy of the results the strongest are spectral interferences formed from solvents (e.g. \(^{40}\)Ar\(^{35}\)Cl\(^-\), interfering with \(^{75}\)As\(^+\) when HCl is used in the digestion) and contamination from reagents and sample containers. \(^{22}\)

A. L. Gray \(^{54}\) was the first to perform solid sampling with LA for ICPMS measurements. By LA, the elemental composition of solids can be accessed with low detection limits (ppb). Since no solvents enter the ICP ("dry" conditions), spectral interferences are reduced. Another important motivation to use LA
instead of solution-based analyses, however, is the spatial resolution of the compositional information. Nowadays, crater sizes down to the low micrometer scale are achievable.\textsuperscript{55-56}

Even though LA is a straightforward solid sampling technique, it has some limitations. One of the major problems of LA has been the so-called elemental fractionation.\textsuperscript{57} More volatile elements were found to vaporize with a faster rate, while in the nucleation-condensation process, the elements with the higher boiling point solidify first and are therefore enriched in larger species. This leads to a deviation of the elemental composition in the aerosol from that of the sample material, which is especially pronounced with ns-LA.\textsuperscript{58} In such a case, quantification requires external standards with similar ablation behavior, which are not always available. Non-matrix matched quantification can be performed and yielded better results with fs-LA.\textsuperscript{59} It was however shown that the accuracy of the quantification depended on the used laser fluence.\textsuperscript{59-60}

Another major drawback of LA-ICPMS is the lacking possibility for a targeted manipulation of the aerosol composition. All elements contained in the aerosol reach the ICP, which can cause spectral interferences. Interfering elements can be eliminated prior to the ICP when using solution-based sample introduction with separation techniques as for example ion chromatography\textsuperscript{61}, high performance liquid chromatography\textsuperscript{62} or solid-phase extraction\textsuperscript{63}.

The operating conditions and correct choice of laser and ICPMS parameters is crucial to obtain sufficient sensitivity and accurate results for the elements of interest. Table 1 shows a summary of parameters and their influence on the measurement.\textsuperscript{2}

<table>
<thead>
<tr>
<th>Sample material</th>
<th>Instrumental parameters</th>
<th>Laser</th>
<th>Transport system</th>
<th>ICP-MS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Absorbance</td>
<td>Reflectivity</td>
<td>Wavelength</td>
<td>Pulse length</td>
</tr>
<tr>
<td></td>
<td>Heat capacity</td>
<td>Heat conductivity</td>
<td>Penetration depth</td>
<td>Surface temperature</td>
</tr>
<tr>
<td>Have influence on</td>
<td>Ablation rate</td>
<td>Surface\textsuperscript{a} composition</td>
<td>Surface\textsuperscript{a} morphology</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Surface in this context extends to the volume, which is affected by the laser radiation and vaporized or melted material.

Table 1 – Overview over laser, ICPMS and sample material parameters and their influence on measurements.\textsuperscript{2}

1.3.2. Lasers

Nowadays, a variety of lasers are available for LA, which differ in their wavelengths, pulse durations and pulse energies. In this work, two ns-lasers were used for ablation, a Nd:YAG laser operating at 213 nm and a ArF excimer laser operating at 193 nm. For fs-LA, a Yb:KGW laser was used, operating at 257 nm or 206 nm. A huge advantage of lasers operating at UV wavelengths is the lower penetration depth of...
the laser radiation into the sample material, which usually leads to reduced elemental fractionation and better defined ablation craters. Especially for transparent materials, the laser-sample coupling is very poor in the near IR region.

1.3.2.1. Nd:YAG ns-Lasers

Nd:YAG (Y3Al5O12) ns-lasers are the most often used solid state lasers in commercial LA set-ups. They belong to the group of solid state lasers using crystals or glasses, which are doped with optically active ions, mostly of transition metals. In the case of an Nd:YAG laser, about 1% of the Y3+ ions are replaced by Nd3+ ions. Stimulated emission can be induced between electronic states that are unoccupied in the ground state. Figure 12 shows the energy level scheme with the most frequent laser transition.

![Energy level scheme of a Nd:YAG laser](image)

Figure 12 – Electronic states involved in the lasing process of a Nd:YAG laser. For lasing, the most important excited states are the \(^{2}F_{5/2}, ^{2}H_{9/2}\) and \(^{4}S_{3/2}, ^{4}F_{7/2}\) levels with a pumping wavelength of 800 and 700 nm, respectively. The excited electrons relax to the upper laser level \(^{4}F_{3/2}\) via fast, radiation-free transitions. The transitions starting from this level have different fluorescence probabilities. The most dominant transmission occurs between the upper \(^{4}F_{3/2}\) and the \(^{4}I_{11/2}\) level, corresponding to a wavelength of 1.064 nm. The lower \(^{4}I_{11/2}\) level is again emptied to the ground level \(^{4}I_{9/2}\) via fast, radiant-free transitions. With frequency doubling, tripling, quadrupling or quintupling,
different wavelengths (532 nm, 355 nm, 266 nm and 213 nm, respectively) can be generated from the initial 1'064 nm.

1.3.2.2. ArF Excimer ns-Lasers

Other ns-lasers that offer ablation with a UV wavelength are ArF excimer lasers, which belongs to the group of diatomic noble gas halogen lasers. Figure 13 shows the energy potentials of a noble gas halogenide complex. The attractive potentials of the excited state and the weakly bound \( ^2\Sigma, X \) or dissociative \( ^2\Pi, A \) potentials of the ground state are the basis for lasing to occur in such systems.

![Figure 13 – Energy potentials of a noble gas halogenide.](image)

In the excited state, the noble gas atoms show a similar chemical behavior as alkali atoms, which form ionic bonds with halogen atoms. Therefore, in the excited state, noble gas halogenides are formed, as excited complexes. These reactions are highly dependent on the gas mixture, pressure and on the type of excitation. The following two reaction channels are the dominant ones:

\[
\begin{align*}
(6) \quad R + h\nu & \rightarrow R^* + e; \quad R^* + X^- + M \rightarrow RX^* + M \\
(7) \quad X_2 + h\nu & \rightarrow 2X; \quad R^* + 2X \rightarrow RX^* + X
\end{align*}
\]

where R is the noble gas atom, X the halogen atom and M a collision partner. Equation (6) corresponds to the photoionization of excited noble gas atoms or molecules or the self-absorption of the excited complex RX\(^*\). Equation (7) shows the photodissociation of X\(_2\). The formation of ArF\(^*\) excited complexes, which have a lifetime around \( \tau = 4.2 \) ns, is equivalent to a population inversion, since the molecules
don’t exist in the ground state. Other complexes have different lifetimes. The laser transition occurs between the first excited bound electronic state back to the ground state ($^2\Sigma, B \rightarrow ^2\Sigma, X$). In the case of the ArF\(^*\) excited complex, this transition corresponds to a wavelength of 193 nm. Pumping of Excimer laser occurs either by an intense electron beam or with the help of an electric high voltage discharge or a combination of both. The gas mixture typically consists of 5 – 50% of the noble gas and 0.1 – 0.5% of the halogen, in combination with a buffer gas (He and/or Ne). The gas pressure lies between 1.5 – 4 bar.

1.3.2.3. Femtosecond Lasers

In the last decade, LA with ultrashort fs-lasers has become an alternative to ns-LA. Poitrasson et al.\(^\text{72}\) showed, that UV-fs-LA-ICPMS is beneficial in terms of internal precision, repeatability and accuracy compared to UV-ns-LA-ICPMS. Especially for (semi-)metallic samples, the pulse duration has a significant impact, where a smaller thermal alteration of the ablated sample leads to a closer representation of the bulk stoichiometry in the aerosol, more stable ICPMS ion signals and a higher sensitivity.\(^3,72\) Differences in ablation processes for the two lasers will be discussed in the following section in more detail.

In this work, a Yb:KGW fs-laser was used, operating at 257 nm (frequency-quadrupling, starting from 1'028 nm) and 206 nm (frequency-quintupling) with a pulse duration of < 190 fs. The femtosecond pulse generated from the laser source has a laser energy that would not be sufficient to reach the ablation threshold on the sample surface. To generate a laser pulse in the femtosecond time frame that has an energy density high enough for ablation, the laser beam must be amplified. The laser system used in this work uses so-called chirped pulse amplification, where the pulse is initially stretched into the higher picosecond (ps-)region, as shown in Figure 14. The stretching occurs via non-linear interactions, where different frequency components are dispersed into different optical path lengths, which leads to the stretching of the pulse (“positive chirp”). The stretched pulse is then amplified and compressed to, ideally, its original duration. In the compressor, the dispersion is arranged in the opposite way as in the stretcher (“negative chirp”).\(^74-77\)

![Figure 14 – Chirped pulse amplification of a fs-laser pulse.\(^78\)](image)

The pulse originating from a fs-laser source, the seed laser, enters the stretcher, which consists of optical grids. The pulse duration is increased about a factor of 10\(^4\) by spectral segmenting. The afocal magnification system causes the optical path of the longer wavelengths to be shorter than that of the
shorter wavelengths. During amplification, a Nd:YAG ns-laser operating at 532 nm pumps the now ps-pulse within the amplifier. This is done by trapping the pulse in a cavity, where it passes through a gain medium for a defined number of times. A stepwise amplification of the pulse occurs in each pass. In the compressor, optical paths are again reversed and the pulse duration is compressed back to the fs-regime.  

1.3.3. The Ablation Process

While different ns-LA-systems have been used over decades in LA-ICPMS set-ups for materials like glass, minerals and even biological tissue, it has been shown in different studies, that especially the quantification of metals has severe limitations. It was shown that the use of fs-LA for ablating metals leads to a closer representation of the bulk stoichiometry in the aerosol. Those observations can be explained by the fundamental differences between the ablation processes for ns- and fs-LA, which emerge from the highly differing time scales of the interaction with the material.

Upon irradiation of a solid by a high-intensity laser beam, initially, the electrons near the sample surface are excited to high temperatures and a fraction of them leaves the material through photoionization. Electron relaxation takes approximately 10 ps and occurs via collisions with the lattice. If the heat transferred is sufficient to reach the vaporization temperature, the ablation threshold is overcome. Because the ns-pulse is significantly longer than the 10 ps needed for energy relaxation, the plume of ablated material starts to expand away from the ablation site while the ns-pulse is still irradiating the sample surface. The incoming pulse further heats the plume, as illustrated in the image on the top left-hand side in Figure 15. This causes a significantly stronger heat dissipation into the bulk material when compared to fs-LA. The ns-LA process therefore is much more affected by the physical properties of the sample (e.g. heat diffusion coefficient). In particular the formation of a melt in the ablation crater (violet region in Figure 15) before evaporation can cause fractionation of elements between melt and vapor. Additionally, diffusion of sample components within the so called “heat-affected-zone” (HAZ, orange region in Figure 15) can change the stoichiometry of the solid.

![Figure 15](image)

Figure 15 – The pulse with nanosecond duration still heats the ablation site while for fs-LA, the laser pulse is already over and the ablated mass can leave the surface.

Since for ultra-short pulses the electron heating and relaxation are essentially separated in time, less heat dissipation occurs via relaxation into the bulk. The image in Figure 15 on the bottom left-hand side...
illustrates that the fs-pulse is already over when the plume of ablated material starts to expand away from the sample surface. The HAZ is therefore significantly smaller for fs-LA (≈ 10 nm) compared to ns-LA (≈ 1 µm). For fs-LA, the subsequent fate of the illuminated sample depends less on the properties of the material. Therefore, it is assumed that the ablation with fs-lasers is more reproducible and deterministic.

Figure 16 – Ejection of particles from the ablation site. For fs-LA, the size distribution of the ejected particles is broader, but the occurrence of splashed particles from hydrodynamic sputtering of the melt is less pronounced than for ns-ablation.

In general, two particle formation mechanisms (Figure 16 and Figure 17) are considered to be relevant during LA in atmospheric conditions: Ejection of particles from the ablation site and nucleation and condensation during vapor expansion from the ablation spot. During nucleation-condensation, typically small (< 60 nm), single particles are formed, which may agglomerate to larger structures with time. This process occurs in ns- and fs-LA to a similar extent. Ejection of particles on the other hand takes place via different pathways for ns- and fs-LA. For fs-ablation, a fast phase transition takes place, which was described as “non-thermal” mechanism, involving a fast, adiabatic phase-explosion. These particles exhibit a broader size distribution compared to the condensate. In the case of ns-ablation, the ejection of droplets from the melt in the ablation crater, the so-called hydrodynamic sputtering, can be pronounced especially for metals, yielding particles with diameters up to the µm-range.
Differences in the aerosol formation mechanism lead to differences in ns- and fs-aerosol morphologies. Koch et al. 73 showed that fs-LA of brass produces mostly particles with diameters < 100 nm, while ns-LA leads to formation of micrometer-ranged particles. 79, 90 Glaus et al. 79 showed that ns-aerosol of brass mostly consists of NP-agglomerates, while the fs-aerosol consists of a mixture of agglomerates and single, spherical particles. For ns-LA, the stoichiometry of the laser generated aerosol was found to strongly deviate from the bulk composition, especially when ablating metals. 91

1.4. Isotope Ratio Measurements with LA-ICPMS

Isotopes of an element differ in their respective neutron numbers in the nucleus, while the number of protons is the same. Most elements in the periodic table consist of more than one isotope and their relative abundancies in nature are, with few exceptions (Li, B, C, N, O), not varying at large scale. Changes in the isotopic abundance ratios can be caused for example by radiogenic decay, or, in an open system, through chemical reactions. Several radioactive decay processes, whose half lives are known, are used in geochronology to date minerals, like for example in the U-Pb, U-Th, or Sr-Rb-Geochronology. Isotopic fractionation summarizes all processes, where the isotopic abundance ratios in a system change. Possible natural fractionation sources are chemical reactions or kinetic processes. In chemical fractionation, an enrichment of the heavier isotope in the molecule with the higher oxidation state can be found, while lighter isotopes are favored in kinetic processes. In unidirectional chemical reactions or biological processes (e.g. removal of reaction products, enzymatic reaction, etc.), the lighter isotope reacts faster, since this is favorable in terms of energy. 92 In physical processes like vaporization, the lighter isotope is favored as well. 93 The variations in isotopic composition that are caused by fractionation effects are more pronounced for the light elements because of the high relative difference between the masses of their isotopes. 94 Changes in the isotopic abundance ratios, which are caused by
fractionation processes, can also be triggered by anthropogenic influence, for example the use of enriched isotopes in isotope dilution analyses or in tracer studies.  

1.4.2. Instrumental Limitations

Fractionation effects during isotope ratio measurements are still a challenge in ICP-MS, especially if a high precision is targeted. The so-called mass bias refers to the systematic offset of the measured isotope ratio to the natural “true” abundance ratio for a pair of stable isotopes. In principle, every step during an analysis can induce a bias, starting with sample preparation steps and the nebulization of the sample. During ion sampling via the vacuum interface and within the ion optics, not all isotopes are transmitted with the same efficiency. Typically, the loss of lighter ions due to collisions and space charge effects is more pronounced. The mass bias is the combination of all the mentioned effects.

The instrumentally induced mass bias can be corrected by external, inter- or intra-element standardization. With the external standardization, the magnitude of mass bias of the isotope ratio of interest is determined using a reference standard with known abundance ratio and used to correct for the mass bias of the same isotope ratio in an unknown sample. This approach requires additional measurements for the calibration solutions and is usually done in standard-sample bracketing mode.

Intra-element standardization can be carried out when the element of interest has at least three isotopes and the abundances for two of them are known precisely. In this case the mass bias can be determined during the measurement directly and extrapolated to correct for the bias of the ratio of interest. For example, the $^{88}\text{Sr}/^{86}\text{Sr}$ ratio is considered to be invariant in nature and the mass bias determined for this pair is used to correct the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio measured with bias. For the inter-element standardization, the mass bias of a stable isotope ratio of another element is used to correct for the mass bias of the isotopic ratio of interest within the same measurement, e.g. Cu-Zn by Maréchal et al. and Pb-Tl by Longerich et al. Belshaw et al. and Woodhead et al. To estimate the magnitude of mass bias, different empirical models have been suggested: The linear, power, exponential and generalized power law. The exponential law (eq. 8) is most frequently used for the mass bias correction.

$$R_{\text{true}} = R_{\text{meas}} \cdot \left(\frac{M_2}{M_1}\right)^f$$

$R_{\text{meas}}$ is the measured isotope ratio, $M_2$ the mass of the heavier isotope, $M_1$ the mass of the lighter isotope, $f$ the mass bias correction factor or fractionation coefficient and $R_{\text{true}}$ the true isotope ratio.

Beneath the mass discrimination, isobaric and polyatomic interferences have to be corrected. One way to correct for such interferences is to measure the signal of an interference-free isotope of the same element. Via the natural isotopic abundance pattern, the contribution of the isotope interfering with the isotope of interest can be calculated. This correction protocol is called peak-stripping and is used for every isobar, which has another isotope that is free of interferences. Following the discussion above, the isotopes used for the correction are also affected by mass bias, which has to be considered before the correction. In the Rb-Sr system, $^{87}\text{Rb}$ interfering with $^{87}\text{Sr}$ is commonly accounted for by using the ion signal of $^{85}\text{Rb}$ and calculating the contribution to $m/Q$ 87 from the natural abundance ratio and, eventually, including the mass bias obtained for $^{88}\text{Sr}/^{86}\text{Sr}$. There are however indications for variability of the magnitude of mass bias amongst the elements.
1.4.3. Techniques and State of the Art

Isotope ratio measurements are usually targeted towards high precision data, in order to allow for small-scale variations amongst different samples. The best attainable precision can be estimated from the total number of counts (N) collected during the measurement of nuclide 1 or 2. Under optimum conditions counting statistics dictate that the best achievable internal precision is:

\[
RSD\% = \frac{1}{\sqrt{N_1}} + \frac{1}{N_2} \cdot 100\%
\]

The precision achievable in sequential isotope measurements by Q- and SCICPMS instruments is modest. The ICP as ion source is relatively ‘noisy’ and the measurement of only isotope per unit time is thus affected even by small variations in the ion currents produced in the source. A compromise between signal correlation and duty cycle of the measurement, as dictated by the number of isotopes, dwell and settling times, is required. In this way, the drift of the signal is compensated for to the best possible extent, however, noise occurring at time scales shorter than the scan cycle of the MS cannot be accounted for.  

The ratio precision achievable with Q-ICPMS instruments is typically ≤ 0.1% RSD, while a precision of ≤ 0.05% RSD can be achieved with a sector field ICPMS instrument operating in low resolution and E-scanning mode. The higher precision of SICPMS instruments can be attributed to the flat top signals in contrast to the near Gaussian shaped peaks observed with a Q-ICPMS. Due to the limited mass stability for signals measured with SICPMS instruments at medium and high resolution, the precisions obtained in this mode are ≤ 0.1% RSD, comparable to Q-ICPMS precisions. Precisions achievable when using a collision/reaction cell can be improved to ≤ 0.05% RSD for Q-ICPMS. For time of flight (TOF) ICPMS, a similar precision can be reached. Ions in a TOF mass filter are accelerated and hit the detector, depending on their m/Q, at slightly different times. Since a full mass spectrum is detected every 33 µs, the detection is considered to be quasi-simultaneous. The improvement compared to quadrupole-based instruments is attributed to the quasi-simultaneous detection, which decreases the time differences of the detection time between the individual isotopes.

With MCICPMS instruments, precisions comparable to ones achieved by Thermal Ionization Mass Spectrometry (TIMS) were reached. MCICPMS instruments are equipped with a detector array consisting typically of up to 15 Faraday cups and several Secondary Electron Multipliers (SEMs), which allows for simultaneous measurement of the isotopes of interest across a large intensity range. Therefore, the influence of signal drift and correlated noise on the precision significantly decreases. With MCICPMS devices, isotope ratio precision below 10 ppm RSD can be reached at low mass resolution. The static mode (constant magnet setting) can be used if every ion beam can be guided onto a Faraday cup. If isotopes outside this range need to be monitored as well, the dynamic mode has to be used, where the magnet settings are scanned across defined masses. At “pseudo” high resolution, where the width of the entrance slit is reduced, internal precisions around 0.005% RSD are achievable. Even though two overlapping signals are not resolved completely, within the wide window, the signal can be measured at a location, where the signal is flat and only the analyte contributes to the intensity.

Traditionally, TIMS, which is also a magnetic sector mass spectrometer, is used for isotope ratio measurements of metals. In TIMS, however, only elements with an ionization potential of ≤ 7 eV can be ionized, which is a large drawback compared to ICP-based instruments, which ionizes nearly all elements of the periodic system. Therefore, in contrast to TIMS, precise isotopic compositions for
poorly ionizing elements like Fe, Cu, Zr, Hf, W can be measured by MCICPMS. However, the energy spread of the ions for TIMS measurements is lower and the mass bias, which can be mainly attributed to fractionated evaporation, is about one order of magnitude lower for TIMS compared to MCICPMS (~1% at mid-masses). In contrast to ICPMS, no solid sampling is possible. Solids must be brought into solution by dissolution protocols before measurements.

1.4.4. $^{87}$Sr/$^{86}$Sr Isotope Ratio Measurements

1.4.4.1. The Sr and Rb Isotopic System

Sr has 4 stable isotopes, $^{84}$Sr, $^{86}$Sr, $^{87}$Sr and $^{88}$Sr. For mass bias corrections in Sr isotope ratio measurements, the natural and stable $^{88}$Sr/$^{86}$Sr abundance ratio of 8.37861 is used. In the Rb isotopic pattern, only $^{85}$Rb is stable, while the $^{87}$Rb isotope undergoes a β-decay with $^{87}$Sr as product. Table 2 and Table 3 summarize the isotopic abundances and ratios.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Mass (amu)</th>
<th>Range of natural variations (mole fraction)</th>
<th>Isotopic composition (atom percent [%])</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{85}$Rb</td>
<td>84.911794</td>
<td></td>
<td>72.1654 ± 0.0132</td>
</tr>
<tr>
<td>$^{87}$Rb</td>
<td>86.909187</td>
<td></td>
<td>27.8346 ± 0.0132</td>
</tr>
<tr>
<td>$^{84}$Sr</td>
<td>83.913430</td>
<td>0.0055 – 0.0058</td>
<td>0.55738 ± 0.00155</td>
</tr>
<tr>
<td>$^{86}$Sr</td>
<td>85.909267</td>
<td>0.0975 – 0.0999</td>
<td>9.85659 ± 0.00337</td>
</tr>
<tr>
<td>$^{87}$Sr</td>
<td>86.908884</td>
<td>0.0694 – 0.0714</td>
<td>7.00152 ± 0.00263</td>
</tr>
<tr>
<td>$^{88}$Sr</td>
<td>87.905619</td>
<td>0.8229 – 0.8275</td>
<td>82.58451 ± 0.00657</td>
</tr>
</tbody>
</table>

Table 2 – Range of natural variations in Sr isotopes in mole fractions and isotopic compositions in atomic percent for Rb and Sr.

<table>
<thead>
<tr>
<th>Isotope Ratio</th>
<th>Abundance Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{88}$Sr/$^{86}$Sr</td>
<td>8.37861 ± 0.003248</td>
</tr>
<tr>
<td>$^{87}$Sr/$^{86}$Sr</td>
<td>0.710339 ± 0.000261</td>
</tr>
<tr>
<td>$^{84}$Sr/$^{86}$Sr</td>
<td>0.056549 ± 0.000143</td>
</tr>
<tr>
<td>$^{87}$Rb/$^{85}$Rb</td>
<td>2.59265 ± 0.00170</td>
</tr>
</tbody>
</table>

Table 3 – Sr and Rb isotope ratios.

