The Potential of Accelerator Secondary Ion Mass Spectrometry in Environmental Sciences

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Abstract

Accelerator Secondary Ion Mass Spectrometry (Accelerator SIMS) originated out of the combination of conventional Secondary Ion Mass Spectrometry (SIMS) with Accelerator Mass Spectrometry (AMS). This has the advantage that interfering molecules in the mass spectrum of SIMS can be destroyed in the accelerator and the fragments are separated in a second mass spectrometer.

The aim of this thesis is to demonstrate the potential of Accelerator SIMS with respect to applications in the environmental sciences. Analytical procedures to reliably measure trace elements over the entire periodic table with AMS have been developed. In addition, ways to analyse electrically insulating sample matrices have been found, as these are commonly encountered when analysing environmental samples. Because of the limitation of Accelerator SIMS to the analysis of negative secondary ions, negative ion yields of trace elements from silicon dioxide have been investigated. And finally, the limits to the analysis of small samples of only 100 ng total sample size have been explored.

The potential of Accelerator SIMS is demonstrated by applying the technique to two applications in the environmental sciences. The results of these measurements show that Accelerator SIMS is capable of analysing trace element concentrations and isotopic ratios in regimes not accessible to any other analytical method presently available. The results also reproduce measurements performed with other analytical techniques nicely demonstrating the reliability of Accelerator SIMS.

The first application that is discussed is in-situ bulk concentration analysis of iridium in sedimentary layers around the Cretaceous-Tertiary transition (KT-boundary). Neutron activation analyses (NAA) revealed that the concentration of iridium is higher in the transition horizon (~56 ng/g) than in the neighbouring sedimentary layers of the Tertiary and the Cretaceous (~0.4 ng/g). This was possibly caused by a meteorite impact 65 million years ago. With Accelerator SIMS it was possible to reproduce the NAA results, but with a lateral resolution orders of magnitude higher (~100 µm compared to ~1 cm) enabling trace element analysis in sedimentary layers at a much smaller lateral scale. Presently, no other technique is capable of performing bulk concentration analysis with such low trace element concentrations and with such a high lateral resolution.
The second application that is addressed is the direct measurement of natural $^{10}\text{Be}/^{9}\text{Be}$ ratios in samples from ferromanganese crusts (carrier-free $^{10}\text{Be}$ AMS). For this application isotopic ratios of $10^{-10}$ have to be measured in samples with a total size of only 100 ng. This alone is a unique achievement in the field of AMS. The natural $^{10}\text{Be}/^{9}\text{Be}$ ratio as a function of depth in a ferromanganese crust gives important information on the growth rate of the crust and is used to date oceanographic events manifested by the concentrations of other radiogenic isotopes. To date, this information has been gained with either the direct measurement of the natural $^{10}\text{Be}/^{9}\text{Be}$ ratio with a SIMS method or with separate measurements of the absolute $^{10}\text{Be}$ and $^{9}\text{Be}$ concentrations with AMS and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) respectively. Accelerator SIMS results not only reproduce previous measurements very nicely, but the method is also more sensitive and measures to a higher precision than the already existing techniques. The new technique can therefore determine time scales in ferromanganese crusts with a higher precision further into the past than the previously existing methods.

Finally, the potential and capabilities of Accelerator SIMS are compared to other analytical techniques presently available. In particular, the method is compared to conventional SIMS and ICP-MS. At present, these are the two state-of-the-art analytical methods. It has been shown that Accelerator SIMS has unique features and some prospects of how these can be exploited in future are presented.
Kurzfassung

Beschleuniger-Sekundärionen-Massenspektrometrie (Beschleuniger-SIMS oder Accelerator SIMS) stammt aus der Erweiterung von herkömmlichem Sekundärionen-Massenspektrometrie (SIMS) mit Beschleuniger-Massenspektrometrie (BMS oder in Englisch AMS). Dies hat den Vorteil, dass die interferierenden Moleküle im Beschleuniger aufgebrochen und ihre Fragmente in einem zweiten Massenspektrometer vom Spurenelement separiert werden können.


Die erste Anwendung, welche vorgestellt wird, ist die Analyse von Iridiumkonzentrationen in Sedimentschichten vom Übergang von der Kreide ins Tertiär (KT-Grenze). Analysen mit Neutronen Aktivierung haben gezeigt, dass die Iridiumkonzentration in der Grenzschicht viel höher ist (~56 ng/g) als in den benachbarten Schichten der Kreide und des Tertiärs (~0.4 ng/g). Dies wurde vermutlich durch den Einschlag eines Meteoriten vor 65 Millionen Jahren erzeugt. Mit Beschleuniger-SIMS war es möglich die Ergebnisse der Neutronen Aktivierungs Analysen zu reproduzieren, aber mit einer örtlichen Auflösung, die um Grössenordnungen besser ist (~100 µm anstatt ~1 cm). Zur Zeit kann mit keiner anderen Analysemethode so geringe Spurenelementkonzentrationen mit einer solch
Kurzfassung

hohen örtlichen Auflösung nachgewiesen werden. Die örtliche Verteilung von Spurenelementen in Sedimentschichten kann also viel genauer erfolgen, und Effekte, welche sich über kleinere Distanzen abspielen, können untersucht werden.

Die zweite Anwendung, welche angesprochen wird, ist die direkte Messung von natürlichen $^{10}\text{Be}/^{9}\text{Be}$-Verhältnissen in Eisen-Mangankrusten (trägerfreies $^{10}\text{Be}$-AMS). Für diese Anwendung müssen Isotopenverhältnisse von $10^{-10}$ in Probenmengen von lediglich 100 ng gemessen werden. Dies alleine ist schon eine einzigartige Leistung auf dem Gebiet der Beschleuniger-Massenspektrometrie. Das natürliche $^{10}\text{Be}/^{9}\text{Be}$-Verhältniss als Funktion der Tiefe in einer Eisen-Mangankruste gibt wichtige Auskunft über die Wachstumsgeschwindigkeit der Kruste und kann zur Datierung von ozeanologischen Ereignissen benutzt werden, welche durch die Konzentrationsverteilungen anderer Radionuklide in der Kruste manifestiert werden.

Bisher wurde diese Information entweder durch die direkte Messung des natürlichen $^{10}\text{Be}/^{9}\text{Be}$-Verhältnisses mit einer SIMS-Methode oder durch zwei separate Messungen der absoluten $^{10}\text{Be}$- und $^{9}\text{Be}$-Konzentrationen mit $^{10}\text{Be}$-AMS respektive mit ICP-MS (Induktiv-gekoppeltes-Plasma Massenspektrometrie) gewonnen. Es wird gezeigt, dass die neue Beschleuniger-SIMS-Methode nicht nur die Messungen der anderen Methoden sehr schön reproduzieren kann, sondern dass sie auch empfindlicher und präziser messen kann als die bisherigen Methoden. Somit können Datierungen an Eisen-Mangankrusten genauer und weiter in die Vergangenheit gemacht werden, als es mit den bisherigen Methoden möglich war.

Zuletzt wird das Potential und die Möglichkeiten von Beschleuniger-SIMS mit denen anderer Analysemethoden, die heute zur Verfügung stehen, verglichen. Insbesondere wird ein Vergleich mit herkömmlichem SIMS und ICP-MS gemacht, da diese heute die vielversprechendsten Analysemethoden sind. Es wird gezeigt, dass Beschleuniger-SIMS einzigartige Eigenschaften hat und mögliche Zukunftsperspektiven für die Methode werden vorgestellt.
The discovery and exploration of the structure of the atom in the first half of the last century triggered the invention of a number of analytical methods to analyse the composition of samples. Over the last fifty years, the available methods have been steadily improved. Today, research, development and manufacturing control could not be imagined without the possibilities of trace element analysis available. Many applications in material science, environmental sciences, and other fields of research rely on the accurate determination of the concentrations of trace elements and their isotopic ratios in samples. But the more progress science makes, the greater the demand for better detection limits and higher lateral resolution gets. The development of new, more sensitive analytical techniques is therefore an important prerequisite for future discoveries in all fields of research.

Accelerator Secondary Ion Mass Spectrometry (Accelerator SIMS) is a recent development. As one can assume from its name, it evolved from the combination of conventional Secondary Ion Mass Spectrometry (SIMS) with Accelerator Mass Spectrometry (AMS). The idea was to suppress molecular interferences in the mass spectrum of conventional SIMS by extending it with an accelerator mass spectrometer. In the nineties, first dedicated Accelerator SIMS facilities were built and tested by analysing trace elements in silicon wafers. Improvements of detection limits by up to two orders of magnitude in comparison to conventional SIMS were observed (Ender et al., 1997a+b+d; Massonet, 1998). Picking up the development of the method from there, the aim of this thesis is to explore the limits of Accelerator SIMS with respect to applications in environmental sciences. It will be demonstrated that Accelerator SIMS has unique features and can perform measurements that no other analytical technique is capable of performing. These features will be compared with the capabilities of other analytical techniques presently available, and prospects for future developments of Accelerator SIMS will be presented.

In this chapter the motivation leading to this thesis will be explained in more detail starting with a short historical review of the development of Accelerator SIMS together with work that has been performed in this field. Following this, the outline of the thesis will be presented.
1.1 SIMS and AMS and their Incommodities

1.1.1 SIMS

In first experiments with ion beams in the thirties it was observed that during bombardment with a primary ion beam secondary ions of the target material itself are emitted out of the surface of a solid. Extracting these secondary ions to a beam and performing mass spectrometry with them gave birth to a method that is now known as Secondary Ion Mass Spectrometry (SIMS). By scanning the primary beam over the sample surface the concentration distribution of a trace element on the surface can be analysed. Also, the three dimensional distribution of a trace element can be measured by eroding the sample layer by layer with the primary beam.

The first dedicated SIMS apparatus was built during a NASA project in the beginning of the sixties. It was built for the analysis of lunar rocks from sample return missions. Due to the ability of the method to produce information on the three dimensional distribution of a trace element in a sample and also to its low detection limits, SIMS soon found a large range of applications in various fields of research and industry. Driven by its own success and the demand for lower detection limits and better lateral resolution the method developed rapidly. Today, state-of-the-art SIMS machines are highly sophisticated devices with - in favourable cases - trace element detection limits in the sub-ppb range and with a lateral resolution of about 30 µm. Reducing sensitivity, mainly due to reducing the intensity of the primary beam, lateral resolutions of about 50 nm have been achieved (de Chambost et al., 1993; Cameca, 2003).

However, in spite of the high mass resolution some particles sputtered from the sample have a mass that is almost identical to the mass of the trace element of interest. For example: When wanting to analyse $^{56}$Fe in a silicon wafer the interfering molecule $^{28}$Si$_2$ has almost the same mass ($M/\Delta M = 5600$). In addition the intensity of the molecular interference is orders of magnitude higher than that of the trace element. Even with a mass spectrometer with a high mass resolution it is difficult to separate this interference from the iron isotope.

1.1.2 AMS

Accelerator Mass Spectrometry is a routine method to detect extremely small amounts of long lived radioisotopes such as $^{10}$Be, $^{14}$C, $^{26}$Al, $^{36}$Cl, $^{129}$I, and others (Wölfli, 1987) in samples of a few hundred microgram. For example radiocarbon isotopic ratios of $10^{-14}$ can be measured to a precision of ~1%. This is only possible with an efficient
suppression of molecular and isobaric interferences, which is done by acceleration of negative secondary ions with a tandem accelerator after a first mass analysis has been performed. In the so-called stripper medium (Ar gas or a carbon foil) located at the high-voltage terminal of the accelerator, electrons are stripped off the ions changing their charge state from negative to positive. All molecules in charge states higher than 2+ are unstable and disintegrate (Weathers et al., 1991). If the trace element is analysed in a charge state higher than 2+ then the atomic fragments of the interfering molecules are separated from the beam in a second mass filter following the accelerator. In addition, the higher energy gained by the acceleration of the ions can be exploited to suppress isobaric interferences in an appropriate detection system (gas ionisation chamber, TOF, gas-filled magnet, etc.). Another advantage of the higher beam energy is that cross sections of scattering processes off residual gas atoms, which can cause a background in the detector, are smaller.

In spite of the enormous suppression of interferences, AMS is not suitable for the analysis of stable trace elements. When analysing radioisotopes of low abundance, contamination resulting from the analysing instrument itself is usually not a problem. This is not the case when analysing stable trace elements where a lot more possibilities of contamination of the sample are possible. Potential sources of contamination are impurities in the primary beam, the quality of the residual gas in the system, and sputtering of electrodes that are exposed to the ion beam. The use of a dedicated ion source is therefore unavoidable in order to perform stable trace element analysis with AMS.

1.2 History of Accelerator SIMS

The use of AMS technology to analyse stable trace elements, i.e. the principles of Accelerator SIMS, was suggested by K. Purser as early as 1977 (Purser, 1977; Purser et al., 1979). In the early eighties first measurements of platinum, iridium and osmium in minerals with an ion source modified for Accelerator SIMS were performed at the University of Toronto. Individual mineral grains were analysed with a caesium beam with a spot size of several hundred micrometers (Rucklidge et al., 1982). However, it was in the light of the rapid development of semiconductor technology that the development of Accelerator SIMS came to life.

In the mid eighties, first test measurements of trace elements in semiconductors were performed in collaboration between Texas Instruments and the University of Arizona. The resulting detection limits were about two orders of magnitude better than the best
detection limits of SIMS at the time (Ender, 1997a+d). Following this, a new Accelerator SIMS system was built specifically for the analysis of semiconductors at the University of Northern Texas, also in collaboration with Texas Instruments (Anthony et al., 1990; McDaniel et al., 1995).

In the early nineties, the American Semiconductor Industry Association indicated the need for more sensitive analytical devices to detect impurities in ultra pure materials and proposed Accelerator SIMS as a possible method (Semiconductor Industry Association, 1994). In the following years more dedicated systems were built worldwide: A new dedicated ion source for Accelerator SIMS was added to the AMS facility in Munich (Massonet, 1998) and a new AMS facility with a micro beam source with a high lateral resolution intended for geological applications was built in Sydney (Sie et al., 1997a+b).

In more recent years, besides the work presented in this thesis, Accelerator SIMS has been applied to the measurement of Os isotope ratios in molybdenite (Sie et al., 2002) and the measurement of tritium depth profiles in walls of fusion reactors (Stan-Sion et al., 2002).

In 1992 a diploma thesis evaluated the potential of stable trace element analysis in semiconductors at the PSI/ETH AMS facility in Zurich (Nebiker, 1992). This led to a doctor thesis (1993–1997) during which the AMS facility was extended with a commercial SIMS source combined with a specially designed sputter chamber. The resulting apparatus was tested on trace element analysis in silicon wafers (Ender, 1997a). The detection limits of various trace elements in silicon were the worlds best, and for some elements, as much as two orders of magnitude better than the best SIMS detection limits at the time. This apparatus was the one used for the experiments presented in this thesis.

Apart from these first developments of Accelerator SIMS, work done at the University of Oxford should be mentioned as well. There, a liquid metal ion source was used to look at the lateral distribution of $^{14}$C in $^{14}$C-labeled biological tissue (Freeman et al., 1994; Jiang et al., 1997). The lateral resolution of the resulting $^{14}$C images was ~1 µm.

1.3 Outline of the Thesis

With the PSI/ETH Accelerator SIMS facility up and running and tested on trace element analysis in silicon wafers, the aim of this thesis is to demonstrate that Accelerator SIMS can also be used for applications in environmental sciences, and
that it has unique features making measurements possible that no other analytical
technique can perform. These unique features, quality, and limits of Accelerator SIMS
measurements will be evaluated by applying the method to two applications out of
environmental sciences and by comparing the results to measurements previously
performed with other analytical techniques. In a final discussion of the potential and
future prospects of Accelerator SIMS, the resulting figures of merit will be compared
with those of other analytical techniques. This leads to the following structure of the
thesis:

In chapter 2 the PSI/ETH Accelerator SIMS facility will be introduced and the
measurements of trace elements in silicon wafers, performed before work towards this
thesis started, will be summarised.

Chapter 3 will give an introduction to parameters influencing an Accelerator SIMS
measurement. In particular, the secondary ion yields of platinum group elements,
gold, and silver (for simplicity abbreviated with PGE) from a silicon dioxide matrix
will be investigated. When confined to analysing negative secondary ions this is of
interest because oxygen is known to enhance the formation of positive secondary ions
in the sputter process, and possibly reduces the negative ion yield as a result. Depth
profiles of implantations of PGE into a silicon dioxide matrix have been measured and
the resulting sensitivities and detection limits will be given.

The procedures used to tune the facility and to measure electrically insulating samples
will also be presented in chapter 3. The PSI/ETH AMS facility in Zurich routinely
analyses radioisotopes only up to a mass of 129 amu. Therefore, when work towards
this thesis commenced, reliable and reproducible procedures to tune the AMS facility
to trace elements of all masses and especially of mass of ~200 amu had to be
developed. Since in most cases environmental samples are electrically non-
conducting, a way to analyse such samples had to be found as well. Technical
improvement of the apparatus and its performance along the way goes without saying.

In chapter 4 the first application will be discussed. It is the in-situ measurement of
iridium concentrations in sedimentary layers around the Cretaceous-Tertiary transition
(KT-boundary). Neutron activation analysis (NAA) revealed that the concentration of
iridium is abnormally high (~56 ng/g) in the transition horizon compared to the
neighbouring sedimentary layers of the Tertiary and the Cretaceous (~0.4 ng/g)
(Pillmore et al., 1987). With Accelerator SIMS it was possible to reproduce the NAA
results, but with a lateral resolution orders of magnitude higher (~100 µm). Presently,
no other technique is capable of performing bulk concentration analysis with such low
trace element concentrations and with such a high lateral resolution. In 1980, Alvarez
proposed that the iridium anomaly was caused by a meteorite impact (Alvarez et al., 1980), but the debate on the origin of the anomalies at the KT-boundary is still ongoing. Due to its capability to perform trace element analysis with a higher lateral resolution, Accelerator SIMS is therefore a tool capable of analysing this problem in greater depth.

