Super-SIMS at DREAMS: Status of a unique and complex endeavour

Rugel, G.; Ziegenrücker, R.; Koll, D.; Lachner, J.; Noga, P.; Vivo Vilches, C.; Renno, A.; Wallner, A.; Wiedenbeck, M.;

Super-SIMS at DREAMS: Status of a unique and complex endeavour

Georg Rugel [a,*], René Ziegenrücker [a], Dominik Koll [a], Johannes Lachner [a], Pavol Noga [b],

Carlos Vivo-Vilches [a], Axel D. Renno [c], Anton Wallner [a], Michael Wiedenbeck [d]

[a]*Helmholtz-Zentrum Dresden-Rossendorf, Institute of Ion Beam Physics and Materials Research, Accelerator Mass Spectrometry & Isotope Research, Dresden, Germany*

[b]*Slovak University of Technology in Bratislava, Faculty of Materials Science and Technology in Trnava, Advanced Technologies Research Institute, Trnava, Slovakia*

[c]*Helmholtz-Zentrum Dresden-Rossendorf, Helmholtz Institute Freiberg for Resource Technology, Freiberg, Germany*

[d]*Helmholtz-Zentrum Potsdam, Deutsches GeoForschungsZentrum (GFZ), Germany*

[*]*Corresponding author: Tel.: +49 351 260 3296; g.rugel@hzdr.de (G. Rugel)*

Abstract

At the DREAMS (DREsden AMS) facility we are implementing a so-called Super-SIMS (SIMS = Secondary Ion Mass Spectrometry) device, which combines the micron-scale spatial resolution of a commercial SIMS (CAMECA IMS 7f-auto) with the very high selectivity through molecule suppression by AMS. We have demonstrated high transmission for major element ions including silicon, fluorine and iodine, however the lack of well characterized calibration materials makes a true quantification of trace and ultra-elements contents difficult. Measurements of P in Si show the linearity of the instrument's relative sensitivity factor over more than three orders of magnitude, and measurements of the isotopic ratio of bromine in ZnS document the reliability of our approach. The goal of the DREAMS Super-SIMS project is to provide quantitative concentration data of ultra-trace elements in geological samples in the context of resource technology.

Keywords: accelerator mass spectrometry, SIMS, trace elements

1. Introduction

Accelerator-based techniques offer great potential for measuring trace elements in many applications due to their great selectivity. The scientific motivation for this approach has been discussed many times; see e.g. Matteson [1] for an overview. Previous efforts at combining secondary ion mass spectrometry (SIMS) with accelerator mass spectrometry (AMS) have demonstrated the challenges in mating-up these two techniques. For a detailed overview of the literature, including a description of the now decommissioned NAUTILUS instrument, see Groopman et al. [2].

While NAUTILUS used exclusively positive ions, the DREAMS (DREsden AMS) facility [3,4] requires negative ions to implement a so-called Super-SIMS device [5]. Our system combines the advantages of a commercial dynamic SIMS (CAMECA IMS 7f-auto) operating as a laterally and depth resolving ion source with the AMS capabilities of an existing multipurpose 6-MV tandem accelerator which is also used for ion implantation and ion beam analysis. SIMS is a well-established technique for trace-element analysis of geological and semiconductor materials. At low concentrations, however, isobaric mass interferences of atoms and molecules can significantly bias the measured signal (e.g. ^{31}P vs. ^{30}SiH in a Si-wafer). To overcome this, SIMS instruments are commonly operated at high mass resolving power (MRP, defined at 10% peak height), which can come at the cost of a loss in signal intensity. The approach of Super-SIMS is to suppress molecular isobars in the secondary ion beam using the AMS capabilities, eliminating any need for elevated MRP above the $M/\Delta M \approx 350$ provided by small geometry machines operating at maximum sensitivity. Super-SIMS aims at the quantification of stable element abundances down to $\sim 10^{-9} - 10^{-12}$ at/at. The total beam transmission of Super-SIMS, which is directly related to both measurement time and test portion mass, will be lower than most SIMS standalone instruments. On the other hand Super-

SIMS offers significantly better limits of detection for stable trace elements. Our intention is to increase the sensitivity by more than an order of magnitude over traditional dynamic SIMS when operated at even moderately high mass resolution (e.g. [1,6]). Our ultimate intent is to apply this technique to the analysis of geological samples in the context of resource technology.

SIMS measurements are characterised by a strong matrix dependency. As a result, the reference materials (RMs) employed for quantification need to meet strict requirements in terms of both being "matrix match" and homogeneneous. The new capabilities of Super-SIMS require the characterisation of an entire new class of RMs for calibrating and validating quantitative determinations at ultra-low concentrations.

2. System set-up

Figure 1 shows an overview of the setup of the low-energy side of the system. At the high-energy side no new devices have been added to the existing AMS system (see, e.g. [3,4]). The following describes the most important features of the new setup.