1.4.4.2. Limitations and State of the Art in spatially resolved $^{87}$Sr/$^{86}$Sr Isotope Ratio Analyses

Several papers demonstrated the ability of the LA-MCICPMS set-up to determine Sr isotope ratios for samples with low-Rb content and [Rb]/[Sr] < 0.002. Vroon et al. summarized the three most important limiting factors for $^{87}$Sr/$^{86}$Sr isotope ratio determinations: The instrumental mass discrimination, the laser-induced isotopic and elemental fractionation and molecular interferences. An
important factor limiting the accurate and precise determination of the $^{87}\text{Sr} / ^{86}\text{Sr}$ ratio is the isobaric interference of the $^{87}\text{Rb}^{+}$ ion signal on the $^{87}\text{Sr}^{+}$ signal. To separate these two signals, a mass resolving power $m/\Delta m \approx 286'000$ would be necessary, which is not available with ICPMS. Other isobaric interferences, are the $^{84}\text{Kr}$ and $^{86}\text{Kr}$, which originate from krypton traces in the argon gas, on $^{84}\text{Sr}$ and $^{86}\text{Sr}$. If the gas blank is stable, the Kr isobars can be subtracted via the gas blank, else, a correction via $^{83}\text{Kr}^{+}$ or $^{85}\text{Kr}^{+}$ signal is necessary and peak-stripping has to be carried out to calculate the $^{84}\text{Kr}$ and $^{86}\text{Kr}$ contribution. In particular when analyzing samples with high [Ca]/[Sr] ratio like plagioclase or carbonates, Ca-based polyatomic interferences like Ca-argides$^{12, 131}$ or Ca-dimers can cause spectral interferences too. These polyatomic ions occur at all $m/Q$ between 76 – 88 except for 77 and 79. The $^{43}\text{Ca}^{44}\text{Ca}$, for example, interferes with $^{87}\text{Sr}$ and the $^{46}\text{Ca}^{40}\text{Ar}$ or $^{44}\text{Ca}^{44}\text{Ca}$ with $^{88}\text{Sr}$. Therefore, for such samples, not only a $^{87}\text{Rb}^{+}$-correction has to be performed, but also a correction for the Ca-based interferences. During the analysis of teeth, $^{40}\text{Ca}^{31}\text{p}^{16}\text{O}$ interferes with $^{87}\text{Sr}$. $^{133}$Oxide interferences can occur from Zn, Ga and Ge. When present in the sample at significant concentration, doubly-charged ions from Er, Yb or Hf can overlap with the Sr isotopes. $^{11-12, 126, 130-131, 134, 128}$ While singly charged isobars are usually not easily identified, interferences from doubly-charged ions can be easily assigned by monitoring the signals of the doubly-charged signals of isotopes with uneven mass. If a sample contains Yb, for example, the doubly-charged $^{173}\text{Yb}^{+2}$ ion can be measured at $m/Q$ 86.5 and used to calculate the $^{176}\text{Yb}^{+2}$ contribution at $m/Q$ 88 or the $^{174}\text{Yb}^{+2}$ contribution at $m/Q$ 87. Additional interferences occur from Ba containing samples, where for example the $^{136}\text{Ba}^{40}\text{Ar}^{+2}$ interferes with the $^{86}\text{Sr}^{+}$ ion signal. $^{135-136}$

Table 4 lists possible isobaric interferences depending on the sample matrix.$^{132}$

<table>
<thead>
<tr>
<th>Source of interference</th>
<th>Mass</th>
<th>82</th>
<th>83</th>
<th>84</th>
<th>85</th>
<th>86</th>
<th>87</th>
<th>88</th>
<th>89</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr</td>
<td>Y</td>
<td>$^{82}\text{Kr}$</td>
<td>$^{83}\text{Kr}$</td>
<td>$^{84}\text{Sr}$</td>
<td>$^{85}\text{Sr}$</td>
<td>$^{86}\text{Sr}$</td>
<td>$^{87}\text{Sr}$</td>
<td>$^{88}\text{Sr}$</td>
<td>$^{89}\text{Sr}$</td>
</tr>
<tr>
<td>Kr</td>
<td>Rb</td>
<td>$^{82}\text{Kr}$</td>
<td>$^{83}\text{Kr}$</td>
<td>$^{85}\text{Rb}$</td>
<td>$^{87}\text{Rb}$</td>
<td>$^{88}\text{Sr}$</td>
<td>$^{86}\text{Sr}$</td>
<td>$^{87}\text{Sr}$</td>
<td>$^{88}\text{Sr}$</td>
</tr>
<tr>
<td>REE</td>
<td>Y</td>
<td>$^{82}\text{Kr}$</td>
<td>$^{83}\text{Kr}$</td>
<td>$^{84}\text{Sr}$</td>
<td>$^{85}\text{Sr}$</td>
<td>$^{86}\text{Sr}$</td>
<td>$^{87}\text{Sr}$</td>
<td>$^{88}\text{Sr}$</td>
<td>$^{89}\text{Sr}$</td>
</tr>
<tr>
<td>Fe/Zn/Ga oxides</td>
<td>Y</td>
<td>$^{82}\text{Kr}$</td>
<td>$^{83}\text{Kr}$</td>
<td>$^{84}\text{Sr}$</td>
<td>$^{85}\text{Sr}$</td>
<td>$^{86}\text{Sr}$</td>
<td>$^{87}\text{Sr}$</td>
<td>$^{88}\text{Sr}$</td>
<td>$^{89}\text{Sr}$</td>
</tr>
<tr>
<td>Ca dimers</td>
<td>Ca</td>
<td>$^{40}\text{Ca}^{40}\text{Ca}$</td>
<td>$^{40}\text{Ca}^{44}\text{Ca}$</td>
<td>$^{40}\text{Ca}^{48}\text{Ca}$</td>
<td>$^{40}\text{Ca}^{49}\text{Ca}$</td>
<td>$^{40}\text{Ca}^{49}\text{Ca}$</td>
<td>$^{40}\text{Ca}^{49}\text{Ca}$</td>
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<td>$^{40}\text{Ca}^{49}\text{Ca}$</td>
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<tr>
<td>Ca argides</td>
<td>Ca</td>
<td>$^{40}\text{Ca}^{40}\text{Ar}$</td>
<td>$^{40}\text{Ca}^{44}\text{Ar}$</td>
<td>$^{40}\text{Ca}^{48}\text{Ar}$</td>
<td>$^{40}\text{Ca}^{49}\text{Ar}$</td>
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<td>$^{40}\text{Ca}^{49}\text{Ar}$</td>
<td>$^{40}\text{Ca}^{49}\text{Ar}$</td>
<td>$^{40}\text{Ca}^{49}\text{Ar}$</td>
</tr>
<tr>
<td>Ca-P</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4 – Possible isobaric or polyatomic interferences.$^{132}$
In mathematical correction protocols, isobars are corrected via the peak-stripping method, which is used to calculate the individual isotope signal contributions for mixed signals and can compensate for these interferences to a certain extent. To calculate the contribution of the $^{87}$Rb on the signal at $m/Q$ 87, for example, the $^{85}$Rb$^+$ ion signal is measured. By assuming a natural abundance ratio of $^{87}$Rb/$^{85}$Rb (2.5927) and considering the mass discrimination of the ICPMS, the $^{87}$Rb$^+$ contribution can be obtained and subtracted. The contribution of the $^{84}$Kr$^+$ contribution at $m/Q$ 84 is calculated in the same way via the $^{83}$Kr$^+$. As more interferences get involved, these corrections can become complex. Contributions from Ca-argide ions or Ca-dimers for example which are, however, not all listed in Table 4 also interfere with the isotopes of Kr, Rb and Sr. The analysis of otoliths shown in Figure 1 in chapter 1.1., for example, is relatively straightforward with LA-ICPMS. Otoliths typically have a low Rb (< 1 ppm) and high Sr concentrations (1'000 ppm). $^{137}$ The isobaric interference of $^{87}$Rb on $^{87}$Sr does not affect the $^{87}$Sr/$^{86}$Sr ratio measurements dramatically, which means that with the mathematical correction, sufficiently high accuracies and precisions are obtained. In this case however, the Ca-based polyatomic ions may become highly relevant. CaAr$^+$ and CaCa$^+$ isotopologues, interfering with the Sr isotopes are however of minor abundance. Only recently it was found that also doubly charged molecular ions of BaAr can be formed $^{135,138}$, which can cause substantial deviations in Sr isotope ratio measurements of Baryte, for example. $^{139}$

For other minerals like silicates, the Rb concentration can however exceed the Sr content by several orders of magnitude and the Rb and Sr concentrations can vary over a relatively large range. In those cases, the influence of the $^{87}$Rb isobar gets more prominent. Jackson et al. $^{20}$ analysed the $^{87}$Sr/$^{86}$Sr ratios of olivine-hosted melt inclusions from nine Samoan basalts, which had a large variability (0.70459 – 0.70926). The reference TIMS value was reproduced within ± 320 ppm. For samples with a [Rb]/[Sr] concentration ratio of 0.04, an error of 145 ppm was obtained, for samples with a [Rb]/[Sr] ratio > 0.14, however, the error increased to 505 ppm. The conclusion of this study was, that for samples with a [Rb]/[Sr] concentration ratio > 0.14, $^{87}$Sr/$^{86}$Sr isotope ratio analyses by LA-ICPMS would not yield a sufficiently high accuracy and precision.

A viable way to mitigate the interference of Rb, when performing isotope ratio measurements with LA-ICPMS is the separation of Sr from Rb by using reaction cell technology. $^{140}$ CH$_3$F as reaction gas can selectively fluorinate Sr via an ion–molecule reaction:

\[
(10) \quad \text{CH}_3\text{F} + \text{Sr}^+ \rightarrow \text{SrF}^+ + \text{CH}_3 \quad \Delta H_r = -31.2 \text{ kcal/mol}
\]

The formation of RbF$^+$ was not observed. The precision of the $^{87}$Sr/$^{86}$Sr isotope ratio measurements was close to counting statistics (0.03%). The deviation of the calculated age to the reference TIMS value was < 1% and the deviation of the calculated age to the reference TIMS value was < 1%.

Hogmalm et al. $^{141}$ performed in-situ dating of K-rich minerals with a LA-ICPMS/MS approach and online chemical separation of Rb and in an N$_2$O- or SrF$_5$- or SrF$_6$ + H$_2$-filled reaction cell, where Sr selectively reacted to dominantly SrO$^+$ at $m/Q$ 104 with N$_2$O or SrF$^+$ at $m/Q$ 107 with SrF$_6$, while no detectable amounts of RbO$^+$ or RbF$^+$ were formed. Both gases showed significantly higher reaction product formation compared to O$_2$, which was used in prior work as reaction cell gas. $^{142}$ For the $^{87}$Sr/$^{86}$Sr isotope ratios, RSDs between 0.1 – 0.4% were obtained after > 8 hours analysis time.

To correct for the combined mass bias effects caused by instrumental mass discrimination and LA-induced fractionation, different mass fractionation laws can be used, which have been mentioned in the
previous chapter. The degree of mass discrimination of the Sr isotopes is by convention estimated using the “true" $^{86}\text{Sr}/^{88}\text{Sr}$ ratio of 0.1194 $^{23}$, which is assumed to be constant. The mass discrimination is commonly calculated from the measured intensity ratio and true $^{86}\text{Sr}/^{88}\text{Sr}$ isotope ratio (in equation (8) in chapter 1.4.2.) and is used to correct the measured $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{85}\text{Rb}$ intensity ratios. The mass discrimination observed for $^{86}\text{Sr}/^{88}\text{Sr}$ may however not be equal to that of $^{87}\text{Rb}/^{85}\text{Rb}$, which is the major source of bias introduced by this correction. The higher the Rb content of a sample, the larger the $^{87}\text{Rb}$ contribution to the signal at $m/Q$ 87 and the error arising from the usage of the $^{86}\text{Sr}/^{88}\text{Sr}$ mass bias factor for correction of the $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{85}\text{Rb}$ ratio increases. The prior elimination of the Rb for $^{87}\text{Sr}/^{86}\text{Sr}$ analyses is therefore the best way to achieve a high precision and accuracy.

The combination of sample matrix dependent peak-stripping steps and the mass bias correction gives a mathematical correction protocol. Vroon et al. $^{132}$ summarized the correction protocols of some publications, as listed in Figure 18.

![Figure 18](image)

Figure 18 – Overview over different correction protocols for $^{87}\text{Sr}/^{86}\text{Sr}$ ratio measurements. $^{132}$

1.5. Electrothermal Vaporization (ETV)

Electrothermal vaporization has been used as sample introduction system for several analytical systems like atomic emission spectroscopy (AES) and mass spectrometry (MS). One of the most popular applications of ETV devices is their use as atomizers in atomic absorption spectroscopy (AAS), e.g. for the determination of trace metals in different matrices. $^{143-144}$ In 1983, Gray et al. $^{145}$ were the first who used an ETV equipped with a graphite rod as sample introduction system for ICPMS to determine transition metal elements in µL sample aliquots. It was shown that the heating of laser-aerosol in an ETV unit can also be used to initiate an element-specific change in the ICPMS signals. $^{146}$ It could also be
shown in earlier work that Rb and Sr react differently to thermal treatment of laser-generated aerosols. Based on these studies there appears to be a significant potential that such an approach may allow for spatially resolved Sr isotope ratio determinations in samples containing excessive amounts of Rb.

1.5.1. ETV-ICPMS

In conventional ETV-ICPMS set-ups, a small sample portion is placed in a heated reservoir, e.g. a graphite furnace or on a metal filament, from where it can evaporate in a controlled manner and get introduced into the ICPMS with a carrier gas. Figure 19 shows the setup of a commercial ETV system (Perkin Elmer HGA-600MS). In position (a), the sample is pipetted into the graphite tube through a small hole. In the first step of an ETV-ICPMS analysis the graphite tube or metal filament is slowly heated to evaporate the solvent while gas is introduced from both ends. The temperature is kept slightly above the boiling point of the solvent and below that of the analyte in the predominant chemical form. The heating rate should not be too fast to avoid analyte losses by explosive boiling. During pyrolysis, the second step of an ETV-ICPMS analysis, the temperature is set to values that are high enough to remove as much of the matrix as possible, but without vaporizing the analytes. Subsequently, vaporization of the analytes is initiated. For that purpose, the seal probe is pushed onto the tube to close the hole and make the system airtight (b) and, subsequently, the carrier gas flow is enabled. The temperature is increased, leading to evaporation of the sample components. The compounds present in the sample are vaporized according to their physical properties and are transported to the ICPMS and detected in a time-resolved manner. At the end of every measurement, a cleaning step is performed, by increasing the temperature to ≈ 2°700°C for a short time to remove residues. Assisted cleaning with modifiers might be desirable to reduce the cleaning step temperature or duration to increase the lifetime of the tube.

Figure 19 – Perkin Elmer HGA-600MS ETV unit with a graphite furnace for (a) the vaporization step with a closed switching valve and (b) an open switching valve to carry the aerosol into the plasma.
One major advantage of ETV as a sample introduction system for ICPMS instruments over alternative systems is its low sample consumption (typically 5 - 20 µl). A further advantage is pre-concentration of the analyte, which can be performed by multiple injections before atomization. Another advantage is the possibility for sequential vaporization of the sample constituents. Potentially interfering elements can be separated based on their vaporization points. Elements of interest can be measured mostly after the vaporization of solvents, for example. In that way spectral and non-spectral interferences can be alleviated, especially polyatomic interferences containing elements from solvents. An improvement in LODs was also reported. Figure 20 gives an overview over relevant parameters that have to be considered before defining a temperature program or before choosing additional modifiers.

One of the most important drawbacks of graphite furnace heaters are the carbon-based interferences that are created during heating, especially at high temperature. \(^{13}C^{18}Ar^+\) on \(^{51}V^+\) or \(^{16}O^{16}O^{13}C^+\) on the monoisotopic \(^{45}Sc^+\) are just two examples of newly introduced polyatomic interferences. Another drawback is the “memory” effect of the graphite tube, where the analyte enters the material of the graphite tube below the inner surface and forms refractory carbides with the graphite. This effect especially gets relevant for high temperatures. The use of pyrolytic graphite–coated tubes is therefore desirable, since the memory effect is reduced during their usage due to the coating, which protects the surface of the tube. Metal coil heaters, on the other hand, interact with oxygen at high temperature, which limits the lifespan of metal-based heaters strongly. Further limitations of ETV-ICPMS are the sample throughput and elemental coverage, eventually. The temperature program can easily require minutes per analysis and highly refractory compounds such as ThO\(_2\) may not be vaporized at the temperatures attainable in an ETV (> 3’000 °C).
1.5.2. LA-ETV-ICPMS

Element-specific vaporization in an ETV was shown by Vaculovic et al. \(^{146}\) to occur during heating of laser-generated aerosols in an ETV. The effect of this online thermal aerosol treatment on the ICPMS ion signals was investigated for a variety of metals. A HGA-600MS ETV unit was combined with an LSX 200 (CETAC Technologies, Omaha, USA) ns-LA-system and an Elan 6000 (PE/Sciex, Ontario, Can) quadrupole-based ICPMS instrument for ion signal detection. It could be shown that an element-selective signal attenuation can be triggered, depending on the order of the melting and boiling points of the metals. As an example, Figure 21 shows the ion signals for Ni, Mo and Zn, which have differing thermodynamic properties, in particular melting and boiling temperatures. Mo is not affected by the increase in ETV temperature, Ni is moderately suppressed, and the Zn signal undergoes a substantial intermediate suppression. While ion signals for Ni only drop by a factor of ~ 2 at a temperature > 2'000 °C, Zn is suppressed by orders of magnitude at that temperature. Furthermore, the profile of Zn does not drop continuously but appears to reach an intermediate “plateau” for temperatures between 1'000°C and 1'500 °C. When exceeding ≈ 2’500 °C both Ni and Zn signals seem to recover to almost the level that was observed without heating.

![Figure 21 - Transient Ni, Mo and Zn signals for during ETV heating. The graphite furnace temperature was increased to 2’700 °C (dotted line) and decreased back to non-heating conditions. \(^{146}\)](image)

Vaculovic et al. \(^{146}\) explained this observation by re-mobilization of condensed material on surfaces downstream the furnace, triggered by the high temperatures. By combining the LA-ETV setup with a particle size measurement system, it was shown, that the number of detected particles decreases in a similar manner as the ICPMS ion signal. This elimination was suggested to take place via vaporization in the graphite furnace and subsequent condensation after the furnace, at cool surfaces of the setup.

The potential of the LA-ETV-ICPMS setup for online interference suppression was initially demonstrated in the PhD thesis of R. Brogioli \(^{147}\), who used a similar LA-ETV-ICPMS setup as before and could show that \(^{87}\)Rb-\(^{87}\)Sr isobar separation is possible. It was shown that accurate and precise \(^{87}\)Sr/\(^{86}\)Sr isotope ratio
measurements could be carried out for samples with a [Rb]/[Sr] concentration ratios up to 0.28 instead of the previously postulated ratio of 0.14 (LA-ICPMS, Jackson et al. 20).

1.6. Aim of this Work

The aim of this work was to better understand the processes involved in the removal of more easily vaporized elements from laser-generated aerosols. The scope was to establish a method for spatially resolved Sr isotope ratio analyses in samples containing substantial amounts of Rb. One major aspect in this view was to investigate the influence of the morphologies of aerosols generated by ns- and fs-LA. Also, the influence of the configurations of the ETV for thermal treatment on the extent of elemental separation was of interest. In this context it was also of interest to which extent fractionated evaporation of isotopes may as well be associated with the elimination of the elements. The experiments outlined in the following sections were targeting at a sensitive, accurate, in-situ analysis of Sr isotope ratios in minerals, in particular for geochronological purposes. By inclusion of the parallel detection of the elemental composition for a fraction of the aerosol, also Rb and Sr concentration ratios of the untreated material should be analysed, using a conventional ICPMS instrument, while isotope ratios were aimed at by using a multi-collector ICPMS available in the lab. Due to a malfunction of the latter the corresponding experiments could however not be included in this work and the better understand of the fundamental processes involved gained more weight.
2. Experimental

In chapter 3.1.1. of the results section, the GeoLas-C ns-laser and the Excite PHAROS fs-laser were used in combination with the ETV-4000 prototype for aerosol morphology studies. The ion signals were recorded with the ELAN 6100 DRCl+ Q-ICPMS instrument, while the PSDs were recorded with an Optical Particle Counter (OPC). The aerosol morphology was studied by collecting the aerosol on filters and analyzing them by Scanning Electron Microscopy (SEM). The outlet of the ETV-4000 was therefore either connected to the Q-ICPMS instrument, the OPC or a membrane pump for aerosol collection. In chapter 3.1.2., the Excite PHAROS fs-laser was connected to the HGA-600MS ETV unit and the ELAN DRCII to record the transient signal behavior of brass samples under a continuous temperature increase. In chapter 3.1.3., the Cu-Zn separation efficiency of the HGA-600MS and ETV-4000 were compared by using the Excite PHAROS fs-laser and either the ELAN DRCII or the ELAN 6100 DRCl+ Q-ICPMS. In chapter 3.2.1., the Rb-Sr separation performance of the HGA-600MS, the ETV-4000 prototype and the tungsten wire based custom-made ETV was compared. For that purpose, the Excite PHAROS fs-laser was connected to one of the ETVs. For the fs-LA-HGA-600MS and fs-LA-prototype combination, the ELAN DRCII was used for ion signal detection, while for the fs-LA-ETV-4000 combination, the Element XR SFICPMS instrument was used. For chapter 3.3.1., either the Excite PHAROS was used in combination with the HGA-600MS ablating with 257 nm or in combination with the ETV-4000 ablating either with 206 nm or 257 nm. For the HGA-600MS measurements, the ELAN DRCII was used for ion signal detection, while for the ETV-4000 measurements, the Element XR was used. For chapters 3.2.2., 3.3. and 3.4., the fs-LA-ETV-4000-Element XR combination at 257 nm was used.

2.1. Laser Ablation Systems

2.1.1. GeoLas-C

The GeoLas-C (Coherent, Göttingen, Germany) system comprises a 193 nm ArF excimer laser with a pulse duration of 14 ns connected to true beam homogenization optics for spot sizes between 4 and 160 μm in diameter. A conventional cylindrical ablation cell with a nozzle inlet was used, which should account for a homogeneous distribution of the aerosol across the transfer lines. The ablation cell can be moved with 0.1 μm/step in x-, y- and z-direction. The system is fully computer controlled. The repetition rate can be adjusted between 1 and 200 Hz and the energy density at the sample surface can reach > 30 J/cm².

2.1.2. Excite PHAROS

For fs-LA, an Excite PHAROS Femtosecond Laser Ablation System (Teledyne CETAC Technologies, Bozeman, MT, USA) was used. The system, which has a fundamental wavelength of 1'028 nm, was operated at the 4th (257 nm) or 5th harmonic (206 nm) with a pulse duration < 10 ps. Repetition rates between 1 – 200 kHz in 1 Hz steps can be used and crater sizes between 1 – 65 μm are adjustable. The stage positioning, illumination and ablation parameters are controlled with the Chromium Software. Laser energies were measured with an external sensor provided by Photon Machines. The system is equipped with a HelEx II Active 2-Volume Ablation Cell with two individually adjustable helium gas flows, the main volume and inner cup flow, as shown in Figure 22.
Figure 22 - Main volume and inner cup helium gas flows in the ablation cell of the Excite PHAROS fs-laser.

2.2. Optical Particle Counter and Dilutor

For PSD experiments, an Ultra-High Sensitivity Aerosol Spectrometer (UHSAS) DOC-0210 OPC (Droplet Measurement Technologies, Colorado, USA) was used in combination with a dilutor. The aerosol, which was generated in the LA-system, was guided through the ETV towards the dilution unit and OPC. The instrument offers a measurement range between 0.06 – 1 µm. Particles are counted in up to 99 user-specified sizing bins with a sizing resolution of 2 – 5%. The particles are confined to a region with 0.5 mm.\textsuperscript{164}

The aerosol was diluted prior to the PSD measurements with a 10-bucket wheel rotating disc diluter (MD19-1i, Matter Engineering, Wohlen, Switzerland), which is shown schematically in Figure 23.

Figure 23 – Sketch of the aerosol dilution unit using a 10-bucket wheel rotating disk diluter. Ar was used as dilution gas.
The magnitude of dilution was adjusted via the speed of the 10-cavity rotating disc (1 – 10), the gas flow of an external dilution gas (Ar, 0.5 – 1.5 L/min) and an internal sample gas flow rate within the OPC (1 – 100 cm$^3$ per minute). The sheath flow was set to 700 cm$^3$ per minute. The dilution factor and ratio plotted against the potential of the dilutor is shown in Figure 24. The dilution was adjusted to a level, where the particle counts of the initial aerosol were as high as possible for non-heating conditions, but just below detector saturation. For non-heating conditions, therefore, a relatively high dilution level was used. Because the particle counts decreased with increasing ETV temperature, the dilution level was decreased whenever necessary. The given numbers in chapter 3.1. are the dilution factors, by which the measured count number was multiplied and subsequently plotted against the diameter range. It should be noted that the dilution principle of the MD-19i may cause particle sizes below 50 nm to be overrepresented in the diluted aerosol fraction. Our own tests also indicated that larger particles are diluted fairly homogeneous. The measurement time was 1 minute, and, for comparison of the PSDs, the count rates were corrected for dilution.

2.3. Aerosol Morphology Studies – SEM Images

For SEM imaging, the aerosol exiting the ETV was collected on 13 mm isopore hydrophilic polycarbonate membrane filters with 0.4 mm pore size (Merck, Germany) during 5 to 8 minutes, depending on the experiment. First, the desired power level was set at the ETV and, subsequently, the ablation and aerosol collection were started. The aerosol was collected with the help of a membrane pump downstream the filter to avoid excess pressure in the ablation cell. SEM images were recorded on a LEO Gemini 1530 SEM (Zeiss, Oberkochen, Germany) using a field emission source and an acceleration of 1 kV.
2.4. Electrothermal Vaporization Units

2.4.1. HGA-600MS

For the first experiment series an HGA-600MS (Perkin Elmer, Norwalk, USA) ETV unit was used. Figure 25 shows the setup of the ETV. Two inert “internal” Ar gas flows enter the ETV before and after the furnace, respectively, when the HGA-600MS is operated in the by-pass mode. The mode is changed with the switch valve. The heating unit is a graphite tube (HGA Pyrocoated Graphite Tubes, Perkin Elmer) with a length of 28 mm and a diameter of 6 mm as shown in Figure 26. The HGA-600MS was originally designed to vaporize liquid aliquots, which were pipetted into the graphite tube via a hole. In this work, laser-generated aerosol was transported from the ablation cell to the ETV through the graphite tube with a He carrier gas flow. The aerosol was thermally treated in the graphite furnace and, subsequently, transported towards the ICP. For LA-ETV-ICPMS measurements, the hole was constantly sealed by the graphite seal probe and the internal gas flows were switched off.

Figure 25 – Setup of the HGA-600MS ETV unit.  

Figure 26 – HGA Pyrocoated L’vov Graphite Tube with 6 mm diameter and 28 mm length. In this work, a graphite tube without platform was used.

The operation of the HGA-600MS was controlled via the Perkin Elmer Elan 3.0 software. Individual temperature steps can be programmed by defining the target temperature, the heating rate, as well as the heating duration.
2.4.2. ETV-4000

The ETV-4000 prototype (Spectral Systems GmbH, Fürstenfeldbruck, Germany) is also equipped with an electrically heated graphite tube. The tube is longer (45 mm) than the one of the HGA-600MS, but has the same diameter (6 mm), as illustrated in Figure 27. The carrier gas continuously flows through the graphite tube and a make-up gas can be added near the tube exit to carry the aerosol and create stable ICP conditions. The furnace temperature cannot be set directly but can be regulated via a power supply between levels 0 (no heating) and 10 (maximum heating). An estimate of the corresponding furnace temperature was made by comparing the onset temperatures from the signal suppression profiles with those from previous experiments performed with the HGA-600MS ETV. This comparison was done for a brass standard (MBH CRM B26). Based on these data, power level 2.5 results in a furnace temperature of about 1000 °C, level 4.5 in about 1’500 °C and level 6 > 2’500 °C. Figure 27 shows the setup of the ETV-4000.

![Figure 27 – Sketch of the ETV-4000 prototype (graphite tube with Ø 6 mm and 45 mm length).](image)

Both graphite tube ETVs are constructed in way that the tube is held between two spring-loaded, water-cooled graphite contacts to maintain an electrical contact to the power supply and at the same time to allow longitudinal expansion of the tube during heating. Gas tightness is thus to some extent depending on the conditions of the contact surfaces and the tension of the spring. In particular during long heating times at high temperatures, the mechanical stress may thus cause leakage and deterioration of the seal.

2.4.3. Custom-made Prototype “Wire ETV”

Figure 28 shows the setup of the custom-made wire ETV prototype. It consists of two concentric quartz glass tubes 1a/b, a metal cap and bottom 5a/b. For cooling, water was guided through the metal caps and in between the two glass tubes. The temperature of the cooling liquid was controlled by a thermostat, which was coupled to the set-up via an inlet 2b at the bottom and outlet 2a at the top cap. A coiled tungsten wire 4b, which was connected to a power supply via electric contacts 4a, was used as heater. The helium/aerosol mixture coming from the LA-system was guided through the inner volume of the smaller quartz glass tube from the inlet 3a (top cap) to the outlet 3b (bottom cap). Aerosol heating was performed by drawing DC electric current through the tungsten wire at different power settings, while the carrier gas was intended to flow through the axis of the wire-coil.
2.4.4. Heating Protocols and Suppression Factor

To determine the ion signal suppression depending on the ETV temperature, different heating protocols were applied. For most experiments, individual measurements with fixed ETV temperatures were carried out and compared to the non-heating conditions. The protocol consisted of four steps, as shown in Table 5. Prior to the measurement, the heating of the ETV was set to the respective power level or temperature. After starting the data acquisition and as soon as stable operating conditions were reached (monitored via the $^{13}$C$^+$ signal), the background signals (BG$_H$) were recorded for 30 s at the desired temperature. Then, a line scan was started and at least 60 s of the stable signal (LA$_H$) was recorded while the graphite furnace was held at the same power level. Then, the heating was turned off while the laser was still ablating the sample. The signal without heating was recorded for at least 60 s (LA$_{RT}$). Subsequently, the ablation was stopped, the aerosol was flushed out of the system and the background signal was measured for at least 30 s (BG$_{RT}$). For the wire ETV, ion signals at different heating powers were recorded in one measurement cycle. The stability of the background was monitored via the $^{184}$W$^{16}$O$^+$ signal before initiating the ablation.