The second application, which will be presented in chapter 5, is the direct measurement of natural \(^{10}\text{Be}/^{9}\text{Be}\) ratios in samples from ferromanganese crusts (carrier-free \(^{10}\text{Be}\) AMS). The instrumental challenge of this application is the reproducible measurement of isotopic ratios in the \(10^{10}\) range in small samples of only 100 ng in size and to a precision of \(\sim\)10%. The natural \(^{10}\text{Be}/^{9}\text{Be}\) ratio as a function of depth in a ferromanganese crust gives important information on the growth rate of the crust and is used to date oceanographic events manifested by the concentrations of other radiogenic isotopes. So far, this information has been gained with either the direct measurement of the natural \(^{10}\text{Be}/^{9}\text{Be}\) ratio with a SIMS method (Belshaw et al., 1995) or with separate measurements of the absolute \(^{10}\text{Be}\) and \(^{9}\text{Be}\) concentrations with AMS and ICP-MS respectively. It will be shown that the Accelerator SIMS results not only reproduce previous measurements very nicely, but that the method is also more sensitive and measures to a higher precision than the already existing methods. This means that time scales in ferromanganese crusts can be determined with a higher precision further into the past.

In chapter 6, the potential of Accelerator SIMS as a method will be compared with other analytical methods. Especially, a comparison to state-of-the-art SIMS and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) will be made. These techniques are widely regarded as the best analytical techniques available today. Advantages and disadvantages of all methods will be summarised. The final discussion will also be held in the light of feasible future developments. Especially, the recent development of small AMS systems (Suter et al., 2000) with high transmissions of heavy elements such as uranium, plutonium and thorium (> 15% for \(\text{Th}^{3+}\)) at terminal voltages of less than 500 kV give reason to assume that Accelerator SIMS technology can be transferred to small AMS systems as well.

And finally, Chapter 7 will briefly summarise the conclusions drawn from this thesis, the main achievements of the thesis, and prospects for the future of Accelerator SIMS.
Chapter 2 Experimental Setup

In this chapter, the general setup of an Accelerator SIMS experiment together with some figures of merit of the apparatus will be presented, even though the details of the experimental setup vary for each of the applications presented in this thesis. But apart from the different samples, the differences between the applications lie mainly in the detection system. Special experimental configurations concerning individual experiments will be introduced in the corresponding chapters.

The tandem accelerator facility in Zurich allows for a wide range of applications in ion beam analysis. The setup used for Accelerator SIMS is almost identical to the one used for AMS measurements. The main difference is that Accelerator SIMS analyses stable isotopes. Contamination coming from the surroundings of the sample in the ion source is therefore a greater problem. The measurements presented in this work were all performed with an ion source specially designed to keep such contamination as low as possible.

2.1 Summary of the Accelerator SIMS Facility

Figure 1 shows the elements of the PSI/ETH tandem accelerator facility that are relevant for Accelerator SIMS. The ion source was attached to the facility in a way that the low-energy spectrometer with the highest mass resolution is used \((m/\Delta m = 330)\). This guarantees a mass resolution of better than one atomic mass unit over the entire mass range of the periodic table. The individual components of the Accelerator SIMS setup are:

- Sputter chamber with the focussed caesium gun
- Secondary ion extraction with small, retractable electrostatic deflector that bends the beam onto the main beam line of the AMS facility
- Low-energy mass spectrometer consisting of an electrostatic and magnetic deflector each with a deflection angle of \(90^\circ\) (heavy ion injector)
- 6MV EN Van de Graaff tandem accelerator
- High-energy mass spectrometer with a \(15^\circ\) electrostatic and a \(90^\circ\) magnetic deflection
Detection chamber with various detector types such as a gas ionisation detector, Faraday cups, a gas filled magnet or time-of-flight spectrometers

2.2 The Caesium Source

The first step of an analysis with Accelerator SIMS is to produce negatively charged ions of the sample material itself. Usually, this is done by bombarding the sample with a caesium ion beam. The caesium ions produce a cascade of collisions between the atoms of the sample that cause particles to be ejected out of the sample. This process is called the sputter process. A certain fraction of the sputtered particles are negatively charged. It is these secondary ions that are extracted, formed to an ion beam, and analysed with the rest of the system.

However, when analysing stable isotopes the primary ion beam is a first source of contamination. Impurities in the caesium are mixed into the sample during sputtering and will influence the detection limits of the corresponding elements. Therefore, demands on the purity of the primary ion beam are high.

The caesium gun used for the measurements in this thesis is a Cs431 from Atomika, Munich. It is an ion source usually used on the Atomika quadrupole SIMS instruments (Wittmaack, 1992). A cross section through the caesium gun is shown in figure 2. Caesium vapour from a heated reservoir is ionised due to surface ionisation on a hot tungsten fritt and an immersion lens accelerates and focuses the ions onto an
intermediate point. The beam energy of the caesium gun used for all measurements was 10 keV. A Wien filter with permanent magnets is used to separate beam components of different mass. The beam is then sent through one of a series of selectable apertures mounted on a wheel and with radii between 1 mm and 10 µm. The objective lens following the aperture focuses the beam onto the sample with a ratio of about 1:10 so that the beam spot size on the sample - defined as the diameter of the one sigma range of the current distribution - is between 110 µm and 3 µm. These focussing optics remained unchanged for all measurements, so, for a given aperture size the beam spot size will stay roughly the same, whereas the caesium current can vary due to variations in the performance of the tungsten fritt. Table 1 shows a summary of typical values of Cs current and beam spot size from the corresponding aperture.

Finally, in order to prevent neutral components in the beam from reaching the sample the beam is subjected to an electrostatic deflection of 1°. Another two pairs of deflection plates have been mounted just before the objective lens allowing one to scan the caesium beam over the sample surface by applying triangular voltage signals to the plates. The area is scanned with a period of 1 Hz and its size can be continuously varied from the maximal area possible down to a stationary beam. At a beam energy of 10 keV the largest area over which the scanning unit is capable of scanning is approximately 1 mm².

![Fig. 2: Cross section through the Atomika CS431 caesium gun.](image)

The current of the primary ion beam is stable to within 5 % over a period of 10 hours. The maximal achievable Cs⁺ current lies around 600 nA. The Cs current depends mainly on the size of the chosen aperture.
<table>
<thead>
<tr>
<th>Aperture $\varnothing$</th>
<th>Current</th>
<th>Beam spot size</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000 $\mu$m</td>
<td>455 nA</td>
<td>110 $\mu$m</td>
</tr>
<tr>
<td>500 $\mu$m</td>
<td>208 nA</td>
<td>60 $\mu$m</td>
</tr>
<tr>
<td>400 $\mu$m</td>
<td>133 nA</td>
<td>50 $\mu$m</td>
</tr>
<tr>
<td>300 $\mu$m</td>
<td>98 nA</td>
<td>40 $\mu$m</td>
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<td>100 $\mu$m</td>
<td>13 nA</td>
<td>12 $\mu$m</td>
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<td>50 $\mu$m</td>
<td>3.3 nA</td>
<td>8 $\mu$m</td>
</tr>
<tr>
<td>10 $\mu$m</td>
<td>0.2 nA</td>
<td>2.5 $\mu$m</td>
</tr>
</tbody>
</table>

Table 1: Typical values of currents and beam spot sizes of the caesium beam for different aperture sizes at a beam energy of 10 keV.

2.3 The Sputter Chamber

The most important aspect while designing the sputter chamber was the suppression of contamination originating from the surroundings of the sample during the sputter process. To achieve this the geometry of the chamber was chosen as open as possible allowing the secondary particles to travel as far away from the sample as possible before colliding with the chamber wall and sputtering particles that could return to the sample as contamination. The design of the chamber together with the nose of the caesium gun and the secondary ion extraction is shown in figure 3. The wall of the chamber is at ground potential, so the negative secondary ions have to be accelerated to ground potential in order to analyse them with the low-energy mass spectrometer and to inject them into the tandem accelerator. This is done by putting the sample holder at a potential of $-30$ kV. The sample holder is mounted on an insulator capable of holding a voltage difference of 40 kV. The insulator, in its turn, is mounted on an xy-stage consisting of two in-vacuum stepping motors of Princeton Research Instruments. The stage allows a movement of 25 mm in steps of 3.3 $\mu$m in each dimension and the position of the sample is monitored with a video camera through a window in the wall of the vacuum chamber. On its largest magnification the camera looks at an area of $4 \times 6$ mm$^2$ on the sample surface. This area is small enough to accurately position a structured sample. In order to minimise cross contamination, samples are brought into the chamber one by one through a vacuum lock. They are mounted in a holder that takes wafer-like objects with a maximal thickness of 4 mm
and side lengths of 28 mm. The design of the holder is such that the surfaces of samples with different thickness are held at the same well-defined place.

Since the sputter processes of not-extracted ions in the vicinity of the sample and the chamber walls are the main source of contamination, the sample holder, the extraction lens, and the caesium gun nose are coated with a 20 µm thick layer of pure gold (99.99%). Gold was chosen because of its availability in a very pure form and because the coating of steel is technically easy. In addition, the geometry of the lenses are such that as little area as possible is visible from the sample and therefore exposed to the unwanted bombardment of secondary ions.

![Diagram](image)

**Fig. 3:** Design of the Accelerator SIMS sputter chamber.

To keep the effects of residual gas in the chamber as low as possible the chamber is built with UHV-technology. It is pumped with a 450 l/s turbo pump which achieves a base vacuum of $3 \times 10^{-10}$ mbar. During measurement, the valve to the main beam line is opened and together with the changing of samples and the operation of the caesium gun the pressure in the chamber rises to $10^{-8}$ mbar. The caesium gun itself is pumped with a 50 l/s getter pump.

As can be seen in figure 3 the primary caesium beam has an angle of incidence of 30° relative to the normal of the sample surface. Symmetrically, the secondary ions are extracted with a three-step extraction lens also at an angle of 30°. This geometry was convenient when attaching the ion source to the rest of the tandem facility, and since
the focal point of the caesium gun is 20 mm in front of the end of its nose, the geometry also allows for an optimal exploit of the physical properties of the sputter process. The angle of incidence of 30° also favours a higher depth resolution when measuring depth profiles. A detailed discussion of the ion optics of the sputter chamber can be found in (Ender, 1997a).

During operation the entire caesium gun with all its control electronics is put on a potential of $-30.8 \text{ kV}$. The nose of the caesium gun is therefore at a potential of $-0.8 \text{ kV}$ relative to the sample stage and the Cs beam is decelerated to an energy of 9.2 keV before hitting the sample. This prevents negative secondary ions from being accelerated back onto the nose of the caesium gun and sputtering contaminating particles. In addition the first electrode of the extraction lens is typically set to a potential of $-27.2 \text{ kV}$. The large potential difference to the sample ensures that as many negative ions as possible are extracted into the beam line. The second extraction electrode is typically set to a potential of $-16.6 \text{ kV}$ that, together with a quadrupole lens and two electrostatic steerer units, guides the secondary ion beam to the object slits of the small electrostatic deflector.

2.4 The Low-Energy Mass Spectrometer

The small, spherical, electrostatic deflector with a trajectory radius of 12 cm bends the beam by 90° onto the beam line of the so-called heavy ion injector shown in figure 4. It creates an image of the object slits in the object plane of the second, larger electrostatic deflection unit. This unit also deflects the beam by an angle of 90°, but with a trajectory radius of 75 cm. Its stigmatic image lies in the objet plane of the 90°, stigmatic injection magnet with a radius of 60 cm. The mass resolution of the resulting mass spectrometer is $m/\Delta m = 330$ and high enough to separate every mass in the periodic system (Synal et al., 1991).

Faraday cups can be inserted into the beam line at the focal points of the larger electrostatic and magnetic deflection units. Even though the beam intensities are usually three orders of magnitude smaller than in AMS measurements, the secondary ion currents of matrix elements are usually strong enough to be measured with in a Faraday cup. However, for the measurement of a conventional SIMS spectrum, weak ion currents can be measured by amplifying the secondary electrons produced by the ion beam in a cup with a channel plate electron multiplier. Using such a secondary electron multiplier the low-energy magnet can be tuned to every mass in the entire mass spectrum (Ender, 1997a; Maden, 1998).
2.5 The Accelerator and High-Energy Mass Spectrometer

After passing the heavy ion injector the negative ions are accelerated towards the terminal of the 6 MV EN tandem accelerator. If not mentioned otherwise, all measurements presented here were performed with a terminal voltage of 5.0 MV. At the terminal the ions pass through a so-called stripper. Due to collisions with the atoms of the stripper medium the ions lose a few electrons and become positively charged. In addition, molecules in charge states higher than 2+ become unstable and disintegrate. The strippers used were either a carbon foil, 3 µg/cm² thick, or differentially pumped argon gas (Niklaus, 1993; Niklaus et al., 1994). The positively charged ions are then accelerated away from the terminal back to ground potential giving them a total energy \( E = U_T (m_{HE}/m_{LE} + q) \cdot e \) where \( U_T \) is the terminal voltage, \( m_{LE} \) the mass of the ion on the low-energy side of the accelerator, \( m_{HE} \) the mass of the ion on the high-energy side after a possible molecular split-up, and \( q \) the charge state of the ion after passing through the stripper.

At the exit of the tandem accelerator a second, retractable channel plate electron multiplier has been installed. It is identical to the one on the low-energy side of the tandem and its purpose is to aid the tuning of the low-energy magnet during measurements. The electron multiplier was installed during work towards this thesis.
and has made tuning of the facility for analysis of trace elements in the entire mass spectrum possible. One could be tempted to use it to improve the resolution of the low-energy mass spectrometer when recording conventional SIMS spectra. Due to its greater distance from the low-energy magnet the mass resolution is indeed improved. However, there has to be a voltage applied to the terminal of the accelerator in order to focus the ion beam onto the Faraday cup. Since molecules are split into their compounds at the terminal and produce different amounts of secondary particles in the accelerator, the composition of the ion beams of two neighbouring masses can be different, and the ratio of the measured currents is not equal to the ratio of the corresponding particle intensities.

![Fig. 5: High-energy side of the PSI/ETH tandem facility.](image)

After the tandem accelerator, the ion beam is subjected to an electrostatic deflection of 15° with a radius of 5.8 m as seen in figure 5. The resolution of this E/q-filter is 1-2 % depending on the width of the aperture following the deflector. A magnetic deflection of 90° with a radius of 1.1 m performs a final p/q-analysis before the ions reach the detector. For a given charge state q the width of the detector window used in a typical experiment gives a resolution \( \Delta p/p \) of 0.4 %.

Apart from the retractable Faraday cup after the accelerator, a retractable cup can be inserted into the beam line after the electrostatic deflector and another cup is installed after the magnetic analyser.

### 2.6 Particle Identification

For bulk concentration analysis of a trace element only two kinds of detectors are necessary. The current of the matrix elements can be measured in a Faraday cup. With the existing setup currents of a few \( 10^{-12} \, \text{A} \) can be measured (1 pA in charge state 1+ corresponds to a particle counting rate of 6 MHz). Particle rates of less than 2 kHz are
measured with a gas ionisation detector. For the experiments presented here, there was no need to close the gap between the two ranges since the concentrations of the measured trace elements are very low.

However, all particles with the same m/q ratio will pass the high-energy mass spectrometer on the same trajectory. This means that the detector has to be able to resolve interferences from the trace isotope of interest. These interferences can be isobars in the same charge state and molecular fragments in different charge states as the trace isotope. The gas ionisation detector used is filled with a mixture out of argon (90%) and methane (10%). The entrance window is a 100 µg/cm² thick mylar foil. The complete design of the detector is shown in figure 6. Ions arriving at the detector penetrate the mylar entrance window and are stopped in the gas of the detector. The gas is ionised along the track of the ions creating charged particles that drift along an electric field perpendicular to the trajectory of the ions until they are collected on its electrodes. The first electrode is 50 mm and second one is 190 mm long. Charge sensitive amplifiers then send the signal on to the data acquisition system.

The electronic stopping power, $dE/dx$, of the incoming ion has a dependency on the nuclear charge of the projectile, $Z$, which can be written as the square of the mean charge of the projectile, $<q(Z)>$, times the stopping power of a proton at the same velocity, $v$. (Betz, 1972 and 1983)

$$\frac{dE}{dx}(v) = <q(Z)>^2 \left( \frac{dE}{dx}(v) \right)_p$$  \hspace{1cm} (2.1)
The amount of detector gas ionised depends on the amount of energy lost by the projectile along a given path length. The charge collected on the electrodes is then proportional to the energy lost by the ion in form of ionisation along the corresponding path lengths.

$$\Delta E = \int_0^l \frac{dE}{dx} \, dx$$

$$E_R = \int_l^{l_0} \frac{dE}{dx} \, dx$$

(2.2)

where $\Delta E$ is the energy signal coming from the first electrode and $E_R$ the residual energy signal from the second electrode. Due to the dependency of the stopping power on the nuclear charge, $\Delta E$ and $E_R$ are also dependent on the nuclear charge of the projectile and a separation of isobaric interferences is possible. The separation of molecular fragments in lower charge states is also very efficient with this detection method due to the lower total energy of these ions. Figure 7 demonstrates the separation of isobars on the example of $^{54}\text{Fe}$ and $^{54}\text{Cr}$ in a histogram of $\Delta E$ versus $E_R$. Gates can be set around a peak in order to accept only the counts of the desired isotope.

**Fig. 7:** Histogram of the energy signals of 40 MeV $^{54}\text{Fe}$ and $^{54}\text{Cr}$ from the gas ionisation detector. The peaks are clearly separated.

Further advantages of gas ionisation counters are that they have virtually no background counting rate and a response probability of 1. In addition, a certain amount of energy that is lost by the projectile via other channels than electronic
stopping is also converted into ionisation of the counter gas. In particular, a large fraction of the projectile energy is transferred to recoiling gas atoms at energies below 0.1 MeV/amu. The energy lost by the projectile in such scattering processes does not ionise the counter gas directly. However, the recoiling gas atom ionises the detector gas during its stopping process and a certain amount of its energy is converted into ionisation energy. When analysing low-energetic beams (< 2 MeV) and heavy trace elements, this property gives gas ionisation detectors a better energy resolution and smaller pulse-height defects in comparison to other detector types, such as semiconductor detectors.

2.7 Data Acquisition

During the construction of the Accelerator SIMS setup the data acquisition system of the AMS facility was modified to accommodate for the needs of Accelerator SIMS (Synal et al., 1997; Ender et al., 1997d). The main difference is that for every trigger event not only the amplitude of the $\Delta E$ and $E_R$ signals are read by the acquisition system, but also the momentary values of two triangular voltage signals that are proportional to the lateral deflection of the Cs beam by its scanning unit. Therefore, not only information on the energy of the particles is acquired, but also information on where on the sample surface the particle originated from.