2.1. Secondary Ion Mass Spectrometry at Super-SIMS

The CAMECA IMS 7f-auto instrument can provide spatial resolution with a primary beam diameter down to a few µm that can optionally be rasterised over a sample area that is commonly 100 µm x 100 µm for Super-SIMS. While most AMS applications require a chemical pre-treatment, this is not necessary for SIMS samples. However, SIMS samples must not outgas as the sample chamber is generally held at ultra-high vacuum (typically below 10^{-8} mbar). Surface roughness over the whole sample must be below 10µm [7], whereas locally near the sputtering region it should be only a few nm when operating in depth profiling mode. A higher surface roughness and/or a domed surface will significantly impact the sputtering process. This can lead to poorly predictable shifts in the elemental and isotopic ratios measured in the sputtered material. In addition, the so-called matrix effect related to changes of ion yields caused by the chemical environment of the matrix will degrade overall reproducibility of the measurements, see e.g. ref. [8-10]. Nevertheless dedicated sample preparation routinely achieves such required surface roughness levels.

Samples used for SIMS quantification can vary from homogeneous and conductive semiconductors to heterogeneous and non-conductive geological materials. In the latter case, electrical charge can build up on the sample, which hinders ions from leaving the sample and may eventually lead to a destruction of the sample due to electrical arcing. Therefore, if positive primary ions are used, as is the case for Super-SIMS using a Cs^+ primary ion source, charge

compensation by means of electron flooding is required in addition to the application of a conductive thin coating for all non- or poorly conducting samples. For our instrument we generally us a 35 nm thick layer of high-purity gold, but other conductive films can also be applied (e.g. carbon, Pt, p- or n- doped but otherwise ultra-pure silicon).

Our CAMECA IMS 7f-auto is not equipped with a pseudo-Wien-filter that pre-filters the Cs^+ beam and that is optionally available in the most recent versions of the instrument (https://www.cameca.com/products/sims/ims7f-auto). Note, in contrast to the typical AMS sputter ion source, which uses metallic Cs in the reservoir, the CAMECA Cs^+ source uses Cs_2CO_3 which is evaporated in an electron impact arrangement. Thus, trace impurities from the Cs_2CO_3 can become significant when studying an element that is only present in low concentrations.

In dynamic SIMS, a continuous and focused primary ion beam impinges on the sample surface. On the so-called primary side of the SIMS (see Fig. 1), the beam diameter, shape, current and position on the sample are defined using lenses, stigmators, steerers and apertures. In the case of Super-SIMS two different modes are available, which can be rapidly interchanged.

For Super-SIMS tuning purposes, a Cs^+ primary beam of several tens of nA, with an impact energy of 20 keV and with a diameter of approximately 50 µm is used to generate (sputter) secondary ions. This - for a SIMS ion source - relatively high Cs^+ current provides a high current of negative secondary ions, typically a few nA, which can be measured using Faraday cups positioned throughout the system. In contrast, actual Super-SIMS measurements are done with a Cs^+-beam that is comparable to a standard SIMS measurement typically employing a primary beam current in the range of 10's of pA to a few nA, resulting in a beam diameter at the sample surface in the range of 10 to 25 µm.

Sputtered secondary ions are passed through an electrostatic filter, which accommodates the large energy spread inherent to the sputter ion spectrum. Ion species are selected by mass using

a double focusing 90° magnet. This ion optical arrangement allows ions of a given mass to be focussed on the exit slit of the mass spectrometer despite having an energy spread of several tens of eV. In the case of the CAMECA IMS 7f-auto data can only be acquired in "mono-collection mode", i.e. a single mass at a time. If several masses need to be measured, data acquisition starts with the lowest mass and proceeds stepwise across the selected mass table. The maximum mass that can be transmitted by the magnet of the SIMS, which depends on the energy of the secondary ions, is 300 amu for 5 keV ions.

In contrast to many SIMS applications, Super-SIMS uses a low MRP as it relies on the subsequent tandem accelerator to quantitatively eliminate all molecular components in the ion beam. For the experiments described hereafter, the technically lowest possible MRP of 400 was chosen, yielding the highest possible beam current for the SIMS, thereby facilitating the quantification of low abundance elements.

The secondary side of the CAMECA IMS 7f-auto is equipped with three different ion detection systems. A discrete dynode electron multiplier (EM) or a Faraday cup (FC) are used to measure the secondary ion intensity as a count rate in the range of 0.1 counts per second (cps) to 1 nA (equivalent to $6.24 \cdot 10^9$ cps). For Super-SIMS, the EM and the FC are used to continuously monitor the signal stability of one or more matrix elements. This provides information about any possible drift in the measurement conditions of the SIMS. The third SIMS detector is a micro-channel plate detector (MCP), which is used to generate a spatially resolved image of the sample surface. The MCP provides only qualitative data about element distributions in the sample; it is very useful for tuning the instrument while setting up a given experiment. Photons generated at the MCP's phosphorous screen are recorded by a digital camera. We modified the 7f with an additional copper mirror, allowing the camera to be placed perpendicular to the beam axis, permitting the entire MCP to be rotated out of the beam axis so that the secondary ion beam can pass to the coupling segment that connects the SIMS with the drift beamline to the

tandem accelerator. As it is essential to mask any insulating surfaces from the charged ion beam, the phosphorous screen has additionally been shielded with a conductive and grounded grid, which is sufficient for protecting the device without significantly affecting the image at the camera.