<table>
<thead>
<tr>
<th>Recorded Signal</th>
<th>Heating</th>
<th>Duration</th>
<th>Laser</th>
</tr>
</thead>
<tbody>
<tr>
<td>BG$_H$</td>
<td>On</td>
<td>30 s</td>
<td>Off</td>
</tr>
<tr>
<td>LA$_H$</td>
<td>On</td>
<td>60 s</td>
<td>On</td>
</tr>
<tr>
<td>LA$_{RT}$</td>
<td>Off</td>
<td>60 s</td>
<td>On</td>
</tr>
<tr>
<td>BG$_{RT}$</td>
<td>Off</td>
<td>30 s</td>
<td>Off</td>
</tr>
</tbody>
</table>

Table 5 – Heating protocol for single temperature measurements.
For some experiments carried out with the HGA-600MS, a different heating protocol was used, which is listed in Table 6. In these cases, the temperature of the graphite tube of the HGA-600MS was continuously increased at a defined rate. At first, the background was again recorded for 30 s (BG\textsubscript{H}). Then, LA was initiated, and the signal was recorded for at least 60 s (LA\textsubscript{RT}). Subsequently, the graphite wall temperature was quickly set to either X = 100 °C or 1'000 °C, depending on the presented data (LA\textsubscript{X}). From that onset point, the temperature was increased with a heating rate of 4.8 °C/s up to 2'500 °C (LA\textsubscript{2500}) before the heating was stopped completely and the graphite tube was allowed to cool down to room temperature (LA\textsubscript{RT}). Subsequently, the ablation was stopped (BG\textsubscript{RT}).

<table>
<thead>
<tr>
<th>Recorded Signal</th>
<th>Temperature</th>
<th>Duration</th>
<th>Heating Rate</th>
<th>Laser</th>
</tr>
</thead>
<tbody>
<tr>
<td>BG\textsubscript{RT}</td>
<td>20 °C</td>
<td>30 s</td>
<td>1 s</td>
<td>Off</td>
</tr>
<tr>
<td>LA\textsubscript{RT}</td>
<td>20 °C</td>
<td>60 s</td>
<td>1 s</td>
<td>On</td>
</tr>
<tr>
<td>LA\textsubscript{X}</td>
<td>100 / 1'000 °C</td>
<td>10 s</td>
<td>1 s</td>
<td>On</td>
</tr>
<tr>
<td>LA\textsubscript{2500}</td>
<td>2'500 °C</td>
<td>504 / 315 s</td>
<td>4.8 °C/s</td>
<td>On</td>
</tr>
<tr>
<td>LA\textsubscript{RT}</td>
<td>20 °C</td>
<td>10 – 20 s</td>
<td>1 s</td>
<td>On</td>
</tr>
<tr>
<td>BG\textsubscript{RT}</td>
<td>20 °C</td>
<td>30 s</td>
<td>1 s</td>
<td>Off</td>
</tr>
</tbody>
</table>

Table 6 – Heating protocol for a continuous increase of the temperature in the HGA-600MS with 4.8 °C/s between 100 °C or 1’000 °C to 2’500 °C, respectively. The other temperature changes were performed with the highest available ramp time (1 s).

In contrast to the heating protocol given in Table 5, a background-correction was only performed with the background recorded without heating (BG\textsubscript{RT}). Release of previously deposited material may thus result in an overestimation of the ion signal intensities. Therefore, this mode was primarily used for a qualitative assessment of the suppression profiles.

The signal suppression factor \( S \) for an ion signal was calculated by normalizing the background-corrected ion signal intensity at the corresponding temperature (\( I_{H} = LA_{H} - BG_{H} \) or \( LA_{H} - BG_{RT} \), when the temperature was ramped) to the background-corrected ion signal intensity at room temperature (\( I_{RT} = LA_{RT} - BG_{RT} \)):

\[
(11) \quad S = \frac{I_{H}}{I_{RT}}
\]

2.5. ICPMS instrumentation

2.5.1. ELAN DRCII and 6100 DRC\textsuperscript{plus}

The ELAN DRC instruments (Perkin Elmer, Norwalk, USA) are essentially identical quadrupole-based ICPMS instruments that are equipped with a dynamic reaction cell (DRC) for interference control. The major difference is that a so-called axial field technology was added to the ELAN 6100 DRC\textsuperscript{plus} after installation, while the ELAN DRCII contains it in its original design. The DRC was however not used in the experiments carried out in these studies and the instrument was always operated in so-called standard mode. The operating conditions were optimized with laser ablation sampling of NIST SRM 610 on a daily basis to ensure highest sensitivity across the \( m/Q \) range (monitored via \(^7\)Li\textsuperscript{+}, \(^{23}\)Na\textsuperscript{+}, \(^{27}\)Al\textsuperscript{+}, \(^{65}\)Cu\textsuperscript{+}, \(^{66}\)Zn\textsuperscript{+}, \(^{140}\)Ce\textsuperscript{+}, \(^{232}\)U\textsuperscript{+} and \(^{232}\)Th\textsuperscript{+}), while limiting oxide-ion formation via \(^{232}\)Th\textsuperscript{16}O\textsuperscript{+}/\(^{232}\)Th\textsuperscript{+} to < 1% and a \(^{238}\)U\textsuperscript{16}O\textsuperscript{+}/\(^{232}\)Th\textsuperscript{+} sensitivity ratio of \( \sim 1 \). An “Autolens” calibration was carried out and the pulse-counting and analog stages of the detector were calibrated for every isotope measured. For all measurements, the peak-hopping mode was used with a dwell time of 10 ms. Typical operating conditions of the ICP were an RF-
forward power of 1’350 W, coolant gas flow rate of 16 L/min, auxiliary gas flow rate of 0.7 – 0.8 L/min and an argon make-up gas flow rate of 0.7 – 0.9 L/min. 167

2.5.2. Element XR

For the Rb elimination efficiency studies and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio fractionation study, the fs-LA-system was used in combination with the ETV-4000 and the Element XR SFICPMS instrument. The Element XR is a double-focusing instrument with a reverse Nier-Johnson mass analyser geometry, offering a low off-peak background intensity (~ 0.2 cps) and high sensitivities (~ 2’000’000 cps per ng/g of a mid $m/Q$ isotope, with solution nebulization for sample introduction). 168 The instrument used in this work was furthermore equipped with the “Jet interface”, which can achieve 5 - 10 x higher sensitivities for dry ICP operating conditions when an additional $\text{N}_2$ flow of 5 – 15 mL/min is admixed to the aerosol stream before the ICP. Mass resolving power can be selected in three steps (300 - low, 4’000 - medium and 10’000 - high) but typically the low-resolution mode was used. Only for the measurements, where polyatomic interferences were investigated, the medium resolution mode was used. The Element XR is additionally equipped with a triple-mode detection system using a conventional dual-stage SEM and a Faraday cup. For isotope ratio measurements, either only the analogue or pulse counting mode of the SEM was used to prevent artefacts originating from detector calibration errors. Optimization was also performed while ablating NIST SRM 610 at a laser energy of 50% with a repetition rate of 25 Hz, a crater size of 55 µm and line scans with 1 µm/s rate. The $^{238}\text{U}^{+}/^{232}\text{Th}^{+}$ was = 1 and the oxide ratio of $^{238}\text{U}^{16}\text{O}^{+}/^{238}\text{U}^{+}$ < 0.3 %. For Sr isotope ratio analyses, the E-scan mode was applied to record ion signals of $^{82}\text{Kr}^{+}$, $^{83}\text{Kr}^{+}$, $^{167}\text{Er}^{++}$, $^{84}\text{Sr}^{+}$, $^{85}\text{Rb}^{+}$, $^{86}\text{Sr}^{+}$, $m/Q$ 87, $^{88}\text{Sr}^{+}$. The magnet mass was set to $^{82}\text{Kr}^{+}$ ($m/Q$: 81.913) and a rapid mass scan was carried out with dwell times of 10 ms per $m/Q$ (mass window of 50%, sample time of 1 ms and 20 samples per peak). Mass calibration and detector cross calibration were performed prior to the measurements. The mass offset determination was done prior to a measurement set for every isotope individually. Typical operating conditions of the ICP were an RF-forward power of 1’300 W, coolant gas flow rate of 12 L/min, auxiliary gas flow rate of 0.7 – 0.8 L/min an argon make-up gas flow rate of 0.8 – 1.1 L/min and a $\text{N}_2$ flow rate of 10 - 13 mL/min.

2.6. Samples

2.6.1. NIST SRM 610 and NIST SRM 987

NIST 610 silicate glass and NIST 987 powder Standard Reference Materials were purchased from the National Institute of Standards and Technology. The NIST SRM 610 contains 61 elements in the glass matrix with concentrations in the range of 100 mg/kg to 500 mg/kg. For 25 elements and the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio (0.7094 ± 0.0002), reference values were given in the certificate. 169 For the other elements, reference values determined by Jochum et al. 170 were used. Table 12 lists the corresponding Rb and Sr concentrations. The NIST SRM 987 SrCO$_3$ powder, which was used to prepare a pellet for LA, has certified $^{88}\text{Sr}/^{86}\text{Sr}$ (8.378 61 ± 0.003 25), $^{87}\text{Sr}/^{86}\text{Sr}$ (0.710 34 ± 0.000 26) and $^{84}\text{Sr}/^{86}\text{Sr}$ (0.056 55 ± 0.000 14) isotope ratios. 171
2.6.2. Li$_2$B$_4$O$_7$ fused disks

Li$_2$B$_4$O$_7$ fused disks (ca. 3 cm diameter and 0.2 cm thickness) containing NIST SRM 987 reference material and Rb-spikes were prepared in-house using an Autofluxer (Breitländer GMBH, Germany) by Brogioli.

The preparation included mixing of Li$_2$B$_4$O$_7$ Spectromelt 100 (Merck, Germany) with powder materials in a Pt/Au (95/5) crucible, gently heating the mixture with the Autofluxer for 2 min, pre-melting for 3 min and melting with agitation for 5 minutes. 15 s before pouring the melt onto Pt/Au conical tapered modules, 1 mg of Ammonium Iodide p.a. (Fluka AG, Switzerland) was added for better casting. Element doping was carried out by mixing the powders or adding standard solutions at defined concentrations and drying overnight. The Rb standard used was Rb$_2$CO$_3$ powder p.a. (Fluka AG, Buchs, CH). The corresponding Rb and Sr concentrations are listed in Table 12.

2.6.3. Biotites provided from the University of Berne

Three biotite samples were kindly provided from K. Mezger from the University of Berne. Reference values for Rb and Sr concentrations were obtained by isotope dilution measurements with a Thermo Fisher Neptune MCICPMS instrument. $^{87}$Sr/$^{86}$Sr isotope ratios were measured with a Thermo Fisher Triton Plus TIMS instrument. The corresponding Rb and Sr concentrations are listed in Table 12. $^{87}$Sr/$^{86}$Sr isotope ratio reference values are shown in Figure 56.

2.6.4. Minerals provided by the University of Lorraine

2 Mounts containing grains of 13 different minerals (biotites, feldspars, orthoclase, muscovite etc.) were provided by J. Mercadier from the University of Lorraine. Reference values for $^{87}$Sr/$^{86}$Sr isotope ratios were measured by SIMS. Quantification results are presented in the Appendix in section 7.5. and $^{87}$Sr/$^{86}$Sr isotope ratio reference values are shown in Figure 57 and Table 21.
3. Results


Authors: Hale Ceren Yilmaz and Bodo Hattendorf

3.1. Fundamental ns- and fs-LA Studies

3.1.1. A Comparison of Signal Suppression and Particle Size Distributions for ns- and fs-LA of Metallic Samples by LA-ETV-ICPMS

It was shown in earlier studies that ns- and fs-LA generates aerosols with different morphologies. Therefore, it can be expected that differences in the signal suppression profiles are observable for a sample undergoing thermal treatment at the same temperature when ablating either with ns- or fs-LA. The goal of this study was to investigate the underlying mechanisms of element separation in more detail and to identify the most suitable LA-system with respect to vaporization efficiency and elemental separation in an ETV. Since the effect of the pulse duration has a strong impact especially on the ablation behavior of metals, for this study, 4 metallic samples were chosen. To study the influence of the sample composition and boiling points, results for brass (MBH CRM B26), pure Cu (BAM M381), pure Zn (BAM M601) and Ta were compared. Figure 29 shows the setup that was used for the experiments. Laser ablation was carried out either with ns- or fs-LA. The laser ablation parameters were chosen in a way that for ns- and fs-LA, the resulting ion signal intensities under no heating conditions were around $10^6$ cps. It was assumed that in that way, similar aerosol masses were generated for both LA-systems. One needs to keep in mind, however, that ns-LA of metals produces a greater fraction of μm-sized particles, which may not be vaporized and ionized completely in the ICP. The total aerosol mass produced with ns-LA may thus be somewhat higher under these conditions.

![Experimental set-up](image)

Figure 29 - Experimental set-up with the (a) Geolas-C ns-laser and (b) Excite Pharos fs-laser for LA, the (c) ETV-4000 unit for thermal treatment of the laser generated aerosol, the (d) Elan 6100 DRCplus-Q-ICPMS for ion signal detection, the (e) UHSAS OPC with a MD19-1i dilutor for PSD measurements and the (f) polycarbonate filters to capture the aerosol for the SEM images.
The ns-LA-system was the GeoLas-C ArF excimer ns-laser, operating at a wavelength of 193 nm. For fs-LA, the Excite Pharos, operating at 206 nm was used. The laser generated aerosol was transported with a 1 L/min He gas flow from the ablation cell through the ETV-4000 for aerosol heating. For ICPMS measurements, the aerosol was transported from the outlet of the ETV to an Elan 6100 DRC\textsuperscript{plus} ICPMS instrument. The $^{13}$C\textsuperscript{+}, $^{63}$Cu\textsuperscript{+}, $^{64}$Zn\textsuperscript{+}, $^{66}$Zn\textsuperscript{+} and $^{181}$Ta\textsuperscript{+} isotopes were monitored. Table 7 summarizes the operating conditions for the two LA-systems.

<table>
<thead>
<tr>
<th>LA-system</th>
<th>Excite Pharos fs-laser</th>
<th>Geolas-C ns-laser</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Yb:KGW</td>
<td>ArF Excimer</td>
</tr>
<tr>
<td>Pulse Duration</td>
<td>190 fs – 10 ps</td>
<td>14 ns</td>
</tr>
<tr>
<td>Wavelength</td>
<td>206 nm</td>
<td>193 nm</td>
</tr>
<tr>
<td>Line scan rate</td>
<td>5 µm/s</td>
<td>5 µm/s</td>
</tr>
<tr>
<td>Energy density</td>
<td>3 – 4 J/cm\textsuperscript{2}</td>
<td>10 – 11 J/cm\textsuperscript{2}</td>
</tr>
<tr>
<td>Repetition Rate</td>
<td>4 Hz</td>
<td>4 Hz</td>
</tr>
<tr>
<td>Spot Size</td>
<td>20 µm (Cu, Zn),</td>
<td>60 µm</td>
</tr>
<tr>
<td></td>
<td>40 µm (brass), 5 µm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Ta)</td>
<td></td>
</tr>
</tbody>
</table>

Table 7 - Operating conditions of the LA-systems.

For thermal treatment, the heating protocol listed in Table 5 in the Experimental was used. For the PSD measurements, the internal dilution gas flow in the OPC and the Ar dilution gas of the dilutor were tuned in a way that no saturation of the detector occurred. The dilution factor was decreased with increasing power level, since a smaller amount of aerosol reached the OPC. Table 8 summarizes the dilution factors used for the different metals and LA-systems. Table 9 lists the melting and boiling points and the thermal conductivity of the investigated metals.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Power Level</th>
<th>ns-LA</th>
<th>fs-LA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Cu (BAM M381)</td>
<td>no heating</td>
<td>98</td>
<td>174</td>
</tr>
<tr>
<td></td>
<td>4.5</td>
<td>21</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>5, 5.5</td>
<td>21</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>6.5</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>Pure Zn (BAM M601)</td>
<td>no heating</td>
<td></td>
<td>174</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td></td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td></td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>3.5, 4</td>
<td></td>
<td>21</td>
</tr>
<tr>
<td>Brass (MBH CRM B26)</td>
<td>no heating</td>
<td>245</td>
<td>625</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td></td>
<td>147</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>38</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>38</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td></td>
<td>21</td>
</tr>
<tr>
<td>Ta</td>
<td>no heating</td>
<td>148</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>148</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>6.5</td>
<td>74</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>38</td>
<td>74</td>
</tr>
</tbody>
</table>

Table 8 - Dilution factors for the different metals and LA-systems at the individual power levels.
### Table 9 - Melting points, boiling points and thermal conductivity of the investigated metals.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Melting point [°C]</th>
<th>Boiling point [°C]</th>
<th>λ, (27°C) [W/m-K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Zn (BAM M381)</td>
<td>420</td>
<td>907</td>
<td>1.16</td>
</tr>
<tr>
<td>Pure Cu (BAM M601)</td>
<td>1'085</td>
<td>2'927</td>
<td>4.01</td>
</tr>
<tr>
<td>Brass (MBH CRM B26)</td>
<td>900 - 940</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pure Ta</td>
<td>3'020</td>
<td>5'425</td>
<td>0.575</td>
</tr>
</tbody>
</table>

Figure 30 shows the signal suppression profiles obtained for ns- and fs-LA of pure Zn, Cu, Ta and brass after heating the respective aerosol within the furnace at increasing power settings. Overall, the profiles of the different metals followed a similar general trend for both LA-systems. As the temperature of the furnace was increased, the signals started to decrease as soon as a certain power level was exceeded.

This onset of suppression occurs at power settings reflecting the order of the boiling points of the studied metals. This agrees with previous studies and indicates that material removal occurs by evaporation and subsequent condensation on cool surfaces downstream the furnace. The $^{66}$Zn$^+$ ion signals started to decrease at power level 2, while the onset of suppression for the $^{65}$Cu$^+$ signals occurred near power level 4. The onset temperatures do not differ for the pure metals and brass. The $^{181}$Ta$^+$ signal did not experience a significant suppression for the power levels used. The extent of the suppression typically increased with furnace temperature, until, for the volatile Zn, the ion signal eventually became indistinguishable from the instrumental background. Furthermore, the signal suppression occurred more pronounced when fs-LA was used. At the highest furnace temperatures studied (power levels > 6), however, the ion signals of $^{65}$Cu$^+$ and $^{66}$Zn$^+$ increased again. Ta on the other hand did only show a slight signal reduction for power levels 6.5 and 7. The highest signal suppression factors were 0.3 (ns-LA) and 0.7 (fs-LA) at power level 7. It is interesting to note that the suppression profiles of Cu and Zn showed an intermediate plateau, which was most pronounced for ns-LA of Zn at signal suppressions of ≈ 0.1 (ns-LA) and near 0.06 (fs-LA) between power levels 2.5 and 3. For Cu, this plateau is moderately distinct only with ns-LA at a signal suppression of ≈ 0.03 between power levels 5 and 5.5. When comparing the signal suppression for pure Cu and Zn to those of brass (Figure 30), a matrix effect became apparent. In particular, there was no clear plateau in the profiles of Zn anymore and the overall suppression of the signal intensities of Cu and Zn appeared more pronounced in brass at power levels above 3.5. Again, the suppression was generally stronger when using fs-LA.
Figure 31 shows the SEM-images of the initial aerosol for all investigated samples for ns- and fs-LA. Areas that were not overloaded with ablated material but still contained a sufficient amount of aerosol, were chosen to record the SEM-images. In that way, the morphology differences of the species were more clearly distinguishable. It is, however not possible to draw quantitative conclusions about the relative fractions of individual species from these images because it is likely, that smaller aerosol particles were buried in the pores of the filter. Nonetheless, the images indicate that the majority of the initial, unheated aerosol consists of very small (<< 60 nm) particles and their agglomerates together with larger solitary particles with diameters that can reach sizes larger than 1 µm in diameter. The relative abundances of agglomerates and solitary particles appeared to depend on the material and laser ablation system used. While for the initial Cu (Figure 31 (a) and (b)) and fs-brass (Figure 31 (d)) aerosols almost exclusively nanoparticles and agglomerates were observable, the SEM-images for the initial Zn (Figure 31 (e) and (f)) and ns-aerosol of brass (Figure 31 (c)) contained also µm-sized droplets. When comparing the ns- and fs-aerosol in general, a smaller degree of branching and extension of the agglomerates is found for fs-LA. For the ns-aerosol of Cu (Figure 31 (a)), for example, the agglomerates appeared more dense and “cloud-like”, while for the fs-aerosol (Figure 31 (b)), longer, branched agglomerates are found. The variability of sizes of the solitary particles, on the other hand, appears to be higher for fs-LA. The aerosol collected for Ta (Figure 31 (g) and (h)) contains a small number of mostly individual NPs with varying diameters. In case of ns-LA, additionally, a few agglomerates with small dimensions are visible. These results are generally in agreement with the PSDs measured with the OPC.
The initial aerosols collected from fs-LA generally showed a broader size distribution between 100 nm and 1 µm (Figure 32) than those from ns-LA. The PSDs for Cu and brass (Figure 32 (a) and (e)) from ns-LA for example indicate that most of the particles were in a size range between < 60 nm and 300 nm, while for fs-LA (Figure 32 (b) and (f)), a significant fraction of particles in a size range up to 700 nm were found. For Zn (Figure 32 (c) and (d)), the ns-LA PSD appears more narrow and mostly contains particles < 200 nm, while the fs-LA PSD is barely distinguishable from that of Cu. Brass and Zn however also produce particles > 1 mm, which are however only visible in the SEM pictures.
On heating, a gradual transformation of the aerosol could be observed in the SEM images and PSDs. In particular, the abundance and size of the agglomerated NPs appeared to continuously decrease with increasing furnace temperature, while the fraction of solitary particles with sizes of several 100 nm increased in the PSDs. For ns-LA of Zn, the thermal treatment at power level 2.5 (Figure 33 (a)) led to a reduction of the number of agglomerates and their structure appeared less dense compared to the initial aerosol (Figure 31 (e) and (f)). The µm-sized particles were not found any more at power levels above 2.5. For fs-LA at power levels 2.5 and 3 (Figure 33 (b) and (d)) and for ns-LA at power level 3 (Figure 33 (c)), “cloud-like”, spherical structures were found, which appear like coagulated agglomerates. Single fractions and branches of the initial agglomerates were still visible in some cases.

![SEM images of pure Zn for ns- (left column) and fs-LA (right column) for power level 2.5 (first row) and power level 3 (second row). The pores of the membrane filters are indicated as black spots, while the laser-generated aerosol appears in white.](image)

For brass, coagulated particles could be found in the aerosol at power level 4.5 (Figure 34 (a)) for ns-LA, while for fs-LA at power level 4.5 (Figure 34 (b)) and for ns-and fs-LA at power level 5.5 (Figure 34 (c) and (d)), exclusively homogenous spherical particles were observed. Agglomerates were not observable for any brass-aerosol that underwent thermal treatment.
The same trend was observed for the Cu aerosol (Figure 35 (a) and (b)). The diameter of the spherical particles was found to get smaller when the temperature was increased and in general, less material was collected on the filters. Differences in morphology seemed to become less pronounced after heating the aerosol. The structure of the coagulation products seemed to get homogenized, yielding homogeneous droplets upon heating.
Further increasing the furnace temperature also led to a steady decrease in particle counts and size distributions recorded with the OPC. In particular for Cu and brass (Figure 32), the OPC data indicated that the majority of the particles appears in a size range < 200 nm when power levels > 4 were applied. The particles of several 100 nm diameter also appeared at similar abundances in the PSDs. Ta also showed a generally wider PSD for fs-LA but no remarkable changes in the OPC data upon heating (Figure 36 (b)). For the ns LA-aerosol on the other hand, an increase in particles between 300 and 700 nm could be observed upon heating (Figure 36 (a)).

For Ta, the SEM pictures show that only a small amount of the aerosol could be collected on the filters. After heating at power level 7, fewer solitary NPs with wider size distribution appeared in the filter collected material (Figure 37 (a) and (b)). For ns-LA on the other hand, the initial aerosol contained a higher fraction of agglomerates and larger solitary particles. After heating the aerosol, it seemed as if the branched agglomerates collapsed to lumps, where the original NPs were still visible within the structure.

Figure 35 - SEM images of pure Cu for ns- (left column) and fs-LA (right column) for power level 5.5 (first row) and power level 6.5 (second row). The pores of the membrane filters are indicated as black spots, while the laser-generated aerosol appears in white.

Figure 36 - PSD for Ta for ns- (left) and fs-LA (right) for the individual power levels. Dilution factors are listed in Table 8.

For Ta, the SEM pictures show that only a small amount of the aerosol could be collected on the filters. After heating at power level 7, fewer solitary NPs with wider size distribution appeared in the filter collected material (Figure 37 (a) and (b)). For ns-LA on the other hand, the initial aerosol contained a higher fraction of agglomerates and larger solitary particles. After heating the aerosol, it seemed as if the branched agglomerates collapsed to lumps, where the original NPs were still visible within the structure.
Figure 37 - SEM images of pure Ta for ns- (left) and fs-LA (right) at power level 7. The pores of the membrane filters are indicated as black spots, while the laser-generated aerosol appears in white.

Apart from the signal suppression observed during heating, the transient signals, in particular for Cu, changed remarkably when increasing the power levels.
Figure 38 - $^{65}\text{Cu}^+$ and $^{13}\text{C}^+$ transient signals for pure Cu for ns-LA (left column) and fs-LA (right column) for power level 5 (first row), power level 5.5 (second row) and power level 6 (third row). The $^{13}\text{C}^+$ signal is used as indicator for the stability of the temperature. Fs-LA was carried out after exchange of the graphite tube, leading to slight changes in the carbon release.

Figure 38 shows the transient $^{65}\text{Cu}^+$ ion signals for ns- and fs-LA for the ablation of pure Cu at different power levels. When looking at the transient $^{65}\text{Cu}^+$ ion signals recorded under heating conditions, spikes are observable. The intensity and occurrence of the spikes is significantly higher for the ns-signals compared to the fs-signals. Especially the ns-$^{65}\text{Cu}^+$ signals at power levels 5.5 and 6 are characterized by individual huge spikes. Theses spikes are also observable in the transient $^{65}\text{Cu}^+$ signal for ns-LA of brass (Figure 39) at higher power levels but were barely visible for the $^{66}\text{Zn}^+$ signal.

Figure 39 - $^{65}\text{Cu}^+$ transient signals for ns-LA of pure Cu and brass recorded while heating at power level 5.5.

For ns-LA of pure Zn at power level 4, only moderate spikes appeared, while for power level 3.5 and for the ns-$^{181}\text{Ta}^+$ signal, no spikes were observed. For fs-LA, in general, a lower number of spikes with a smaller intensity were observed. Without heating, there were also indications for spikes, but they appeared to be less pronounced due to the higher signal intensity. This supports observations made in earlier work. 58 The spikes are most likely caused by large particles, which do not evaporate inside the ETV until high power levels are reached. The peak intensities seemed to gradually decrease as the
furnace temperature was increased, while the frequency of their occurrence appeared to increase. This would indicate that NP-agglomerates collapse to droplets upon melting, as seen in the SEM images and PSDs, which arrive at the ICP as particles of several 100 nm in size and produce the short and sharp individual peaks. The fact that the spikes were absent during ablation of Zn can be explained by an efficient vaporization of the heated aerosol in the ICP. For fs-LA of Cu, the spikes were much less intense compared to ns-LA, which may be a result from the generally lower agglomeration state of the original aerosol, as seen in the SEM-images of the filter-collected material. It has to be noted that the calculated signal suppression factors, which are shown in Figure 30, were calculated from the mean intensities during the respective transient heating periods and therefore also include the spike signals. The resulting suppression factors may therefore be overestimated for ion signals with large or high number of spikes, since the large particles that cause the spikes might not be completely ionized in the ICP or may get lost during the transport in the tubing.