In figure 8 one can see the most important spectra used during a measurement. These are the multichannel spectra of $\Delta E$ and $E_R$ and the two 2-dimensional histograms in which on one hand the intensity distribution of $\Delta E$ and $E_R$ are plotted and on the other hand the distribution of the trace isotope on the sample surface. The spectra are recorded in a way that at first all events are plotted in the $\Delta E$-spectrum. In the $E_R$-spectrum, however, only those events will be plotted that lie in a so-called pre-gate in the $\Delta E$-spectrum. And further, only those events will be plotted in the 2-dimensional $\Delta E/E_R$-histogram which lie in a second pre-gate in the $E_R$-spectrum. Last of all, only those events lying in a gated area of the $\Delta E/E_R$-plane will be taken into the histogram with the xy-distribution. This procedure reduces the number of interfering particles step by step.

During a measurement the number of counts in the gates is measured over an adjustable length of time, the so-called cycle time, before they are written into the database. Depending on the experiment the cycle time is chosen between 10 and 60 seconds. After a cycle the measurement is paused for a couple of seconds to write the acquired data to the database and to start a new cycle. One parameter written into the
database is the effective measuring time of the cycle. This takes instabilities of the terminal voltage, dead time of the detector, and the low-energy bouncing system into account. The real counting rate in the detector is therefore the number of acquired counts per effective measuring time.

![Histograms](image)

**Fig. 8:** To illustrate the data acquisition system the two multi-channel spectra of the $\Delta E$- and $E_R$-signals are shown (top row) together with the two 2-dimensional histograms, the $\Delta E/E_R$-spectrum and the lateral distribution of the events on the sample surface. Only events lying within the rectangular gate of the $\Delta E/E_R$-spectrum are plotted in the $xy$-histogram.

There is also the possibility to gate an area of the $xy$-plane. This is useful when measuring depth profiles, which are recorded by regarding the counting rate of the detector as a function of time and then normalising to the depth of the sputtered crater. For all depth profiles presented in this work the central 15% of the $xy$-plane was gated. This fraction was chosen based on the fraction of a sputter area of 500 x 500 $\mu$m$^2$ that is left when the size of the area is reduced by two beam diameters (two times ~110 $\mu$m) in both dimensions. Of course, this reduces the analysed volume of the sample by a factor of 7 but also increases the depth resolution, because the sensitive area is confined to the central, plane part of the sputter crater and concentration differences on the crater wall are ignored.

### 2.8 Figures of Merit of Accelerator SIMS

Before the work towards this thesis began, the Accelerator SIMS setup had been tested on the detection of trace elements in silicon wafers. Bulk detection limits of various trace elements, depth resolution, and lateral resolution had been determined...
and found to be the best in the world. This section will give a short summary of the most important results. It should be kept in mind that the apparatus has been improved over the last four years and with it the detection limits have been reduced. The values presented here are therefore to be regarded as upper limits. It is estimated that the figures have been improved by more than one order of magnitude mainly due to higher transmission through the mass spectrometers and the tandem. This was mainly achieved by using a different ion optical configuration to inject the ion beam into the tandem accelerator. In addition, the designs of the extraction lens and the small electrostatic deflection unit were improved to achieve better stability of the secondary ion currents.

For the determination of the detection limits of the elements B, Al, P, Fe, Ni, Cu, As and Sb it was possible to use silicon wafers with a known concentration of the trace elements as standards. The measured counting rates were then compared to the counting rate coming off a corresponding blank and the ratio of the two give the detection limit. This procedure has also been described in (Maden, 1998). Table 2 summarises the detection limits.

<table>
<thead>
<tr>
<th>Trace Element</th>
<th>Detection limit [at./Si]</th>
<th>Detection limit [cm$^{-3}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>$1 \cdot 10^{-10}$</td>
<td>$7 \cdot 10^{12}$</td>
</tr>
<tr>
<td>Al</td>
<td>$7 \cdot 10^{-11}$</td>
<td>$4 \cdot 10^{12}$</td>
</tr>
<tr>
<td>P</td>
<td>$3 \cdot 10^{-10}$</td>
<td>$2 \cdot 10^{13}$</td>
</tr>
<tr>
<td>Fe</td>
<td>$1 \cdot 10^{-9}$</td>
<td>$1 \cdot 10^{14}$</td>
</tr>
<tr>
<td>Cu</td>
<td>$1 \cdot 10^{-9}$</td>
<td>$1 \cdot 10^{14}$</td>
</tr>
<tr>
<td>As</td>
<td>$9 \cdot 10^{-12}$</td>
<td>$5 \cdot 10^{11}$</td>
</tr>
<tr>
<td>Sb</td>
<td>$2 \cdot 10^{-10}$</td>
<td>$1 \cdot 10^{13}$</td>
</tr>
</tbody>
</table>

Table 2: Bulk detection limits of trace elements in a silicon matrix of the Zurich Accelerator SIMS facility.

The capability of the facility with respect to depth profiling is shown in figure 9. It shows an example of a depth profile of a 300 nm thick Al doped layer on a pure silicon substrate. The top picture is a light microscope image of the sputter crater together with a profile of the crater measured with a Dectac profilometer (middle). The bottom picture shows the intensity of the Al signal as a function of depth into the sample. The layer thickness in which the Al intensity drops from 84% down to 16% is 23 nm, thus giving the depth resolution.
Chapter 2  Experimental Setup

Fig. 9: Light microscope picture of a sputter crater (top) and the corresponding profile measured with a Dectac profilometer (middle). The roughness of the bottom of the crater is 5 nm. The bottom picture shows the relative intensity of sputtered Al as a function of depth into the sample.

A nice demonstration of the imaging properties of the facility is shown in figure 10. An area (500 µm x 500 µm) of an integrated circuit chip (shown as an optical micrograph in the right hand picture) was analysed with respect to its lateral phosphorous concentration. The resulting image is shown in the top left hand image. The P concentration is grey scale coded with white being regions with a high P concentration and black the regions with low concentration. The bottom left hand picture shows the concentration distribution along a line scan on the same area (dashed line in the top left hand picture). The lateral resolution of the image is 4 µm.
Fig. 10: Distribution of phosphorous on an area of an integrated circuit chip (500 µm x 500 µm). The P concentration varies between $10^{14}$ and $10^{17}$ at./cm$^3$ and the lateral resolution of the image is 4 µm.
Chapter 3  
Accelerator SIMS Analysis of a 
SiO$_2$ Matrix

Accelerator SIMS measurements are subjected to the same physical constraints as conventional SIMS measurements are. Both methods primarily rely on an optimal yield of secondary ions from a sample. Owing to the fact that positive ions are not accelerated to the terminal of the tandem accelerator, Accelerator SIMS is additionally confined to the analysis of negative secondary ions. In addition, for in-situ analysis no chemical preparation of the sample precedes the measurement. In cases, this can make it more difficult to find a suitable reference material to use as a standard sample. This becomes more apparent when noting that the size of a sample is a lot larger than the beam spot of the Cs beam. If the distributions of the matrix elements are homogeneous throughout the sample an adequate standard can usually be found. In a sample with a non-uniform matrix composition, however, the secondary ion yield of a given trace element will vary with the lateral position of the Cs beam even if the concentration of the element is homogeneous throughout the sample.

For this reason it is vital to study the sputter properties of a sample matrix when assessing the feasibility of applying Accelerator SIMS to an application in a field of research. This chapter will demonstrate the importance of this issue on the example of the analysis of platinum group elements, gold and silver, which for simplicity will be referred to as PGE in the following, in silicon and silicon dioxide matrices, a topic of great interest for the application of Accelerator SIMS in the field of geology. The results of the discussion will then be applied to a practical problem in chapter 4 where Accelerator SIMS measurements of PGE in sedimentary layers at the Cretaceous-Tertiary transition (KT-boundary) are presented.

3.1 Formalisms

First, however, a few terms should be introduced. This section makes no claim for completeness and will only introduce terms necessary to understand the procedure of an Accelerator SIMS analysis and the following discussion. A more complete treatise can be found in (Benninghoven et al., 1989).
3.1.1 Sputter yields

The physical details of the sputter process have not been understood in detail yet. It is clear that the incident primary ion produces a cascade of collisions between the atoms of the sample resulting in particles being ejected out of the sample. Several models and simulations of the sputter process exist (Sigmund et al., 1974; Ziegler et al., 1985), but often the direct measurement remains the securest source of information.

For the purpose of Accelerator SIMS, however, it is not necessary to know the details of the sputter process. The formalisms used regard the sputter process as a black box. All one needs to know is how many target atoms are sputtered on average per incoming primary ion and the probability of formation of a secondary ion.

The amount of sample material used in a measurement is determined by the total sputtering yield, \( Y_{\text{tot}} \). It is defined as the average number of sample atoms ejected out of the sample per incoming primary ion. For example, the total sputter yield of pure silicon resulting from 10 keV Cs\(^+\) ions incident at 30° from the sample normal has been measured to be \( Y_{\text{tot}} = 2.4 \) (sputtered Si atoms per Cs ion) (Ender, 1997a).

Usually the composition of the sample matrix is not monatomic, but consists of several elements (A, B, C, …) with a molecular stoichiometry \((A_iB_jC_k)\) defining the relative concentrations of the matrix elements. In this case, the total sputter yield is given in units of number of sputtered molecules \(A_iB_jC_k\) per incident primary ion.

The types of secondary particles sputtered from the sample are plentiful. Apart from secondary electrons, they can be either single atoms or molecular particles of all possible compositions and in different charge states. If \( Y_q(M) \) is the sputter yield of molecule \( M \) in charge state \( q \), i.e. the average number of molecules in charge state \( q \) sputtered per incoming primary ion, then the total sputter yield of a specific element \( A \), \( Y_{\text{tot}}(A) \), is given by summing over all charge states \( q \) and molecule types \( M_l = A_iB_jC_k \)

\[
Y_{\text{tot}}(A) = \sum_q \sum_l i Y_q(M_l) = \sum_q \sum_{i,j,k} i Y_q(A_iB_jC_k)
\]

(3.1)

The total sputter yield of the sample is the sum of the total specific sputter yields of all the elements in the matrix.

\[
Y_{\text{tot}} = Y_{\text{tot}}(A) + Y_{\text{tot}}(B) + Y_{\text{tot}}(C) = \frac{Y_{\text{tot}}(A)}{\alpha} = \frac{Y_{\text{tot}}(B)}{\beta} = \frac{Y_{\text{tot}}(C)}{\gamma}
\]

(3.2)

where \( \alpha, \beta \) and \( \gamma \) are such that the matrix stoichiometry can be written as \( A_\alpha B_\beta C_\gamma \) with \( \alpha + \beta + \gamma = 1 \). 

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Chapter 3 Accelerator SIMS Analysis of a SiO\(_2\) Matrix

28
The same formalism can be used for elements consisting of more than one isotope. In this case the sum in equation 3.1 also runs over the different isotopes of element A as well. Thus

\[ Y_{tot}(A) = \sum_{N} Y_{tot}(A^N) = \frac{Y_{tot}(A^N)}{r(A^N)} \]  

(3.3)

where \( A^N \) symbolises an individual isotope of element A, and \( r(A^N) \) is the corresponding isotopic abundance.

Here it has been assumed that the total sputter yields of all elements in the matrix are linearly correlated to their relative concentrations, so-called stoichiometric sputtering. Therefore there is no enrichment of an element or an isotope during the sputter process. By general reasons every equilibrium sputter process is stoichiometric. This also means that the fractional concentration, \( c(A) \), of element A can also be written as

\[ c(A) = \frac{n(A)}{n_{tot}} = \frac{Y_{tot}(A)}{Y_{tot}} \]  

(3.4)

With \( n(A) \) being the volume density of element A in the sample [atoms/cm\(^3\)] and \( n_{tot} \) the total number of target atoms per cm\(^3\).

### 3.1.2 Secondary ion currents

The total sputter yield of a sample matrix is useful to estimate the total amount of sample material required to perform an analysis for a certain time interval. The quantities measured during a measurement, however, are currents of secondary ions. The probability of the creation of a secondary ion in the sputter process therefore influences the characteristics of a measurement. Occasionally it is of advantage to analyse a sputtered molecule \( P \) instead of the atomic ion \( A \) itself, because not all elements form stable negative ions and also only a few per cent of the sputtered particles leave the sample as ions. Over 90\% of the particles are sputtered as neutrals. Therefore, if \( A \) is the element of interest for an analysis and \( P = A^N B^M C^L \) is a particle containing isotope \( N \) of element \( A \), then one can define the probability of ionisation, \( \alpha^q(P) \), of isotope \( A^N \) contained in particle \( P \) into a given charge state \( q \) as follows:

\[ \alpha^q(P) = \frac{Y^q(P)}{Y_{tot}(A)} \]  

(3.5)

After extracting ions of charge state \( q \) to a beam and passing them through a mass spectrometer the resulting current, \( I^q(P) \), can be described as
Chapter 3  Accelerator SIMS Analysis of a SiO₂ Matrix

\[ I^q(P) = I_p \cdot c(A) \cdot Y_{tot} \cdot \alpha^q(P) \cdot q \cdot T^q(P) \cdot \varepsilon(P) \]  \hspace{1cm} (3.6)

where \( I_p \) is the current of the primary beam, \( c(A) \) the fractional concentration of A, \( T^q(P) \) the transmission probability of P through the mass spectrometer, and \( \varepsilon(P) \) the efficiency of the detector.

Equation 3.6 is enough to calculate the secondary ion current for SIMS, that is, for an ion current that has passed through a single mass spectrometer. For Accelerator SIMS one could at most claim validity for atomic ions extracted from the sample. This is because the ion beam is additionally passed through the tandem accelerator and the high-energy spectrometer breaking up molecules in the stripper. Hence for Accelerator SIMS equation 3.6 becomes

\[ I^q(A^N) = I_p \cdot c(A) \cdot Y_{tot} \cdot \alpha^q(P) \cdot T_{LE}^q(P) \cdot \beta^q_E(A^N) \cdot q \cdot T_{HE}^q(A^N) \cdot \varepsilon(A^N) \]  \hspace{1cm} (3.7)

where the transmission \( T^q(P) \) has been substituted with the product of the transmission of the negatively charged particle P through the low-energy spectrometer, \( T_{LE}^q(P) \), the probability of the isotope N of element A populating charge state q after having passed the stripper at energy E, \( \beta^q_E(A^N) \), and the transmission through the high-energy spectrometer, \( T_{HE}^q(A^N) \).

This distinction between SIMS and Accelerator SIMS will not be made in the following. Since the secondary electrons follow the same trajectory as singly negative ions until they reach the first magnetic deflection, the first place in the beam line that a pure ion current can be measured is after the low-energy magnet. For the PSI/ETH Accelerator SIMS facility it is therefore advantageous to make the following definitions. The product \( \beta^q_E(A^N) \cdot T_{LE}^q(P) \cdot \varepsilon(A^N) \) is described as the transmission, \( T_E^q(A^N) \), of isotope A\(^N\) in charge state q and at energy E. Likewise the yield, \( N_{M}^q(P) \), of a specific secondary ion P from a sample is understood to be the product \( \alpha^q(P) \cdot T_{LE}^q(P) \), that is, the probability of an isotope A\(^N\) reaching the low-energy side of the accelerator as a negative ion P per sputtered atom of element A. As will be shown in section 3.1.4 the yield depends on the type of matrix M the ion is sputtered from. And finally, the product of the yield and the transmission is called the overall useful yield, \( U_{p,M}^q(E)(A^N) \). It describes the probability of detecting an isotope A\(^N\) in charge state q per sputtered atom A from the sample while analysing at energy E.

\[ U_{M}^{q,E}(A^N) = N_{M}^q(P) \cdot T_{E}^q(A^N) = \alpha^q(P) \cdot T_{LE}^q(P) \cdot \beta^q_E(A^N) \cdot T_{HE}^q(A^N) \cdot \varepsilon(A^N) \]  \hspace{1cm} (3.8)
3.1.3 Quantification formalisms

There are different formalisms used to make a quantification of the concentration of a trace element in a measurement. Two of them shall be presented briefly.

The first one uses so-called Relative Sensitivity Factors (RSF). This formalism relies on the availability of a standard sample with a known concentration of the trace element in order to determine the value of the RSF. Further, exactly identical analytical conditions are assumed for the measurement of the standard sample and for that of the unknown sample. And last of all, the concentrations of the trace element in the standard and the sample have to be so low that its secondary ion current is proportional to the absolute concentration of the trace element. This is the case, if the concentration is below ~1%. If these conditions are fulfilled, it is sufficient to measure the secondary ion current of one of the isotopes of trace element S and the ion current of one of isotopes of the matrix element A of the sample matrix \( M = A_i B_j C_k \) in order to obtain the concentration of the trace element in the sample:

\[
    n(S) = \frac{I_q^N(S^N)}{I_q^K(A^K)} \cdot RSF_M^{A^K}(S^N)
\]

Here \( n(S) \) is the concentration [atoms/cm\(^3\)] of the trace element S in the sample. \( I_q^N(S^N) \) is the measured secondary ion current of isotope N of the trace element S in charge state q, and \( I_q^K(A^K) \) is the measured ion current of isotope K of element A in charge state q’. The relative sensitivity factor, \( RSF_M^{A^K}(S^N) \), is also calculated from equation 3.9, but with the values gained from the measurement of the standard sample. It is clear from equation 3.9 that the use of a given RSF is limited to trace element analysis performed under exactly identical experimental conditions. In particular, this includes the isotope \( S^N \) of the analysed trace element, the matrix isotope \( A^K \), and the stoichiometry \( A_i B_j C_k \) of the sample as well.

Equation 3.9 is strikingly simple and concentration calibration for a measurement becomes an easy task. However, it is also clear that the RSF has the dimensions of a number density [atoms/cm\(^3\)]. This can be irritating in as much that the absolute value of the RSF is inversely proportional to the relative sensitivity of Accelerator SIMS analysis of different trace elements in a given matrix.