The beam line height of the 6-MV tandetron accelerator is at about 1.8 m above the laboratory's floor whereas the SIMS IMS 7-f auto has a beam line height of only 0.9 m. Therefore, the IMS 7f-auto had to be positioned on a massive block of natural diorite (1.8 m x 1.4 m x 0.9 m), which works also as a vibration damper. The electronics are placed in racks on the platform around the diorite. Diorite was selected as the material for making the instrument platform because of its intrinsically low concentration of natural radioactive elements, making it favourable to fulfil low radiation level constraints. Because the entire IMS 7f-auto must be floated at high voltage (see below) and because diorite is not a particularly good electrical insulator, the diorite platform is additionally isolated from ground by a 5 mm thick glass-fibre reinforced plastic plate of Isoval® TM from ISOVOLTA AG, which has a breakdown voltage of 13 kV/mm. Conductive Cu-tape is used on top of this plate, as well as on the lower and upper surface of the rock, to define equipotential surfaces. With these modifications, the platform of the SIMS can be charged up to a potential of -30 kV relative to laboratory ground. Combined with the 10 kV extraction energy of the secondary ions from the SIMS, our design can deliver ions with energies up to 40 keV, which is fully sufficient for the low-energy AMS beam optics. This approach, however, causes further challenges: All the necessary support infrastructure required for the SIMS (e.g. gases, electrical power, instrument chill water supply, communications) must bridge this potential difference. Furthermore, the SIMS needs to be fully remote controlled. In our case, the instrument was already designed for remote control.

2.2. Coupling Segment

The vacuum level required for the SIMS operation is some two orders of magnitude better than what is typically present in the AMS ion source region. Therefore, we designed a differential pumping arrangement between these two sections that are separated by a low conductance beam tube.

The negative ion beam is transported about 10 m from the exit of the SIMS until it reaches the accelerator with the low-energy beam optics being optimised for ions with energies of about 30 keV. The transition of the -30 kV potential to ground is accomplished with a coupling lens consisting of 5 individual electrodes (internal diameter 50 mm, length 50 mm and spacing 20 mm), with the 1st, 3rd, 4th and 5th electrodes connected in series via resistors to ground potential. The 2nd electrode within the coupling lens is connected to an additional power supply (0 to +10 kV with respect to SIMS potential). This configuration ensures a gradual potential change and avoids over-focusing of the beam within the coupling segment as well as flexible operation covering the whole operating range of SIMS platform potentials (-30 to 0 kV) and injected ion energies.

At the highest platform potential, -30 kV in addition to the -10 kV SIMS extraction potential, the lens will focus the beam to the injector FC, working merely as an accelerating tube, whereas at lower energies the 2nd electrode can be used to adjust the focus. When the SIMS operates at ground potential, the system reduces to an Einzel lens in accel-decel mode. The coupling lens is followed by a steering device consisting of 4 separate steerers: 2 plates for x and two plates for y.

Recently we added a retractable perforated steel sheet using the same material used at the VERA facility [11]. This sheet acts as an attenuator, can be remotely inserted into the beam path, providing a reproducible reduction of the beam intensity by a factor of between 50 and 95. This additional device is helpful when tuning the ion beam downstream through the system

to the gas ionization chamber (GIC). The attenuator is sometimes also used for the measurement of samples, which have a high concentration of the element of interest.

2.3. DREAMS setup adaptions

The 6-MV facility is shared with other users having specific demands for the ion beam quality. We adapted the system [3,4] for Super-SIMS to transport the ion beam past several beam injection lines prior to entering the tandem accelerator.

Our Faraday cups are capable of measuring ion currents even below 1 nA if we replace the standard current measuring device with a low-current amperemeter (e.g. a Keithley 6485). For convenience, we use its 0-10 V output signal via a 1 MΩ resistance to amplify our ion currents into the range of about 100 nA; this amplified signal is used for scanning procedures of the control software that was delivered with the accelerator system. All three injection magnets that are passed by the beam from the SIMS in the low-energy beamline are demagnetized to "0" mT while the Einzel lenses and steerers are used for further tuning. An overview of the different components is shown in Figure 1. As usual, Ar gas is used to strip the injected negative ions to produce positive charge states while also destroying all poly-atomic ions present in the ion beam. A high-energy 90° magnet, a 35° ESA and a vertical 30° magnet act as additional filters before the beam enters the ionisation chamber. The pressure in the GIC is adjusted to stop all isotopes of interest within the detector volume. The shaping time of the main amplifier can be adjusted to accommodate count rates roughly from 1 to 10,000 ions per second. To measure ratios of isotopes in the detector with reproducible stable setups, we group the isotopes of interest such as ^{19}F with ^{35,37}Cl and ^{79,81}Br with ^{129}I and, we use different charge states for the isotopes to minimize the needed changes. When alternating between different isotopes provided by the SIMS, only the electrostatic elements (i.e. the terminal voltage and the 35° ESA) need

to be manually changed. Measurement intervals of typically 60 s are used for data collection. For each trace element, we measure the ratio of the trace element versus a proxy of the matrix element. For example, this can be a molecule with rare isotopes in the case of a silicon wafer ($^{29}Si^{30}Si^-$), or a low abundant isotope such as ^{36}S in case of sphalerite (ZnS) sample. These measurements of the proxy beams are performed both at the SIMS and, if possible, at the GIC. If needed, the ion beam intensity representing the matrix element can be reduced by the attenuator. In order to achieve quantitative and metrologically traceable data from Super-SIMS, a new class of matrix-matched reference materials needs to be developed, as the goals of our initiative differ significantly from those of "conventional" SIMS routines with established SIMS reference materials.