The ICPMS signal suppression and changes in the aerosol morphology and PSDs during the transport through the heated furnace can hardly be explained by a single underlying process. The observed changes in morphology and the signal suppression profiles are most certainly the result of a combination of thermal effects and gas dynamics. Higher furnace temperatures accelerate melting, surface evaporation before the boiling point is reached and boiling of the liquid droplets, while at the same time the aerosol residence time in the furnace is decreased. There are thus at least two competing processes that determine the state of an individual aerosol particle. If the gas temperature is sufficiently high and the residence time within the hot gas sufficiently long, the particle or droplet will reach thermal equilibrium.

Differently sized particles however will reach different bulk temperatures during their residence time in the furnace. Smaller, solitary particles will start to melt and evaporate at an earlier stage inside the furnace, while bigger particles may still remain solid. At the same time, agglomerates appear to form lumps upon melting of their individual constituents, which are expected to behave similarly to the larger particles or droplets. At lower temperatures, only the small, solitary NPs and constituents of the agglomerates start to melt. In parallel, surface evaporation may set in. At this point, the degree of melting will decrease with increasing particle sizes because larger particles have a larger volume/surface ratio and thus need more time to accumulate the amount of energy required to reach the molten state. Further increasing the furnace temperature will cause the larger particles to eventually undergo melting completely, while the smallest particles may already reach the boiling point and evaporate rapidly. Thus, the initial, gradual signal suppression would reflect surface evaporation. Figure 40 illustrates the processes taking place for the individual species under thermal treatment.
In particular for Cu and Ta, this must be the dominating process for material removal because the furnace temperature cannot reach the boiling point of the metals under the conditions used here. The magnitude of the signal suppression at lower temperatures (e.g. at level 2.5 for Zn or level 4.5 for Cu) thus depends on the fraction of particles that can be heated to temperatures that are sufficiently high to trigger at least surface evaporation. The drop in signal intensities therefore reflects the fraction of these particles relative to the total aerosol mass. The plateau-like region observed in particular in the suppression profiles for Zn is therefore interpreted as a state, where most of the solitary NPs have evaporated, while the intermediate and large particles still remain in the particle phase when exiting the furnace. The fact that the plateau appears most pronounced for Zn when using ns-LA (Figure 30 (a)) can then be explained by the smaller size distribution in the initial aerosol. In the PSDs of the Cu-aerosol and the fs-generated Zn-aerosol, a much larger diameter variability is found, which causes the evaporation of solitary particles to occur across a wider temperature range. The larger fraction of the particles remains in the aerosol up to high power levels due to their large volume/surface ratio. The spikes can be attributed to the presence of the large particles, which are not evaporating until high power levels are reached. They remain within the aerosol and therefore continuously contribute to the ICPMS signal. This is particularly prominent for ns-LA of Cu, where these particles appear as individual spikes in the transient signals. Their intensity seems to gradually decrease as the furnace temperature increases and the frequency of their occurrence increases. This indicates a collapse of agglomerates to droplets and thereby an increase of the number of particles with diameters of several 100 nm, which also appear in the PSD (Figure 32 (a)) after aerosol heating. The fact that the spikes were absent during ablation of Zn can be explained by an efficient vaporization of the heated aerosol in the ICP. For fs-LA of Cu, the spikes were much less intense compared to ns-LA, which may be a result from the generally lower agglomeration state of the original aerosol, as seen in the SEM-images (Figure 31 (a)) of the filter-collected material. The maximum signal suppression is obtained as soon as the residence time of the aerosol in the furnace is sufficiently high to reach the boiling point of the material. For the Zn aerosols studied here, an elimination of more than 5 orders of magnitude could be achieved in pure metal and
brass. Cu and Ta can only be removed at higher temperatures and, in the case of Cu, less efficiently for the pure metal. This is in good agreement with the higher boiling temperatures of the bulk metals compared to brass. Only for the fs-LA generated aerosol of brass, a similarly high elimination of Cu was possible, which indicates that the alloy has slightly higher surface evaporation rates as the pure metal. The observation that Zn can be removed to such a great extent from the aerosol indicates that the evaporation does not occur under equilibrium conditions. It must thus be assumed that the density of metal vapor inside the tube remains sufficiently low to prevent significant condensation of Zn on the aerosol particles even after exiting the heated zone.

Deposition of the vapor occurs thus most likely on the tube's cooled downstream contact and the transfer tube. At power levels > 6 the ion signals of Cu and Zn became detectable above the instrumental background again. Such a behavior had already been observed in earlier studies and was initially thought to be caused by re-evaporation of condensed vapor downstream the furnace. Currently, however, this is rather attributed to be a result of the decrease in aerosol residence times inside the furnace during the heating process. Otherwise, one would expect these signals to decrease with time as the reservoir of the condensed material is consumed continuously. However, no such decrease was observed, and the signals remained stable during ablation for the entire heating period. Additionally, there was a clear intensity increase between the gas blank signal and the laser ablation signal.

3.1.2. Cu-Zn Separation Efficiency in Dependence on the Composition of Brass

In the following section, the dependency of the Cu-Zn separation efficiency on the \([\text{Cu}]/[\text{Zn}]\) concentration ratio was investigated for brass. Three brass standards (MBH CRM B22, B24 and B26) with significantly differing Cu and Zn contents (Table 11) were analysed. The measurements in this case were carried out with the ELAN DRCII. The operating conditions are listed in Table 10. In contrast to chapter 3.1.1., the Excite PHAROS was used at a wavelength of 257 nm. Since no significant difference is observable between the suppression factor profile of the MBH CRM B26 ablated with 206 nm (chapter 3.1.1., Figure 30) and the profile for LA with 257 nm (chapter 3.1.3., Figure 41), the effect of the wavelength and fluence differences are expected not to be substantial. To achieve a similar ablation yield as in the experiments discussed in chapter 3.1.1., the laser parameters were set in a way that the resulting \(^{65}\text{Cu}^+\) plus \(^{66}\text{Zn}^+\) ion signal intensities under no heating conditions were around \(10^6\) cps. It has to be noted, however, that the ionization efficiency is not equal for Cu and Zn, which leads to differences in sensitivities for the two elements.

<table>
<thead>
<tr>
<th>LA-system</th>
<th>Excite PHAROS fs-laser</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Yb:KGW</td>
</tr>
<tr>
<td>Pulse Duration</td>
<td>190 fs – 10 ps</td>
</tr>
<tr>
<td>Wavelength</td>
<td>257 nm</td>
</tr>
<tr>
<td>Energy</td>
<td>100%</td>
</tr>
<tr>
<td>Energy density</td>
<td>7 J/cm²</td>
</tr>
<tr>
<td>Repetition Rate</td>
<td>5 Hz</td>
</tr>
<tr>
<td>Spot Size</td>
<td>20 µm</td>
</tr>
</tbody>
</table>

Table 10 – Operating conditions of the Excite PHAROS fs-laser.
The HGA-600MS was used as ETV, because, in contrast to the ETV-4000, temperature ramping was available. The temperature of the graphite furnace was increased with a rate of 4.8 °C/s from 100 °C to 2’500 °C for the MBH CRM B24 and B26 and from 1’000 °C – 2’500 °C for the MBH CM B22. The heating protocol is summarized in Table 6 in the experimental section. Background-correction was performed only with the background recorded under no heating conditions. Previous experiments however showed that the background signals for Cu and Zn did not change substantially when applying higher temperatures to the ETV.

<table>
<thead>
<tr>
<th>Percentage element by weight</th>
<th>MBH B22</th>
<th>MBH B24</th>
<th>MBH B26</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>82.47</td>
<td>95.65</td>
<td>62.93</td>
</tr>
<tr>
<td>Zn</td>
<td>15.92</td>
<td>1.99</td>
<td>30.30</td>
</tr>
<tr>
<td>Cu suppression at 1’800 °C</td>
<td>0.12175</td>
<td>0.11148</td>
<td>0.10952</td>
</tr>
</tbody>
</table>

Table 11 – Cu and Zn contents of the MBH B22, B24 and B26 brass standards and the ⁶⁵Cu⁺ ion signal suppression factor at a graphite tube temperature of 1’800 °C.

Figure 41 shows the transient ⁶⁵Cu⁺ and ⁶⁶Zn⁺ ion signals (a1 – a3) and the corresponding signal suppression profiles (b1 – b3).
Figure 41 - $^{65}\text{Cu}^+$ and $^{66}\text{Zn}^+$ transient signals (left) and signal suppression transient profiles for $^{65}\text{Cu}^+$ and $^{66}\text{Zn}^+$ ion signals (right) for the MBH CRM B22 (first row), the MBH CRM B24 (second row) and the MBH CRM B26 (third row).

The $^{66}\text{Zn}^+$ signal suppression started near 750 °C, while the $^{65}\text{Cu}^+$ ion signal showed a suppression onset around 1'000 °C for all brass standards. The decrease of the $^{66}\text{Zn}^+$ signal was relatively steep and continuous. Near 1'250 °C, the $^{66}\text{Zn}^+$ ion signal could not be distinguished from the instrumental background any more for MBH CRM B22 and B24, which contain 15.92% and 1.99% of Zn, respectively. Due to the higher Zn content (30.30%) of the MBH CRM B26, the instrumental background was not reached, but the $^{66}\text{Zn}^+$ suppression factors between 1'250 – 2'500 °C reached a minimum ($5\times10^{-4}$). The $^{65}\text{Cu}^+$ signal decreased relatively slowly between 1'000 – 1'700 °C. The intermediate minimum observed between 1’000 – 1’500 °C is currently attributed to the non-specific suppression regime, which was already observed by Brogioli. This regime is assumed to be an artefact of the HGA-600MS (detailed discussion in the Appendix in section 7.1.) and is therefore not considered in the discussion here. For temperatures > 1'700 °C – 2'500 °C, the $^{65}\text{Cu}^+$ ion signal decreased relatively fast to suppression factors around 0.01. When the $^{65}\text{Cu}^+$ and $^{66}\text{Zn}^+$ transient suppression factors for the three brass standards are compared, no significant differences are observable. The signal intensities and suppression factors for the different standards at the same temperature are very similar. It can be concluded that the $[\text{Cu}]/[\text{Zn}]$ concentration ratio of a brass standard does not affect their relative suppression caused by thermal treatment. This indicates that the vaporization process is largely independent of the elemental composition in samples within the same type of matrix, which means that the physical properties of the elements are the governing factors of the suppression onset and magnitude.

For temperatures > 1’000 °C, spikes were observable in the transient $^{66}\text{Zn}^+$ ion signal in contrast to the observations made in chapter 3.1.1. Also, for the $^{65}\text{Cu}^+$ signal > 2’000 °C, the transient signal consisted of a comparably larger number of spikes for fs-LA. The most likely reason for the occurrence of the spikes in this case is the shorter graphite tube length of the HGA-600MS (28 mm) compared to the one of the ETV-4000 (45 mm) used before. As will be discussed in more detail in the following section, the HGA-600MS appears to be less efficient for aerosol heating, which may lead to a larger fraction of particles with diameters of several 100 nm remaining in the aerosol after the ETV. The evaporation of approximately 90% of the Zn occurs at temperatures < 1’000 °C for all samples in the HGA-600MS. This indicates that evaporation of Zn from the NPs and agglomerates occurs relatively independent of the concentration. The remaining spikes observed, especially for the MBH CRM B24, indicate however that some of the remaining particles that also cause the spikes in the Cu signals contain small fraction of Zn.
Due to the higher boiling point, Cu seems to start to evaporate only at temperatures < 1'800 °C. For higher temperatures, the intermediately-sized and large particles still contribute to the ICPMS signal as spikes even do at the highest temperatures.

3.1.3. Comparison of the Cu and Zn Suppression Factors for the HGA-600MS and the ETV-4000 Prototype for Brass

The Cu-Zn separation efficiency for the two GF-ETVs is finally compared for the MBH CRM B26 brass standard. Figure 42 shows the signal suppression factors for the $^{65}$Cu$^+$ and $^{66}$Zn$^+$ ion signals for the (a) HGA-600MS and (b) ETV-4000. The HGA-600MS data were extracted from the previously discussed experiments by averaging the suppression factors for a temperature interval of 96 °C at selected points. The ETV-4000 data were identical to the ones shown in Figure 30 in chapter 3.1.1.

The decrease of the suppression factor achieved with the (b) ETV-4000 prototype was steeper for both Cu and Zn signals when compared to the profile obtained with the (a) HGA-600MS. The onset of suppression occurred at power level 2 for $^{66}$Zn$^+$ and at power level 3.5 for $^{65}$Cu$^+$. The $^{65}$Cu$^+$ ion signal dropped below the instrumental background at power levels > 4.5 and re-increased above the background for power levels 6 and 6.5. The ion signal of $^{66}$Zn$^+$ dropped below the background for power levels > 4 and re-increased at power level 6.5. For power level 4, a Cu-Zn separation of more than 3 orders of magnitude is achieved. The Cu/Zn ratio of ~2 of the original aerosol increases to a suppression factor ratio of ~3'600 at power level 4 due to the selective Zn suppression. For the (a) HGA-600MS, the onset of the $^{66}$Zn$^+$ ion signal is found between 500 – 750 °C and the onset for the $^{65}$Cu$^+$ ion signal at 1'000 °C. The decrease of the $^{65}$Cu$^+$ ion signal was only moderate compared to that of $^{66}$Zn$^+$. Between 1'000 – 1'500 °C, a short stabilization regime was observable, where the signal did not decrease significantly. The lowest achieved suppression factor for the $^{65}$Cu$^+$ ion signal was 0.03 at 2'250 °C and 0.0005 for the $^{66}$Zn$^+$ ion signal. The highest separation achieved with the HGA-600MS occurred at 1'250 °C, where the $^{65}$Cu$^+$ and $^{66}$Zn$^+$ signals were separated by almost 3 orders of magnitude. Due to the selective Zn suppression, the Cu/Zn ratio of ~2 of the original aerosol increased to a suppression factor ratio of ~
700 at 1'250 °C. The instrumental background was not reached within the investigated temperature range.

Considering the Cu-Zn separation attainable with both ETVs, it is apparent that the ETV-4000 achieves an almost fivefold higher efficiency compared to the HGA-600MS. The ETV-4000 prototype thus offers a potentially higher vaporization efficiency and more efficient separation of volatile and non-volatile elements in metals. The higher performance of the ETV-4000 can most probably be attributed to its longer graphite tube (45 mm) compared to the HGA-600MS (28 mm). The aerosol has significantly more time to undergo vaporization, which explains the steeper and stronger suppression of the two signals. At the temperature settings, where a re-increase is observed, the suppression and increase in gas velocity compete. The non-specific suppression appears absent when the ETV 4000 is used.

SUMMARY

In the first part of this chapter, the transformation of ns- and fs-aerosols upon thermal treatment was investigated. Findings from earlier studies were confirmed, which reported that a higher amount of single particles is found in fs-aerosols, while the ns-aerosol consisted of a larger fraction of NP-agglomerates. Differences in aerosol transformation, by thermal treatment can therefore be traced back to the initial ns- and fs-aerosol morphology. It was shown that surface melting of single particles can cause the collapse of NP agglomerates, which ultimately form larger spherical droplets. Furthermore, it was shown that surface evaporation sets in already below the boiling point of the elements. The fs-aerosol had a broader PSD, but mostly consisted of single particles of varying diameters. Those particles were continuously vaporized according to their sizes, which led to the steady ICPMS signal decrease. The large particles formed after the collapse and homogenization of the agglomerates in the ns-aerosol, however, were vaporized only at high temperatures. This explains the higher vaporization and Cu-Zn separation efficiency achieved for fs-LA. Suppression onset temperatures for Zn in brass were shifted to higher temperatures and to lower temperatures for Cu, compared to the pure metals. This indicated that the vaporization onset and efficiency is governed by the physical properties of the bulk.

The similarities in suppression profiles for three brass samples with highly differing [Cu]/[Zn] concentration ratios indicate that the composition of the sample does not influence the vaporization efficiency of the elements to a measurable extent for sufficiently similar matrix compositions. This supports the finding of the first subsection of this chapter that the vaporization behavior is mostly governed by material characteristics of the matrix. The independence of the vaporization efficiency from the sample composition is a significant advantage when thermal treatment of the aerosol shall be used for samples of similar matrix, but unknown composition.

For the MBH CRM B26 brass standard it was shown that the ETV-4000 can achieve a higher Cu-Zn separation than the HGA-600MS. The signal decrease was steeper for the $^{65}$Cu$^+$ and $^{66}$Zn$^+$ ion signals and the instrumental background was reached for Cu and Zn, which was not observed when the HGA-600MS was used. This significant increase of the vaporization in general and the increase in elemental separation can most certainly also be attributed to the longer graphite tube in the ETV-4000 prototype. The longer residence time of the material in the furnace triggers a more extensive vaporization process. Brogioli$^{147}$ observed a slightly different suppression profile for the MBH CRM B26 with ns-LA. While the $^{66}$Zn$^+$ signal suppression profile showed similar suppression factors at similar temperatures, the $^{65}$Cu$^+$
ion signal was stronger suppressed in the data shown by Brogioli. In contrast to the experiments discussed here, a significantly lower helium gas flow was used (0.5 L/min). The higher vaporization efficiency of the Cu therefore can be explained by the higher residence time of the aerosol in the furnace, which seems to have a larger influence in this case than the morphology differences between ns- and fs-aerosols. It can be expected that with fs-LA under a similarly low gas flow, stronger suppression factors would be measured compared to ns-LA. It has to be noted that additionally to the element-specific suppressions, the non-specific suppression regime was observed by Brogioli, which was not the case for the profiles shown here. As discussed in the Appendix in section 7.1., this regime was considered to be an artefact of the HGA-600MS ETV unit.

3.2. Rb Suppression and Rb-Sr Separation using Thermal Treatment of Laser-Generated Aerosols

The initial experiments described in this chapter were aiming at a comparison of the different ETV systems in order to identify potential differences in isobar separation in dependence on temperature, geometry and heater material. The suppression factors of the $^{85}\text{Rb}^+$ and $^{88}\text{Sr}^+$ signals were investigated for the three ETV systems to compare the Rb elimination and the Rb-Sr separation efficiency in particular. The characterization was carried out using different synthetic materials (NIST SRM 610 silicate glass and fused pellets of SRM 987 doped with different levels of Rb). In the second part of this chapter, the Rb$^+$ suppression and Rb-Sr separation efficiency were investigated for 3 biotite minerals, kindly provided by Klaus Mezger from the University of Berne. As it could be shown for the metal samples in the previous chapter, fs-LA appeared to be advantageous in terms of elemental separation according to volatility in metals. Therefore, the studies in this chapter were all performed using the Excite PHAORS fs-LA-system. Different wavelengths were used, and the detection was carried out by different ICPMS as by availability and suitability. The materials used in this chapter covered a wide range of Rb-Sr concentration ratios and Rb and Sr concentrations. Table 12 lists the data for the individual samples used in this study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type</th>
<th>Sr [mg/kg]</th>
<th>Rb [mg/kg]</th>
<th>[Rb]/[Sr]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIST SRM 610</td>
<td>Silicate glass</td>
<td>516</td>
<td>426</td>
<td>0.83</td>
<td>GeoReM $^{170}$</td>
</tr>
<tr>
<td>1:1</td>
<td>Li-tetraborate</td>
<td>1118</td>
<td>1074</td>
<td>0.96</td>
<td>In-house $^{147}$</td>
</tr>
<tr>
<td>3:1</td>
<td>Li-tetraborate</td>
<td>868</td>
<td>2740</td>
<td>3.16</td>
<td>In-house $^{147}$</td>
</tr>
<tr>
<td>131102-4</td>
<td>Biotite</td>
<td>10.324</td>
<td>210.088</td>
<td>20.35</td>
<td>TIMS $^{172}$</td>
</tr>
<tr>
<td>KR36-04</td>
<td>Biotite</td>
<td>5.3251</td>
<td>349.853</td>
<td>65.70</td>
<td>TIMS $^{172}$</td>
</tr>
<tr>
<td>KR65-10</td>
<td>Biotite</td>
<td>37.864</td>
<td>655.14</td>
<td>17.30</td>
<td>TIMS $^{172}$</td>
</tr>
</tbody>
</table>

Table 12 – List of samples.
Figure 43 – LA-ETV-ICPMS setup with the (a) ETV-4000 prototype, the (b) HGA-600MS and (c) the wire ETV for thermal treatment in combination with either the ELAN DRCII (bottom) or the Element XR (top).

Table 13 lists the operating parameters for the Excite PHAROS fs-laser. The parameters were chosen in a way that the intensity of the $^{88}\text{Sr}^+$ ion signal for NIST SRM 610 was $\sim 10^6$ cps for non-heating conditions for the ELAN DRCII and Element XR measurements. The Ar make-up gas was added right before the ICP in both cases. After thermal treatment, the aerosol was guided towards the Elan DRCII Q-ICPMS in the measurements where the (b) HGA-600MS or (c) wire prototype was used or towards the Element XR SFICPMS when the (a) ETV-4000 was used. Figure 43 shows the used experimental setups. For thermal treatment with all ETVs, the heating protocol listed in Table 5 in the Experimental section was used.

<table>
<thead>
<tr>
<th>ICPMS instrument</th>
<th>(b) Elan DRCII</th>
<th>(c) Elan DRCII</th>
<th>(a) Element XR</th>
<th>(a) Element XR</th>
</tr>
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<tbody>
<tr>
<td>ETV</td>
<td>HGA-600MS</td>
<td>Wire prototype</td>
<td>ETV-4000</td>
<td>ETV-4000</td>
</tr>
<tr>
<td>Sample(s)</td>
<td>NIST SRM 610</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wavelength</td>
<td>257 nm</td>
<td>206 nm</td>
<td>257 nm</td>
<td></td>
</tr>
<tr>
<td>Ablation style</td>
<td>line, 5 µm/s</td>
<td>single spot, 300 shots</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Energy</td>
<td>100%</td>
<td>50%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Energy density</td>
<td>7 J/cm²</td>
<td>7 J/cm²</td>
<td>5 J/cm²</td>
<td>8 – 8.5 J/cm²</td>
</tr>
<tr>
<td>Repetition Rate</td>
<td>25 Hz</td>
<td>5 Hz</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spot Size</td>
<td>55 µm</td>
<td>40 µm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>He carrier gas</td>
<td>1.0 L/min (0.5 L/min each)</td>
<td>0.9 L/min (0.45 L/min each)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 13 – Operating conditions for the Excite PHAROS fs-laser for the (a) ETV-4000 prototype, the (b) HGA-600MS and the (c) wire ETV.
3.2.1. Comparison of the Rb and Sr Suppression for the HGA-600MS, the ETV-4000 Prototype and the Homemade ETV Prototype

The performance in terms of Rb-Sr separation efficiency and Rb and Sr suppression was investigated for three different ETV units, the two GF-ETVs (HGA-600MS or ETV-4000) and the custom-made wire ETV prototype for NIST SRM 610 and two Li-tetraborate samples. Figure 44 shows the suppression profiles of the $^{85}\text{Rb}^+$ and $^{88}\text{Sr}^+$ ion signal for NIST SRM 610 and two Li-tetraborate pills after thermal treatment in the HGA-600MS, the ETV-4000 and the wire prototype.

The first thing that gets apparent is the selective $^{85}\text{Rb}^+$ suppression, which is observable for all samples when using GF-ETVs. For the wire prototype on the other hand, the profile was dominated by a large non-specific signal loss. Differences exist not only between the profiles of the different ETVs, but also between the suppression profiles of the silicate and tetraborate pills. For NIST SRM 610, the onset of the $^{85}\text{Rb}^+$ suppression was observed at 1'600 °C, when using the HGA-600MS for thermal treatment. Subsequently, the signal decreased steadily until it reached a minimum at 2’300 °C, where a suppression factor of 0.035 was measured. The signal suppression stayed relatively constant until 2’500 °C. For the ETV-4000, the onset of the $^{85}\text{Rb}^+$ suppression occurred at power level 4. After the onset of the
suppression, the signal decreased significantly faster compared to the suppression profile of the HGA-
600MS. The minimum of the signal was reached at power level 6.5, where a suppression factor of 0.0015
was reached. The suppression of all signals started around 100 W when using the wire prototype as ETV.
A relatively large $^{85}$Rb$^+$ suppression was observed at 170 W (0.008), however, in parallel, also a high Sr-
loss to factors around 0.03. For the two GF-ETVs, the $^{88}$Sr$^+$ signal did not undergo a significant
suppression in the investigated temperature range. Because the $^{85}$Rb$^+$ suppression observed with the
ETV-4000 was one order of magnitude stronger compared to the HGA-600MS, the resulting Rb-Sr
separation efficiency at power level 6.5 ($^{85}$Rb$^+$/88Sr$^+$ = 0.002) was also one order of magnitude higher
compared to the one achieved with the HGA-600MS at 2'300 °C ($^{85}$Rb$^+$/88Sr$^+$ = 0.03). This performance
difference between the two GF-ETVs is even more pronounced than for the Cu-Zn separation discussed
in chapter 3.1.3. Because of the large signal loss observed with the wire prototype, the Rb-Sr separation
was poor ($^{85}$Rb$^+$/88Sr$^+$ = 0.44). The highest Rb-Sr separation efficiency was therefore achieved with the
ETV-4000.

For the tetraborate pills, on the other hand, a suppression of both the $^{85}$Rb$^+$ and $^{88}$Sr$^+$ signal was
observed for all ETVs. In between the two tetraborate samples, however, only small differences in their
suppression profiles were found. The $^{85}$Rb$^+$ suppression onset was around 1’000 °C when heating with
the HGA-600MS. The signal dropped to suppression factors 0.05 around 1’700 – 1’800 °C and 0.07 at
1’300 °C for the 1:1 and 3:1 [Rb]/[Sr] tetraborate, respectively. Subsequently, a re-increase of the signal
was observed. The $^{85}$Rb$^+$ signal of the 1:1 sample re-increased to factors around 0.07 - 0.08 between
1’800 – 2’400 °C, before decreasing to 0.05 at 2’500 °C. The 3:1 $^{85}$Rb$^+$ signal profile was similar, with a
re-increase to values around 0.2 between 1’300 – 2’000 °C followed by a decrease to factors around
0.05 for 2’300 – 2’500 °C. The onset of the $^{88}$Sr$^+$ signal suppression occurred at power level 1’500 °C for
both Li-tetraborates and decreased to factors around 0.1 – 0.2 at 2’500 °C. With the ETV-4000, the $^{85}$Rb$^+$
suppression onset was found at power level 3 for both Li-tetraborates, which was followed by a fast,
strong decrease to suppression factors < 10$^{-5}$ at power level 4.5. For higher power levels, the $^{85}$Rb$^+$ signal
dropped below the instrumental background. For the $^{88}$Sr$^+$ signal, a suppression was observed as well,
starting at power level 4 and decreasing to a factor of 0.6 at power level 4.5. The suppression profiles
of the Li-tetraborates resembled that of NIST SRM 610 when using the wire prototype for thermal
treatment. The suppression of both elements was steady and relatively fast. At 190 and 200 W, $^{85}$Rb$^+$
suppression factors of 0.0035 and 0.0045 were measured for the 3:1 and 1:1 sample, respectively. This
suppression however occurred almost in parallel with a Sr-loss, which exhibited suppression factors
around 0.035 at 190 and 200 W.