To overcome this problem the introduction of Scaled Sensitivity Factors (SSF) and Scaled Sensitivity Ratios (SSR) has been proposed (Wittmaack, 1995). Starting from equation 3.7 one can define a Scaled Sensitivity Factor for a specific matrix M and element S as follows
As can be seen from its units [(counts/s)/(nA \cdot \text{atoms/cm}^3)] the Scaled Sensitivity Factor describes the secondary ion current of an element S to be expected from matrix M per unit current of the primary beam and per unit concentration of the trace element S. Likewise a Scaled Sensitivity Factor, $SSF_M^A$, can be defined for a matrix element A as well. Taking the ratio of the two SSF defines the so-called Scaled Sensitivity Ratio, $SSR_{A,M}^S$

$$SSR_{A,M}^S \equiv \frac{SSF_M^S}{SSF_M^A} = \frac{N_M^-(P) \cdot T_E^q(S^N) \cdot \varepsilon(S^N) \cdot Y_{tot}}{N_A^-(A) \cdot T_E^q(A^K) \cdot \varepsilon(A^K)} = \frac{I^q(S^N) \cdot r(A^K) \cdot n(A)}{I^q(A^K) \cdot r(S^N) \cdot n(S)}$$ (3.11)

Just like for Relative Sensitivity Factors the Scaled Sensitivity Ratio has to be measured with the aid of a standard sample. Concentration calibration is now performed based on the following equation

$$\frac{n(S)}{n(A)} = \frac{I^q(S^N) \cdot r(A^K)}{I^q(A^K) \cdot r(S^N)} \cdot \frac{1}{SSR_{A,M}^S}$$ (3.12)

Comparing equation 3.12 with equation 3.9, it becomes clear that the SSR is basically an RSF with the dependence on the concentration of the matrix element A decoupled from it. In addition, the dependence on the isotopic ratio has been removed making the SSR a more instructive measure for planning an experiment, since it is the ratio of the overall useful yields of the two elements under consideration. Its absolute value is therefore directly proportional to the sensitivity of SIMS analyses of a trace element S in a given matrix M when using the element A as a reference. The currents can also be estimated with the Scaled Sensitivity Factors.

However, since a change in the matrix composition would cause an unpredictable change in the secondary ion yields, the SSF, and with them the SSR, would change imposing the same restriction as on the RSF: the Scaled Sensitivity Ratio is only valid for trace element analyses performed under exactly identical experimental conditions as the ones during the analysis of the corresponding standard sample, in particular, the same matrix composition.

### 3.1.4 Parameters influencing secondary ion yields

Both formalisms presented above require measuring a standard sample with a known concentration of the trace element before a concentration calibration can be made for an unknown sample. To date, these are the most reliable calibration methods. This is
due to the lack of a theoretical model capable of predicting the secondary ion yields of trace elements from a matrix. All that is available are semi-empirical models based on collections of data on secondary ion yields form different matrices. Usually, a model is only valid within a group of matrices with similar physical properties. The different models use different parameters to predict the secondary ion yield. In the following, the secondary ion yield data gained from measurements on metals, metal-silicides and semiconductors with \( \text{Cs}^+ \) and \( \text{O}^+ \) primary beams will be discussed as an example.

For a given set of primary ion beam parameters the properties influencing the secondary ion yield have to be related to the trace element on one hand and the sample matrix on the other. This is clear, because the secondary ion yields vary for different trace elements sputtered from the same matrix and for a given trace element sputtered from different matrices (Deline et al., 1978a). Specifically, considering the case of different trace elements in a matrix of the kind mentioned above, it has been found that the secondary ion yield forms a Saha relation with the electron affinity \( \Omega_T \) for negative secondary ions and with the ionisation potential \( \Phi_T \) for positive secondary ions. That is

\[
\alpha^+ (S) \propto e^{-\Omega_T} \\
\alpha^- (S) \propto e^{-\Phi_T}
\]  

In the second case, where a given trace element is sputtered from different matrices \( M \), it was found that the linear sputter rate \( S_{l,M} \) [nm/s], i.e. the speed at which the sample surface is eroded, influences the secondary ion yield. The reason being that the concentration of the element of the primary beam at the surface of a sample influences the properties of a matrix with respect to the sputter process. The concentration of the primary species, for example \( n(\text{Cs}) \), at the sample surface is proportional to the inverse of the linear sputter rate: \( n(\text{Cs}) \sim 1/S_{l,M} \). The overall relation between the secondary ion yield and the linear sputter rate for some matrices has been found to be (Deline et al., 1978b)

\[
\alpha^+ (S) \propto \left[ \frac{1}{S_{l,M}} \right]^{\frac{1}{\nu}} \propto [n(O)]^{\frac{1}{\nu}}
\]  

or

\[
\alpha^- (S) \propto \left[ \frac{1}{S_{l,M}} \right]^{\frac{1}{\nu}} \propto [n(\text{Cs})]^{\frac{1}{\nu}}
\]
The primary species $O^+$ and $Cs^+$ were chosen as examples, because an $O^+$ beam favours the yield of positive secondary ions and a $Cs^+$ beam favours negatively charged secondary ions. The exponents $x_s^\pm$ vary from trace element to trace element and it is not yet clear on which parameters they depend. Table 3 gives their values for some trace elements.

![Graph showing Si- yield versus the reciprocal of the linear sputtering rate $S_{l,M}$ for various metal silicides measured on an AEI-IM20 ion microprobe (Deline et al., 1978b).](image)

**Fig. 11:** Useful Si$^-$ yield versus the reciprocal of the linear sputtering rate $S_{l,M}$ for various metal silicides measured on an AEI-IM20 ion microprobe (Deline et al., 1978b).

Relations 3.1.14 and 3.1.15 also hold for a given matrix element sputtered from different binary compound matrices. This has been demonstrated on the yield of negative silicon ions from different metal silicides as can be seen in figure 11.

<table>
<thead>
<tr>
<th>Element</th>
<th>$x_s^+$</th>
<th>$x_s^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>$2.8 \pm 0.1$</td>
<td>$2.1 \pm 0.1$</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td>$2.0 \pm 0.1$</td>
</tr>
<tr>
<td>P</td>
<td>$2.8 \pm 0.3$</td>
<td>$2.4 \pm 0.2$</td>
</tr>
<tr>
<td>As</td>
<td>$3.3 \pm 0.1$</td>
<td>$2.6 \pm 0.1$</td>
</tr>
<tr>
<td>Sb</td>
<td>$2.9 \pm 0.3$</td>
<td>$3.4 \pm 0.2$</td>
</tr>
</tbody>
</table>

**Table 3:** Exponents of the reciprocal of the linear sputtering rate, $S_{l,M}$, for positive and negative ionisation probabilities with an O+ or a Cs+ primary beam respectively (Deline et al., 1978b)
3.2 Negative Secondary Ions from a SiO$_2$ Matrix with a Cs$^+$ Primary Beam

By the nature of the method, Accelerator SIMS is limited to analysing negative secondary ions. This can be a problem if a sample matrix contains oxygen as one of its main compounds, for example SiO$_2$. As mentioned above, the presence of oxygen favours the yield of positive secondary ions. When experimentally confined to using a negative ion enhancing caesium beam the question arises as to how the coexistence of Cs and O will influence the yield of negative secondary ions from a matrix such as SiO$_2$. This question is an important issue when wanting to apply Accelerator SIMS to geological samples, the matrices of which often contain oxides. Traditionally, SIMS analysis of geological samples is performed with an oxygen primary beam while extracting positive secondary ions. In the following, an experiment performed at the PSI/ETH Accelerator SIMS facility with the goal to measure the yield of negative secondary ions from a SiO$_2$ matrix will be presented. The trace elements used for this experiment were the platinum group elements, gold, and silver (PGE), because of their potential for environmental applications.

3.2.1 Samples and implantation technique

As mentioned in chapter 2, the design of the sputter chamber requires samples of wafer-like shape. Therefore, the idea was to take a structured wafer containing a SiO$_2$ layer and a Si substrate, and to implant a given PGE at different energies but on the same place on the wafer. This way a concentration maximum of the PGE is produced both in the SiO$_2$ layer and the substrate. The ion yield of the PGE in SiO$_2$ relative to the yield from a Si matrix can then be determined by measuring a depth profile of the implantation with Accelerator SIMS.

The wafer chosen for the experiment was produced with the bond-and-etch-back technique, but for simplicity it will be referred to as a SIMOX wafer (separation by implantation of oxygen). Its surface consists of a 200 nm thick layer of silicon. Beneath it is a 100 nm thick SiO$_2$ layer, which in its turn is on a silicon substrate. Figure 12 shows a cross section through the wafer. An important aspect to the choice of the wafer is that the silicon surface layer acts as an electrically conducting protection on top of the insulating silicon dioxide layer. Charging of the sample from the primary beam is therefore prevented.

The implantations were made by inserting a pure metal PGE cathode (with the exception of osmium where an OsCl$_3$ cathode was used) into the high-current source
of the AMS facility (see also figure 29 in chapter 5). For each element the isotope with the highest abundance was selected with the low-energy mass spectrometer. The implantation targets were placed at the focal point of the beam behind the high-energy electrostatic deflector. Thus a charge state of the positive ions produced at the stripper can be selected and together with the terminal voltage of the tandem accelerator the final implantation energy is known to better than 1%. The PGE beam was scanned over an aperture just in front of the implantation target. The size of this aperture defines the size of the implantation area on the target surface. It was set to 4 x 4 mm and left unchanged for all implantations. Measuring the mean current of the scanned ion beam in a Faraday cup behind the aperture before and after exposing the target to the ion beam, together with the measured time of exposure, the implantation fluence can be determined to within 2%.

The isotopes $^{103}$Rh, $^{106}$Pd, $^{107}$Ag, $^{192}$Os, $^{193}$Ir, $^{195}$Pt, and $^{197}$Au of the PGE were selected for the experiment. Implantation energies were 0.60 MeV and 2.00 MeV for the isotopes $^{103}$Rh, $^{106}$Pd, and $^{107}$Ag and the isotopes $^{192}$Os, $^{193}$Ir, $^{195}$Pt, and $^{197}$Au were implanted at 0.95 MeV and 3.50 MeV.

![Layer structure of a SIMOX wafer with the direction of incidence of the PGE indicated](image)

The energies were chosen based on TRIM simulations. The only criterion was to achieve a concentration maximum in the centre of the SiO$_2$ layer, and separate from it, a concentration maximum in the substrate. Figure 13 shows such a simulation of the
depth dependence of the concentration of $^{195}$Pt in the SIMOX wafer. It is representative for all the implanted isotopes and shows that not all of the projectiles of the lower implantation energy are stopped in the SiO$_2$ layer. Average ranges and longitudinal straggling ($1\sigma$) of the different isotopes in the SIMOX wafer are summarised in table 4. The differences in the ranges for isotopes of nearly the same mass lie within the error of the simulation. Therefore, in table 4 only a distinction between the light PGE (Pd, Rh, Ag) and the heavy PGE (Os, Ir, Pt, Au) has been made.

![Fig. 13: TRIM simulation of the concentration of $^{195}$Pt as a function of depth in the SIMOX wafer.](image)

<table>
<thead>
<tr>
<th>Isotopes</th>
<th>Range at low energy</th>
<th>Straggling at low energy</th>
<th>Range at high energy</th>
<th>Straggling at high energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{103}$Rh, $^{106}$Pd, $^{107}$Ag</td>
<td>245 nm</td>
<td>64 nm</td>
<td>822 nm</td>
<td>160 nm</td>
</tr>
<tr>
<td>$^{192}$Os, $^{193}$Ir, $^{195}$Pt, $^{197}$Au</td>
<td>244 nm</td>
<td>52 nm</td>
<td>780 nm</td>
<td>150 nm</td>
</tr>
</tbody>
</table>

Table 4: Ranges and longitudinal straggling ($1\sigma$) taken from the TRIM simulation for the implanted isotopes.
The aim was to implant doses of $1 \times 10^{14}$ atoms/cm$^2$ for all isotopes at each energy. Due to variations in the ion current during exposure of the wafer, the implanted doses - with the exception of Pd - were up to 10% away from this value. The small current extracted from the Pd cathode only allowed implantation doses of $1 \times 10^{13}$ atoms/cm$^2$. The implantations at the higher energy were performed first as not to disturb the shallower lying profile during implantation at the higher energy. In addition, the incident angle of the PGE beam was set to 15° from the surface normal to avoid possible channelling effects in the substrate.

As can be seen from figure 13, the distribution of ranges for a given energy is close to Gaussian. The concentration $n(S^N, x)$ of a trace isotope from an implantation of a given energy as a function of depth $x$ into the wafer can therefore be approximated with

$$n(S^N, x) = \frac{D(S^N)}{\sqrt{2\pi \cdot \Delta R_p^2}} \cdot \exp \left( -\frac{(x - R_p)^2}{2 \cdot \Delta R_p^2} \right)$$

(3.16)

where $D(S^N)$ is the implanted dose [atoms/cm$^2$], $R_p$ is the range, and $\Delta R_p$ is the longitudinal straggling of the trace element.

$R_p$ and $\Delta R_p$ can be read out of table 4. In particular the maximal concentration $n_{\text{max}}(S^N)$ of the trace element at depth $R_p$ can be calculated:

$$n(S^N, R_p) = n_{\text{max}}(S^N) = \frac{D(S^N)}{\sqrt{2\pi \cdot \Delta R_p^2}}$$

(3.17)

3.2.2 Accelerator SIMS results

Depth profiles of the prepared SIMOX wafers were measured with Accelerator SIMS and are shown in figures 15 to 21. They show the counting rate acquired from the gated, central 15% of the scanning area of the Cs beam against time. The only correction made to the data is for dead time. The caesium currents used for the measurement of depth profiles in the SIMOX wafers were varied from measurement to measurement between 53 and 290 nA depending on the chosen aperture in the primary ion source, and the sputter areas were varied between 300 x 300 $\mu$m$^2$ and 650 x 650 $\mu$m$^2$. This explains the differences in the times needed to sputter through the Si and the SiO$_2$ layers.

All measurements were performed with a terminal voltage of 5 MV, and carbon foil strippers were used because of a limitation imposed by the maximal field strength of the high-energy magnet. On the high-energy side heavy PGE were analysed in charge
state 9+. According to a model by Sayer, their charge state yield was only ~17%, whereas the yield of charge state 8+, which is the charge state with the highest population at 5 MeV, would have been ~21%. Transmission was around 5 per mil for the heavy PGE. The light PGE were analysed in charge state 8+, which has the highest charge state yield at 5 MeV, but transmission was similar to that of heavy PGE. For all elements the atomic ion was injected into the tandem. The PGE-Si and PGE-O secondary molecules were also investigated, but their yields were more than one order of magnitude smaller than those of the atomic secondary ions.

Due to the high concentrations of PGE in the SIMOX wafers, tuning the system was no problem. First a calibration setup for the day was obtained by injecting mass 28 amu and analysing $^{28}\text{Si}^{6+}$ on the high-energy side of the accelerator. The current of this ion can be measured in a Faraday cup next to the detector. This setup can be used to calculate the settings of the ion optical elements on the high-energy side for all other elements to be analysed. For the analysis of PGE, the ion optical elements of the injector were optimised by measuring the current produced by molecules, such as Si$_7$, with the secondary electron multiplier just after the tandem. The fragments of such molecules, for example $^{28}\text{Si}^{2+}$, can give a counting rate of a few hundred Hertz in the detector. Tuning the facility to analyse such fragments can be of advantage in order to briefly check the calibration setting from the analysis of $^{28}\text{Si}^{6+}$. Its ion optical setup lies between the calibration setting and those settings needed for the analysis of PGE and, if necessary, can therefore be used as a second calibration setup. It is then no problem to predict and find the settings for the PGE of interest.

When analysing a SIMOX wafer, the concentrations of the PGE in the sample are high enough to produce counting rates that can easily be used for a final fine-tuning of the setup. This is not always the case. In chapter 4 the analysis of minute concentrations of iridium in sedimentary layers will be presented. In this case, the ion optical setup can be checked with clusters containing caesium ions. For example, $^{133}\text{Cs}^{28}\text{Si}^{16}\text{O}_2$ has a mass of 193 amu and the Cs$^{6+}$ fragment has an intensity of a few hundred Hertz when sputtered from an appropriate matrix. The ion optical setup to focus the Cs$^{6+}$ beam into the detector is very close to the setup for the analysis of $^{193}\text{Ir}^{9+}$. Only slight changes in the field strengths of the high-energy electrostatic and magnetic deflectors are necessary to change to the setup of $^{193}\text{Ir}^{9+}$. This makes it easier to check the stability of the measurement during analysis of sedimentary layers.

Technically it was not possible to simultaneously monitor the current of a matrix element in order to make a correction for fluctuations in the ion currents. This is due to the large mass differences between silicon and the PGE meaning that a quasi-simultaneous injection with the beam bouncing system of the low-energy magnet is
not possible. Possibilities on how to solve this problem will be presented in chapter 6. However, as can be seen in figure 14 the current of Si$^{6+}$ measured in a Faraday cup next to the detector remains stable to within 10% in a given layer of the sample. It has therefore been assumed that the transmission remains constant throughout the measurement of a depth profile.

**Fig. 14:** Gated $^{28}$Si$^{6+}$ current as a function of time during a depth profile of a SIMOX wafer. The current was measured in a Faraday cup situated next to the gas ionisation detector. The scanning area of the Cs beam was 450 x 450 µm.

**Fig. 15:** Depth profile of $^{195}$Pt implantation in SIMOX wafer. The counting rate has only been corrected for dead time. The Cs current was 53 nA and the scanning area was set to 450 x 450 µm.
Fig. 16: Depth profile of $^{197}$Au implantation in SIMOX wafer. The counting rate has only been corrected for dead time. The Cs current was 115 nA and the scanning area was set to 300 x 300 µm.

Fig. 17: Depth profile of $^{193}$Ir implantation in SIMOX wafer. The counting rate has only been corrected for dead time. The Cs current was 126 nA and the scanning area was set to 450 x 450 µm.
**Fig. 18:** Depth profile of $^{192}$Os implantation in SIMOX wafer. The counting rate has only been corrected for dead time. The Cs current was 290 nA and the scanning area was set to 650 x 650 µm.

**Fig. 19:** Depth profile of $^{107}$Ag implantation in SIMOX wafer. The counting rate has only been corrected for dead time. The Cs current was 290 nA and the scanning area was set to 650 x 650 µm.
Fig. 20: Depth profile of $^{103}$Rh implantation in SIMOX wafer. The counting rate has only been corrected for dead time. The Cs current was 126 nA and the scanning area was set to 450 x 450 $\mu$m.

Fig. 21: Depth profile of $^{106}$Pd implantation in SIMOX wafer. The counting rate has only been corrected for dead time. The Cs current was 126 nA and the scanning area was set to 450 x 450 $\mu$m.