2.4. Super-SIMS tuning procedures

After optimizing beam transport to the FC at the front end of the GIC, the beam output of the SIMS is decreased by reducing the SIMS primary ion current. As mentioned above, it is often useful to reduce further the beam intensity with the attenuator, as this allows the primary beam conditions at the SIMS to be kept unchanged. We found that it is important to end the tuning with a final fine-tuning of the SIMS magnet to secure optimal beam transport to the GIC. With this SIMS magnet mass calibration procedure, we were able to get stable results while stepping the beam between the different isotopes.

3. Status of Super-SIMS – some milestones

As the first step in setting up an analytic process, a stable transmission of the ion beam from the SIMS to the detector needs to be established. We use for this initial tuning step a ^{28}Si beam

produced from a silicon wafer. In the normal case where the output of the ^{28}Si$^-$ beam is too intense for the SIMS-FC, both ^{29}Si and ^{30}Si are used in conjunction with the known natural isotopic abundance ratios. Subsequently a ^{28}Si$^-$ signal is measured at the low-energy side of the accelerator and then in the FC at the front end of the GIC. Under these conditions, ^{28}Si$^-$ ions are transported with a transmission of 88% from the FC of the SIMS to the FC in front of the accelerator (FC LE-side). For a terminal voltage of 4.6 MV the transmission from the FC LE-side to the front end of the GIC (FC GIC) is 35% for ^{28}Si^{4+}. This corresponds very closely to the 4+ charge state yield as calculated according to Sayer [12], meaning there is minimal loss due to the ion optics of the system. The total transmission from the SIMS FC to the GIC is thus 31% (see Table 1). Experiments with other prolific beams such as ^{19}F or ^{127}I show similar results for their beam transmissions.

3.1 The example of ^{31}P in Si

Semiconductor materials are widely available and are generally assumed to be homogeneous at the SIMS nanogram sampling scale. Trace stable phosphorous (monoisotopic ^{31}P) determination in silicon by standard SIMS is possible at a MRP of M/ΔM = 3950, which is required to resolve ^{31}P from the molecular interference ^{30}Si^{1}H. Such a relatively modest MRP can be readily achieved even by small geometry dynamic SIMS instrument, albeit at a large loss of transmission. However, at the low P abundances typical for high-purity silicon, background signal becomes dominant due to scattered ions as well as dark noise on the standard SIMS ion counter (around 0.01 ions per second in the case of the CAMECA IMS 7f-auto). Furthermore, operating the CAMECA IMS 7f-auto at M/ΔM = 4000 results in a roughly 90% loss of transmission. At Super-SIMS, ^{31}P^{28}Si$^-$ molecules are used as a proxy for the P content in the sample and ^{29}Si^{30}Si$^-$ molecules are used as a control for establishing the relative sensitivity factor for a given experiment. These specific molecules were chosen as both having

nominal masses of 59 amu, meaning that both can be detected at the GIC without any need to modify parameters on the SIMS side — only the AMS side needs to be changed, which greatly simplifies the analyses. The $^{29}Si^{30}Si^{-}$ beam was attenuated by a factor of 81.3 ± 1.0, to be able to monitor the beam transmission from the low-energy side to the GIC while avoiding significant peak pile-up.

The lack of well-matched reference materials is a major hindrance for the absolute quantification of data. We are now undertaking the characterisation of such materials for specific applications of interest. In the test case of P in Si we were able to use a suite of materials developed earlier as intra-laboratory reference materials. Our data show a good reproducibility of the relative sensitivity factor for P in Si across a wide range of P concentrations. The sample with the highest phosphorous concentration of $5.5 \cdot 10^{18}$ P atoms per cm^3 of Si (corresponding to $1.1 \cdot 10^{-4}$ at$_P$/at$_{Si}$) was used as a calibrant for quantifying the P-concentrations of other samples (Figure 2). These samples and their concentration values were taken from the ultra-clean injector project in Munich. These samples with its presumed trace element concentrations from $8.6 \cdot 10^{14}$ to $5.5 \cdot 10^{18}$ P atoms per cm^3 are described in Ref. [13] and [14]. Only an upper limit is given for the blank sample. Our blank value at $3.4 \cdot 10^{14}$ P atoms per cm^3 of Si, which is about a factor of three lower than the previously reported upper limit [13,14], is encouraging. However, we are aware that blank values can be much lower as e.g. given at the web page of CAMECA cited above. For these experiments on our primary reference sample, we achieved a 1σ repeatability of ±1% from eight measurements of the ^{31}P to ^{30}Si ratio. This suite of analyses indicates that the measurement conditions are stable and there is no significant background due to contamination, interferences, etc. in the respective concentration range. None of our four samples was found to have significantly higher P-concentrations as compared to the independently established reference values, confirming that no meaningful background is present in our analytical design. In one specific case, we cannot exclude the mislabelling of a

sample that showed a significantly lower concentration than expected from Ref. [13, 14]. We obtained the original silicon discs and it is planned to prepare new material for further measurements as these first results are very promising. Our work demonstrates that this method of using molecules generated from the bulk material as reference allows quantitative measurements.