The Rb-Sr separation (0.001 at power level 4) was slightly stronger for the Li-tetraborates compared to
NIST SRM 610 when using the ETV-4000 for thermal treatment. The $^{85}$Rb$^+$/88Sr$^+$ intensity ratios for the
1:1 and 3:1 sample at power level 4 were 0.00103 and 0.00131, respectively, and 0.8616 and 2.155 for
non-heating conditions. For the HGA-600MS, the contrary was the case. An about one order of
magnitude less efficient Rb-Sr separation was observed for the Li-tetraborates compared to NIST SRM
610 (0.1 vs. 0.04). The $^{85}$Rb$^+$/88Sr$^+$ intensity ratio dropped from 0.62 for the 1:1 sample to 0.064 at 1’300
°C and from 1.84 for the 3:1 sample to 0.19 at 1’500 °C. The separation of the two elements was similarly
poor as for the wire prototype, where for all three samples $^{85}$Rb$^+$/88Sr$^+$ ratios around 0.1 – 0.3 were
measured. The intensity ratios dropped from 0.671 to 0.273 and from 1.765 to 0.292 for the 1:1 and
3:1 samples, respectively. The most efficient Rb-Sr separation was therefore achieved with the ETV-
4000, as it was already the case for NIST SRM 610. Furthermore, it can be concluded that the $^{85}$Rb$^+$/88Sr$^+$
intensity ratio is suppressed to similar values at the temperature setting with the highest Rb-Sr
separation efficiency for the two teraborrates, even though the 3:1 Li-tetraborate contains significantly more Rb.

When comparing the profiles for NIST SRM 610 to the ones of the tetraborrates, clear differences can be observed, when using the GF-ETVs. The onset temperatures of suppression were clearly shifted to lower temperatures for the Li-tetraborates compared to the NIST SRM 610. Furthermore, for the tetraborrates, at lower temperatures, stronger suppression factors were reached than for the NIST SRM 610. These are clear indicators for a matrix effect, which supports the findings made in chapter 3.1.1. that the vaporization efficiency is governed by material characteristics.

No significant differences between the suppression profiles of the two Li-tetraborate samples were observed. The [Rb]/[Sr] concentration ratio does not seem to play an important role for the Rb-Sr separation efficiency within the concentration range studied. Again, the conclusions drawn in chapter 3.1.1. are supported here. Two elements in samples with different concentration ratios do not show a significantly altered vaporization efficiency, as long as they are embedded in the same matrix type.

It has to be noted that Brogioli observed a slightly stronger suppression for the $^{85}$Rb$^+$ for NIST SRM 610 when using the HGA-600MS in combination with ns-LA. In contrast to the profile here, a slight Sr suppression occurred starting around 2'200 °C. The Rb signal underwent a re-increase after reaching a minimum at 2'000 °C. At 2'000 °C, a $^{85}$Rb$^+$/$^{88}$Sr$^+$ ratio of 0.01 was obtained, which was slightly lower than the one obtained at 2'300 °C (0.04) in the data shown here. The onset temperature for the Rb suppression was however similar to the one observed here. The slightly better Rb-Sr separation performance can be explained by the significantly lower helium gas flow of 0.5 L/min and lower repetition rate of 5 Hz that was used for Brogioli’s measurements. In the experiments discussed here, a gas flow of 1 L/min was used. The effect of gas flow rate on the suppression of Sr and Rb was investigated for the ETV 4000 in this work and results are presented in the Appendix in section 7.4.

With the wire prototype, for all samples, a strong non-selective elimination was observed. Starting around 100 W, the $^{85}$Rb$^+$ and $^{88}$Sr$^+$ signals underwent a steady and fast decrease. A more pronounced $^{85}$Rb$^+$ suppression was observable, starting around 120 W. For $^{85}$Rb$^+$, suppression factors of 0.003 - 0.009 were measured between 170 – 200 W. However, the strong parallel $^{88}$Sr$^+$ signal suppression to suppression factors around 0.03 led to a poor Rb-Sr separation efficiency. The whole setup of the custom-made prototype strongly differs from the one of the GF-ETVs. The volume of the inner glass cylinder is significantly larger compared to the volume of the graphite tubes of the HGA-600MS and ETV-4000. This means that the heated aerosol has much more space available to cool before it comes into contact with the water-cooled walls. Since the same helium gas flow was used as for the GF-ETV experiments, the resulting aerosol residence time in the prototype is significantly longer. The temperature gradient and heat distribution differ strongly from the GF-ETVs. The temperature drop occurs from the wire towards the walls, while the temperature drops towards the middle of the graphite tube for the other ETVs. The differences in ETV and heater geometry and heater material, most probably affect the vaporization-condensation process to a large extent. A selective Rb vaporization is observable; however, the strong suppression of the Sr signal is an indicator for an overlapping non-selective elimination process. Due to the significantly longer residence time compared to the GF-ETVs, a lot more time for aerosol-ETV interactions is available. This could lead to coagulation of aerosol particles which may deposit within the inner section of the prototype or in the tubing due to their large sizes. This would cause high aerosol losses and is a possible explanation for the non-selective signal suppression. Another, however less probable explanation is a deposition of the aerosol on the tungsten wire. Since a large
fraction of the aerosol would have to come into direct contact with the wire, this assumption is less probable.

3.2.2. Rb-Sr Separation in Natural Samples

To characterize the Rb and Sr suppression in minerals with higher [Rb]/[Sr] concentration ratios and range, three biotite minerals (Table 12) were selected. In these experiments, the thermal treatment was performed only with the ETV-4000 due to the high Rb-Sr separation performance, at power levels between 2 and 6 with the heating protocol listed in Table 5 in the Experimental section. The Element XR was used for ion signal detection. Due to the smaller grain sizes, single spot ablation had to be carried out, and experiments with and without heating were done at separate grain positions. In order to monitor the reproducibility of the system and to calculate the suppression factors of the previous measurements, a measurement without thermal treatment was performed after every 5th measurement. The fact that ablation was performed for different positions on the grains for every power level, however, introduces some uncertainty because these natural samples show a certain degree of heterogeneity. Considering the obtained transient signals and the mean intensities, however, the Rb and Sr concentrations between the grains did not vary to an extent that would falsify the results. Figure 45 shows the transient signal of the 131102-4 biotite. When considering especially the $^{85}\text{Rb}^+/^{88}\text{Sr}^+$ intensity ratio of the biotite phase between 40 – 60 s, it gets obvious that the sample is heterogeneous. Two transient signals of the KR36-04 and KR65-10 recorded under non-heating conditions are shown in the Appendix in section 7.3.

Figure 45 – $^{85}\text{Rb}^+$ and $^{88}\text{Sr}^+$ transient ion signals and the corresponding $^{85}\text{Rb}^+/^{88}\text{Sr}^+$ intensity ratio of the 131102-4 biotite.

Small-scale variations are visible when comparing the suppression factor profiles for the three biotites in Figure 46 to those of NIST SRM 610 and the Li-tetraborates (Figure 44). Overall, however, the profiles for Sr in particular appear less smooth, which may be a result of the heterogeneities, but probably also the generally lower Sr concentrations (Table 12).
Figure 46 - $^{85}\text{Rb}^+$, $m/Q\ 87$ and $^{88}\text{Sr}^+$ ion signal suppression factors for biotite 131102-4 (top left), KR36-04 (top right) and KR65-10 (bottom).

A selective suppression of the $^{85}\text{Rb}^+$ and $m/Q\ 87$ signal is observable, starting at power level 3.5, 2 and 3 for the 131102-4, KR36-04 and KR65-10 biotite, respectively. Compared to the NIST SRM 610, the suppression onset of the Rb suppression is shifted to lower temperatures. Apart from the greater variability in the $^{88}\text{Sr}^+$ signal of the biotites compared to the NIST SRM 610 and tetraborate pills, no significant suppression appeared to occur for the investigated power levels. The suppression profiles for the $^{85}\text{Rb}^+$ ion signal, seemed to differ amongst the biotites. For the KR36-04 and KR65-10, the decrease of the signal started at power levels 2 and 3.5, respectively, was initially flat, and then dropped relatively fast up to power levels 5.25 and 5.5. For the 131102-4 biotite, the initial drop was rather moderate but steady, starting between power levels 3 and 4 and until power level 5.5. The magnitude of the $^{85}\text{Rb}^+$ ion signal suppression also differed between the three samples. While for the 131102-4 and the KR65-10 suppression factors around $10^{-3}$ are achieved, for the KR36-04, a suppression in the order of $10^{-4}$ was obtained. Those differences are caused most likely by differences in sample composition and the corresponding physical properties. Additionally, in contrast to the KR65-10, the Li-tetraborates and the NIST SRM 610, for the 131102-4 and the KR36-04 biotites, a re-increase of the signal was observed, starting from power levels 5.5 and 5.25, respectively. As it was already discussed in chapter 3.1.1, it can be assumed that at those power levels, the higher temperature inside the tube and the shorter residence time compete and, finally, the higher gas velocity superimposes the suppression. The $^{85}\text{Rb}^+$ re-increase for biotites 131102-4 and KR36-04 ultimately resulted in suppression factors of 0.7 and 0.0015, respectively. The maximally achieved $^{85}\text{Rb}^+$ signal suppression factors are 0.0025 for the 131102-4, 0.0009 for the KR65-10 and 0.0001 for the KR36-04 biotite. The $^{85}\text{Rb}^+/^{88}\text{Sr}^+$ intensity ratios measured under non-heating conditions was suppressed from $\approx 44$, $\approx 43$ and $\approx 25$ for the 131102-4, KR36-04 and KR65-10 biotite, respectively, to 0.11, 0.15 and 0.04 at power levels where the maximal
Rb-Sr separation efficiency was achieved. Due to the heterogeneity of the biotites (Figure 45) it is difficult to draw a conclusion about the dependence of the Rb-Sr separation efficiency on the [Rb]/[Sr] concentration ratio. Even though the most efficient separation was achieved for the KR65-10 biotite, which also has the lowest [Rb]/[Sr] concentration ratio, it is possible that this observation is caused by matrix inhomogeneities and not a real dependence of the separation efficiency on the concentration ratio. The most reasonable explanation for the differences in the Rb-Sr separation efficiency between the three biotites and also between the biotites and the other materials is therefore the presence of a matrix effect. The Rb-Sr separation efficiencies at the power levels, where the maximal separation was measured, are summarized in Table 14 for all samples investigated in this chapter.

SUMMARY

When the suppression profiles for the Li$_2$B$_4$O$_7$ disks, the NIST SRM 610 and the biotites are compared, a matrix effect became obvious when one of the two GF-ETVs is used. The onset of the $^{85}$Rb$^+$ signal suppression is near 1'600 °C for NIST SRM 610, while it was observed around 1'000 °C for the Li-tetraborate pills for the HGA-600MS. For the ETV-4000, the signal suppression began at power level 4.25 for NIST SRM 610 and shifted to power level 3 for the Li-tetraborates. The decrease of the signals with increasing power level was much steeper for the Li-tetraborates. These observations are most probably an effect of the lower boiling point of the Li$_2$B$_4$O$_7$ (917° C) compared to the glass or the minerals. For the wire ETV, however, no significant matrix dependency was observed for the two materials. Either no matrix effect is present for this ETV, or, more likely, it was not detectable due to the pronounced non-selective aerosol loss. For none of the used ETV units, a significant difference in the Rb elimination efficiency was observed between the two Li-tetraborate pills. This indicates that the [Rb]/[Sr] concentration ratio does not have a significant influence on the element-specific elimination within this type of matrix.

Overall, the highest Rb elimination and Rb-Sr separation efficiency was achieved with the ETV-4000 for NIST SRM 610, the two Li-tetraborates, in a similar fashion as the Cu-Zn separation in brass. This can be explained by the longer graphite tube of the ETV-4000 (45 mm) compared to the HGA-600MS (28 mm). The residence time of the aerosol in the heated tube is almost twice as high in the ETV-4000, which makes this furnace much more efficient in terms of elemental separation compared to the shorter graphite tube of the HGA-600MS. The wire prototype did not result in an appreciable Rb-Sr separation for the studied materials. Modifications of the heating zone, which are summarized in the Appendix in section 7.2., were attempted in order to test whether an improvement is possible but showed no success.

The Rb-Sr separation efficiency for three biotites was found to display greater variabilities in the suppression profiles and in the $^{85}$Rb$^+/^{88}$Sr$^+$ intensity ratio suppression, which is again most likely caused by matrix effects within the biotites. Generally, the onset of Rb suppression was shifted to lower temperatures but also occurred over a wider range than for example in NIST SRM 610. This may partly also be related to the higher Rb content of these materials but is currently assumed to represent a matrix dependency.

Table 14 gives an overview over the Rb-Sr separation efficiencies and onset temperatures for the suppression of Rb and Sr for the different combinations of ETV and sample types.
Table 14 – Summary of the maximally achievable $^{88}$Rb$^+$ suppression, the corresponding temperature setting, the corresponding $^{88}$Sr$^+$ suppression factor and the onset temperature of both signal suppressions.

<table>
<thead>
<tr>
<th></th>
<th>$\text{Max. } ^{86}\text{Rb}^+/^{88}\text{Sr}^+$ separation</th>
<th>$T$ at max. separation</th>
<th>onset-$T$ $^{86}\text{Rb}^+$</th>
<th>onset-$T$ $^{88}\text{Sr}^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIST SRM 610 ($^{86}\text{Rb}^+/^{88}\text{Sr}^+ = 0.83, [\text{Rb}]/[\text{Sr}] = 0.83$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HGA-600MS</td>
<td>0.03</td>
<td>2'300 °C</td>
<td>1'600 °C</td>
<td>2'500 °C</td>
</tr>
<tr>
<td>ETV-4000</td>
<td>0.002</td>
<td>PL 6.5</td>
<td>PL 4</td>
<td>&gt; PL 6.5</td>
</tr>
<tr>
<td>Wire ETV</td>
<td>0.44</td>
<td>170 W</td>
<td>100 W</td>
<td>100 W</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{Li}_2\text{B}_2\text{O}_5$ ($^{86}\text{Rb}^+/^{88}\text{Sr}^+ = 0.96, [\text{Rb}]/[\text{Sr}] = 1$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HGA-600MS</td>
<td>0.0641</td>
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<td>1'000 °C</td>
<td>1'500 °C</td>
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<tr>
<td>ETV-4000</td>
<td>0.001</td>
<td>PL 4</td>
<td>PL 3</td>
<td>PL 4</td>
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<td>Wire ETV</td>
<td>0.273</td>
<td>200 W</td>
<td>&lt; 100 W</td>
<td>&lt; 100 W</td>
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<td>HGA-600MS</td>
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<td>0.0013</td>
<td>PL 4</td>
<td>PL 3</td>
<td>PL 4</td>
</tr>
<tr>
<td>Wire ETV</td>
<td>0.292</td>
<td>190 W</td>
<td>&lt; 100 W</td>
<td>&lt; 100 W</td>
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<tr>
<td></td>
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<td><strong>Biotite 131102-4</strong> ($^{86}\text{Rb}^+/^{88}\text{Sr}^+ = 42.6, [\text{Rb}]/[\text{Sr}] = 20.35$)</td>
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<tr>
<td>ETV-4000</td>
<td>0.1052</td>
<td>PL 5.5</td>
<td>PL 3.5</td>
<td>&gt; PL 6</td>
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<td></td>
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<td><strong>Biotite KR36-04</strong> ($^{86}\text{Rb}^+/^{88}\text{Sr}^+ = 35.9, [\text{Rb}]/[\text{Sr}] = 65.70$)</td>
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<tr>
<td>ETV-4000</td>
<td>0.1455</td>
<td>PL 5.25</td>
<td>PL 2</td>
<td>&gt; PL 6</td>
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<td><strong>Biotite KR65-10</strong> ($^{86}\text{Rb}^+/^{88}\text{Sr}^+ = 25.6, [\text{Rb}]/[\text{Sr}] = 17.30$)</td>
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<td></td>
</tr>
<tr>
<td>ETV-4000</td>
<td>0.0387</td>
<td>PL 5.5</td>
<td>PL 3</td>
<td>&gt; PL 6</td>
</tr>
</tbody>
</table>

3.3. Rb-Sr Separation Efficiency Depending on Mass Load and Sample Composition

R. Brogioli \(^{147}\) had observed that increasing the aerosol mass flow through the HGA-600 MS ETV caused a reduction in Rb suppression when ns-LA was used. NIST SRM 610 was studied and the mass load varied by changing the laser ablation spot size and frequency at a furnace temperature of 2'200°C. The suppression was found to change by more than an order of magnitude when the mass flow was increased by a factor of 8. Due to the difference in aerosol morphologies between fs- and ns-LA, it may be expected that the effect of mass load effect on the Rb-Sr separation efficiency differs.

Therefore, in the first part of this chapter, the dependency of the separation efficiency from the mass load in the furnace was tested for fs-LA for NIST SRM 610. Thermal treatment was performed using the HGA-600MS or ETV-4000 as shown in Figure 43 (b) and (a), respectively. For the HGA-600MS measurements, the ELAN DRCII was used for ion signal detection while for the ETV-4000 measurements, the Element XR was used. In order to study the possible influence of laser wavelength ablation was performed using 257 nm and 206 nm.

The Rb-Sr separation efficiency was studied for 2 of 6 mineral samples, which were provided by J. Mercadier from the University of Lorraine. They had additionally been analysed for their major, minor and trace element composition in order to assess the composition and abundance of REEs in particular. The results are given in detail in the Appendix in section 7.5. For ablation, in the second and third subsection, the Excite PHAROS fs-laser was used operating at a wavelength of 257 nm. The separation efficiency measured for the minerals was lower compared to the performance measured for NIST SRM 610 under the same operational parameters. In order to test, whether the Rb-Sr separation efficiency could be increased by increasing the aerosol residence time in the furnace, in the second part of this chapter, the influence of the helium carrier gas flow through the ETV on the separation efficiency was...
investigated for two minerals. The ETV-4000 was used for thermal treatment and the Element XR for ion signal detection.

Additional mass load experiments were carried out in the last subsection of this chapter with the ETV-4000 - Element XR combination for 6 mineral samples. The experiments were carried out during different periods and therefore, slightly different operating conditions of the LA and ICPMS were used. For the HGA-600MS, the operating conditions were adjusted to simulate the conditions used previously with ns-LA as closely as possible. In experiments using the ETV-4000, however, single spot ablation was used for NIST SRM 610 and the mineral samples in order to account for the small-scale heterogeneity observed in the natural material (see Appendix in section 7.5.). In the framework of the studies of the brass samples, it had been found that no significant variations of the suppression factors were observed between line scan and single spot ablation, as shown in the Appendix in section 7.8. Mass load changes were performed by changing the laser repetition rate and spot size. Due to the Gaussian beam profile of the fs-laser used, larger spot sizes may however not lead to a proportionally higher mass ablation rate. Therefore, instead of calculating a mass load index, the suppression is plotted against the $^{88}\text{Sr}^+$ sensitivities for the same laser settings under non-heating conditions as indicator for the mass aerosol mass flow in the graphite furnace. The ICPMS optimization was generally following the strategy outlined in the Experimental section. Operating conditions are summarized in Table 15. Thermal treatment was performed according to Table 5.

<table>
<thead>
<tr>
<th>LA-system</th>
<th>(a) ELAN DRCII</th>
<th>(b) Element XR</th>
<th>(c) Element XR</th>
<th>(d) Element XR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>257 nm</td>
<td>206 nm</td>
<td>257 nm</td>
<td></td>
</tr>
<tr>
<td>ETV</td>
<td>HGA-600MS</td>
<td>ETV-4000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample</td>
<td>NIST SRM 610</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ablation style</td>
<td>line, 10 µm/s</td>
<td>single spot, measurement time = 1 min</td>
<td>line scans, 1 µm/s, 5 µm/s (55 µm, 100 Hz)</td>
<td></td>
</tr>
<tr>
<td>Energy</td>
<td>100%</td>
<td>50%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Energy density</td>
<td>7.5 J/cm²</td>
<td>3 J/cm²</td>
<td>7 J/cm²</td>
<td>6 - 7 J/cm²</td>
</tr>
<tr>
<td>He carrier gas</td>
<td>1.0 L/min (0.5 L/min each)</td>
<td>0.9 L/min (0.45 L/min each)</td>
<td>0.2 L/min (0.15 L/min main volume and 0.05 L/min inner cup)</td>
<td></td>
</tr>
<tr>
<td>Temperature settings</td>
<td>2'200 °C</td>
<td>PL 5.75, 6</td>
<td>PL 5.5, 5.75, 6, 6.5</td>
<td>PL 6</td>
</tr>
</tbody>
</table>

Table 15 – Operating conditions for the Excite PHAROS fs-laser for the HGA-600MS and ETV-4000 for the different samples.

3.3.1. Comparison of the Influence of the Mass Load on the Rb-Sr Separation Efficiency for NIST SRM 610

The influence of the mass load in the graphite furnace of the HGA-600MS and ETV-4000 on the Rb-Sr separation efficiency was investigated. Figure 47 shows the $^{85}\text{Rb}^+/^{88}\text{Sr}^+$ ratios and the suppression factors for the $^{88}\text{Sr}^+$ ion signals plotted against the $^{88}\text{Sr}^+$ sensitivities for the ETV-4000 with LA with (a) 206 nm at power levels 5.5 – 6.5 and (b) 257 nm at power levels 5.75 and 6 and the (c) HGA-600MS at 2'200 °C. For the measurements performed with LA at 206 nm and the ETV-4000, the $^{85}\text{Rb}^+/^{88}\text{Sr}^+$ ratios and the $^{88}\text{Sr}^+$ suppression factors for the individual power levels were in the same order of magnitude.
Due the lower Rb-intensities obtained for the lower mass load settings (i.e. $^{88}$Sr$^+$ sensitivities) the signal was almost suppressed to the instrumental background causing a larger variability in the calculated suppression factors. For the measurements performed with 257 nm LA and thermal treatment in the ETV-4000, also no significant change in the $^{85}$Rb$^+$/$^{88}$Sr$^+$ intensity ratios or the $^{88}$Sr$^+$ suppression was observed for the different mass load settings within the individual power levels. Compared to the 206 nm data for power levels 5.75 and 6, the ratios were slightly less suppressed. This might either be due to the fact that the measurements were performed on different days or related to the smaller mass load introduced with 206 nm. For the HGA-600MS measurements, again no differences in the $^{85}$Rb$^+$/$^{88}$Sr$^+$ intensity ratios and the $^{88}$Sr$^+$ suppression factors for different mass load settings were observed. It has to be noted, however, that a significantly smaller mass load range was studied compared to the ETV-4000 measurements, because the primary goal was a comparison with the conditions used during the ns-LA measurements with this ETV. In general, the $^{85}$Rb$^+$/$^{88}$Sr$^+$ ratios for both GF-ETVs and both wavelengths were in a range between $10^{-3} – 10^{-2}$. The ratios in the HGA-600MS data are found to be slightly less than $10^{-2}$ which is similar to the results obtained for ns-LA and the HGA-600MS at intermediate mass load settings. The $^{88}$Sr$^+$ suppression factors were around 0.5 – 1 for both ETVs and wavelengths, which means that most of the Sr is retained in the aerosol during heating. In general, these experiments did indicate that the mass load effect obtained with ns-LA and the HGA-600MS appears to be reduced or even absent when using fs-LA. The Rb-Sr separation was found to be largely independent and greater with the ETV-4000 and only a minute increase was found with 257 nm fs-LA at the highest mass load studied.

![Figure 47 - $^{85}$Rb$^+$/88Sr+ ratio and $^{85}$Rb+ and $^{88}$Sr+ ion signals suppressions plotted against the $^{88}$Sr+ sensitivity for NIST SRM 610 for the (a) ETV-4000 with LA with a wavelength of 206 nm, (b) ETV-4000 with LA with 257 nm and the (c) HGA-600MS with LA with 257 nm. The $^{88}$Sr$^+$ sensitivity is used as proxy for mass load index. For (c), a different x-axis is used to achieve a better depiction of the data.](image-url)
3.3.2. Effect of the Helium Gas Flow Rate on the $^{85}$Rb$^+$ and $^{88}$Sr$^+$ Suppression

When testing the Rb-Sr separation for the mineral samples, it became obvious, that Rb signals could not be suppressed to near instrumental background levels, even at the highest power levels applied to the ETV-4000. This was due to the fact that some of the minerals had a significantly higher Rb concentration and [Rb]/[Sr] concentration ratio than NIST SRM 610 or the Li-tetraborates. The remaining $^{85}$Rb$^+$/$^{88}$Sr$^+$ intensity ratios were therefore one to two orders of magnitudes higher than for the other samples. One factor that certainly influences the Rb vaporization efficiency to a strong extent is the residence time of the aerosol in the graphite furnace. It was shown for NIST SRM 610 (see Appendix, section 7.4.), that when the helium gas flow is increased from 0.7 – 1.1 L/min in 0.1 L/min steps, the $^{85}$Rb$^+$ suppression factor profile is shifted to higher power levels. This means that for a certain power level, the factor decreases with increasing flow rate. The Rb-Sr separation efficiency can therefore be manipulated by varying the carrier flow rate. Therefore, in this chapter, gas flow variation experiments were carried out to find operating parameters, which yield a greater Rb suppression. In contrast to the data shown in the Appendix in section 7.4 for NIST SRM 610, the gas flow rate was varied across a wider range, between 0.2 and 0.9 L/min in 0.1 L/min steps. For initial experiments, the AM13 1F feldspar was used, which has the highest Sr concentration and additional experiments were carried out with AM13 1B biotite, which has a significantly higher [Rb]/[Sr] concentration ratio. Table 16 lists the laser parameters. For thermal treatment, the ETV-4000 was used at power level 6 with the heating protocol listed in Table 5 in the Experimental.

<table>
<thead>
<tr>
<th>LA-system</th>
<th>Excite PHAROS fs-laser</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>257 nm</td>
</tr>
<tr>
<td>Ablation style</td>
<td>single spot, 300 shots</td>
</tr>
<tr>
<td>Energy</td>
<td>50%</td>
</tr>
<tr>
<td>Energy density</td>
<td>12 J/cm²</td>
</tr>
<tr>
<td>Repetition Rate</td>
<td>5 Hz</td>
</tr>
<tr>
<td>Spot Size</td>
<td>40 µm</td>
</tr>
</tbody>
</table>

Table 16 – Operating conditions of the Excite PHAROS fs-laser.

Table 17 lists the Sr and Rb concentrations and the [Rb]/[Sr] concentration ratio for the two samples, which were investigated in this chapter.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type</th>
<th>Sr [mg/kg]</th>
<th>Rb [mg/kg]</th>
<th>[Rb]/[Sr]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM13 1B</td>
<td>Biotite</td>
<td>5</td>
<td>925</td>
<td>25</td>
<td>this work</td>
</tr>
<tr>
<td>AM13 1F</td>
<td>Feldspar</td>
<td>767</td>
<td>358</td>
<td>0.5</td>
<td>this work</td>
</tr>
</tbody>
</table>

Table 17 – Samples used for the gas flow variation experiments.