The ratio of the total sputter yields of a Si matrix and a SiO$_2$ matrix can be easily read out of both figure 14 and the depth profiles of the PGE (figures 15 to 21). This is due
to the fact that on one hand the extracted Si current is different for the 2 matrices (figure 14) and on the other hand that there is a large increase in the counting rate of the PGE at the interfaces between the SiO$_2$ and the silicon layers. Averaging over several measured profiles one calculates that the Cs beam sputters through the 200 nm thick silicon surface layer in 0.60 of the time it takes it to sputter through the 100 nm of SiO$_2$. Limited by the cycle time, which was chosen between 10 and 30 seconds, this value is precise to within 10%. The total sputter yield of a silicon matrix for the primary beam parameters used for these measurements has been measured by (Ender, 1997a) and found to be 2.4 Si atoms per Cs atom. Together with the atomic densities of silicon and SiO$_2$ the total sputter yield of a SiO$_2$ matrix can therefore be calculated: 0.34 SiO$_2$ molecules per Cs atom.

Looking at figure 13 and the measured depth profiles it is clear that a significant fraction of the implanted ions of the lower energy are stopped outside the SiO$_2$ layer. In the depth profiles this is manifested by the peaks of the counting rate at the interfaces between the SiO$_2$ and the Si layers. This makes it difficult to evaluate the depth profiles with methods using the integral of the counting rate from an implantation peak. A detailed evaluation revealed that a Gaussian fit to the counting rate in the SiO$_2$ layer can only be used to estimate the maximal counting rate in the layer. More details on this topic will be presented later on. For the following evaluation every implantation of a given element and energy is regarded independently, and only maximal counting rates in the depth profile are compared with the corresponding concentration maximum derived with the SRIM simulation allowing one to calculate the Sensitivity Factors and detection limits of PGE in the corresponding matrix.

Scaled Sensitivity Factors (SSF) are readily calculated using equation 3.10, where the reference concentration $n(S)$ is the maximal concentration in the implantation profile as calculated from equation 3.17, but additionally corrected for the isotopic abundance. Its corresponding counting rate, $I_q^0(S^N)$, is determined out of the depth profiles for both the SiO$_2$ layer and the Si substrate. $I_q^0(S^N)$ is the maximum of a Gaussian fit to the counting rate of an implantation peak. Together with the known primary beam currents, $I_p$, during the individual measurements the SSF can be calculated. Table 5 summarises the Scaled Sensitivity Factors for platinum group elements, gold, and silver in silicon and SiO$_2$. Additionally, the ratio of the two SSF of a given PGE for the same atomic densities (atoms/cm$^3$) is given indicating the reduction in absolute sensitivity when changing from one sample matrix to the other. On average the sensitivity drops by a factor of ~50.
Table 5: Accelerator SIMS Scaled Sensitivity Factors of PGE for Si and SiO₂ matrices.

From figure 14 it is also possible to determine a SSF for sputtered Si ions. The average Si current sputtered from the SiO₂ layer is 0.15 nA and the Si current coming from the Si substrate is 4.0 nA. Taking into account that the Si ions are analysed in charge state 6+ one gets:

\[
SSF_{Si}^{Si} = 1.5 \cdot 10^{-16} \text{(counts/s)/(nA·at./cm}^3\text{)}
\]

\[
SSF_{SiO₂}^{Si} = 1.2 \cdot 10^{-17} \text{(counts/s)/(nA·at./cm}^3\text{)}
\]

Following the discussion in section 3.1.3, it is now possible to calculate the Scaled Sensitivity Ratios (SSR) of the PGE relative to Si⁶⁺ ions from the Si and SiO₂ matrices. These are summarised in table 6 together with the ratios of the SSR in the different matrices. In comparison to table 5 the ratio of the SSR indicates the relative difference of the sensitivities when analysing a given PGE in these matrices. As can be seen the reduction is less than one order of magnitude. This means that most of the sensitivity is lost due to a reduced probability of the formation of negative secondary ions in the sputter process caused by the presence of oxygen in the sample matrix. Generally, this means that large variations in sensitivities have to be expected when analysing different matrices.
Chapter 3  Accelerator SIMS Analysis of a SiO$_2$ Matrix

<table>
<thead>
<tr>
<th>Element</th>
<th>Au</th>
<th>Pt</th>
<th>Ir</th>
<th>Os</th>
<th>Ag</th>
<th>Pd</th>
<th>Rh</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSR in Si</td>
<td>0.038</td>
<td>0.073</td>
<td>0.054</td>
<td>0.008</td>
<td>0.008</td>
<td>0.006</td>
<td>0.010</td>
</tr>
<tr>
<td>SSR in SiO$_2$</td>
<td>0.008</td>
<td>0.027</td>
<td>0.009</td>
<td>0.003</td>
<td>0.004</td>
<td>(0.014)</td>
<td>(0.020)</td>
</tr>
<tr>
<td>$\frac{SSR_{PGE}^{Si,Si}}{SSR_{PGE}^{SiO_2,Si}}$</td>
<td>5.0</td>
<td>2.7</td>
<td>5.9</td>
<td>2.3</td>
<td>2.2</td>
<td>(0.4)</td>
<td>(0.5)</td>
</tr>
</tbody>
</table>

**Table 6:** Accelerator SIMS Scaled Sensitivity Ratios of PGE and Si ions analysed in Si and SiO$_2$ matrices.

Another interesting value that can be estimated from the measured data is the detection limit of a PGE in the two matrices. Again, using the Gaussian fit to the measured counting rate and the corresponding simulated maximal trace element concentration of the implantation and assuming a background counting rate of 0.01 Hz for all PGE (except for Au, where 1 Hz is a realistic background counting rate) the detection limit, DL, can be calculated from:

$$DL(S) = \frac{0.01 \text{ Hz}}{I(S)} \cdot \frac{n_{\text{max}}(S^N)}{r(S^N)}$$

(normalised to the full scanning area and to a primary Cs beam current of 500 nA before inserting into equation 3.18, gives the detection limits for PGE in Si and SiO$_2$ as presented in table 7. Again, the effect of the smaller negative ion yields from the SiO$_2$ matrix can be seen in the worse detection limits.

<table>
<thead>
<tr>
<th>Element</th>
<th>Au</th>
<th>Pt</th>
<th>Ir</th>
<th>Os</th>
<th>Ag</th>
<th>Pd</th>
<th>Rh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detection limit in Si [at./cm$^3$]</td>
<td>3\cdot10^{14}</td>
<td>5\cdot10^{12}</td>
<td>4\cdot10^{12}</td>
<td>4\cdot10^{13}</td>
<td>3\cdot10^{13}</td>
<td>8\cdot10^{13}</td>
<td>1\cdot10^{13}</td>
</tr>
<tr>
<td>Detection limit in Si [at./Si atom]</td>
<td>7\cdot10^{-9}</td>
<td>1\cdot10^{-10}</td>
<td>8\cdot10^{-11}</td>
<td>8\cdot10^{-10}</td>
<td>7\cdot10^{-10}</td>
<td>2\cdot10^{-9}</td>
<td>3\cdot10^{-10}</td>
</tr>
<tr>
<td>Detection limit in Si [ng/g]</td>
<td>48</td>
<td>0.7</td>
<td>0.5</td>
<td>5</td>
<td>3</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>Detection limit in SiO$_2$ [at./cm$^3$]</td>
<td>2\cdot10^{16}</td>
<td>2\cdot10^{14}</td>
<td>3\cdot10^{14}</td>
<td>1\cdot10^{15}</td>
<td>9\cdot10^{14}</td>
<td>(4\cdot10^{15})</td>
<td>(8\cdot10^{13})</td>
</tr>
<tr>
<td>Detection limit in SiO$_2$ [at./SiO$_2$]</td>
<td>9\cdot10^{-7}</td>
<td>7\cdot10^{-9}</td>
<td>1\cdot10^{-8}</td>
<td>5\cdot10^{-8}</td>
<td>4\cdot10^{-8}</td>
<td>(2\cdot10^{-8})</td>
<td>(3\cdot10^{-9})</td>
</tr>
<tr>
<td>Detection limit in SiO$_2$ [ng/g]</td>
<td>2800</td>
<td>23</td>
<td>36</td>
<td>150</td>
<td>65</td>
<td>(30)</td>
<td>(6)</td>
</tr>
</tbody>
</table>

**Table 7:** Accelerator SIMS detection limits of PGE in Si and SiO$_2$. 

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Looking at the depth profiles of Pd and Rh in figures 20 and 21 it seems as if the concentration maximum of the 600 keV implantation lies close to the interface between the SiO$_2$ layer and the silicon substrate. This is probably due to a channelling effect during implantation of the trace elements. The fit of the Gaussian distribution to the counting rate in the SiO$_2$ layer is therefore not reliable and distorts SSF, SSR and detection limits derived from the depth profile for these two elements in this matrix. This is why the values for Pd and Rh in a silicon dioxide matrix have been set in parentheses.

Before concluding, a word should be said about the reliability of the presented numbers. First of all, the depth profiles shown in figures 15 to 21 were not all measured on the same day. Variations in the transmission from day to day can be significant. The fluctuations in the transmissions due to this are not expected to be larger than a factor 2 - 3.

In addition, it should also be kept in mind, that the concentration maxima of the implantation profiles simulated with TRIM probably overestimate the real concentrations. This is because the longitudinal straggling of heavy elements in the energy range applicable here is underestimated by TRIM due to the difficult prediction of nuclear stopping. This results in the assumption of a narrower Gaussian concentration distribution of the trace isotope and therefore an overestimation of the maximal concentration of the profile. A detailed evaluation of the depth profiles revealed that the TRIM prediction of the range $R_p$ is accurate to with 20%. This was checked by calculating the sputter rate with the time needed to erode through the 200 nm thick surface layer. With this information the depth, $R_p$, at which the substrate implantation is located can be calculated with the time it takes to reach the maximum in the counting rate after having passed the second interface assuming that the second interface lies at a depth of 300 nm. This also gives a depth scale to which one can compare the width of the Gaussian fit to the depth profile. It turned out that TRIM underestimates the longitudinal straggling by 20 – 50 %. Therefore, the simulated concentrations are overestimated by 20 – 50% and the Scaled Sensitivity Factors given here are to be regarded as lower limits whereas the detection limits can be regarded as upper limits to the true values.

The widths of Gaussian distributions fitted to the depth profiles in the region of the SiO$_2$ layer, however, didn’t correspond to the predictions made by TRIM. The fits only reproduced the longitudinal straggling to within a factor of 2. This is also due to the fact that the depth profiles are difficult to fit in this region, due to the presence of the large interface peaks. Therefore, only the maximal counting rates measured in the SiO$_2$ layer were compared to the TRIM simulations.
Also, the assumed background counting rate of 0.01 Hz in equation 3.18 is only a practical assumption. In many cases virtually no background was measured over a period of up to 20 minutes!

In total, all SSF, SSR and detection limits given here are correct to within about a factor of 5 and are only meant to demonstrate the capabilities of Accelerator SIMS.
Chapter 4  Platinum Group Elements at the KT-Boundary

As announced earlier on, this chapter deals with the application of the insights gained in chapter 3 to in-situ bulk concentration analysis with Accelerator SIMS in the field of geology. The advantages of Accelerator SIMS in comparison to other analytical methods will be demonstrated on the measurement of platinum group elements (PGE) in sedimentary layers at the transition from the Cretaceous to the Tertiary period (KT-boundary). In particular, the measurement of a concentration peak of iridium (56 ng/g at the maximum) at the transition line between the two periods will be looked at. This is a perfect topic to test the abilities of Accelerator SIMS, since the processes involved in evolutionary history at the transition from the Cretaceous to the Tertiary have received much attention over the last two decades resulting in a wealth of information to compare Accelerator SIMS test measurements to. Accelerator SIMS measurements reproduce data gained with Neutron Activation Analysis (NAA) very nicely. But the lateral resolution of Accelerator SIMS is orders of magnitude higher (~100 µm instead of ~1 cm) making it possible to study trace elements in sedimentary layers at a much smaller lateral scale.

4.1 Introduction to the KT-Boundary

In 1980 Luis Alvarez and his co-workers proposed that the mass extinction at the end of the Cretaceous period, 65 million years ago, was provoked by a comet or asteroid of some ten kilometres in diameter colliding with Earth. This novel explanation of the observed anomalies at the transition between the two periods was only based on a peak in the iridium concentration at the transition line in the corresponding sedimentary layers, supposedly material from the extraterrestrial projectile. The theory stands in opposition to the proposition that massive volcanic eruptions also could have transported dust from the Earth’s mantle, containing an excess of iridium relative to the Earth’s crust, into the atmosphere to form a concentration peak of iridium in sedimentary layers. The debate triggered a worldwide search for the impact crater and other evidence to support the theories (Goss Levi, 1992). Today, a lot more evidence has been gathered and - even if the KT-debate is still ongoing - it is believed that a structure beneath the Yucatàn peninsula in the Gulf of Mexico, the so-called
Chicxulub crater, is the remains of the impact site. Its age was determined by $^{40}$Ar/$^{39}$Ar-dating to $64.98 \pm 0.05$ Ma, which is a strong indication that the crater is related to the KT-boundary (Swisher et. al, 1992).

Whatever the theory, a significant amount of PGE rich dust was blown into the atmosphere and distributed globally before it fell out, creating a small excess of platinum group elements in sedimentary layers as they formed at that time. The element abundances and isotope ratios of the PGE in the sedimentary layers are therefore a key to answering the question as to whether a meteorite struck Earth of whether volcanic eruptions lead to the climate change resulting in the mass extinction at the end of the Cretaceous.

From a meteorite fragment found in the KT-boundary sediments in the Pacific Ocean it has been anticipated that the asteroid was a chondrite of type CV, CO, or CR (Kyte, 1998). These chondrites carry a high abundance of platinum group elements ($\sim 700$ ng/g of Ir, $\sim 1000$ ng/g of Pt, and others) in comparison to the Earth’s crust ($\sim 1$ ng/g of Ir, $\sim 5$ ng/g of Pt). Therefore, not only a peak in the concentration of iridium is expected in sedimentary layers, but a peak in the platinum concentration would be expected as well. Alvarez determined an iridium peak concentration of around $42$ ng/g in samples found in Denmark, a concentration that - according to the results of chapter 3 - should be measurable with Accelerator SIMS in an adequate sample matrix.

### 4.2 Sample Description

The samples used for the Accelerator SIMS experiments were provided through the courtesy of Dr. Beda Hofmann, Natural History Museum Bern. They were taken from sedimentary layers at the Starkville South section, Raton basin, Colorado. Figure 22 shows a picture of the sampling site with a Swiss Army Knife on the right hand side of the picture to illustrate the size scale. The light layer, in front of which the knife has been placed, is kaolinitic clay typical for the sedimentary structure of the KT-boundary in Northern America. In Alvarez’ theory this is basically material that fell out immediately after the impact (Pillmore et al., 1987). Immediately above it is a slightly darker and redder layer of finer grain. This is predominantly dust that fell out during the years after impact and should contain the highest fraction of extraterrestrial material.
Fig. 22: Excavation site at the Starkville South section, Raton basin, Colorado. The KT-boundary samples used for Accelerator SIMS experiments came from this site. A Swiss Army Knife on the right indicates the size scale.

Fig. 23: Continuous cross section of the sedimentary layers around the KT-boundary from Starkville, Colorado. 1-2: Carbonaceous shale of the Cretaceous; 2-3: Kaolinitic clay layer (immediate impact fall-out); 3-4: KT-horizon (material of very fine grain containing post-impact dust fall-out); 4-5: Coal layer of the Tertiary.

About one millimetre thick cross sections were cut out of the layer structure described above and glued onto glass object slides. The region of interest was distributed over two slides. Figure 23 shows a photograph of these slides. Together they represent a continuous section of the sedimentary layers starting at the carbonaceous shale of the Cretaceous (region 1-2) followed by the layer of caolinitic clay (2-3). The KT-horizon consisting of post-impact dust sediments lies between 3-4, and 4-5 is the coal layer of
the early Tertiary period. The iridium peak is expected to be between 3-5 (Hofmann, 1999).

Unfortunately, both object slides had to be cut to size after the samples had already been glued on to them in order for the samples to fit into the sample holder of the Accelerator SIMS chamber. During this process the smaller sample of the Tertiary layer split perpendicular to the direction of sedimentation. This, however, did not affect the measurements. As can be seen in figure 24, which shows the samples prepared for analysis, it sufficed to press the two fragments as close together as possible and not to measure in the direct vicinity of the crack between the two halves.

In order to prevent electrical charging of the samples by the primary beam, the samples were coated with a 50 nm thick carbon layer. This gives the samples the silvery look in figure 24. Unfortunately, it turned out that the carbon layer contained a platinum contamination and a reliable measurement of the platinum concentration in the sediments was not possible. This would have been of great interest, because of the high platinum abundance in CV, CO and CR chondrites.

4.3 Measurements and Results

Accelerator SIMS measurements were performed with the same analytical setup as the measurements presented in chapter 3. The terminal voltage was set to 5 MV and carbon foil strippers were used. The low-energy mass spectrometer was tuned to inject mass 193 amu and on the high-energy side of the tandem accelerator $^{193}\text{Ir}^{9+}$ was analysed. The machine was tuned with iridium implantations in a silicon matrix before measurements on the sedimentary layers were performed. Detailed information on the tuning procedure was given in section 3.2.2.

The main interest was in reproducing the lateral concentration distribution of iridium in the sedimentary layers (Pillmore et al., 1987) and all Accelerator SIMS measurements were performed along the dashed white line in figure 24. In order to measure the low concentrations of iridium the primary caesium current had to be maximised. For this reason a beam spot size of ~100 µm was chosen, which is also a lot larger than the size of the mineral grains in the samples (~1 µm). Therefore, the measurement was not influenced by the microscopic structure of the samples.

It turned out that iridium could only be found in the coal layer of the Tertiary. For this reason the matrix composition of the sedimentary layers was analysed with Rutherford Backscattering Spectrometry (RBS). This way the main matrix components could be easily identified and a possible change in the secondary ion
yield due to changes in the matrix composition across the sample monitored. The RBS analyses were performed in 1 mm steps along the same dashed line indicated in figure 24 and the results are summarised in figure 25 together with the Ir concentrations measured with Accelerator SIMS.