3.2 The example of C, N, O in Si

Another experimental topic is the analysis of C, N and O in silicon. Despite a pressure of $<10^{-8}$ mbar, these elements can be present in significant concentrations in the residual gas of the SIMS analysis chamber, making this analytical task particularly challenging. For the experiments undertaken, we use the approaches of Gnaser [15] and Kudriavtsev et al. [16] developed for traditional SIMS analysis. In their approaches, the primary beam intensity of the SIMS is kept constant, while the raster size on the sample is reduced stepwise. With each step, the signal intensity of the elements originating from the sample increases, while the signals dominated from the residual gas stay constant. We adapted these procedures to the lower detection limits provided by Super-SIMS. An additional challenge is the presence of traces of such elements in the primary Cs^+ beam (again it should be noted that the starting material for generating the Cs^+ ions is Cs_2CO_3). We have tested a type of pseudo-Wien-filter as a mass filter built from a set of two permanent magnets outside of the beamtube and the existing electrostatic steerers and apertures in the primary column. The first results for the lightest element in this series – carbon – are encouraging (Figure 3). For the heavier element O, our setup with permanent magnets provisionally mounted outside the beamtube needs to be improved to achieve the necessary mass separation.

3.3 The example of halides in sphalerite

The analysis of halogen concentrations in natural sulphide minerals as a reference measurement for the study of geological samples is desirable for two reasons. First, the concentrations of halogens in the crystal lattices of such minerals can help characterize the ore-forming aqueous solutions, not only in terms of their chemical compositions but also in terms of other physicochemical parameters [17, 18]. Secondly, negatively charged secondary ions from the halogens form prolifically under typical sputtering conditions, meaning that fewer analytical challenges were to be expected on the SIMS side of the experiment.

The involved masses span a large mass range, thus the experiment needed to be split between the lighter elements (fluorine and chlorine) and the heavier elements (bromine and iodine). As a reference mass for the SIMS, we used the rare matrix isotope ^{36}S, that even at 0.02 % natural abundance still required the use of the attenuator in order to measure it with the GIC. We could not detect a competing background signal in the energy loss spectrum of the GIC for any of the ion species of interest, meaning that the total energy signal could be used for ion counting. For this case, a detector with a simpler design could be used in the future.

As with any other quantitative SIMS measurements, the availability of matrix-matched reference materials is essential for obtaining accurate quantitative results. As we could not find any proven determinations of fluorine contents in either natural or synthetic sphalerite, we had to rely on a direct comparison of the different signal intensities. For the elements Cl, Br and I we used nanopowder tablets [19] of natural sphalerites [18], from which we have started to determine the corresponding contents using both bulk analytical and spatially resolved chemical methods, which currently remains a work in progress. An alternative approach for the preparation of matrix matched reference materials would be the ion implantation of the isotopes of interest into synthetic sphalerites by the method described by Wu et al. [20]. However, this experimental approach is time-consuming, since a series of different RMs with different

concentrations must be prepared and it also requires corrections for the initial concentrations of the implanted isotopes in the starting materials.

Signals for the isotopes ^{19}F, ^{35}Cl, ^{37}Cl, ^{79}Br, ^{81}Br and ^{127}I could be detected in all investigated samples, meaning that a qualitative detection of these isotopes was possible for all the investigated sphalerite samples. For bromine, both isotopes ^{79}Br and ^{81}Br were measured as a proxy for the stability of the measurement, and the ratio was found to be both stable within statistical uncertainties (~5%) and yielded a mean value of 1.07, which is close to its natural abundance ratio of 1.03.

The ratio of the count rates of ^{79}Br to ^{36}S was between 0.3 and 1.8 for a set of five samples at the detector. The corresponding standard deviation from counting statistics ranges from 5% to 16%.

For sphalerite there are no published validated concentrations of ^{19}F in the crystal lattice of the mineral. Non-spatially resolved bulk chemical measurements of the fluorine content are unsuitable since fluid inclusions are likely present in such materials and it would be expected that even small amounts of such fluids would dominate the fluorine budget. The ^{19}F concentration in the crystal lattice of the sphalerite can give significant information about different physicochemical conditions during crystallization, e.g. temperature, pressure or chemical activities of the mineral-forming solutions.

So far our measurements on sphalerite have shown that all halide isotopes were detectable in all tested sphalerite samples. The lowest standard deviation from four measurement cycles in one spot for ^{35}Cl was less than 1%, in other samples up to 8% which could indicate heterogeneities in the Cl-content and not the stability of the setup. In addition, in some cases our spatially resolved analyses point to minor, albeit detectable heterogeneities in some of our test samples. However, the number of measurements is still too small at this stage to allow for any crystal chemical interpretation from the observed differences. Due to the lack of any matrix-

matched reference materials, the quantification of the absolute halogen concentrations is not yet possible.