Figure 48 shows the change of the (a) $^{85}$Rb$^+$ and (b) $^{88}$Sr$^+$ transient ion signals and the (c) $^{85}$Rb$^+$/88Sr$^+$ intensity ratio at power level 6 for different gas flows for the AM13 1F feldspar.
Figure 48 – $^{88}\text{Sr}^+$ (top left) and $^{85}\text{Rb}^+$ transient signals (top right) and $^{85}\text{Rb}^+/^{88}\text{Sr}^+$ intensity ratios (bottom) for helium gas flows between 0.2 – 0.9 L/min for the AM13 1F feldspar. Thermal treatment was performed by heating with power level 6.

The $^{85}\text{Rb}^+$ and $^{88}\text{Sr}^+$ ion signal suppression became more pronounced when the helium flow was lowered from 0.9 to 0.2 L/min. It has to be noted that for gas flow rates < 0.2 L/min, no ion signals above the instrumental background were detected at the Element XR, indicating that the aerosol is not efficiently transported out of the ablation cell anymore. With a lower flow rate, the intensity of the $^{88}\text{Sr}^+$ signal decreased gradually from $3 \times 10^7$ cps to $10^6$ cps, while the $^{85}\text{Rb}^+$ signal decreased from $10^6$ cps to approach the instrumental background of $3 \times 10^4$ cps at a gas flow rate of 0.2 L/min. At the same time, however the background signals for $^{88}\text{Sr}^+$ decreased by almost an order of magnitude while the background signals of $^{85}\text{Rb}^+$ increase by a factor of ≈ 4. The $^{85}\text{Rb}^+$ suppression therefore reaches 2 orders of magnitude, while the suppression of $^{88}\text{Sr}^+$ was only one order of magnitude increased with the lower gas flow. The reason for the change in background signals is not fully clear. Rb is typically found in the background spectra of the Element XR and may result from ionized vaporized material, previously deposited on the interface cones and extraction lens. A lower He gas flow rate leads to a higher plasma temperature and thus more material may be removed from the sampler and skimmer cones. The decrease in $^{88}\text{Sr}^+$ backgrounds, on the other hand, is less clear. Memory effects may be excluded, leaving varying levels of molecular ions (e.g. ArC$_4^+$) as most likely explanations. The background signals also varied between individual measurement sessions. The influence of the gas flow rates on the Rb-Sr separation efficiency...
for a mineral with higher [Rb]/[Sr] ratio, was further studied for the AM13 1B biotite with gas flow rate of (a) 0.9 and (b) 0.2 L/min at power level 6 (Figure 49).

The net intensities of the $^{86}$Sr$^+$ and $^{88}$Sr$^+$ ion signals were found to decrease more strongly than for the AM13 1F feldspar. When lowering the gas flow from 0.9 to 0.2 L/min, Sr was suppressed by almost an order of magnitude here. Due to the high background signals (dominated by $^{86}$Kr$^+$), the signal/background ratio of $^{86}$Sr$^+$ is very low when a gas flow of 0.2 L/min is used. The effect on $^{85}$Rb$^+$ ion signal suppression was less pronounced, which is partly related to the fact that most of the Rb is already removed from the aerosol at the higher gas flow rate. The background signals however did not change substantially. Both Rb and Sr background intensities only varied within a factor of 2.

The decrease of the sensitivity caused by lowering the helium gas flow rate could partly be compensated for by increasing the argon make-up gas flow rate of the Element XR from 0.96 to 1.225 L/min. The Rb-Sr separation on the other hand was not affected. Under these conditions, the measurements at power level 6 were performed for the 1F and 1B. Table 18 summarizes the resulting suppression factors and the $^{85}$Rb$^+$/88Sr$^+$-intensity ratios for heating and non-heating conditions for the 1F and 1B with a helium gas flow of 0.2 L/min.

Table 18 – Summary of the signal suppression factors of the $^{85}$Rb$^+$, $^{86}$Sr$^+$, $^{87}$m/Q and $^{88}$Sr$^+$ signals for the AM13 1B biotite and the AM13 1F feldspar. Mean and standard deviation from 3 replicates.

The measured $^{85}$Rb$^+$/88Sr$^+$ intensity ratio for both samples could be suppressed across three orders of magnitude. Compared to the suppression factors and intensity ratios obtained for the different grains of the leucogranite biotite LB (Appendix, section 7.6.), a significant improvement in terms of accuracy.
and reproducibility could be achieved. This is either a result of the lower gas flow and the higher Rb-Sr separation efficiency, or it is attributed to the lower [Rb]/[Sr] concentration ratios of the 1F and 1B compared to the LB. Since the $^{85}\text{Rb}^{+}/^{88}\text{Sr}^{+}$-intensity ratios of the 1F and 1B were both suppressed by three orders of magnitude, it can be assumed that the improvements in terms of reproducibility can be attributed to the lower gas flow setting.

It can be concluded that a helium gas flow of 0.2 L/min is advantageous for the separation of Sr and Rb, when analyzing minerals. This effect is certainly caused by the higher residence time in the furnace and the resulting higher temperature of gas and aerosol.

3.3.3. Influence of the Mass Load on the Rb-Sr Separation Efficiency for Minerals

It was shown in chapters 3.2.2. and chapter 3.3.2. that the Rb concentration and the helium gas flow are relevant parameters affecting the measured $^{85}\text{Rb}^{+}/^{88}\text{Sr}^{+}$ intensity ratios after thermal treatment for minerals. While the separation efficiency decreased with increasing concentration ratio, it was advantageous to lower the helium gas flow to 0.2 L/min. The effect of the mass load on the Rb-Sr separation efficiency for the 6 minerals provided by J. Mercadier was investigated, using the same operating conditions as listed in Table 15 with a Ar make-up gas flow of 1.225 L/min. In contrast to the results obtained for NIST SRM 610 (Figure 44) however, the mass load had a more pronounced effect on the separation efficiency under these conditions.

Figure 50 shows the $^{85}\text{Rb}^{+}/^{88}\text{Sr}^{+}$ intensity ratios and the $^{87}\text{Rb}^{+}$ and $^{88}\text{Sr}^{+}$ ion signal suppression factors as function of the ablated mass, in this case again indicated by the $^{88}\text{Sr}$ sensitivity for non-heating conditions in 6 minerals. The mass load was varied over a wider range here. This was tested mainly to increase $^{88}\text{Sr}^{+}$ ion signal intensities, because the Sr concentrations in some minerals were relatively low. Due to the different Rb and Sr concentrations of the samples, the $^{85}\text{Rb}^{+}/^{88}\text{Sr}^{+}$ intensity ratios vary over a relatively wide range. The $^{88}\text{Sr}^{+}$ ion signal suppression factors can be found in a range between 0.05 – 1, however, they do not show a pronounced correlation with the change in mass load or Sr concentration of the samples.

Figure 50 – The $^{85}\text{Rb}^{+}$ and $^{88}\text{Sr}^{+}$ ion signal suppression (right) and the $^{85}\text{Rb}^{+}/^{88}\text{Sr}^{+}$ ratios (left) as a function of the $^{88}\text{Sr}^{+}$ sensitivity for the AM13 feldspar 1F, the ponsac orthose PF, the brame feldspar BF, the AM13 biotite 1B, the brame biotite BB and the leucogranite muscovite LM.
The $^{85}\text{Rb}^+$ suppression, on the other hand, appears to be relatively similar for a given mass load setting and the resulting $^{85}\text{Rb}^+/^{88}\text{Sr}^+$ intensity ratios correspond to the concentration ratios in the minerals. Across the different materials, a suppression of $^{85}\text{Rb}^+$ by almost 4 orders of magnitude can be achieved (Table 19), when a low mass load is resulting from ablation. The Rb-Sr separation efficiency, however, decreases substantially with increasing mass load in the furnace for all samples studied. Thus, even though a significantly lower helium gas flow rate was used, the increased residence time in the furnace does not appear to sufficiently increase the vaporization efficiency when a larger aerosol mass is introduced into the ETV. Still, the slight $^{88}\text{Sr}^+$ ion signal suppression, which was observed in these experiments, would indicate that the Sr already starts to undergo vaporization under the used operating conditions, which would mean that the lower separation efficiency is not only due to the gas and aerosol temperature. It will need further dedicated studies to isolate the reason for this behavior. This observation may however still be a limiting factor for $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio measurements, where the concomitant reduction of the $^{86}\text{Sr}^+$ signal will ultimately affect accuracy and precision of the measurement. The latter is less critical for the feldspars studied here, which have Sr concentrations of > 100 ppm. For samples with much lower Sr concentrations like the biotites, on the other hand, this may impose a clear limitation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sr [ppm]</th>
<th>$^{88}\text{Sr}$ supression</th>
<th>Rb [ppm]</th>
<th>$^{85}\text{Rb}$ supression ($10^{-4}$)</th>
<th>$^{85}\text{Rb}^+/^{88}\text{Sr}^+$, no heating</th>
<th>$^{85}\text{Rb}^+/^{88}\text{Sr}^+$, heating</th>
</tr>
</thead>
<tbody>
<tr>
<td>1F</td>
<td>767</td>
<td>0.43</td>
<td>358</td>
<td>1.4</td>
<td>0.4</td>
<td>0.00014</td>
</tr>
<tr>
<td>PF</td>
<td>195</td>
<td>0.73</td>
<td>212</td>
<td>3.9</td>
<td>0.2</td>
<td>0.0011</td>
</tr>
<tr>
<td>BF</td>
<td>168</td>
<td>0.33</td>
<td>458</td>
<td>3</td>
<td>2.4</td>
<td>0.0013</td>
</tr>
<tr>
<td>1B</td>
<td>5</td>
<td>0.73</td>
<td>925</td>
<td>2.2</td>
<td>150</td>
<td>0.034</td>
</tr>
<tr>
<td>BB</td>
<td>2</td>
<td>0.64</td>
<td>1235</td>
<td>1.3</td>
<td>674</td>
<td>0.14</td>
</tr>
<tr>
<td>LM</td>
<td>4</td>
<td>0.39</td>
<td>1242</td>
<td>3.9</td>
<td>117</td>
<td>0.12</td>
</tr>
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</table>

Table 19 – Summary of the Rb and Sr suppression factors and concentrations and the $^{85}\text{Rb}^+/^{88}\text{Sr}^+$ for heating and no heating conditions when using the lowest mass load setting (5 Hz, 20 μm). Thermal treatment for the 1F, PF and BF was performed at power level 5.5 and at power level 5 for the 1B, BB and LM.

**SUMMARY**

In the first subsection of this chapter it was shown that the Rb suppression from fs-LA generated aerosols appears to be affected to a different extent by mass load effects in an ETV compared to aerosols generated by ns-LA. For NIST SRM 610, the Rb-Sr separation efficiency and the $^{88}\text{Sr}^+$ suppression factors did not depend on the mass load in the furnace, when fs-LA with 206 nm or 257 nm was used and the thermal treatment was carried out in the ETV-4000 or the HGA-600MS. In contrast to the findings made in this chapter, Brogioli observed a decrease of the Rb-Sr separation efficiency for thermal treatment in the HGA-600MS for similar ablation conditions while using ns-LA at 213 nm and a lower helium flow of 0.5 L/min. Again, the ETV-4000 provided a higher separation efficiency for the more volatile element Rb, while the laser wavelength does not seem to influence the Rb-Sr separation efficiency to a notable extent. It was found, however, that the Rb-Sr separation is significantly less efficient for 6 silicate mineral samples than NIST SRM 610 glass when using the same experimental conditions. By reducing the carrier
gas flow and therefore extending the residence time of the aerosol inside the furnace, the separation could however be increased significantly, even though a slight suppression of the Sr⁺ ion signals occurred in parallel. After optimization of the other operating parameters, a Rb suppression of 4 orders of magnitude was achieved with small suppression of Sr, which was practically independent of the sample material studied. Due to the different [Rb]/[Sr] concentration ratios, however, the remaining ⁸⁵Rb⁺/⁸⁸Sr⁺ intensity ratios varied. It was found that with the current setup, the ⁸⁵Rb⁺ ion signal can be suppressed down to the instrumental background for minerals with Rb < 1’000 ppm and [Rb]/[Sr] ≤ 25. For samples with Rb < 1’250 ppm and [Rb]/[Sr] up to ~ 700, the ⁸⁵Rb⁺/⁸⁸Sr⁺ can be suppressed to < 0.14. In contrast to the NIST SRM 610 experiments mentioned before, a mass load effect was present when analysing the 6 mineral samples under a helium gas flow of 0.2 L/min. Despite the longer residence time, the ⁸⁵Rb⁺/⁸⁸Sr⁺ intensity ratios were found to increase with increasing mass load in the furnace after thermal treatment. The ⁸⁸Sr⁺ suppression factors were fairly reproducible but frequently below 1, which indicates that the Sr starts to take part in the vaporization process under the used conditions. The dependency of the Rb-Sr separation efficiency on the mass load thus appears to depend on the actual aerosol composition. While NIST SRM 610 glass mainly consists of Si-, Ca-, Na- and Al-oxides, the minerals are silicates with variable composition. In particular, the biotites are rich in Ti and Fe while the feldspars contain more Na. The corresponding melting points of the aerosol particles will thus be different. The fact that the degree of Rb-evaporation from the aerosol was practically independent of the composition, however, would imply that the thermodynamic properties of the material is of lesser importance. At the current state, it appears as if the mass load effect observed in section 3.3.3 results primarily from the fact that the ablated mass in these experiments was varied over a much wider range. For mass loads corresponding to a ⁸⁸Sr⁺ sensitivity < 10⁴ cps in these experiments, the situation is similar to the experiments using NIST SRM 610. Here, fs-LA generated aerosols however appear to be advantageous over ns-LA sampling. Yet also with fs-LA, excessive mass load in the ETV causes a reduced Rb-Sr separation.

This chapter has made clear that finding the optimal operating parameters is not always straightforward. To keep the balance between a high ⁸⁵Rb⁺ suppression while retaining the ⁸⁸Sr⁺ sensitivity it is especially important for example for the biotites, where Sr concentrations can be so low that the instrumental background is a possible limiting factor to detect all relevant isotopes. For samples with high Sr concentrations the focus can be set on the Rb suppression and the operational parameters can be chosen in a way that the highest possible Rb elimination is achieved. Therefore, the combination of a low mass load and high power level is desirable to achieve a high heat distribution within the aerosol. For samples with low Sr content, however, already a slight suppression of the Sr signals could suppress the ⁸⁶Sr⁺ ion signal below the instrumental background. For samples with high Rb and low Sr concentrations, the operational parameters have to be chosen with great care.
3.4. $^{87}\text{Sr}/^{86}\text{Sr}$ Isotope Ratio Fractionation and Dependence on the $[\text{Rb}]/[\text{Sr}]$ Concentration Ratio and Gas Flow

3.4.1. $^{87}\text{Sr}/^{86}\text{Sr}$ Isotope Ratio Fractionation as a Function of the Furnace Temperature

Because fractionation occurs for example during evaporation in TIMS, it has to be assumed, that a fractionated evaporation of Sr isotopes also occurs during thermal treatment of laser-aerosols at high ETV temperatures. It was described before that $\text{Sr}^+$ ion signal intensities were getting suppressed in the ETV-4000 at different power levels, depending on the sample composition. It is thus of particular importance to be able to correct for the Sr isotope fractionation that may be caused by aerosol heating. Conventionally, ICPMS isotope ratio measurements are using models adapted from TIMS to correct for mass discrimination of the MS, which are originally used to correct for thermally induced effects on the isotopes. The question whether such a model is sufficient to correct also for the combined mass fractionation in the MS and thermal fractionation in the ETV has to be answered.

In this chapter, the $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{86}\text{Sr}/^{88}\text{Sr}$ isotope ratio fractionation was investigated for a synthetic pressed pellet of NaCl, containing NIST SRM 987 SrCO$_3$, which is certified for Sr-isotope ratios. The pellet was prepared by milling NaCl (Ultrapure, Merck, DE) with the SrCO$_3$ powder for 1 h in a wiggle bag mixer/mill (SPEX 8000) in order to pulverize the carbonate and homogenize the mixture. The pellet contained 31.5 weight-% SrCO$_3$ to ensure that a sufficient fraction of the aerosol consisted of Sr and potential spectral interferences arising from NaCl (e.g. $^{40}\text{Ar}^{23}\text{Na}^+$, $^{40}\text{Ar}^{35}\text{Cl}^{12}\text{C}^+$) occur at correspondingly low abundances. The addition of NaCl as a binder was necessary to produce stable pellets, which could not be obtained from pure NIST SRM 987 powder. The aim of this study was to determine if fractionated evaporation of the Sr isotopes is detectable under conditions where Sr is suppressed by thermal treatment and whether such a fractionation may be corrected for by the conventional mass bias correction protocol.

<table>
<thead>
<tr>
<th>LA-system</th>
<th>Excite PHAROS fs-laser</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>257 nm</td>
</tr>
<tr>
<td>Ablation style</td>
<td>line scans, 5 µm/s</td>
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<tr>
<td>Energy</td>
<td>50%</td>
</tr>
<tr>
<td>Energy density</td>
<td>5 J/cm$^2$</td>
</tr>
<tr>
<td>Repetition Rate</td>
<td>5 Hz</td>
</tr>
<tr>
<td>Spot Size</td>
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</tr>
<tr>
<td>He carrier gas</td>
<td>0.2 L/min (0.15 main volume, 0.05 L/min inner cup flow)</td>
</tr>
</tbody>
</table>

Table 20 – Operating conditions for the Excite PHAROS fs-laser.

Laser ablation was carried out using the Excite PHAROS with operating conditions given in Table 20 and the aerosol was heated in the ETV-4000 with the heating protocol listed in Table 5. The Element XR with Jet interface was used for the measurement of the Kr-, Rb and Sr isotopes. Ion signals were recorded for $^{83}\text{Kr}^+$, $^{85}\text{Kr}^+$, $^{84}\text{Sr}/^{86}\text{Kr}^+$, $^{85}\text{Rb}^+$, $^{86}\text{Sr}/^{88}\text{Kr}^+$, $^{87}\text{Sr}/^{88}\text{Rb}^+$ and $^{88}\text{Sr}^+$ at 10 ms dwell time and averaging 10 sweeps per data point if not indicated otherwise. Some experiments were carried out using the analogue detector mode of the instrument exclusively to minimize potential artefacts from the detector cross...
calibration. The He carrier gas flow rate was set to 0.2 L/min. The $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios were determined for non-heating conditions and for power levels 3 to 6.

The isotope ratios were calculated after background subtraction using the gas blank signals without ablation. Mass discrimination was then corrected for by using the exponential law via the measured $^{86}\text{Sr}^+/^{88}\text{Sr}^+$ intensity ratios and the commonly accepted “true” isotope ratio of 0.1194. It should be kept in mind that the pellet may not have a truly homogeneous distribution of the SrCO$_3$ in the NaCl matrix, which, in combination with the sequential isotope detection, may limit the attainable precision of the isotope ratio measurements. Unfortunately, the multi-collector instrument available in the laboratory was not functioning properly at the time when these measurements were carried out.

Figure 51 shows the transient $^{88}\text{Sr}^+$ and $^{86}\text{Sr}^+$ ion signals at power level 3 (a) and power level 5.5 (b). Changes in mass ablation rate and small-scale heterogeneities were observed in the transient signals. The $\text{Sr}^+$ ion signals do not only change slightly during a line scan but show also a reproducible peak-pattern at the ablation start. $^{85}\text{Rb}^+$ ion signals above the instrumental background were not observed at any power level.

![Graph](image)

Figure 51 - $^{88}\text{Sr}^+$ and $^{86}\text{Sr}^+$ transients for power level 3 (left) and power level 5.5 (right).

Figure 52 shows the $\text{Sr}^+$ suppression factors as a function of the power level applied. It is apparent that the suppression of Sr is initiated already at comparably low temperatures for this aerosol composition. At power levels above 4, the $\text{Sr}^+$ signals were substantially suppressed. At power level 3, the suppression is already 50% and approaches $10^{-4}$ at power levels above 5. The suppression of the $\text{Sr}^+$ isotopes occurs largely in parallel, which seems to indicate that fractionated evaporation does not occur on a significant scale.
Figure 52 – $^{86}\text{Sr}$*, $^{87}\text{Sr}$* and $^{88}\text{Sr}$* suppression factors of the pellet as a function of the power levels.

Figure 53 shows the mass bias correction factor $f$ obtained from the measured $^{86}\text{Sr}/^{88}\text{Sr}$ intensity ratios as a function of the power levels. A clear dependence of the magnitude of the factor on the furnace temperature is observable. At room temperature and power levels $\leq 4$, $f$ is near -1, which would correspond to an isotopically lighter $^{86}\text{Sr}/^{88}\text{Sr}$ ratio than certified, while mass fractionation usually discriminates against the lighter isotopes. Similar fractionation factors at a larger magnitude were found in previous studies [147], where values near -2 were found in MCICPMS measurements. It is however unexpected and not fully understood which process would cause the heavier isotopes to become depleted. Possible reasons are spectral interference on $^{86}\text{Sr}$* from $^{40}\text{Ar}^{23}\text{Na}_2^+$ due to the NaCl matrix, an altered mass discrimination in the Jet interface of the Element XR or a non-linearity of the detection system. Possible further, but less likely, interferences occurring from this matrix could be $^{23}\text{Na}^{13}\text{C}_4^+$ or $^{40}\text{Ar}^{35}\text{Cl}^{13}\text{C}^+$ on $^{88}\text{Sr}$*, $^{40}\text{Ar}^{35}\text{Cl}^{12}\text{C}^+$ on $^{87}\text{Sr}$*, $^{40}\text{Ar}^{23}\text{Na}_2^+$ on $^{86}\text{Sr}$* and $^{35}\text{Cl}^{13}\text{C}_4^+$ on $^{85}\text{Rb}$*. None of them were however found in mass scans carried out at $> 10'000$ mass resolving power with the Element XR.

With increasing power level, however, the mass bias correction factors became less negative, indicating a change in isotope fractionation and/or a shift to isotopically heavier ratios as it would be expected under fractionated evaporation. It needs to be kept in mind, however, that the comparably strong suppression at power levels above 4.5 increases the uncertainty substantially and the values should be interpreted with care.
Figure 53 - Mass bias correction factor $f$ as a function of the ETV temperature.

Figure 54 shows the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios obtained from these measurements after mass bias correction as a function of the power level of the ETV. The red line indicates the reference value of NIST SRM 987 (0.71034 ± 0.00026). Due to the lighter measured $^{86}\text{Sr}^+/^{88}\text{Sr}^+$, the corrected $^{87}\text{Sr}/^{86}\text{Sr}^+$ isotope ratios also appeared light under non-heating conditions and initially decreased further when the aerosol was heated. At the highest power levels with strongest Sr suppression, the ratios approached the reference values again, but the data scattering was significant.

Figure 54 - $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios as a function of the power levels.

These results indicate that the mass bias correction via the exponential law using $^{86}\text{Sr}^+/^{88}\text{Sr}^+$ as reference is not fully compensating for the effects occurring in these measurements. It is not fully clear why the ratios appear isotopically lighter. Spectral interferences appeared to be not significant in this case, but the deviation cannot be completely described. The fact that the $^{87}\text{Sr}^+/^{86}\text{Sr}^+$ is getting heavier with increasing furnace temperature however indicates that isotope fractionation through evaporation has to be taken into consideration, in particular when a significant suppression of Sr occurs.
3.4.2. \(^{87}\text{Sr}/^{86}\text{Sr}\) Isotope Ratio Measurements in Glass and Silicates containing Rb

The dependence of the \(^{87}\text{Sr}/^{86}\text{Sr}\) isotope ratio accuracy and precision on the Rb-Sr separation efficiency was investigated for NIST SRM 610 and three biotites. The isotope ratios were calculated from the data set obtained from the Rb-Sr separation efficiency measurements discussed in chapter 3.2.2.

3.4.2.1. NIST SRM 610

The \(^{87}\text{Sr}/^{86}\text{Sr}\) isotope ratios were determined for non-heating conditions and power levels 3 – 6.5 of the ETV-4000. In order to achieve the highest possible signal correlation with the Element XR, doubly charged REEs were not measured and thus not included in the mathematical correction. Previous results \(^{147}\) also indicated that the contribution of these interferences in NIST SRM 610 was not affecting the accuracy significantly.

Figure 55 shows the resulting \(^{87}\text{Sr}/^{86}\text{Sr}\) isotope ratios plotted as a function of the power levels. The \(^{87}\text{Sr}/^{86}\text{Sr}\) reference value of NIST SRM 610 is indicated as blue line in the plot. Due to the high concentration of Rb, the ratio is found to be 5 times too high under non-heating conditions, indicating that the error originating from the unknown mass bias of the \(^{87}\text{Rb}/^{85}\text{Rb}\) isotopes is substantial. By eliminating the Rb selectively with thermal treatment, the influence of this error is decreased. The \(^{87}\text{Sr}^+\) ion signal can therefore be measured with higher accuracy. The \(^{87}\text{Sr}/^{86}\text{Sr}\) isotope ratio ultimately converges closer to the reference value with increasing temperature and decreasing \(^{87}\text{Rb}^+\) contribution on the \(m/Q\) 87 signal. As it was the case for NIST SRM 987, initially, the \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios were found to become isotopically lighter as soon as the temperature was increased. After power level 5, where the majority of the Rb is suppressed, however, the certified ratio was obtained. Due to the fact that the \(^{88}\text{Sr}^+\) suppression in NIST SRM 610 was not pronounced until power level 6.5 (Figure 44 (a1)), fractionated evaporation is assumed to be minimal in the graphite tube of the ETV.

![Figure 55 - \(^{87}\text{Sr}/^{86}\text{Sr}\) isotope ratios as a function of the power level. The reference value is indicated as blue line.](image)

3.4.2.2. Three Biotites provided by the University of Berne

The \(^{87}\text{Sr}^+/{^{86}\text{Sr}^+\text{r}}\) isotope ratios for the three biotites provided by K. Mezger, University of Berne, were calculated from the data set obtained from the Rb-Sr separation efficiency measurements discussed in chapter 3.2.2. Table 12 shows the reference data for Rb and Sr concentrations and the resulting [Rb]/[Sr] concentration ratios. Compared to NIST SRM 610, the Rb and Sr concentrations occurred at a larger
spatial variability in these minerals. This was shown already in Figure 45, where the transient LA signal for the 131102-4 biotite shows an order of magnitude variations of the $^{85}$Rb$^+$/Sr$^+$ intensity ratio. The biotite phase is observable between 40 – 60 s, followed by a Sr-rich inclusion or another phase. Such regions are generally particularly interesting for Rb-Sr geochronology, because the changes in concentration are directly reflected in the $^{87}$Sr isotope data. The initial characterization in this chapter however focused primarily on the attainable precision and accuracy of the $^{87}$Sr/$^{86}$Sr isotope ratios for the phases which are rich in Rb. Selected points of the grains were tested for potential interferences from doubly charged REEs and contributions from Ca-argidos via the $^{82}$Kr$^+$ and $^{83}$Kr$^+$ signals. However, no doubly-charged REE species were observed and the intensities were thus only corrected by blank subtraction, $^{87}$Rb$^+$ peak-stripping and mass bias correction via the $^{86}$Sr/$^{88}$Sr ratio, assuming natural abundances (0.1194).