One can clearly see that in the coal layer of the Tertiary carbon is the dominant matrix element with an atomic fraction of more than 60%. At the transition line to the sediments of the KT-boundary the carbon concentration drops sharply and the oxygen concentration on the other hand rises. This rise in the oxygen abundance is caused by the increasing presence of silicon and aluminium. The concentration of aluminium is not shown in figure 25, but the oxygen abundance goes hand in hand with a mixture of SiO$_2$ and Al$_2$O$_3$ of about 2:1 in the matrix. It is also nicely demonstrated that within a given sedimentary layer the matrix composition does not vary and stays constant. In the layer of the carbonaceous shale of the Cretaceous the carbon concentration rises again and the oxygen and with it the SiO$_2$ and Al$_2$O$_3$ compounds diminish.
Fig. 25: Summary of the atomic concentration measurements performed on the sedimentary layers at the KT-boundary. Iridium was measured with Accelerator SIMS and carbon, silicon and oxygen abundances were determined with RBS.
In the light of this change of matrix composition it becomes clear why no iridium could be detected with Accelerator SIMS in the kaolinitic clay layer. According to the results of chapter 3, the sensitivity of Accelerator SIMS with respect to iridium drops in a SiO₂ dominated matrix by almost two orders of magnitude. In such a matrix even the highest expected iridium concentration of 56 ng/g lies close to the detection limit of Accelerator SIMS (table 7 in chapter 3). Carbon, however, has much more the same properties as a silicon matrix and the detection limit of Ir is therefore much lower. This is why iridium is detected in the carbonaceous layer of the Tertiary even though the iridium concentration is much lower there. Figure 25 shows four iridium concentration measurements in the coal layer. It nicely reproduces the form of the iridium concentration profile published by Pillmore et al., 1987, which lies between 1 and 10 ng/g in the layer under consideration.

It would also be possible to perform the Accelerator SIMS measurements with a lateral resolution corresponding to the beam spot size of around 100 µm. To emphasise this, figure 26 shows a magnification of a section of figure 24 The thin black lines are marks made by the caesium beam of the Accelerator SIMS source. They were made by moving the sample in 150 µm steps under the stationary caesium beam with a beam diameter of about 100 µm (the largest aperture of the ion source was used). One can clearly see the sputter spots of the individual steps meaning that the beam spot size of the caesium beam is significantly smaller than the step size.

Fig. 26: Magnification of the area marked in figure 24 indicating the sputter marks made by the Accelerator SIMS primary beam.
The absolute iridium concentration in the coal layer was determined by producing a standard with the implantation technique described in chapter 3. An $^{193}\text{Ir}$ fluence of $1.0 \times 10^{13}$ cm$^{-2}$ was implanted into a graphite plate at an energy of 1 MeV. Graphite is a suitable approximation to the matrix of the carbonaceous layer, and it is expected that the secondary ion yield of iridium from graphite is close to its yield from the carbonaceous sediment layer.

Following the procedures used in chapter 3 the range and longitudinal straggling of the profile were simulated with TRIM 2000 and with equation 3.17 the maximal concentration of the profile can be estimated. The simulation gave a range, $R_p$, of 221 nm and a longitudinal straggling, $\Delta R_p$, of 31 nm. This gives a maximal concentration of $1.3 \times 10^{18}$ Ir atoms/cm$^{-3}$. An Accelerator SIMS depth profile of the implantation was measured prior to the analysis of the carbonaceous layer. The measured maximal counting rate was then used as a reference for concentration calibration taking into account that depth profiles are evaluated out of the central 15% of the scanning area of the caesium beam. The iridium concentrations presented in figure 25 were calculated by comparing the maximal counting rate of the profile to the counting rates of the measurements on the carbonaceous sediment layer. Figure 27 shows the measured profile together with a Gaussian fit. As discussed in chapter 3, the range straggling of the implantation is probably higher than the value calculated with TRIM. This can also be seen in figure 27. Assuming, according to the
simulation, that the maximal counting rate was measured at a depth of 221 nm, then the variation of the concentration distribution is 46 nm. For the same reason as mentioned in chapter 3 this results in an additional systematic error of the concentration measurements of 50%.

For comparison, by using the same procedure as explained in chapter 3, one calculates a detection limit of $1.5 \cdot 10^{12} \text{ cm}^{-3}$ ($1.3 \cdot 10^{-11}$ Ir atoms/C atom or 0.2 ng/g) for iridium in graphite.

4.4 Conclusions

It has been demonstrated that Accelerator SIMS is an analytical method suited to perform trace element analysis of platinum group elements in ng/g-concentrations in geological samples with a lateral resolution of ~100 µm. In well-suited matrices, such as carbonaceous layers, even sub-ng/g detection limits can be reached. This represents an improvement to in-situ bulk concentration analysis, which before could not be performed at such low concentrations with such high lateral resolution. Scientific problems at this lateral scale can be studied now. The value of such analytical methods is also apparent in the light of the recent observation of another iridium anomaly at the transition between the Triassic and Jurassic periods (TJ-boundary) that might have the same origin as the iridium anomaly at the KT-boundary (Olson et al., 2002).

To date, the analyses at the KT-boundary have been performed with Neutron Activation Analysis (NAA) and laser ablation ICP-MS (Inductively Coupled Plasma Mass Spectrometry) for iridium (Alvarez et al., 1980; Lichte, 1992). AMS measurements of the concentrations of platinum and iridium in sedimentary layers have also been performed by Rucklidge et al., 1982, and isotopic ratios of PGE in rocks have been measured by Chew et al., 1984. But these methods have the disadvantage that either they cannot measure with the same lateral resolution achievable with the PSI/ETH Accelerator SIMS apparatus (NAA, AMS) or the sensitivity of the method is impaired by molecular interferences (LA-ICP-MS). Also, in contrast to NAA, Accelerator SIMS is more or less equally sensitive to all PGE, therefore it is a universal method with higher sensitivity and higher lateral resolution for PGE analysis in sedimentary layers. The analysis of other trace elements also has to be considered.

A more detailed comparison of Accelerator SIMS to other analytical methods will be made in chapter 6.
Monitoring the composition of the matrix, however, is a must when analysing heterogeneous samples. This also poses the problem of finding a suitable standard sample. If this is not possible, the implantation of the trace element of interest directly into the sample and measuring a depth profile of the implantation is a method to produce a concentration calibration. For trace element concentration measurements it should generally be possible to reach an accuracy of 40% and better.
Chapter 5  Direct Measurement of Natural $^{10}\text{Be}/^{9}\text{Be}$ Ratios

In chapter 4 the limits of Accelerator SIMS with respect to in-situ analysis of trace element concentrations were explored. When wanting to analyse small samples, such as individual mineral grains, it is clear that the limit to the size of an analysable mineral grain in a thin section is set by the beam spot size of the primary caesium beam. This restriction is removed when a mineral grain is removed out of its native rock and is set into a pure matrix that will not interfere during trace element analysis. This method requires more effort to prepare the sample for analysis, but on the other hand objects far smaller in size can be analysed.

In this chapter the limits of the required sample size for an Accelerator SIMS measurement shall be explored. However, the following discussion contains more than just simply exploring the limit to the size of a sample in order to make a comparison with other analytical techniques. The work presented here is basically a new method for routine measurement of natural $^{10}\text{Be}/^{9}\text{Be}$ ratios in ferromanganese crusts and will be presented in this way. The sample sizes that will be regarded here are in the range of 100 ng of beryllium, a total sample size that so far has never been measured with AMS. The application of this new technique to the analysis of carrier-free samples of other radioisotopes routinely analysed with AMS is therefore also a prospect for the future.

By comparing results from test samples from ferromanganese crusts it will become clear that precision and sensitivity of this new Accelerator SIMS method is higher than with methods previously used to gain the same information. These methods are on one hand two separate measurements of the $^{10}\text{Be}$ and $^{9}\text{Be}$ concentrations with AMS and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) respectively, and on the other hand a method developed on an ISOLAB-120 SIMS instrument in Oxford (Belshaw et al., 1995).

5.1 Introduction

The cosmogenic nuclide $^{10}\text{Be}$ has found many applications as a tracer in the environmental sciences over the last two decades and is one of the most frequently measured radionuclides with AMS. Although it is mostly the $^{10}\text{Be}$ concentration in the
original sample that is of interest, there are applications in which the abundance of
cosmogenic $^{10}\text{Be}$ relative to terrestrial $^{9}\text{Be}$ provides important information (von
Blanckenburg et al., 1996b; Robinson et al., 1995). One such application that will be
addressed in the following is the measurement of the $^{10}\text{Be}/^{9}\text{Be}$ ratio as a function of
depth in ferromanganese crusts. With this information growth rates of crusts are
determined and past oceanographic events reflected by changes in the radiogenic
isotope composition in the crusts are dated (Ling et al., 1997; Frank et al., 1998).

Because of the relatively low concentration of $^{9}\text{Be}$ in ferromanganese crusts (1–
10 ppm) sample sizes are too small (~100 ng of $^{9}\text{Be}$) to be analysed with methods
presently used in conventional AMS. But due to the high sensitivity of AMS several
hundred micrograms of $^{9}\text{Be}$ carrier can be added to the sample during chemical pre-
concentration bringing the sample size into the range measurable with AMS.

However, this way information on the natural $^{10}\text{Be}/^{9}\text{Be}$ ratio is lost and can only be
obtained by performing an additional measurement of the $^{9}\text{Be}$ concentration in the
sample, for example with ICP-MS, which introduces additional uncertainty in the
determination of the $^{10}\text{Be}/^{9}\text{Be}$ ratio. Therefore, apart from a more simple chemical
preparation of the sample, it was also anticipated that a direct measurement of the
natural $^{10}\text{Be}/^{9}\text{Be}$ ratio would be more precise than two individual measurements.

A method based on SIMS for the direct measurement of the natural $^{10}\text{Be}/^{9}\text{Be}$ ratio has
been developed by a group in Oxford (Belshaw et al., 1995). The detection of $^{10}\text{Be}^+$
with SIMS, however, is hampered by the presence of $^{9}\text{BeH}^+$ and $^{10}\text{B}^+$ in the secondary
ion beam. Because of the use of an accelerator, Accelerator SIMS has additional
possibilities of suppressing these interferences. The extension of the range of
measurable ratios towards smaller ratios is therefore not to be excluded.

When measuring carrier-free samples with the focussed caesium beam of the
Accelerator SIMS source the resulting secondary ion currents are about three orders
of magnitude smaller than those produced by high current sources used for
conventional $^{10}\text{Be}$ AMS measurements. Because $^{10}\text{Be}/^{9}\text{Be}$ ratios in carrier-free
samples are also about three to four orders of magnitude higher, this means that three
to four orders of magnitude smaller amounts of beryllium oxide can be analysed for
long enough to measure the natural $^{10}\text{Be}/^{9}\text{Be}$ ratio to a precision of a few per cent.

5.2 Sample Preparation and Loading

For each sample 30 – 130 mg of material was taken from the ferromanganese crust.
Chemical purification and preconcentration of the Be followed a previously published
method (von Blanckenburg et al., 1996a) with some modifications, mainly a miniaturisation and a reduction to the first two column separation steps and was gratefully performed under the supervision of Martin Frank, Institute for Isotope Geology and Mineral Resources, ETH Zurich. The detailed recipe of the procedure can be found in Appendix A. It enables a high-purity separation of nanogram amounts of beryllium from the matrix of the ferromanganese crust. At the end of chemical pretreatment the samples are evaporated in small Teflon vials.

As we have seen in chapter 2, the design and geometry of the sample stage require that only objects of wafer-like shape with a plane surface of about 20 x 20 mm can be mounted onto the sample stage in the sputter chamber. Following dissolution in 1-3 µl of 65% HNO₃ the samples were pipetted onto stainless steel wafers held at a temperature of 65°C. The dimensions of the wafer are 24 mm x 24 mm x 0.1 mm and stainless steel was chosen because of its hygroscopic surface allowing the pipetted drops to disperse on the surface thereby distributing the beryllium evenly over the wafer after the solvent has evaporated. Without further precautions the resulting spots of beryllium are 2 – 3 mm in diameter. The beryllium is deposited on the wafer as BeNO₃ and by baking it at 850°C for two hours the beryllium nitrate decomposes to beryllium oxide. A second reason for the choice of stainless steel is its resistivity against high temperatures and the solvent acid. The wafers are therefore resistant to corrosion during the baking process.

For sample sizes of ~100 ng the area over which the drop disperses has to be controlled by creating a hydrophobic ring around a hygroscopic area of about 1 mm diameter. This is done by heating the wafer to 225°C and then drawing a ring by hand on the surface of the wafer with the end of a plastic capillary tube usually used for pipetting µl-amounts of liquid. 225°C is sufficient for the plastic to change the hygroscopic properties of the steel surface, but still low enough for the plastic not to melt completely. The plastic ring subsequently evaporates in the baking process.

Controlling the size of the area over which the sample is allowed to disperse is important, because the beryllium has to be distributed evenly over the surface of the wafer but at the same time a certain thickness of the beryllium layer is necessary. The analysis time available before the primary beam has sputtered through the beryllium layer and has to be moved to a fresh spot on the sample increases with the thickness of the layer. On the other hand mounds or an uneven structure of beryllium on the plane surface of the stainless steel will cause different ion optical conditions for different positions of the primary beam on the sample. The mass fractionation that is caused by this can be as large as a few percent.
For this experiment only one unknown sample was pipetted onto a single stainless steel wafer. In addition, standards and blanks were pipetted onto the same wafer as the unknown sample. Due to the larger amounts of beryllium in standards and blanks the hydrophobic ring on the steel surface is not necessary. The standard used for the measurements presented here is the M3 fraction of the dilution series published by Hofmann et al., 1987, with a nominal $^{10}\text{Be}/^{9}\text{Be}$ ratio of $3.64 \cdot 10^{-8}$. This standard is dissolved in 0.1 N HCl, an acid that readily corrodes stainless steel during the baking process. To reduce this corrosion, the standard consisting of 1 µl of original M3 solution was evaporated at 150°C in a Teflon vial before being redissolved in 2 µl of 65% HNO$_3$ and transferred to the wafer. 1 µl of the blank solution (1000 ppm $^9\text{Be}$ carrier solution routinely used for $^{10}\text{Be}$ AMS) was pipetted directly onto the wafer. Because the beryllium is dissolved in 0.5 N HNO$_3$ no pretreatment of this solution was necessary.

Since the beam spot of the primary beam is a lot smaller than the size of the sample, the electrically insulating beryllium oxide has to be made conducting so that charging of the sample is not a problem during analysis. To achieve this, the entire stainless steel wafer with the samples on it is covered with a 20 nm thick, electrically conducting layer by evaporating high purity gold onto it.

![Sample mounting procedure. Last steps before measurement.](image)

**Fig. 28:** Sample mounting procedure. Last steps before measurement.
Figure 28 schematically summarises the procedure of mounting samples on stainless steel wafers. Before measurement the shapes and sizes of the samples are observed with a pair of binoculars in order to recognise and hold back samples that are likely to be problematic to measure. Especially, samples that are too small for measurement (<50 ng) can be held back.

With this sample mounting technique cross contamination between the sample to be measured, the standards and the blanks on the steel wafer is possible. The obvious places where cross contamination cannot be controlled are the baking of the wafer in the oven and during the actual measurement. At temperatures of 800°C more volatile beryllium compounds can degas from the sample and diffuse to another sample on the same wafer. On the other hand, during measurement beryllium that is sputtered from the sample as neutrals will be deposited on the surfaces of electrodes close to the sample. They can return to the wafer as tertiary particles sputtered by not-extracted secondaries and possibly contaminate samples on it. These contamination channels have been investigated by loading wafers with either only blanks (blank ratio measured by conventional $^{10}\text{Be}$ AMS: $\sim10^{-15}$) or blanks together with standards with $^{10}\text{Be}/^{9}\text{Be}$ ratios in the range of $10^{-7}$-$10^{-9}$. It was found that the background ratio is better than a few times $10^{-13}$ for blanks on a wafer holding only blanks (95% confidence level for zero $^{10}\text{Be}$ counts recorded during the charge collection corresponding to $\sim10^{13}$ $^{9}\text{Be}$ atoms). However, if the wafer has been prepared with a standard on it, the background ratios of the blanks are three orders of magnitude lower than the measured ratio of the sample irrespective of whether the blank is the first sample to be analysed on a given wafer or not. Cross contamination therefore occurs during the baking process in the oven. However, if the ratios of the sample to measure and the standard do not lie more than two orders of magnitude apart then this should not impose a problem for the measurement.

5.3 Instrumentation

The experimental setup used for the measurement of carrier-free samples is different from the one used for the measurements presented in chapters 3 and 4. However, the only difference between the setup of a routine $^{10}\text{Be}$ AMS measurement performed at the PSI/ETH AMS facility and the measurement of carrier-free $^{10}\text{Be}$ samples is the use of a different ion source. BeO$^-$ ions are extracted from the ion source and the switching system of the low-energy magnet injects mass 25 amu and 26 amu sequentially into the tandem accelerator, which is run at 5.6 MV with a gas stripper. Like in routine measurements the $^{16}\text{O}^{5+}$ fragment from the break-up of the $^{9}\text{Be}^{16}\text{O}^-$
molecule is analysed and used for normalisation on the high-energy side of the accelerator. The $O^{5+}$ current is measured in a Faraday cup situated behind the analysing magnet. The $^{10}\text{Be}^{3+}$ beam additionally passes a second stripping foil and a second magnetic deflection to reduce the isobaric interference $^{10}\text{B}$ due to a different charge state distribution at the higher energy. The remaining $^{10}\text{B}$ in the beam is stopped in a gas absorber just in front of the gas ionisation detector.

Fig. 29: Relevant elements for the measurement of carrier-free beryllium samples on the low-energy side of the PSI/ETH AMS facility.

Fig. 30: Relevant elements for the measurement of carrier-free beryllium samples on the high-energy side of the PSI/ETH AMS facility.
For clarification figure 29 shows the relevant elements of the low-energy side of the PSI/ETH AMS facility and figure 30 shows the equivalent on the high-energy side of the tandem accelerator.

When setting up the facility for carrier-free $^{10}$Be AMS, the high-current source is used first to tune the facility identically as for a routine $^{10}$Be AMS run. Its cathode potential is then set to match the sample potential of the Accelerator SIMS source. Once the facility is tuned the high current source is turned off and the electrostatic deflector just after the source (ED 3) is retracted out of the beam line. Also, the integrator used to measure the $^{16}$O current has to be changed to one suitable for the measurement of 100 pA-currents and the pulse of the beam bouncing system, during which $^{9}$Be$^{16}$O$^-$ is injected into the accelerator, is increased from 200 $\mu$s to 20 ms. The extraction unit of the Accelerator SIMS source is roughly tuned by maximising the current measured in a Faraday cup before the low-energy analysing magnet. Fine-tuning of the extraction is done by maximising the current of the fragments of the injected $^{9}$BeO$^-$ ions in the Faraday cup following the accelerator and after that in the Faraday cup following the high-energy analysing magnet. Except for minor retuning of the low-energy magnet, none of the settings of the ion optical elements tuned with the high-current source are changed during measurement.