4. Conclusions

The combination of SIMS with AMS is an ongoing challenge. We reached high beam transmission for the ions of interest and we have also demonstrated that Super-SIMS can quantitatively eliminate molecular isobaric backgrounds generated during the sputtering process. The high energies from the 6-MV tandem were not actually required for our background suppression capabilities. A more compact machine could, in fact, also be used for Super-SIMS. So far, most of our measurements were done on artificial samples, though the ultimate aim is to use Super-SIMS for highly sensitive analysis of geological samples in the context of resource technology.

A major impediment for quantitate applications remains the lack of suitable reference materials that will be essential for calibrating absolute abundance data from all future Super-SIMS determinations. A promising approach is the use of nanopowder materials, which have only recently become of metrological interest. Furthermore, additional developments aimed at simplifying the software and optimizing the measurement procedure are being pursued.

References

[1] S. Matteson, Issues and opportunities in accelerator mass spectrometry for stable isotopes. Mass Spectrom Rev. 27(5) (2008) 470-84. https://doi.org/10.1002/mas.20174.

[2] Evan E. Groopman, David G. Willingham, Albert J. Fahey, Kenneth S. Grabowski, An overview of NRL's NAUTILUS: a combination SIMS-AMS for spatially resolved trace isotope analysis, J. Anal. At. Spectrom. 35 (2020), 600. http://dx.doi.org/10.1039/C9JA00344D.

[3] S. Akhmadaliev, R. Heller, D. Hanf, G. Rugel, S. Merchel, The new 6 MV AMS-facility DREAMS at Dresden, Nucl. Instr. Meth. B. 294 (2013) 5. doi:https://doi.org/10.1016/j.nimb.2012.01.053

[4] G. Rugel, S. Pavetich, S. Akhmadaliev, S.M. Enamorado Baez, A. Scharf, R. Ziegenrücker, S. Merchel, The first four years of the AMS-facility DREAMS: Status and developments for more accurate radionuclide data, Nucl. Instr. Meth. B. 370 (2016) 94. doi:https://doi.org/10.1016/j.nimb.2016.01.012.

[5] J. M. Anthony, D. J. Donahue, A. J. T. Jull, Super-SIMS for ultrasensitive impurity analysis, MRS Proceedings 69 (1986) 311-316.

[6] C. Maden, The potential of accelerator secondary ion mass spectrometry in environmental sciences, Dissertation ETH Zurich, Switzerland (2003) https://doi.org/10.3929/ethz-a-004598699.

[7] N.T. Kita, T. Ushikubo, B. Fu, J.W. Valley, High precision SIMS oxygen isotope analysis and the effect of sample topography, Chemical Geology 264 (2009) 43–57.

[8] L. Ottolini, F. Camara, S. Bigi, An investigation of matrix effects in the analysis of fluorine in humite-group minerals by EMPA, SIMS and SREF, American Mineralogist, 85 (2000) 89-102. https://doi.org/10.2138/am-2000-0110.

[9] D.R. Bell, R.L. Hervig, P.R. Buseck, S. Aulbach, Lithium isotope analysis of olivine by SIMS: Calibration of a matrix effect and application to magmatic phenocrysts: Chemical Geology, 258 1-2 (2009) 5-16. https://doi.org/10.1016/j.chemgeo.2008.10.008.

[10] R. Taylor, C. Clark, S.M. Reddy, The effect of grain orientation on secondary ion mass spectrometry (SIMS) analysis of rutile: Chemical Geology, 300-301 (2012) 81-87. https://doi.org/10.1016/j.chemgeo.2012.01.013.

[11] M. Martschini, D. Hanstorp, J. Lachner, C. Marek, A. Priller, P. Steier, P. Wasserburger, R. Golser, The ILIAMS project – An RFQ ion beam cooler for selective laser photodetachment at VERA, Nucl. Instr. Meth. B. 456 (2019) 213-217, https://doi.org/10.1016/j.nimb.2019.04.039.

[12] R.O. Sayer, Rev. Phys. Appl. 12 (10) (1977) 1543-1546. DOI: 10.1051/rphysap:0197700120100154300.

[13] Th. Brunner, Beschleunigermassenspektrometrie mit stabilen Isotopen, Diploma thesis, Technische Universität München, Germany (1991).

[14] St. Massonet, Beschleunigermassenspektrometrie mit stabilen Isotopen und primordialen Radionukliden, Dissertation Technische Universität München, Germany (1998).

[15] H. Gnaser, Greatly enhanced detection sensitivity for carbon, nitrogen, and oxygen in silicon by secondary-ion-mass spectrometry, Applied Physics Letters, 79 (2001) 497-499. doi:https://doi.org/10.1063/1.1388876.

[16] Yu. Kudriavtsev, A. Villegas, A. Godines, R. Asomoza, SIMS analysis of residual gas elements with a Cameca IMS-6f ion microprobe, Applied Surface Science, 252 (2006) 3406-3412. DOI: 10.1016/j.apsusc.2005.05.064.

[17] D.E. Harlov, L. Aranovich, The Role of Halogens in Terrestrial and Extraterrestrial Geochemical Processes : Surface, Crust, and Mantle (Springer International Publishing, Cham, 2018) p. 1-19. https://doi.org/10.1007/978-3-319-61667-4_1.