Figure 56 shows the $^{87}$Sr/$^{86}$Sr isotope ratios as function of the power level. Reference values are indicated as blue lines. In all cases, the ratios are offset under non-heating conditions by more than an order of magnitude but approach the reference values at higher temperatures. The value of the ratios for the 131102-4 biotite decreased slowly until power level 4.5, after which a strong decrease occurred, and the ratios were close to the reference value. For power level 6, the re-increase of the $^{87}$Sr/$^{86}$Sr is ratios reflected in the re-increase of $^{85}$Rb$^+$ (Figure 46). The ratios for KR65-10, on the other hand, converged relatively slowly and steadily towards the reference value. For power levels 5 – 6, a good agreement was obtained. For the KR36-04, after power level 2, a strong and steady decrease of the ratio was observable, but the ratio never seemed to stabilize near the reference value.

Overall, and despite the heterogeneity of the biotites, the $^{87}$Sr/$^{86}$Sr isotope ratios followed the same trend as for NIST SRM 610. The suppression of the $^{87}$Rb isobar reduced the error resulting from the difference in mass bias between $^{87}$Rb/$^{85}$Rb and $^{86}$Sr/$^{88}$Sr, and, as a consequence, the accuracy of the $^{87}$Sr/$^{86}$Sr isotope ratios improved. While for the 131102-4 and KR65-10 biotites, the closest agreement was found for the power levels with the highest Rb-Sr separation efficiency, the KR36-04 did not show a stable region. This can most certainly be attributed to the heterogeneity of the sample or incomplete separation of Rb as this sample had the highest [Rb]/[Sr] concentration ratio. To obtain a higher accuracy and, additionally, also a high precision, either choosing line scans over single spot ablation would probably be advantageous, where the integration range can be chosen more freely, or measuring and averaging a significantly larger amount of data sets.
Figure 56 – $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios for the 131102-4 (top left), KR36-04 (top right) and the KR65-10 (bottom) biotite.

3.4.3. $^{87}\text{Sr}/^{86}\text{Sr}$ Isotope Ratio Measurements for Samples with highly variable [Rb]/[Sr] Concentration Ratios

The $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio of three mineral samples (LB, 1B, 1F) provided by J. Mercadier from Université de Lorraine, for which the Rb-Sr separation efficiency was studied in chapter 3.3.3., were also analysed. Initial experiments were however done with a helium gas flow of 0.9 L/min. After considering the results obtained for the three biotites in chapter 3.4.2.2., it was decided to use line scans for the Sr isotope ratio measurements here, in order to extend the measurement time of the experiments. It was assumed that a relatively slow scan rate improves signal stabilities, while regions with varying Rb-Sr concentration ratios and the associated change in isotope ratios can be separated during data evaluation.

Another important point that has to be kept in mind with regard to $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio measurements is the fact that in samples with low Sr concentrations, the $^{86}\text{Sr}^+$ signal intensities in some cases (biotite LB in particular) were barely visible above the instrumental background of $^{86}\text{Kr}^+$. This was in particular the case when the lower carrier gas flow rate of 0.2 L/min was used. Because Kr in the ICP is assumed to primarily originate from the liquid Ar supply, a compressed gas Ar bottle with quality 5.0 (Pan Gas, Dagmersellen, Switzerland) was tested for its effect on the Kr contribution. However, no change in background intensities was obtained.
The $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio measurements were performed for different grains of the three samples. Thermal treatment of the aerosol was carried out at power level 6 for the entire measurement period. To avoid overheating of the ETV-4000 power was on for a maximum time of 15 minutes followed by 5 minutes cool-down. The $\text{N}_2$ flow was optimized to 12.3 mL/min, where the highest $^{86}\text{Sr}^+$ signal/background ratio was obtained. Doubly-charged REE isotopes were not monitored, because quantification results of the 1F and 1B (Appendix, section 7.5) and transients of the LB did not indicate that REEs were contained in the minerals. For data evaluation, background subtraction, Rb peak-stripping and mass bias correction via $^{86}\text{Sr}/^{88}\text{Sr}$ assuming natural abundance was carried out. Figure 57 shows an overview over the calculated $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and precision in individually analysed grains.

It is again obvious that the attainable accuracy and precision depended strongly on the $[\text{Rb}]/[\text{Sr}]$ concentration ratio of the sample. For LB in particular, the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios for the different grains showed variability by almost an order of magnitude. For some measurements, the precision was low with relative variations of $> \pm 50\%$. Furthermore, the mean calculated isotope ratio (15.617 ± 5.467) strongly deviated from the mean of the reference values (1.980 ± 0.179). Several factors can be made responsible for the low precision and accuracy. An important factor is the low $^{86}\text{Sr}^+$- signal intensity, introducing a significant uncertainty into the ratio calculation. Another potential source of error is the
heterogeneity of the grains. Individual spikes were not considered in the data evaluation, but only relatively short periods of stable signal within the transients could be integrated for the data evaluation. The shown values are therefore means of only a small number of data points. On top of that, the $^{87}$Rb$^+$ ion signal was not sufficiently suppressed. Even though the $^{85}$Rb$^+/^{88}$Sr$^+$ intensity ratio was reduced by more than three orders of magnitude from values of $>10^3$ in the unheated aerosol to $10^3$, for most grains, $^{85}$Rb$^+/^{88}$Sr$^+$ intensity ratios $>0.14$ were measured at power level 6. Therefore, the need for correction of the $^{87}$Rb$^+$ isobar still had a strong impact on the accuracy of the $^{87}$Sr$^+$ ion signal evaluation.

The LB has a high mean [Rb]/[Sr] concentration ratio of 75. The AM13 1B biotite and the AM13 1F feldspar, which have [Rb]/[Sr] concentration ratios of 25 and 0.5, respectively, showed significantly better reproducibility and agreement with the reference values. A summary of the results is given in Table 21. It can be seen that for a carrier gas flow rate of 0.9 L/min, the agreement of the measured and reference values was getting better with lower [Rb]/[Sr] concentration ratios. However, even for 1F, which had a [Rb]/[Sr] concentration ratio of 0.5, a significant deviation by almost 20% of the measured Sr isotope ratio from the reference value was obtained. In order to further reduce the abundance of Rb in the aerosol, the $^{87}$Sr/$^{86}$Sr isotope ratios were analysed with a carrier gas flow rate of 0.2 L/min, which has been shown to be advantageous in terms of Rb-Sr separation efficiency for the minerals (chapter 3.3.2.). Due to the high deviation of the isotope ratios obtained in sample LB (Figure 57 (a)), it was assumed that not an appreciable accuracy would be attainable, even under a lower gas flow. Therefore, the Sr isotope ratios were not re-measured under for the LB, but only for the 1B and 1F. For 1B and 1F under a helium flow of 0.2 L/min, the $^{85}$Rb$^+$ ion signal was almost completely suppressed to the instrumental background. The $^{87}$Sr/$^{86}$Sr isotope ratios obtained under these conditions are also are listed in Table 21. While a reasonable agreement with the reference value can now be obtained for sample 1F, the values for 1B still deviate by more than a factor of 2 from the reference data. Here, the low Sr concentration certainly affects the accuracy and precision to an appreciable extent.

<table>
<thead>
<tr>
<th>Sample</th>
<th>He [L/min]</th>
<th>$^{87}$Sr/$^{86}$Sr</th>
<th>Absolute precision</th>
<th>Ref. value</th>
<th>Rb [ppm]$^{1/2}$</th>
<th>Sr [ppm]</th>
<th>$^{[Rb]/[Sr]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LB</td>
<td>0.9</td>
<td>15.617</td>
<td>5.467</td>
<td>1.98 ± 0.179</td>
<td>1'738</td>
<td>23</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>4.307</td>
<td>0.073</td>
<td>1.864 ± 0.008</td>
<td>925</td>
<td>5</td>
<td>25</td>
</tr>
<tr>
<td>1B</td>
<td>0.9</td>
<td>5.359</td>
<td>0.505</td>
<td>1.864 ± 0.008</td>
<td>925</td>
<td>5</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>4.307</td>
<td>0.073</td>
<td>1.864 ± 0.008</td>
<td>925</td>
<td>5</td>
<td>25</td>
</tr>
<tr>
<td>1F</td>
<td>0.9</td>
<td>0.887</td>
<td>0.029</td>
<td>0.728 ± 6.032·10$^{-5}$</td>
<td>358</td>
<td>767</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>0.740</td>
<td>0.012</td>
<td>0.728 ± 6.032·10$^{-5}$</td>
<td>358</td>
<td>767</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Table 21 – Summary of the $^{87}$Sr/$^{86}$Sr isotope ratios obtained for LB, 1B and 1F with high (0.9 L/min) and low (0.2 L/min) carrier gas flow rate.

SUMMARY

It was shown for a synthetic NIST 987-NaCl pellet that a Sr-fractionation occurs, which cannot be completely corrected for via the mass bias correction over the natural $^{86}$Sr/$^{88}$Sr ratio. The fractionation was especially pronounced (mass bias correction factor $f$ variations between -2 and $>2$) at high temperatures, where Sr started to take part in the vaporization process and a substantial Sr$^+$ ion signal suppression was measured with factors in the order of $10^4$. Because significant fractionation can only occur when Sr is evaporated (i.e. suppression factors $<1$), it is of high importance to maintain the Sr in the aerosol. Amongst the samples analysed in this work, the NIST SRM 987-NaCl pellet and Li-
tetraborates would be affected by the fractionation, since only for them, a significant Sr suppression was observed.

The mass bias correction factor $f$ under non-heating conditions was close to -1, which would correspond to an isotopically lighter $^{86}\text{Sr}/^{88}\text{Sr}$ ratio compared to the certified one, which is in contrast to typically observed discriminations. At the moment, the source of this observation is unknown. Possible sources are isotopic fractionation of i.e. the aerosol transport in the furnace or processes taking place in the ICPMS. Another explanation would be the occurrence of matrix- or carbon-induced polyatomic interferences. However, no interferences were found at > 10'000 mass resolving power. Further studies have to be carried out to identify the source of the bias and to develop a suitable correction protocol for it.

One major factor that limits the accuracy and precision of $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio measurements is the heterogeneity of natural samples. However, the extent of heterogeneity remains unknown for measurements where the Rb is suppressed to a substantial extent and the transient $^{85}\text{Rb}^+/^{88}\text{Sr}^+$ intensity ratio cannot be used as control. Local variations in Sr$^+$ signal intensities can occur when the samples are not perfectly homogeneous and due the fact that the ion beams are not detected simultaneously, this is a limitation for $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio measurements. The uncertainty caused by heterogeneities increases when low gas flows are used to achieve a sufficient Rb suppression for the minerals. Due to the pronounced aerosol mixing in the ablation cell under these conditions, the isotope signatures of different regions will become less distinguishable.

It could be shown for NIST SRM 610 silicate glass and different minerals that the best agreement of the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio can be obtained at the temperature where the highest Rb-Sr separation is achieved. Furthermore, it was shown that the lower the $[\text{Rb}]/[\text{Sr}]$ concentration ratio of a sample is, the higher the accuracy and precision of the ratio. In general, it can be said that the lower the Rb contribution, the higher the accuracy and precision of the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio.

Sr suppressions < 1 should be avoided, not only because fractionation effects increase with the Sr suppression, but also because the $^{86}\text{Sr}^+$ signal might be suppressed below the instrumental background when analysing low Sr containing samples. A critical point is therefore the $^{86}\text{Kr}^+$ baseline, which might limit Sr isotope ratio measurements. Ideally, the Kr-contamination source has to be identified and reduced substantially. In this work, the signal-to-background at $m/Q$ 86 was tuned to a maximum by varying the $\text{N}_2$ flow required for maximum sensitivity with the Jet interface, while the use of higher purity Ar did not lead to a decrease of the background.

A complete $^{85}\text{Rb}^+$ ion signal suppression for minerals containing Rb < 1'000 ppm and concentration ratios $[\text{Rb}]/[\text{Sr}] < 25$ was achieved under optimal (highest possible $^{85}\text{Rb}^+$ suppression and $^{86}\text{Sr}^+$ sensitivity) conditions. For samples with $[\text{Rb}]/[\text{Sr}] > 100$, a complete suppression of the $^{85}\text{Rb}^+$ signal is difficult to achieve by modifying the operating parameters. However, for every investigated sample, higher Rb-Sr separation efficiencies compared to the HGA-600MS were achieved. This can most probably be attributed to the longer residence time of the aerosol in the heated furnace rather than to the graphite wall temperature.
4. Conclusion and Outlook

It was shown that different species present in laser-generated aerosols undergo different transformations during thermal treatment. Findings from earlier studies were confirmed, showing that fs-aerosols consist of a larger fraction of single particles, while ns-aerosols consist of a larger fraction of NP agglomerates and µm-sized particles. It was shown for the first time in the frame of this work that the agglomerates formed from the nanoparticles after the laser ablation event initially collapses and subsequently form homogeneous droplets of varying sizes. The single particles and droplets experience surface evaporation already before the boiling point of the bulk material. The extent of evaporation in the heated tube depends on the initial particle sizes. It must therefore be assumed that the agglomerated NPs are only evaporating as rapidly as individual particles of similar total mass within the furnace, which explains the higher vaporization efficiency and stronger volatile-non-volatile element separation observed for fs-LA. At the onset of the suppression profiles, most likely, surface evaporation of molten, solitary NPs takes place. Removal of evaporated material is assumed to take place via condensation at cooler parts downstream the furnace. The onset and magnitude of the suppression caused by the surface evaporation is reflecting the boiling points of the material.

In contrast to ns-LA, different mass loads did not appear to influence the suppression of volatile elements, when fs-LA was used with 206 or 257 nm for ablation of NIST SRM 610. This may also be attributed to the higher fraction of single nm-sized particles in fs-aerosols and the resulting higher vaporization efficiency. Even though a higher number of single particles is present in the furnace per unit time when the mass load is increased, they can be heated comparably fast as with the lower mass load. Comparing fs-ablation with different UV wavelengths, showed no significant influence on the Rb-Sr separation efficiency. This would indicate that ablation with the two different wavelengths generated aerosols of similar morphology.

The onset and magnitude of the suppression was typically found to reflect the physical properties of the material. The onset of suppression of Cu and Zn was shifted to lower, respectively higher temperatures for brass due to the different melting point of the alloy compared to the pure metals, which confirms that melting of the aerosol particles is a critical step in the element-selective evaporation. Similar differences were observed for the suppression onset regimes of Rb and Sr between silicates and Li-tetraborates, which were shifted to lower temperatures for the Li-tetraborates compared to the silicates. The absolute concentration of trace or minor elements in samples, which have the same major matrix composition, on the other hand, did not have an observable influence on the suppression profile and onset. This was demonstrated for brass samples with differing \([\text{Cu}]/[\text{Zn}]\) concentration ratios, Li-tetraborates and minerals with different \([\text{Rb}]/[\text{Sr}]\) concentration ratios. This indicates that different amounts of the elements within the aerosols and within the investigated range can be brought to vaporization in the same amount of time and therefore do not limit the elimination efficiency.

A matrix effect was also observed for the Rb-Sr separation efficiency between NIST SRM 610 glass and the silicate minerals. The efficiency of the separation was much smaller for minerals when the same operating parameters were used. It was shown, however, that increasing the residence time and ultimate temperature of the aerosol in the furnace by lowering the carrier gas flow, increases the Rb-Sr separation. In the following, an attempt is made to explain the influence of the gas flow, while the temperature of the ETV tube walls is assumed to remain constant. For a too high gas flow, resulting in a low residence time and lower gas temperature, the point of the maximum Rb-Sr separation (position
2 in Figure 58, left) would be outside the heating zone. Only a moderate separation can be achieved at point 1) inside the ETV. When the carrier flow is lowered, position 2) can be reached within the heating zone and maximum separation is obtained due to the longer residence time (middle). For a too low gas flow (right), Sr may start to evaporate (position 3) and the Rb-Sr separation efficiency is reduced again.

Figure 58 – Point of completion of processes triggered by thermal treatment for a high (left), moderate (middle) and low (right) carrier gas flow through the furnace.

Thus, a longer heating zone would in particular make sense in cases, where a sufficient Rb suppression cannot be achieved even at the lowest reasonable carrier gas flow setting.

In these experiments it could be shown that a reduced gas flow and the corresponding longer residence time in the furnace improved the accuracy of $^{87}$Sr/$^{88}$Sr isotope ratio measurements, even when the gas flow reduction also caused a decrease in Sr sensitivity. Thus, for silicate glass and minerals, the $^{87}$Sr/$^{86}$Sr isotope ratios were closest to the reference values for the temperature setting, where the highest Rb-Sr separation was obtained. This demonstrates the substantial effect of the unknown $^{87}$Rb/$^{85}$Rb mass discrimination and the resulting bias from the $^{87}$Rb isobar correction. It needs furthermore to be expected that the evaporation of Rb from the aerosol causes an additional isotope fractionation, as it was observed for Sr. This process would change the degree of $^{87}$Rb/$^{85}$Rb mass discrimination relative to $^{86}$Sr/$^{88}$Sr even more and in an uncontrollable way. Thus, ultimately, a complete Rb elimination will be required in particular in samples containing high Rb concentrations. Operating parameters like mass load and ETV temperature, however, have to be chosen in a way to retain the Sr sensitivity as much as possible and to avoid for the $^{86}$Sr$^+$ signal to become indistinguishable from the instrumental background. A combination of low mass loads and a longer residence time would thus be ideal for these applications. A major limitation for the detection of $^{86}$Sr$^+$ that can severely affect the accuracy and precision was the high $^{85}$Kr$^+$ background of several 10'000 cps, which was equivalent to ppm levels of Sr for typical laser ablation and heating conditions.

A major limitation for online $^{87}$Sr/$^{86}$Sr isotope ratio measurements with the current setup, however, was a bias in the measured isotope ratios from an unknown source, which could not be corrected via the measured $^{86}$Sr/$^{88}$Sr mass discrimination factor. The reason for the measured isotope ratios being unexpectedly lighter could not be determined. Possible sources could be unresolved spectral interferences, minute changes in the Kr-baseline or a non-linear ion detection system.

Under the reduced gas flow, for minerals, $^{85}$Rb$^+$ suppression factors $\sim 10^{-4}$ could be achieved while $^{88}$Sr$^+$ suppression factors were never below 0.1. For samples with a Rb concentration < 1'000 ppm, a complete suppression of the $^{85}$Rb$^+$ ion signal was achieved. In these cases, however, a mass load effect was observed, which indicates that also here, the aerosol composition affects the separation efficiency inside the furnace. Since variations in mass load potentially alter the Rb-Sr separation efficiency for minerals, the operating parameters have to be investigated for every sample type individually.
With the current setup, promising initial Rb-Sr separation and $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio measurements could be carried out. In order to be able to perform routine $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio measurements with high accuracy and precision, however, a certain number of obstacles still has to be overcome. Major limitations are currently imposed by the Rb elimination, which is not always complete, a high $^{86}\text{Kr}^+$-baseline and the potential fractionation of the Sr isotopes at high temperatures. Thus, with the current setup, operating parameters have to be tuned and chosen with great care for every sample type individually. This is a highly time-consuming process and is not applicable in routine analyses.

Thus, to allow for spatially resolved Sr isotope ratio analyses in heterogeneous materials containing appreciable amounts of Rb, several issues will have to be addressed. Most importantly, a practically complete suppression of Rb$^+$ ion signals must be achieved while minimizing evaporation of Sr from the aerosol. A longer heating zone is the most promising parameter in this respect. It should not only allow for a more efficient removal of Rb but also allow for the use of higher carrier gas flow rates. The latter will be in particular important in order to retain the spatial information, because less aerosol mixing will occur inside the ablation cell compared to lower carrier gas flow rates. In geochronological applications, furthermore, the Rb and Sr concentrations in the initial aerosol have to be monitored in parallel in order to be able to construct an isochron from different phases of a mineral, for example. This will require a “split-flow” setup where a fraction of the original aerosol is guided to a second ICPMS for conventional analysis. Attempts made in the frame of this work, however, yielded highly unstable gas flow patterns between the two instruments, causing the respective aerosol fractions to change unpredictably. Finally, the isotope ratio determination by multi-collector ICPMS would be highly advantageous over the currently used setup. In particular when heterogeneous samples are being analysed, the parallel detection of all isotopes of interest significantly improves the correlation of the individual ion signals and would result in the highest possible precision and accuracy.
5. Bibliography


96


46. Cameca, Attem ES, High Resolution ICP-MS. *Brochure*.


78. C. Antoncini, Ultrashort Laser Pulses. Script Department of Physics, University of Reading.


6. Curriculum Vitae

Personal Information

Date/place of birth 08.01.1990, Iskenderun, Turkey
Nationalities Swiss/Turkish
Marital Status Single

Record of Employment

02/2014 – 12/2017 ETH Zurich, Group of Trace Element and Micro Analysis, PhD Candidate
02/2017 – 05/2017 Teaching assistant (20%), ETH Zurich
02/2016 – 05/2016 Teaching assistant (20%), ETH Zurich
02/2015 – 05/2015 Teaching assistant (20%), ETH Zurich
08/2012 – 11/2013 Assistant (20%), Dangel Asset Management, Zurich
05/2012 – 09/2013 Private teacher (10%), Learning Institute, Zurich/Olten
12/2011 – 04/2012 Google AdWords administrator (20%), Safi Concept GmbH, Zurich
02/2010 – 02/2011 Employee at the Customer Service Center (20%), UBS AG, Olten

Education

09/2014 – 12/2017 ETH Zurich, Group of Trace Element and Micro Analysis, PhD Candidate
09/2012 – 07/2014 ETH Zurich, Master of Science ETH in Chemistry
09/2009 – 09/2012 University of Zurich, Bachelor of Science UZH in Chemistry
09/2007 – 09/2009 ETH Zurich, Bachelor’s Studies in Physics
08/2000 – 06/2007 Kantonsschule Olten
Presentations

H. C. Yilmaz, B. Hattendorf, Sr isotope ratios and Rb-Sr ages by LA-ICPMS with isobar separation by online electrothermal vaporization, Beatenberg, Berne, Switzerland, CIna Analysis, April 10-11, 2015. (Poster)

H. C. Yilmaz, B. Hattendorf, Sr isotope ratios and Rb-Sr ages by LA-ICPMS with isobar separation by online electrothermal vaporization, Tucson, Arizona, USA, Winter Plasma Conference, January 10-16, 2016. (Oral presentation)

H. C. Yilmaz, B. Hattendorf, A comparison of signal suppression and particle size distribution for ns- and fs-LA-ETV-ICPMS, Ulm, Baden-Württemberg, Germany, DAAS, April 6-8, 2016. (Oral presentation)

H. C. Yilmaz, B. Hattendorf, Lasers in Heat – The influence (or not) of laser pulse duration on the particle size distribution of metal aerosols and the ICPMS signal response to different temperatures, Zurich, Zurich, Switzerland, LAC Christmas Symposium, December 14, 2016. (Oral presentation)

H. C. Yilmaz, B. Hattendorf, Lasers in Heat – The influence (or not) of laser pulse duration on the particle size distribution of metal aerosols and the ICPMS signal response to different temperatures, St. Anton am Arlberg, Tirol, Austria, European Winter Plasma Conference, February 18-24, 2017. (Oral presentation)


Publications


7. Appendix

Abbreviations

Δm  difference in mass
AC  alternating current
B  magnetic field
BG<sub>RT</sub>  background signal without heating
BG<sub>X</sub>  background signal at temperature X
CCD  charge-coupled device
β  β-particle
d  gap between the inner and outer plate of the electrostatic analyser
DC  direct current
E  differential voltage of the electrostatic analyser
e.g.  exempli gratia
E<sub>kin</sub>  kinetic energy
ESA  electrostatic analyser
et al.  et alii
etc.  et cetera
ETV  electrothermal vaporization unit
ETV-ICPMS  electrothermal vaporization inductively coupled plasma mass spectrometry
eV  electron volt
fs-LA  femtosecond laser ablation
f  mass bias correction factor
I<sub>RT</sub>  background-corrected mean laser ablation ion signal without heating
I<sub>X</sub>  background-corrected mean laser ablation ion signal with heating
i.e.  id est
ICP  inductively coupled plasma
ICPMS  inductively coupled plasma mass spectrometry
ICPTOFMS  inductively coupled plasma time-of-flight mass spectrometry
λ  decay constant or thermal conductivity
LA<sub>RT</sub>  laser ablation signal without heating
LA<sub>X</sub>  laser ablation signal at temperature X
LA-ICPMS  laser ablation inductively coupled plasma mass spectrometry
LA-ETV-ICPMS  laser ablation electrothermal vaporization inductively coupled plasma mass spectrometry
LOD  limit of detection
m  mass
M<sub>x</sub>  isotope mass
mbar  millibar
m/Q  mass-to-charge ratio
MCICPMS  multi-collector inductively coupled plasma mass spectrometry
MS  mass spectrometry
N<sub>x</sub>  number of counts
ns-LA  nanosecond laser ablation
OPC  optical particle counter
ppm  parts per million
ppq  parts per quadrillion
PSD  particle size distribution
Q    decay energy or ion charge
Q-ICPMS quadrupole-based inductively coupled plasma mass spectrometry
[Rb]/[Sr] [Rb]/[Sr] concentration ratio
R_{meas} measured isotope ratio
R_{true} true isotope ratio
REE  rare earth elements
RF   radiofrequency
r_e  radius in the electrostatic analyser
r_m  radius in the magnetic sector
RSD% internal precision
S    suppression factor
SEM  secondary electron multiplier or scanning electron microscope
SCICPMS single-collector inductively coupled plasma mass spectrometry
SFICPMS sector field inductively coupled plasma mass spectrometry
SIMS secondary ion mass spectrometry
τ    half time
TIMS thermal ionization mass spectrometry
U    acceleration potential
ū    anti-neutrino
v    velocity
vs.  versus
7.1. Non-specific signal suppression in the HGA-600MS

Brogioli\textsuperscript{147} observed an element non-specific signal suppression regime in a temperature range ~1’000 – 1’300 °C when using the HGA-600MS for thermal treatment. In this regime, which occurred additionally to the element-specific suppression, the signals of all observed isotopes decreased to a minimum and re-increased to a certain extent. The exact temperature range, broadness and suppression factors of the regime were material- and gas flow-dependent. When looking at Figure 44 in chapter 3.2.1., however, no such regime is observable. During other measurements that were performed earlier in this work, the regime was observable. Table 22 shows operating conditions used for the Excite PHAROS. The ELAN DRCII was used for ion signal detection with the operating conditions listed in Table 13 (a).

<table>
<thead>
<tr>
<th>LA-system</th>
<th>Excite PHAROS fs-laser</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>257 nm</td>
</tr>
<tr>
<td>Ablation style</td>
<td>line, 5 μm/s</td>
</tr>
<tr>
<td>Energy</td>
<td>100%</td>
</tr>
<tr>
<td>Energy density</td>
<td>6 J/cm(^2)</td>
</tr>
<tr>
<td>Repetition Rate</td>
<td>20 Hz</td>
</tr>
<tr>
<td>Spot Size</td>
<td>40 μm</td>
</tr>
<tr>
<td>He carrier gas</td>
<td>1.0 L/min (0.5 L/min each)</td>
</tr>
</tbody>
</table>

Table 22 – Operating conditions for the Excite PHAROS fs-laser.