With the facility tuned and ready for analysis, the stainless steel wafers prepared according to section 5.2 are brought into the Accelerator SIMS source one by one. With the x/y-stage the sample to measure is placed under the primary beam and extraction of the secondary ions is optimised by adjusting the steerers and lenses in the extraction of the source. If possible, the extraction unit is left unchanged until the next wafer is brought into the chamber thus assuring identical analytical conditions for all the samples on a given wafer. However, the tuning of the extraction unit should be checked before every measurement in order to minimise the possibility of mass fractionation during analysis due to a not-quite-optimal extraction of the secondary ions.

The measurement procedure of a wafer is as follows. First, a blank sample is measured to determine the background. Then, alternately, the sample and the standard are measured three times for approximately 10 minutes each. Figure 31 illustrates a typical measurement of 10 minutes length by plotting the $^{10}$Be counting rate and $^{16}$O$^{5+}$ current together with the resulting $^{10}$Be/$^{9}$Be ratio as a function of time. For technical reasons this particular measurement was performed with a Cs$^+$ current of about 100 nA. The strong increase in current after about 450 seconds is caused by moving the sample under the caesium beam by a few tens of micrometers with the
stepping motors of the x/y-stage. The measured ratio is not influenced by this increase in current.

**Fig. 31:** Typical run of a sample showing the $^{10}\text{Be}$ counting rate and the $^{16}\text{O}^{5+}$ current as well as the resulting $^{10}\text{Be}/^{9}\text{Be}$ ratio as a function of time. For technical reasons the Cs$^+$ current during this measurement was about 100 nA.

Finally the blank is measured again to monitor possible changes in the background of the measurement.

Taking the weighted mean of the three measurements gives the final $^{10}\text{Be}/^{9}\text{Be}$ ratio of the sample. Samples with a $^{10}\text{Be}/^{9}\text{Be}$ ratio of $10^{-9}$ can be measured to a precision of about 3%. Counting statistics is the limiting factor in the uncertainty, and in the limited amount of data available at present no external error is observed. With a Cs$^+$ current of 600 nA, the $^{16}\text{O}^{5+}$ current is typically 200 - 300 pA with a yield of secondary BeO$^-$ ions of about 1%. This yield is comparable to the yields of other ion sources (1-2 %). The 30 minutes of analysis time mentioned above do not use up all of the sample. Under analytically acceptable conditions analysis time can be extended up to 1.5 hours, which makes the measurement of $^{10}\text{Be}/^{9}\text{Be}$ ratios in the $10^{-10}$ range possible to an accuracy of around 10%. Not all of the sample beryllium can be consumed during measurement and the overall useful yield of a single sample is around 4·$10^{-4}$. Background ratios are ~3·$10^{-11}$ when normalising to standard solution M3.
5.4 Results and Discussion of first Measurements

In order to test this new Accelerator SIMS method, three samples each were taken from ferromanganese crusts ROM96 and GMAT 14D and two samples were taken from crust D11-1. The \(^{10}\text{Be}/^{9}\text{Be}\) ratios at various depths in crusts GMAT 14D and D11-1 have previously been measured with the ISOLAB-120 SIMS instrument in Oxford (Ling et al., 1997; Frank et al., 1999). The \(^{10}\text{Be}/^{9}\text{Be}\) ratio as a function of depth in crust ROM96 was derived by individually measuring the absolute \(^{10}\text{Be}\) and \(^{9}\text{Be}\) concentrations in the crust with AMS and ICP-MS respectively, and then calculating the corresponding ratios. Figures 31, 32, and 33 show the results of the original measurements connected with straight lines together with the results of the Accelerator SIMS measurements. The horizontal bars through the data points indicate the depth range out of which the corresponding sample was taken. The vertical error bars represent the 1σ-error of the \(^{10}\text{Be}/^{9}\text{Be}\) ratio of the sample, which, in the case of the ISOLAB-120 measurements, is counting statistics convoluted with an empirically determined external error. A possible external error in the Accelerator SIMS measurements is too small to be quantified with the amount of data available from a single wafer. But because Accelerator SIMS measures ratios normalised to a standard on the same wafer, the reproducibility between wafers holding the same sample is not an issue. The error of 3% in the nominal value of the M3 standard was not included into the errors.

Belshaw et al., 1995, report a discrepancy between the published ratio of the M3 standard and the ratio measured with the ISOLAB-120 when calibrating to the NIST SRM-951 boron standard. To take this into account all ratios measured with Accelerator SIMS were normalised to the ratio of the M3 standard measured with ISOLAB-120 (3.09 \(\times\) 10^{-8}) (Belshaw et al., 1995, table 1).

As can be seen from figures 32 and 33 the Accelerator SIMS measurements fit the data previously measured with ISOLAB-120 very well, apart from two exceptions (CM13 and CM14) in crust GMAT 14D which will be discussed later on. Especially, for the sample, for which a direct comparison of the ratio is possible from the depth range out of which it was taken, the Accelerator SIMS measurement yielded an identical result to the ISOLAB-120 measurement to within statistics. This is true for the other samples as well and is quite astonishing, because the crusts were literally resampled in comparison to taking an aliquot from a reservoir of already sampled material. All measured ratios and errors are listed in tables in Appendix B. A complete list of the ratios measured with ISOLAB-120 and the combination of \(^{10}\text{Be}\) AMS and ICP-MS for the three crusts is given there as well.
Fig. 32: $^{10}$Be/$^9$Be ratio as a function of depth in ferromanganese crust D11-1 comparing the samples measured with Accelerator SIMS (CM16 and CM17) with data published by (Ling et al., 1997).

Fig. 33: $^{10}$Be/$^9$Be ratio as a function of depth in ferromanganese crust GMAT 14D comparing the samples measured with Accelerator SIMS (CM13, CM14 and CM15) with data published by (Frank et al., 1999).
The large sampling ranges in crust D11-1 are only due to the fact that CM16 and CM17 were not intended for a direct comparison of methods. As can be seen from the data of the other crusts, taking greater care while sampling results in a better depth resolution.

Exceptions are the two data points CM13 and CM14 from crust GMAT 14D. These samples contained less than 50 ng of Be and were too small for reproducible analysis, i.e. repetitive measurements gave ratios that scattered by more than the internal error of the individual measurements. The small samples can be explained with the high growth rate of the GMAT 14D crust. No measurements of the absolute $^9$Be concentration in GMAT 14D have been made, but with ~10 mm/Ma it has grown 5-6 times faster than the other crusts which means that the $^9$Be concentration is about the same amount less than in the other crusts (Frank, 2003a). This will yield a lot smaller samples, if roughly the same amount of material is taken from the ferromanganese crusts. Because of the uncertainty in the $^9$Be concentration of GMAT 14D it is expected that the limit to the sample size is smaller than 50 ng of beryllium.

In figure 34 the Accelerator SIMS results of samples from crust ROM96 are compared with results gained from the combination of $^{10}$Be AMS and $^9$Be ICP-MS. (Frank et al., 2003b)

![Fig. 34: $^{10}$Be/$^9$Be ratio as a function of depth in ferromanganese crust ROM96 comparing the samples measured with Accelerator SIMS (CM10, CM11 and CM12) with ratios obtained with $^{10}$Be AMS and $^9$Be ICP-MS. (Frank et al., 2003b)](image-url)
measurement, the day-to-day reproducibility of the absolute \(^{9}\text{Be}\) concentration with ICP-MS is about 15\%. This introduces a large uncertainty to the measured absolute ratios, even if the relative variations can be measured accurately. In general, it is also the ICP-MS measurements that contribute to the large errors of the data points. By correcting the ratios of one method by 22\%, both methods give identical results within statistical uncertainty. However, it is Accelerator SIMS that produces the more reliable results for both absolute ratios as well as relative variations between data points.

Generally, it can also be said that the precision of the Accelerator SIMS measurements is better than those of the ISOLAB-120 measurements as well as the combination of \(^{10}\text{Be}\) AMS and ICP-MS.

### 5.5 Conclusions

First measurements of natural \(^{10}\text{Be}/^{9}\text{Be}\) ratios with Accelerator SIMS have been performed successfully, and the analysed total sample sizes of about 100 ng of Be represent a unique achievement in the field of AMS. It demonstrates that samples of \(~10^{16}\) atoms in total can be measured reliably and even isotopic ratios of \(10^{-10}\) can be measured to a precision of \(~10\%\), higher ratios can be measured to a precision of \(~3\%\). The good agreement of the Accelerator SIMS results with results from other methods demonstrate that this new method is ready to be used for routine measurements of carrier-free \(^{10}\text{Be}\) samples.

In addition, the expectations to develop a more precise and more sensitive method for the measurement of natural \(^{10}\text{Be}/^{9}\text{Be}\) ratios were fulfilled. This means that growth rates and therefore time scales of ferromanganese crusts can be measured to greater precision. The measurement of smaller ratios (\(10^{-10}\)) in comparison to the method based on SIMS (\(10^{-9}\)) also means that the period, over which the time scales are measured, can be increased from \(~10\) Ma to \(~15\) Ma (3 half-lives of \(^{10}\text{Be}\)). For ratios of \(10^{-10}\), which are either not measurable (SIMS) or the precision of the measurements is bad (AMS/ICP-MS), the higher precision of Accelerator SIMS makes the extrapolation of the time scale to deeper layers of the crust, where \(^{10}\text{Be}/^{9}\text{Be}\) ratios cannot be measured anymore, more accurate. It is planned to apply the Accelerator SIMS method to the measurement of \(^{10}\text{Be}/^{9}\text{Be}\) ratios in ferromanganese crusts from sea-mounds in the Mediterranean out-flow zone on the Atlantic side of Gibraltar. The method will be able to give reliable information on how the water circulation through the sea-passage changed in the past.
It also might be possible to transfer the technique developed with this method to the measurement of carrier-free samples of other radioisotopes. In the light of the development of small AMS-facilities with terminal voltages of less than 1 MV the potential of using a focused ion beam to analyse samples could be significant (Suter et al., 2000).

The results of this chapter combined with the results of chapters 3 and 4 also demonstrate that it is be possible to measure the presence of trace elements in ppb-concentrations in samples of 100 ng in size. But for the measurement of isotopic ratios of trace elements to the precision required in the environmental sciences (better than 1%) ppm concentrations should be available.
Chapter 6  
Comparison with other Analytical Techniques

It remains to compare the measured figures of merit of Accelerator SIMS with those of other analytical methods. A detailed comparison of all existing Accelerator SIMS facilities with every single analytical technique in the wide variety of techniques available would take too long at this point. Therefore, Accelerator SIMS will mainly be compared with the two state-of-the-art analytical techniques presently available: SIMS and ICP-MS.

Ideally, the decision on which analytical method is used for an application is made by choosing the best analytical method for the set problem. However, it is not only properties such as sensitivities or detection limits of a technique that influence the decision. Other factors such as sample throughput, sample preparation, availability of the analytical apparatus, etc. have a large influence on the final choice. These boundary conditions are unique from application to application and from laboratory to laboratory. Therefore, the following discussion will only compare quantifiable properties of the PSI/ETH Accelerator SIMS facility with the capabilities of other analytical methods.

Possible improvements to Accelerator SIMS will be presented after this comparison. There are a variety of technical improvements that can still be made in order to improve performance and sensitivity. A few of them will be discussed.

6.1 Detection Limit and Lateral Resolution

For bulk concentration analysis of trace elements it is usually the detection limit for a given lateral resolution that determines the potential of a technique for applications. A comparison between methods can therefore be made by creating a graph in which trace element concentration is plotted against analytical spot size. In this graph every technique is represented by an area that is defined by its detection limits for a given lateral resolution. Figure 35 shows such a graph with various areas corresponding to some techniques. Additional techniques that only allow imaging or concentration analysis are plotted along the corresponding axis. The figure is based on a website of the Charles Evans and Associates analytical group (Charles Evans and Associates, 2000).
Chapter 6  Comparison with other Analytical Techniques


Fig. 35: Detection limits against lateral resolution: A comparison of regimes accessible to various analytical methods.
The area in which Accelerator SIMS can operate is shown in figure 35 as well. It is based on results of measurements performed at the PSI/ETH Accelerator SIMS facility. In addition, the area gained by extrapolating detection limits to expected values, after the sensitivity of the apparatus had been improved, has been included as well. As can be seen, the area is basically the regime represented by conventional SIMS extended towards lower detection limits by more than one order of magnitude. This was to be expected, since Accelerator SIMS has the advantage of suppressing molecular and isobaric interferences with the additional use of an accelerator mass spectrometer. Accelerator SIMS does not rival the high lateral resolutions achievable with SIMS due to the fact that no state-of-the-art SIMS source has ever been attached to an accelerator mass spectrometer yet. However, when looking at figure 35 the following should be kept mind: in chapter 3 it was demonstrated that the sensitivity of Accelerator SIMS for bulk concentration analysis of a given trace element can vary by orders of magnitude according to the secondary ion yields of the different elements in different sample matrices. This feature is not unique to Accelerator SIMS. Other methods suffer from the same or a similar disadvantage and in some cases a trace element cannot be analysed with a given technique at all. Figure 35 should therefore not be interpreted as showing the detection limits for all trace elements in all samples for a certain lateral resolution, but more as the envelope defined by the sum of convenient analytical conditions. The decision of which technique is suitable for an application can therefore not be made based on figure 35 alone.

6.2 Analysis of Small Samples

As was seen in chapter 5, the challenge of analysing small samples lies in the art of mounting the samples in a way that they can be analysed reproducibly. However, the following discussion is not going to focus on this aspect. A more general view of aspects to be considered for such analyses will be given; be it for bulk concentration analysis or isotopic ratio measurements. Again, a detailed comparison of all possible techniques would take too long at this point and the following discussion is by no means exhausting.

Assuming that a sample can be mounted in a way that reproducible measurement is possible, then the smallest sample size analysable with a given application is determined by the overall useful yield of the analytical technique under consideration, or, in other words, on the fraction of atoms that are not detected during analysis and are therefore lost. A graphical visualisation of such losses suffered by different
Chapter 6  Comparison with other Analytical Techniques

techniques is attempted in figure 36 where Accelerator SIMS is compared with SIMS and ICP-MS. The example used for discussion is the measurement of carrier-free $^{10}$Be samples presented in chapter 5.

It is assumed that a sample of given size - in this case 100 ng of beryllium (100 ng Be = 6.6\times10^{15} Be atoms) with a rare isotope abundance of 10^{-10} (in this case $^{10}$Be with 6.6\times10^5 atoms) - is prepared for the analysis in the best possible way. For SIMS the main losses will then be due to the low ion yield in the sputter process. In this example, SIMS analyses positive beryllium ions, which have a yield of about 1% when sputtered from pure beryllium oxide (Benninghoven et al., 1989). The transmission probability through the mass spectrometer is above 90% and losses are therefore negligible. This is a feature that Accelerator SIMS has in common with SIMS. By coincidence, the yield of negative beryllium oxide ions is also about 1%.

However, for Accelerator SIMS additional losses in the intensity of the ion beam are suffered by additionally sending the ion beam through the accelerator mass spectrometer. For the specific example being discussed the transmission of $^{10}$Be$^{3+}$ is 15%. Generally, the transmission can range from 0.1% for heavy elements through a spectrometer with no special design up to 50% and higher for lighter elements through a dedicated system (Jacob et al., 2000).

![Figure 36: Comparison of the analysis of carrier-free $^{10}$Be samples with Accelerator SIMS, SIMS and ICP-MS. The losses in sensitivity due to overall useful yield, detector background, molecular and isobaric interferences and the resulting dynamic range are indicated for the individual techniques.](image-url)
In figure 36 the fractions of sample atoms lost during analysis are indicated with horizontal lines for the individual techniques. Ideally, the intensity of the signal of the rare isotope, which is measured with a technique, should then be proportional to the remaining number of atoms that make it through the analytical instrument. However, detector background or interferences that could not be completely suppressed can reduce the sensitivity of the method. The combination of the overall useful yield and the different backgrounds that are present define the lower limit of the dynamic range in which an analytical technique can detect a rare isotope.

ICP-MS cannot be compared as directly to Accelerator SIMS and SIMS, because the analytical process is different. The sample is usually dissolved in a weak acid. This solution is then transported to a so-called nebuliser where it is sprayed into a carrier gas (usually argon). Generally, the salinity of the solution injected into the nebuliser is not allowed to be higher than 10 mg/ml (or 10 mg/g) otherwise the nebuliser will clog (Knüsel, 1999). The sample is then carried to the plasma where only a few percent of the argon flow is injected into the plasma (Beauchemin, 2002). The analysis of beryllium with ICP-MS is additionally hampered by the presence of $^{10}\text{B}^+$ and $^{40}\text{Ar}^{4+}$ in the mass spectrum. These interferences cannot be resolved completely and even for thoroughly purified samples the detection limit of $^{10}\text{Be}$ has been found to be about 1 ng/g (Knüsel, 1999). Using a hot plasma all the atoms entering the plasma are ionised and almost all molecules will be destroyed, so $^9\text{BeH}^+$ is not a problem. However, only a fraction of the ions produced by the plasma can be accepted by the mass spectrometer. Especially, if a magnetic sector field spectrometer with a high mass resolution is used the overall useful yield will suffer and in cases can be as low as $10^{-6}$ which is not in favour of the analysis of small samples (Beauchemin, 2002; Turner et al., 2000).

If the salinity of the sample solution is not allowed to be higher than 10 mg/ml then $^{10}\text{Be}/^9\text{Be}$ ratios of $10^{-7}$ are the smallest ratios that can be measured with ICP-MS. However, this is the highest ratio ever found in the environment (von Blanckenburg et al., 1996a). Without wanting to perform tedious isotopic enrichment of $^{10}\text{Be}$ in the sample, ICP-MS is therefore not suitable for this application as can be seen in figure 36 as well.

To do ICP-MS justice, however, it should be said that the overall useful yield depends strongly on the type of transport system used to inject the sample into the plasma and on the type of mass spectrometer used to analyse the ions. In some cases detection limits of a few fg/g have been achieved (Winefordner et al., 2000; Günther et al., 1999; Beauchemin, 2002). These are, however, instrumental backgrounds and should not be confused with the general performance of ICP-MS. The real advantage of ICP-
MS lies in the analysis of vacuum incompatible samples. For example, with Laser Abolation ICP-MS fluid inclusions in minerals can be analysed (Halter et al., 2002).