[18] M. Frenzel, N.J. Cook, C.L. Ciobanu, A. Slattery, B. Wade, S. Gilbert, K. Ehrig, M. Burisch, M.R. Verdugo-Ihl, P. Voudouris, Halogens in hydrothermal sphalerite record origin of ore-forming fluids, Geology 48 8 (2020), 766-770. DOI: 10.1130/G47087.1.

[19] D. Garbe-Schönberg, S. Müller, 2014, Nano-particulate pressed powder tablets for LA-ICP-MS: J. Anal. At. Spectrom., 29 6 (2014) 990-1000.

[20] H. Wu, R. Böttger, F. Couffignal, J. Gutzmer, J. Krause, F. Munnik, A.D. Renno, R. Hübner, M. Wiedenbeck, R. Ziegenrücker, 'Box-Profile' Ion Implants as Geochemical Reference Materials for Electron Probe Microanalysis and Secondary Ion Mass Spectrometry: Geostandards and Geoanalytical Research, 43 4 (2019) 531-541.

.

Tables:

Table 1: Values for the transmission of ^{28}Si from the FC of the SIMS to the FC at the front of the accelerator (FC LE-side) to the FC at front end of the GIC (FC GIC). The value for ^{28}Si$^-$ of the SIMS is scaled from the other Si-isotopes as the FC of the SIMS can handle maximal 1 nA. The stripping yield at 4.6 MV of 37% to the 4+ charge state is calculated according to Sayer [12], pointing to a maximum transmission of the ^{28}Si^{4+} of 31% to the detector.

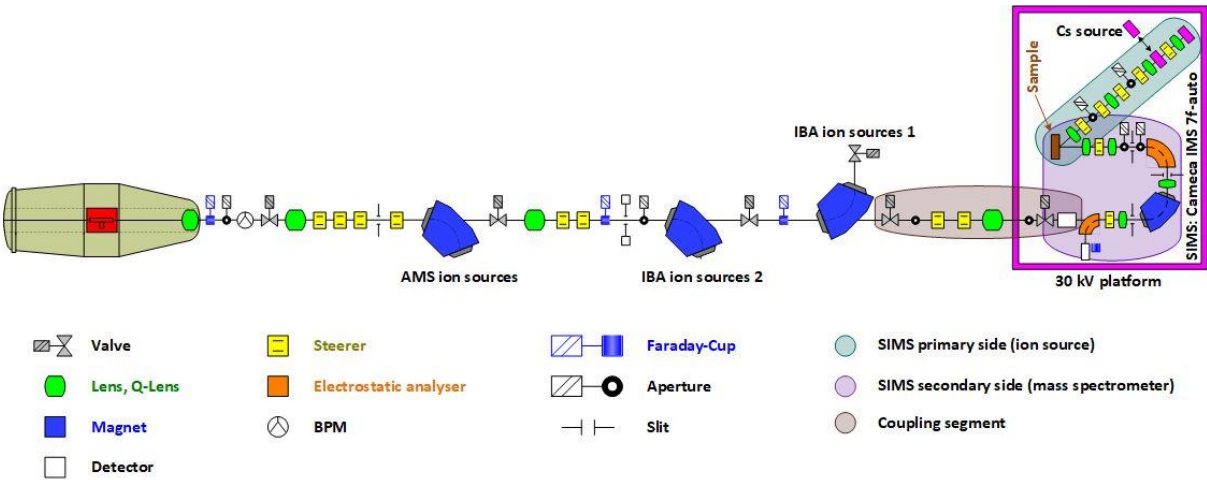|	^{28}Si$^-$		^{28}Si^{4+}
	FC-SIMS	FC LE-side	FC GIC
ion current [nA]	1.5	1.3	1.9
relative transmission [%]	100%	88%	31%

.