The temperature of the HGA-600MS was increased continuously from 1’000 – 2’500 °C, as shown in Table 6 in the Experimental in chapter 2.4.4. Figure 59 shows the transient \(^{85}\text{Rb}^+\), \(^{m/Q\ 87}\) and \(^{88}\text{Sr}^+\) signals of a measurement for NIST SRM 610, where the non-specific regime was observable. All signals underwent a decrease and re-increase between 1’000 – 1’500 °C. Around 1’250 °C, the signals reached a minimum. This regime was described as element non-specific suppression regime by Brogioli\textsuperscript{147}, because it was observable for all signals.

![Figure 59](image-url)

Figure 59 – \(^{85}\text{Rb}^+\), \(^{m/Q\ 87}\) and \(^{88}\text{Sr}^+\) transient signals for NIST SRM 610. Additionally, to the element-specific suppressions, the non-specific suppression regime is observable between 1’000 – 1’300 °C.
After > 1'500 °C, the selective $^{85}\text{Rb}^+$ suppression starts, while the suppression of the $^{88}\text{Sr}^+$ signal sets in at higher temperatures, around 2'400 °C.

The magnitude and occurrence of the non-specific regime was not reproducible and when the ETV-4000 or homemade ETV prototype were used, the regime was never observed. It was therefore assumed that the non-specific suppression regime is an artefact of the HGA-600MS. Potential sources are mechanical changes within the ETV, triggered by heating, which lead to a leak and aerosol loss. The hole in the graphite tube is a possible weak spot of the setup.

7.2. Set-up modifications of the homemade prototype

For the custom-made wire ETV, a high non-selective aerosol loss and poor Rb-Sr separation efficiency were observed. To limit the Sr-loss, the setup of the wire ETV was modified in different ways. As a first approach, the inner quartz glass tube was isolated by wrapping it with aluminum foil. The goal was to improve the temperature storage and prevent heat radiation losses to the environment. In another approach, the ETV was turned upside down and the aerosol was guided through the ETV from the bottom to the top. The goal was to increase the interaction of the aerosol with the heated tungsten wire by inverting the gas flow direction in the ETV. It was hoped that the longer interaction time would trigger an onset of the selective Rb elimination at lower power settings, where the Sr suppression factors were not yet in the order of $10^{-2}$. However, neither the isolation, nor change of the gas flow direction led to a decrease of the Sr-loss. Since the suppression factors were significantly more element-selective for the GF-ETVs, pieces of a HGA-600MS graphite tube were integrated in different ways into the tungsten wire heater. The pieces were either wrapped with the wire or were integrated into the heater to serve as current conducting parts. Later, parts of graphite foil were integrated into the tungsten wire in a similar way. However, no decrease of the Sr-loss was observed.

In a last step, the influence of the laser parameters on the signal suppression was investigated. A very high repetition rate of 200 Hz was combined with a slow scan rate of 1 µm/s to generate a high aerosol mass load in the ETV. The goal was to reduce the heat distribution efficiency in the aerosol by increasing the amount of material in the ETV, while keeping the gas flow constant. It was hoped that this would lead to a decrease of the Sr-loss. However, no improvement was observed. Subsequently, the influence of the mass load was investigated in general by generating a significantly lower mass load. A low repetition rate of 15 Hz was combined with a fast scan rate of 10 µm/s. A decrease of the Sr signal suppression factors was expected, however, no changes were observable.

None of the approaches that were made to decrease the Sr-loss and to increase the Rb-Sr separation for the wire ETV were successful. For future studies, the use of this ETV for thermal treatment of laser-aerosols was not considered.

7.3. Three Biotites provided from the University of Berne

Additionally to the transient signal of the 131102-4 biotite shown in chapter 3.2.2. in Figure 45, the two transients of the KR36-04 and KR65-10 are shown here in Figure 60. Heterogeneities in the Rb and Sr concentrations are observable for the two biotites, in particular for the biotite phase of the KR36-04.
Figure 60 - $^{85}$Rb$^+$ and $^{88}$Sr$^+$ transient ion signals and the corresponding $^{85}$Rb$^+$/$^{88}$Sr$^+$ intensity ratio of the KR63-04 (left) and KR65-10 (right) biotite.

7.4. Influence of the Gas Flow Rate on the Rb-Sr Separation Efficiency

To find the ideal helium gas flow rate for the Rb-Sr separation, the $^{85}$Rb$^+$ and $^{88}$Sr$^+$ ion signal suppression factors for helium gas flows between 0.7 – 1.1 L/min were investigated as a function of the graphite furnace temperature. The ETV-4000 was used for thermal treatment, since it achieved the highest Rb-Sr separation for different materials. While the main volume of the Excite PHAROS fs-laser was kept constantly at 0.45 L/min, the inner cup flow was varied between (0.25 - 0.65 L/min). Ion signals were recorded with the Element XR. Table 23 lists the operating parameters of the Excite PHAROS.

<table>
<thead>
<tr>
<th>LA-system</th>
<th>Excite PHAROS fs-laser</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>206 nm</td>
</tr>
<tr>
<td>Ablation style</td>
<td>single spot, 300 shots</td>
</tr>
<tr>
<td>Energy</td>
<td>50%</td>
</tr>
<tr>
<td>Energy density</td>
<td>7 J/cm$^2$</td>
</tr>
<tr>
<td>Repetition Rate</td>
<td>5 Hz</td>
</tr>
<tr>
<td>Spot Size</td>
<td>40 µm</td>
</tr>
<tr>
<td>He carrier gas</td>
<td>0.35 – 0.65 L/min inner cup variations (0.45 L/min main volume constant)</td>
</tr>
</tbody>
</table>

Table 23 – Operating parameters of the Excite PHAROS fs-laser.
Figure 61 – Signal suppression factors of the $^{85}$Rb$^+$, m/Q 87 and $^{88}$Sr$^+$ ion signal suppression factors for a main volume flow of 0.45 L/min in combination with an inner cup flow of 0.25 L/min (top left), 0.35 L/min (top middle), 0.45 L/min (top right), 0.55 L/min (bottom left) and 0.65 L/min (bottom right), resulting in total helium flows of 0.7 – 1.1 L/min through the ablation chamber and the ETV.

Figure 61 shows the $^{85}$Rb$^+$, m/Q 87 and $^{88}$Sr$^+$ ion signal suppression factors for the different helium carrier gas flows. For all gas flow settings, the overall suppression profile did not change significantly. The onset of suppression for the $^{85}$Rb$^+$ ion signal was at power level 3.5 – 4, while the $^{88}$Sr$^+$ ion signal did not undergo a notable suppression. When comparing the $^{85}$Rb$^+$ suppression factors at power level 5.5, however, a decrease of the factor with increasing gas flow rate gets apparent. While the factor is in the order of $5 \cdot 10^{-3}$ for a total helium flow rate of 0.7 L/min, a suppression factor of $2 \cdot 10^{-2}$ is observed for a flow rate of 1.1 L/min. This means that with increasing helium gas flow rate, the vaporization efficiency of the Rb slightly decreases and, in parallel, also the Rb-Sr separation efficiency. The reduced residence time of the aerosol in the furnace therefore seems to limit the vaporization efficiency of the Rb in particular.
7.5. Quantification of the 6 mineral samples provided from the University of Lorraine

For further analysis, 6 of the 13 samples obtained from the University of Lorraine were chosen. A criterion was to have a wide range of Rb and Sr concentrations and \([\text{Rb}] / [\text{Sr}]\) concentration ratios across the chosen samples. Table 24 lists the ICPMS and laser parameters.

<table>
<thead>
<tr>
<th>ICPMS</th>
<th>Element XR</th>
<th>LA-system</th>
<th>Excite PHAROS fs-laser</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar make-up gas</td>
<td>0.975 L/min</td>
<td>Wavelength</td>
<td>257 nm</td>
</tr>
<tr>
<td>Auxiliary gas</td>
<td>0.77 L/min</td>
<td>Ablation style</td>
<td>single spot, 300 shots</td>
</tr>
<tr>
<td>Plasma gas</td>
<td>14 L/min</td>
<td>Energy</td>
<td>50%</td>
</tr>
<tr>
<td>(\text{N}_2) flow rate</td>
<td>12.3 mL/min</td>
<td>Energy density</td>
<td>10 J/cm²</td>
</tr>
<tr>
<td>RF Power</td>
<td>1400 W</td>
<td>Repetition Rate</td>
<td>5 Hz</td>
</tr>
<tr>
<td>x-, y-, z-pos.</td>
<td>2.6 mm, 0.3 mm, -0.7 mm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dwell time / Isotope</td>
<td>10 ms</td>
<td>Spot Size</td>
<td>40 (\mu)m</td>
</tr>
<tr>
<td>Isotopes monitored</td>
<td>see Table 25 and Table 26</td>
<td>He carrier gas</td>
<td>0.2 L/min (0.15/0.05 L/min main/inner cup)</td>
</tr>
</tbody>
</table>

Table 24 – ICPMS and laser parameters.

To ensure that no REE are present in the samples, a full quantification of the 6 chosen samples was performed against NIST SRM 610. Reference values for Sr and Rb concentrations ([ppm]), \([\text{Rb}] / [\text{Sr}]\) concentration ratios (weight-%) and \(^{87}\text{Sr} / ^{86}\text{Sr}\) isotope ratios were obtained by SIMS. The following Figure 62 shows the 6 samples with their elemental composition in the weight-% concentration region.

![Figure 62 – Quantification result of 6 silicate-based geologic materials.](image)

For REE, no signals higher than instrumental background were measured for any of the samples. Therefore, for Sr isotope ratio calculations, no correction for doubly-charged isobaric REE signals was performed. Table 25 and Table 26 show the elemental composition of the 6 minerals and the standard deviation.
<table>
<thead>
<tr>
<th>Element</th>
<th>1F Mean</th>
<th>SD n=3</th>
<th>PF Mean</th>
<th>SD n=3</th>
<th>BF Mean</th>
<th>SD n=3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
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<td>0.6</td>
<td>700</td>
<td>500</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>Ti</td>
<td>73</td>
<td>8</td>
<td>66</td>
<td>47</td>
<td>51</td>
<td>7</td>
</tr>
<tr>
<td>V</td>
<td>0.027</td>
<td>0.013</td>
<td>0.8</td>
<td>0.6</td>
<td>0.6</td>
<td>0.9</td>
</tr>
<tr>
<td>Cr</td>
<td>12</td>
<td>0.9</td>
<td>18</td>
<td>9</td>
<td>15.7</td>
<td>1.6</td>
</tr>
<tr>
<td>Mn</td>
<td>3.8</td>
<td>0.1</td>
<td>14</td>
<td>4</td>
<td>18</td>
<td>10</td>
</tr>
<tr>
<td>Fe</td>
<td>43</td>
<td>5</td>
<td>1'300</td>
<td>1'100</td>
<td>150</td>
<td>100</td>
</tr>
<tr>
<td>Co</td>
<td>0.022</td>
<td>0.013</td>
<td>0.28</td>
<td>0.29</td>
<td>0.079</td>
<td>0.086</td>
</tr>
<tr>
<td>Ni</td>
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<td>0.08</td>
<td>1.6</td>
<td>1.2</td>
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<td>0.25</td>
</tr>
<tr>
<td>Cu</td>
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<td>30</td>
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<td>2.9</td>
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<tr>
<td>Zn</td>
<td>10</td>
<td>4</td>
<td>45</td>
<td>41</td>
<td>5.9</td>
<td>1.3</td>
</tr>
<tr>
<td>Rb</td>
<td>400</td>
<td>4</td>
<td>310</td>
<td>240</td>
<td>340</td>
<td>230</td>
</tr>
<tr>
<td>Sr</td>
<td>810</td>
<td>83</td>
<td>130</td>
<td>50</td>
<td>173</td>
<td>18</td>
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<tr>
<td>Y</td>
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<td>0.005</td>
<td>0.2</td>
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<td>0.3</td>
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<tr>
<td>Cs</td>
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<td>8</td>
<td>4</td>
<td>3.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Ba</td>
<td>2'700</td>
<td>260</td>
<td>400</td>
<td>500</td>
<td>600</td>
<td>400</td>
</tr>
<tr>
<td>La</td>
<td>6.7</td>
<td>1.1</td>
<td>5</td>
<td>4</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>Ce</td>
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<td>0.8</td>
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<td>6</td>
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<td>7</td>
</tr>
<tr>
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<td>0.6</td>
<td>0.6</td>
<td>0.7</td>
</tr>
<tr>
<td>Nd</td>
<td>0.6</td>
<td>0.06</td>
<td>1.7</td>
<td>1.6</td>
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<tr>
<td>Sm</td>
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<td>0.04</td>
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<td>0.5</td>
<td>0.6</td>
<td>0.29</td>
<td>1</td>
<td>0.1</td>
</tr>
<tr>
<td>Gd</td>
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<td>0.025</td>
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<td>0.13</td>
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</tr>
<tr>
<td>Tb</td>
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<td>0.004</td>
<td>0.017</td>
<td>0.011</td>
<td>0.026</td>
<td>0.025</td>
</tr>
<tr>
<td>Dy</td>
<td>0.022</td>
<td>0</td>
<td>0.06</td>
<td>0.04</td>
<td>0.07</td>
<td>0.1</td>
</tr>
<tr>
<td>Ho</td>
<td>0.001</td>
<td>0.0004</td>
<td>0.021</td>
<td>0.016</td>
<td>0.014</td>
<td>0.014</td>
</tr>
<tr>
<td>Er</td>
<td>0.002</td>
<td>0.0008</td>
<td>0.02</td>
<td>0.01</td>
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<td>0</td>
</tr>
<tr>
<td>Tm</td>
<td>0.007</td>
<td>0</td>
<td>0.01</td>
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<tr>
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<td>0.012</td>
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</tr>
<tr>
<td>Lu</td>
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<td>0.0013</td>
<td>0.05</td>
<td>0.03</td>
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<tr>
<td>Pb</td>
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<td>10</td>
<td>40</td>
<td>50</td>
<td>78</td>
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</tr>
<tr>
<td>Th</td>
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<td>0.13</td>
<td>0.35</td>
<td>0.30</td>
<td>0.03</td>
<td>0.04</td>
</tr>
<tr>
<td>U</td>
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<td>1</td>
<td>0.7</td>
<td>0.03</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Table 25 – Elemental composition of the feldspars.
<table>
<thead>
<tr>
<th>[ppm]</th>
<th>1B</th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean SD n=3</td>
<td>Mean SD n=3</td>
<td>Mean SD n=3</td>
<td>Mean SD n=3</td>
<td>Mean SD n=3</td>
<td>Mean SD n=3</td>
<td>Mean SD n=3</td>
</tr>
<tr>
<td>⁴²Ca</td>
<td>610 170 1’000</td>
<td>100 2’000</td>
<td>400</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>⁵¹V</td>
<td>160 1.8 220</td>
<td>52 39 24</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>⁵²Cr</td>
<td>30 6 100</td>
<td>80 60 40</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>⁵⁵Mn</td>
<td>620 12 1’500</td>
<td>130 450</td>
<td>130</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>⁵⁹Co</td>
<td>40 0.7 40</td>
<td>1.8 1 0.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>⁶⁰Ni</td>
<td>9 0.3 30</td>
<td>0.7 30 40</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>⁶⁵Cu</td>
<td>3.8 0.21 3</td>
<td>0.4 4 3</td>
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<td></td>
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<td></td>
<td></td>
</tr>
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<td>⁶⁵²Zn</td>
<td>1’000 40 1’300</td>
<td>26 200</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>⁸⁵Rb</td>
<td>1’100 21 1’500</td>
<td>28 2’000</td>
<td>600</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>⁸⁸Sr</td>
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<td>2.8 4.3 2.1</td>
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<td>0.0024 0.0017 0.0017</td>
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<td>0.0011 0.0026 0.0017</td>
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<td>0.007 0.017 0.0019</td>
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<td>0.021 0.089 0.039</td>
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</tbody>
</table>

Table 26 – Elemental composition of the biotites.
7.6. Rb-Sr Separation Efficiency for a Helium Gas Flow of 0.9 L/min

The $^{85}\text{Rb}^+$ and $^{88}\text{Sr}^+$ suppression and the suppression of the $^{85}\text{Rb}^+/^{88}\text{Sr}^+$ intensity ratio for four grains of the leucogranite biotite (LB), which has a $[$Rb$]/[\text{Sr}]$ ratio of 75, were investigated at power level 6.5. The experiments were aiming at identifying possible limiting factors for $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios measurements and at tuning operating conditions in a way that the highest possible accuracy and precision is achieved. In addition to the isotope list shown in the Experimental, the $^{171}\text{Yb}^{++}$ and $^{173}\text{Yb}^{++}$ ion signals were recorded. The operational parameters are listed in Table 27.

<table>
<thead>
<tr>
<th>LA-system</th>
<th>Excite PHAROS fs-laser</th>
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</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>257 nm</td>
</tr>
<tr>
<td>Ablation style</td>
<td>single spot, 300 shots</td>
</tr>
<tr>
<td>Energy</td>
<td>50%</td>
</tr>
<tr>
<td>Energy density</td>
<td>6 J/cm²</td>
</tr>
<tr>
<td>Repetition Rate</td>
<td>5 Hz</td>
</tr>
<tr>
<td>Spot Size</td>
<td>40 µm</td>
</tr>
<tr>
<td>He carrier gas</td>
<td>0.9 L/min (0.45 L/min each)</td>
</tr>
</tbody>
</table>

Table 27 – Operating conditions for the Excite PHAROS fs-laser.

The transient ion signals of two grains (grain 1: (a1) and (a2); grain 2: (b1) and (b2)) are shown in Figure 63. For (a1) and (b1), no thermal treatment was performed during ablation. For (a2) and (b2), the ETV-4000 was kept at power level 6.5. Initial tests performed for the leucogranite biotite showed that the highest Rb-Sr separation with a gas flow of 0.9 L/min is achievable at power level 6.5. Therefore, the same power level was used for the data shown here. During the measurements, however, it got apparent that power level 6.5 is too high for long measurement times. Therefore, in chapters 3.3.2. and 3.4.3., power level 6 was used for thermal treatment. When comparing the signal intensities of (a1) to (a2) and (b1) to (b2), it gets apparent that not only the $^{85}\text{Rb}^+$ ion signal is suppressed. The Sr$^+$ ion signals are also slightly suppressed at the chosen operational settings. For the $^{86}\text{Sr}^+$ signal, only a low sensitivity was measured. This is a strong limiting factor for the precision of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio measurements for samples with similar or lower Sr concentrations. Furthermore, it can be seen that the sample is not homogeneous in its Rb and Sr concentrations. Since spot ablation was used and the signals under heating and non-heating conditions therefore represent different positions on a grain, the inhomogeneity is a possible error source. Figure 64 makes this problematic clearer by showing the $^{85}\text{Rb}^+/^{88}\text{Sr}^+$ transient.
As it can be seen from the Figure 63, no $^{82}$Kr$^+$, $^{83}$Kr$^+$ ion signal increase was observable when the ablation was started. This means that the background subtraction is sufficient to correct for the isobaric $^{84}$Kr$^+$ signal on $^{84}$Sr$^+$ and $^{86}$Kr$^+$ signal on $^{86}$Sr$^+$. No signals over the instrumental background for REEs were measured and therefore, no doubly-charged REE correction had to be performed. The doubly-charged REEs were deleted from the method for subsequent measurements, for future $^{87}$Sr/$^{86}$Sr ratios measurements to achieve a higher correlation. The fact that only a very low sensitivity was achieved for the $^{86}$Sr$^+$ signal can partly be explained by the low Sr concentration of the sample, but also by the high $^{86}$Kr$^+$ background coming from impurities in the argon. Therefore, an Ar bottle with quality 5.0 (Pan Gas, Dagmersellen, Switzerland) was connected to the setup, which had a higher purity grade than the previously used argon from the internal laboratory supply. It was hoped that the $^{86}$Kr$^+$ background (40'000 cps) would decrease with the new argon source. However, this was not the case. It is also possible that the N$_2$ supply was the major or an additional source responsible for the Kr contamination. Since no improvement in terms of background reduction was achieved, tuning for the highest $^{86}$Sr$^+$ sensitivity was performed by changing the N$_2$ flow until the best signal-to-background ratio was found. With increasing N$_2$ flow, the $^{86}$Sr$^+$ signal increased, but also the background at m/Q 86. Since this correlation was not linear, the optimal setting was found to be 13 mL/min (12.3 mL/min readout of the mass flow controller), which was used for all future measurements. Table 28 shows the signal suppression factors for the $^{85}$Rb$^+$, m/Q 87 and $^{88}$Sr$^+$ signals and the $^{85}$Rb$^+$/$^{88}$Sr$^+$ intensity ratio for heating and non-heating conditions.
Table 28 – Signal suppression factors of the $^{85}\text{Rb}^+$, m/Q 87 and $^{88}\text{Sr}^+$ signals.

The $^{85}\text{Rb}^+$ suppression was around 2 – 3 orders of magnitude. The $^{85}\text{Rb}^+/^{88}\text{Sr}^+$ intensity ratio dropped from the order of $10^3$ under no thermal treatment to orders of $10^1$ when heating at power level 6.5, which means that the suppression occurred across three orders of magnitude. The $^{85}\text{Rb}^+/^{88}\text{Sr}^+$ ratio and suppression factors differ strongly for the different grains. This shows that the leucogranite biotite is not a homogenous sample. Figure 64 shows the high variability in the transient $^{85}\text{Rb}^+/^{88}\text{Sr}^+$ intensity ratios for grain 1 and 2. Spikes in the transient of grain 1 were not considered for the $^{85}\text{Rb}^+/^{88}\text{Sr}^+$ ratio calculation and for $^{87}\text{Sr}/^{86}\text{Sr}$ calculations (chapter 3.4.3.). Only signal ranges with a stable signal were used for integration.

Figure 64 - $^{85}\text{Rb}^+/^{88}\text{Sr}^+$ transient intensity ratios for power level 6.5 for grain 1 and 2, respectively.

The low $^{86}\text{Sr}^+$ sensitivity, the inhomogeneous grains and the fact that the $^{85}\text{Rb}^+$ ion signal was not suppressed below the instrumental background are all factors that could limit the accuracy and precision for future $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios measurements. In chapter 3.4., $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios were measured for leucogranite biotite grains to investigate the achievable accuracy and precision.
7.7. Rb-Sr Separation Efficiency for 1B and 1F under a reduced Helium Gas Flow

It was shown earlier that a lower helium gas flow (0.2 L/min) was advantageous in terms of Rb suppression when analyzing minerals. Under the reduced helium flow, the $^{85}\text{Rb}^+$ signal was almost suppressed down to the instrumental background and the $^{86}\text{Sr}^+$ and $^{88}\text{Sr}^+$ ion signals were also suppressed to a stronger extent. For the AM13 1B biotite, the $^{86}\text{Sr}^+$ sensitivity was very low due to the increased suppression.

$^{85}\text{Rb}^+$ and $^{88}\text{Sr}^+$ ion signal suppressions were measured after fs-LA of the AM13 1F feldspar and AM13 1B biotite and thermal treatment with the ETV-4000 at power level 6. The same operating conditions as in chapter 3.4.3. were used. Table 29 gives an overview over the suppression factors for the AM13 1B biotite and the AM13 1F feldspar.

<table>
<thead>
<tr>
<th></th>
<th>$^{85}\text{Rb}^+$; RSD</th>
<th>$^{88}\text{Sr}^+$; RSD</th>
<th>$^{85}\text{Rb}^+/^{88}\text{Sr}^+$ no heating; SD</th>
<th>$^{85}\text{Rb}^+/^{88}\text{Sr}^+$ power level 6; SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1F</td>
<td>0.00185; 0.00048</td>
<td>0.830; 0.122</td>
<td>0.412</td>
<td>0.000729; 0.000149</td>
</tr>
<tr>
<td>1B</td>
<td>0.000374; 0.000031</td>
<td>0.679; 0.006</td>
<td>77.71</td>
<td>0.03191; 0.00449</td>
</tr>
</tbody>
</table>

Table 29 – Summary of the signal suppression factors of the $^{85}\text{Rb}^+$ and $^{88}\text{Sr}^+$ signals for the AM13 biotite (1B) and the AM13 feldspar (1F).

Compared to the RSDs obtained for the leucogranite biotite in the chapter before, a slight improvement can be observed. This can possibly be attributed to the lower [Rb]/[Sr] concentration ratio of the 1B and 1F. This would indicate, however, that for the 1F a higher precision should be measured as for the 1B, which is not the case. Therefore, the more probable explanation is that the lower helium gas flow and increased residence time leads to an increase in the precision of the suppression factors, even though the samples are not perfectly homogeneous in their concentrations. The $^{85}\text{Rb}^+/^{88}\text{Sr}^+$ intensity ratio drops across three orders of magnitude for both samples and seems not to be dependent on the initial [Rb]/[Sr] ratio. This indicates a highly efficient Rb-Sr separation efficiency amongst the minerals and under the same operating conditions. The same observation was already made for the Li-tetraborates in chapter 3.2.1., for which the Rb-Sr separation efficiency was also independent of the initial [Rb]/[Sr] ratio. Another explanation for the increase in precision compared to the LB data could be the use of line scans instead of spot ablation, which increases the signal stability essentially. Inhomogeneities or unstable signal ranges can be specifically neglected during data evaluation.

7.8. Line Scans versus Single Spot Ablation

The suppression factors obtained by using either line scans with a scan rate of 5 μm/s or single spot ablation were compared in the scope of the fundamental ns- and fs-LA fundamental study discussed in chapter 3.1. Pure Zn, Cu, Ta and brass were analysed with the Geolas-C ns-laser and the ELAN DRC$^+$ 6100. The HGA-600MS was used for thermal treatment with the heating protocol listed in the Experimental in Table 5. Table 30 lists the operating conditions of the Geolas-C.
<table>
<thead>
<tr>
<th>LA-system</th>
<th>Geolas-C ns-laser</th>
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<tr>
<td>Wavelength</td>
<td>193 nm</td>
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<td>Ablation style</td>
<td>line scan, 5 µm/s</td>
</tr>
<tr>
<td>Energy density</td>
<td>10 J/cm²</td>
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<td>Repetition Rate</td>
<td>4 Hz</td>
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<tr>
<td>Spot Size</td>
<td>60 µm</td>
</tr>
<tr>
<td>He carrier gas</td>
<td>1 L/min</td>
</tr>
</tbody>
</table>

Table 30 – Operating conditions of the Geolas-C ns-laser.

Figure 65 shows the suppression factors for the $^{66}$Zn$^+$, $^{65}$Cu$^+$ and $^{181}$Ta$^+$ ion signals as a function of the HGA-600MS temperature. No significant differences between the suppression factors obtained for line scans and single spot ablation are observable at the same temperature.

Figure 65 – $^{66}$Zn$^+$, $^{65}$Cu$^+$ and $^{181}$Ta$^+$ ion signal suppression factors for the pure metals (left) and brass (right) for line scans (dotted lines) and single spot ablation (straight lines).