Figures

Figure 1: Layout of the low-energy side of the Super-SIMS setup with all elements relevant for the ion beam optics.
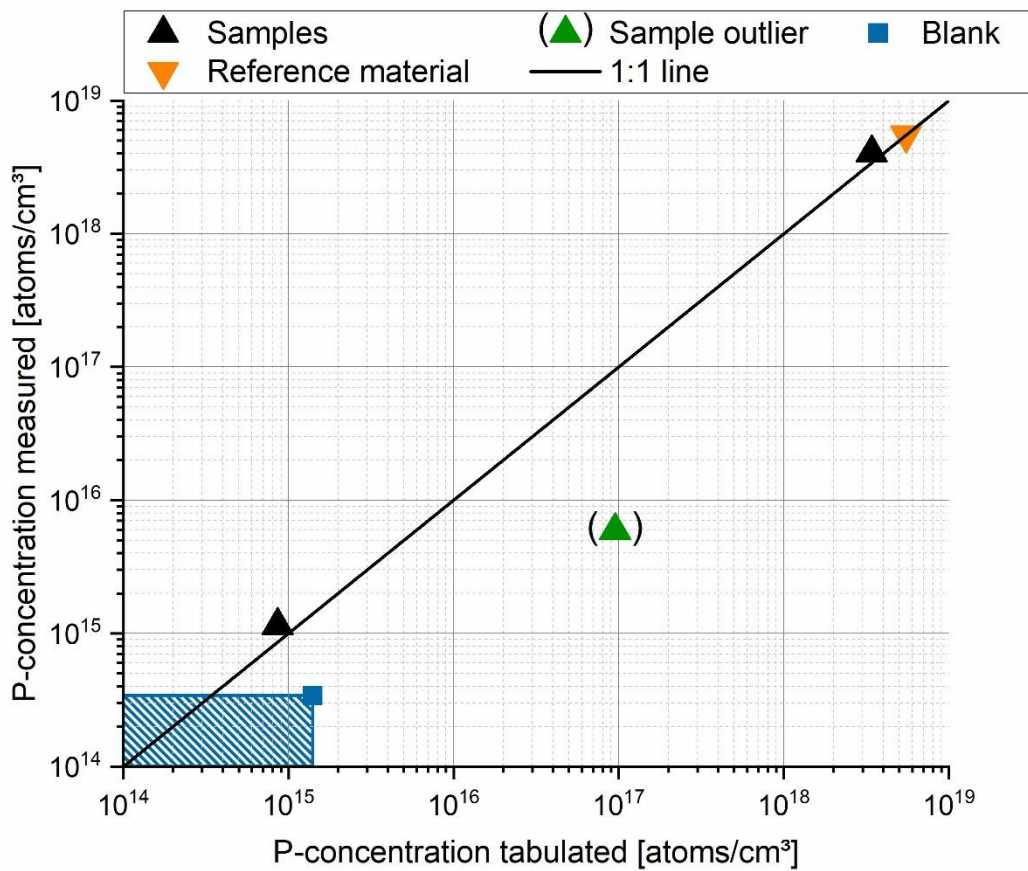
Figure 2: P-concentration measured using the tabulated value [13, 14] of the highest labelled silicon sample as a reference. The tabulated value for the blank was an upper limit, our value is a about a factor of three lower.
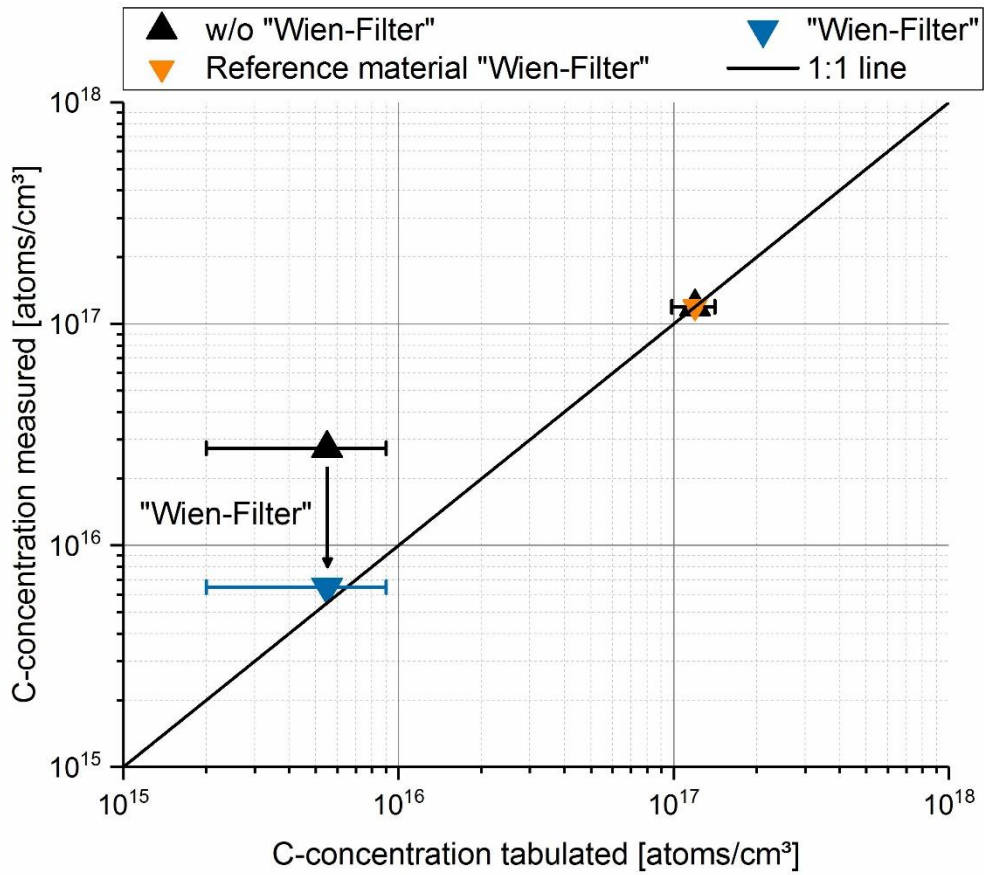
Figure 3: Concentration of the trace element carbon in silicon. Two samples with known concentrations of carbon were measured. The known range of concentration is indicated together with its mean value. The higher concentration sample was used as a reference. The lower concentration of the sample can only be reproduced when applying the pseudo Wien-filter, demonstrating the need for such a device.