The upper limit of the dynamic range would have to be reduced by at least two orders of magnitude in figure 36, if the bulk concentration of a trace element were to be analysed instead of an isotopic ratio. If the trace element concentration rises above 1% then its secondary ion current is no longer proportional to its concentration (Benninghoven et al., 1989). If the trace element is present in such high abundance then a calibration curve of secondary ion current versus trace element concentration would have to be established first, a method that would introduce additional uncertainties to the measured results. In addition, the matrix and trace elements will have different ion yields which has an additional influence on the overall useful yields and therefore on the dynamic range as well.

The combined results presented in this thesis demonstrate that it is possible to measure the presence of trace elements in ppb concentrations in samples of 100 ng in size. But for the measurement of isotopic ratios of trace elements to the precision required in the environmental sciences (better than 1%) ppm concentrations should be available.

### 6.3 Improvements to Accelerator SIMS

The full potential of Accelerator SIMS has not been exploited yet. However, further technical improvements to the existing facility or the design of a new apparatus have to be made for this. Higher precision and an extension of the capabilities of Accelerator SIMS would be the result.

By extending the variety of detectors available at the PSI/ETH AMS facility, the beam bouncing system of the low-energy magnet could be used for quasi-simultaneous injection of different masses. This would be of advantage for the measurement of both isotopic ratios of trace elements as well as trace element concentrations. Because of the possibility to monitor the transmission during measurement or the possibility to quasi-simultaneously detect different isotopes of a trace element, the results of Accelerator SIMS measurements would be a lot more precise and would also extend the capabilities of Accelerator SIMS to analytical regimes, which are not accessible to other techniques.

For example, the transmission is not monitored during the measurement of platinum group elements and corrections for a possible variation cannot be made. The main reason for this is that measurements are presently limited to the use of only one
detector and the measurement of ion currents in Faraday cups. Because the trace elements analysed are a lot heavier than the main compounds of the sample matrix, the bouncing system of the low-energy magnet cannot bridge the gap in order to measure an ion current related to the sample matrix in a Faraday cup. However, a possible candidate to monitor a beam related to the matrix would be the Cs$^{6+}$ fragment coming from the break-up of an intense molecule with a mass close to the mass of the trace element of interest, for example, the $^{133}$Cs$^{28}$Si$_2$ molecule. The injection mass of 189 amu would lie within the reach of the bouncing system when the low-energy magnet is tuned to the mass of one of the heavy platinum group elements. In order to be able to monitor the Cs$^{6+}$ beam at the position of the detector additional bouncing of the high-energy electrostatic deflector would be required. This, however, has already been implemented and does not impose a technical problem (Suter et al., 1984). A greater challenge lies in the detection system. The field value of the high-energy magnet has to remain constant during measurement and the resulting separation of the Cs$^{6+}$ beam and, for example, the Au$^{9+}$ beam at the position of the detector would be ~40 mm. With either two small detectors or with a position-sensitive gas ionisation detector with a broad entrance window (~76 mm) both elements could be monitored quasi-simultaneously. The same principle could also be used to measure isotopic ratios of heavy trace elements, for example the $^{191}$Ir/$^{193}$Ir ratio.

A different constraint presently imposed on Accelerator SIMS is that it has only been performed at large accelerator facilities and accordingly measurements are more complex and more expensive. To make the method more accessible to scientists wanting to use Accelerator SIMS, a smaller instrument would have to be developed that could fit into a regular laboratory. Recent development and commercial success of small AMS facilities for radiocarbon dating (Suter et al., 1999; Jacob, 2001) and results obtained for the measurements of other radioisotopes on a small AMS facility (Stocker et al., 2003) indicate that a versatile compact AMS facility for the measurement of a wide variety of radioisotopes with similar sensitivities and precision as on large facilities can be designed. Table 8 summarises the present transmissions and background levels of radioisotopes measured with the compact 600 kV PSI/ETH AMS facility. The extremely high transmission of heavy elements such as uranium, plutonium and thorium in charge state 3+ (15%) is striking (Fifield et al., 2003) and is almost two orders of magnitude higher than the transmission of similar elements through the accelerator mass spectrometer used for this thesis. However, generally the transmission would increase by a factor of 2 to 5. In addition, at the lower energies increasing background in the detector hampers measurements.
The results of this thesis and the insight gained with the design of compact AMS facilities suggest that the design of a small compact Accelerator SIMS instrument operating at low energies is feasible. The compact and with it simpler design of such a machine would also improve the precision of Accelerator SIMS measurements. The great distances covered by the ion beam as it travels through the high-energy mass spectrometer would be shortened considerably making the system less vulnerable to instabilities of all kinds. The higher transmission through a compact system means that generally the overall useful yields would improve relative to the accelerator mass spectrometer used for the measurements presented in this thesis. Correspondingly, assuming that no additional background problems arise, the detection limits would improve as well. First test measurements investigating the feasibility of trace element analysis with stable trace elements are being made at the compact 600 kV PSI/ETH AMS facility at present (von Wartburg, 2003).

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Charge state</th>
<th>Energy [keV]</th>
<th>Transmission [%]</th>
<th>Background ratio / Detection limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{10}$Be</td>
<td>2+</td>
<td>1500</td>
<td>13 [$^9$Be]</td>
<td>$10^{-13}$</td>
</tr>
<tr>
<td>$^{14}$C</td>
<td>1+</td>
<td>970</td>
<td>40 – 45</td>
<td>$5\cdot10^{-15}$</td>
</tr>
<tr>
<td>$^{26}$Al</td>
<td>3+</td>
<td>2455</td>
<td>9</td>
<td>$7\cdot10^{-14}$</td>
</tr>
<tr>
<td>$^{41}$Ca</td>
<td>1+, 2+, 3+</td>
<td>1000 - 2000</td>
<td>15 – 20</td>
<td>$10^{-12}$</td>
</tr>
<tr>
<td>$^{129}$I</td>
<td>4+</td>
<td>2500</td>
<td>4</td>
<td>$10^{-12}$</td>
</tr>
<tr>
<td>Th</td>
<td>3+</td>
<td>1240</td>
<td>15</td>
<td>-</td>
</tr>
<tr>
<td>Pu</td>
<td>3+</td>
<td>1200</td>
<td>10 - 15</td>
<td>$10^6$ atoms</td>
</tr>
</tbody>
</table>

*Table 8: Charge state, resulting energy after acceleration, transmission and background levels for radioisotopes evaluated at the 600 kV PSI/ETH AMS facility. Taken from (Stocker et al., 2003)*

Another advantage of a compact Accelerator SIMS facility in comparison to sector field mass spectrometers is that Accelerator SIMS only requires the use of spectrometers with a relatively low mass resolution in comparison to state-of-the-art sector field spectrometers. This means that the ion optics of the system are simpler and the instrument would be easier to operate and easier to maintain than a high-resolution sector field spectrometer. The most delicate part of the system would then be the primary ion source.

The disadvantage of only being able to analyse negative secondary ions could be compensated with the use of charge-changing canals. In this arrangement positive
secondary ions would be extracted from the sample and passed through an alkali vapour placed between the low-energy magnet and the tandem accelerator. In this charge-changing canal the secondary ions would be converted either to neutrals or to negative ions with an efficiency of, in cases, more than 50% (Heinemeier et al., 1978a+b; Litherland et al., 1997).
Chapter 7  Final Conclusions

The main goal of this thesis, namely evaluating the potential of Accelerator SIMS with respect to its application in the environmental sciences, has been met. It can be said that Accelerator SIMS is superior to any other analytical method available for specific applications. The applications discussed in chapters 4 and 5 could not have been performed with the same sensitivity or lateral resolution by any other method available at present. Therefore the potential of Accelerator SIMS lies in its use for specific applications in the environmental and other sciences. These can be all sorts of trace element or isotopic ratio analyses in solids. Applications with radioisotopes other than $^{10}$Be are to be considered as well. The individual achievements are summarised in the following.

When work towards this thesis commenced, instrumental setups for reproducible analysis of the trace elements of interest for the applications discussed in this thesis were non-existent. Isotopes heavier than iodine had never been analysed in trace element abundances at the PSI/ETH AMS facility before. The facility was technically upgraded to the extent to make measurements of the kind presented in this thesis possible. Procedures required for time-efficient start-up of the AMS facility had to be developed. These tuning procedures can be applied to trace element analysis in the entire mass range and in different sample matrices. The ability to reliably tune the PSI/ETH Accelerator SIMS facility is a prerequisite to tackle future applications. With the procedures developed for the two applications, know-how has been gained with respect to the sample forms necessary for a reliable Accelerator SIMS analysis and for quicker tuning of the instrument itself. Future applications are able to substantially benefit from this.

In addition, the design of the ion optical elements was improved to achieve a better stability of the secondary ion currents. The transmission through the system could be increased by a factor of more than ten for all elements, thereby improving the sensitivities and detection limits by the same factor.

The sensitivities and detection limits of platinum group elements, gold, and silver (PGE) analysed in a silicon dioxide matrix were studied by implanting PGE into SIMOX-wafers at two different depths and evaluating the resulting depth profiles measured with Accelerator SIMS. It was shown that the sensitivity of Accelerator...
SIMS drops by nearly two orders of magnitude in comparison to the analysis of PGE in a silicon matrix. This is mainly due to a reduction in the ionisation probability in the sputter process. The type of matrix a trace element is analysed in therefore greatly influences the properties of a measurement.

For the in-situ analysis of PGE in sedimentary layers of the KT-boundary, additionally a procedure to analyse electrically non-conducting samples had to be developed. Best results were achieved by covering the samples with a few nanometer thick electrically conducting layer. Subsequently, in-situ bulk concentrations of less than 1 ng/g of iridium in sedimentary layers were measured. The lateral resolution of the measurements was 100 µm. To date, such concentrations have so far only been measurable with NAA and AMS, methods mainly suitable for bulk concentration analysis only and without any significant lateral resolution. With Accelerator SIMS it has therefore become possible to study concentration distributions of trace elements in the ng/g-range at a lot smaller scale.

A similar situation was encountered when work towards the measurement of carrier-free \(^{10}\text{Be}\) samples commenced. In this case a procedure had to be found in order to tune the facility to be able to reliably analyse the asthmatic currents of a few hundred pA extracted from 100 ng-samples (total sample size) and to measure their isotopic ratios of \(10^{-10}\) to a precision of ~10%. Analysis of such small samples has never been performed in the field of AMS before and the greatest challenge was to find an adequate way to load the samples onto wafers so that, on one hand, they did not drop off the wafers and on the other that their geometrical shape enabled reproducible measurement. The developed procedure has been explained in detail in chapter 5. Test measurements gave a good agreement with results obtained with already existing methods and showed that the new Accelerator SIMS method measures more precisely than the other methods. This means that growth rates and therefore time scales of ferromanganese crusts can be measured to greater precision. The measurement of smaller ratios (\(10^{-10}\)) in comparison to the method based on SIMS (\(10^{-9}\)) also means that the period over which the time scales are measured can be increased from ~10 Ma to ~15 Ma (3 half-lives of \(^{10}\text{Be}\)). For ratios of \(10^{-10}\), where the precision of the previously available methods gets worse, the higher precision of Accelerator SIMS makes the extrapolation of the time scale to deeper layers of the crust, where \(^{10}\text{Be}/^{9}\text{Be}\) ratios cannot be measured anymore, more accurate.

With the two applications discussed here, it has been demonstrated that Accelerator SIMS has unique properties and can perform measurements that cannot be performed with any other analytical technique. However, the technique can still be made more flexible and more powerful. As described in section 6.3 extensions made to the
available detection systems at the PSI/ETH AMS facility would make the measurement of isotopic ratios of trace elements possible and the precision of results would be improved by monitoring transmission during measurement. Charge changing canals could compensate the restriction to only being able to analyse negative secondary ions.

In order to make Accelerator SIMS more competitive to other state-of-the-art analytical methods, the size of the apparatus has to be reduced. Recent success of compact AMS facilities suggests that Accelerator SIMS is possible at low energies as well ( < 2 MeV ). In this case Accelerator SIMS would also profit from the higher transmissions that have been achieved with such facilities and which would result in higher sensitivities and better detection limits. Mass spectrometers with only a relatively low mass resolution would have to be used for a compact Accelerator SIMS facility, making the system simpler and operation easier than with sophisticated sector field spectrometers. This way Accelerator SIMS would become more accessible to scientists in all fields of research and would develop to be a more powerful tool than it already is.
Appendix A  Beryllium Chemistry

The recipe below is the one used for chemical preconcentration and purification of beryllium from ferromanganese crusts. Sample material was removed from the crust by sawing a rut into a cross section of the crust with a fine saw. The dust collected from this process was fed into the chemical purification process.

**Sample dissolution**
Dissolve ~100 mg of Fe-Mn-crust in 1.3 ml 6M HCl at low heat (7 ml Savillex Vial)
Transfer the solution to a centrifuge tube leaving the coarse residue in the vial
Centrifuge at 10'000 Rpm for 5 Min.
Transfer solution to a 15 ml centrifuge tube
pH 8 precipitation with NH₃
Centrifuge and discard supernate
Dissolve precipitate in 1 ml 6M ΔHCl

**Column Fe**
2ml Biorad (Dowex) 1x8 100-200 mesh in small Biorad Column stored in 1M ΔHCl
Open column and let storage liquid drop out
2ml Millipore H₂O: clean resin
2ml 1M ΔHCl: clean resin
5ml + 5ml 6M ΔHCl: Condition resin
Load sample (1ml 6M HCl)
0.5ml + 0.5ml + 1ml + 2ml: 6M ΔHCl
2ml 1M ΔHCl: clean resin
2ml Millipore H₂O: clean resin
2ml 1M ΔHCl: clean resin
Seal and store columns in 1M ΔHCl
Evaporate samples
Dissolve precipitate in 2 ml Oxalic acid

**Column Be (Small Column B)**
1 ml Biorad (Dowex) AG50-X8 (200-400 mesh) in small Biorad Column stored and sealed in 6M HCl
Open column and let acid drop out
2 ml ~3M ΔHCl: clean resin
10 ml 6M ΔHCl: clean resin
2 ml ~3M ΔHCl: clean resin
3 ml + 2 ml Millipore H2O: Remove HCl from resin
3 ml + 2 ml: 0.4M Oxalic Acid: Condition resin
Load sample (in 2 ml Oxalic acid)
1 ml + 1 ml + 2 ml 0.4M Oxalic Acid: Wash down sample and elute Fe, Al, Ti, etc.
1 ml + 2 ml Millipore H2O: Remove Oxalic Acid from Column
10 ml 0.5M ΔHCl: Elute Na
2 ml 1M ΔHCl
6 ml 1M ΔHCl: Collect Be in 7 ml Savillex beaker
~ 2 ml ~3M ΔHCl: clean resin
5 ml 6M ΔHCl clean resin
Seal & store column in ~6M ΔHCl
Evaporate samples

AG MG 50 (Small Column A)
Dissolve sample in 1 ml 0.4M Oxalic Acid
1ml Biorad AG MP-50 in small Biorad Column stored in H2O
Open column and let storage liquid drop out
1 ml 3M ΔHCl: clean resin
10 ml 6M ΔHCl: clean resin
1 ml 3M ΔHCl: clean resin
1 ml H2O: clean resin
1 ml 3M ΔHCl: clean resin
10 ml 6M ΔHCl: clean resin
1 ml 3M ΔHCl: clean resin
2 ml H2O: clean resin
2ml + 2ml 0.4M Oxalic Acid: Condition resin
Load sample in 1 ml 0.4M Oxalic Acid
0.5ml + 0.5ml 0.4M Oxalic Acid: Wash sample down
4ml + 4ml 0.4M Oxalic Acid: Elute Al, Fe, Ti, REE, etc.
2ml + 2ml H2O: Wash Oxalic Acid out
3 ml 1M ΔHCl: wash
5 ml 1M ΔHCl: Collect Be (in cleaned Savillex beaker)
1 ml 3M ΔHCl: clean resin
6 ml 6M ΔHCl: clean resin
2 ml 3M ΔHCl: clean resin
2 ml 1M ΔHCl: clean resin
Seal and store columns in 1M ΔHCl
Evaporate samples
Appendix B    Results of the Carrier-free $^{10}$Be Measurements

The following tables summarise mean $^{10}$Be/$^9$Be ratios, $<R>$, and the corresponding errors of the mean ratios, $\sigma_R$, of the carrier free beryllium samples CM10 to CM17 as measured with Accelerator SIMS and presented in chapter 5. If a direct comparison to a published ISOLAB or AMS/ICP-MS measurement is possible these figures are given as well (Ling et al., 1997; Frank et al., 1999; Frank et al., 2003b).

The mean ratios are error-weighted means of three to five individual measurements. Errors of the individual measurements are usually dominated by counting statistics. Weighting the measurements with their errors is therefore similar to weighting them with the integrated charge of the $^{16}$O$^{5+}$ current collected during the corresponding measurement. This is justified considering that in some measurements the samples hardly gave any current at all. The definitions of the individual parameters are given below.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Accelerator SIMS</th>
<th>ISOLAB or AMS/ICP-MS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$&lt;R&gt;$ [⋅10^{-9}]</td>
<td>$\sigma_R$ [%]</td>
</tr>
<tr>
<td>CM10</td>
<td>35.2</td>
<td>2.25</td>
</tr>
<tr>
<td>CM11</td>
<td>6.15</td>
<td>3.55</td>
</tr>
<tr>
<td>CM12</td>
<td>1.21</td>
<td>5.82</td>
</tr>
<tr>
<td>CM13</td>
<td>100</td>
<td>2.71</td>
</tr>
<tr>
<td>CM14</td>
<td>108</td>
<td>2.97</td>
</tr>
<tr>
<td>CM15</td>
<td>31.8</td>
<td>3.49</td>
</tr>
<tr>
<td>CM16</td>
<td>78.2</td>
<td>3.22</td>
</tr>
<tr>
<td>CM17</td>
<td>13.8</td>
<td>4.29</td>
</tr>
</tbody>
</table>

Table 9: Measured $^{10}$Be/$^9$Be ratios with their corresponding errors.

If N is the number of $^{10}$Be/$^9$Be ratio measurements, $R_i$, of a given sample with the 1σ-errors, $\sigma_i$, then the weighted mean ratio $<R>$ is calculated with:

$$< R > = \frac{\sum_{i=1}^{N} \frac{1}{\sigma_i^2} R_i}{\sum_{i=1}^{N} \frac{1}{\sigma_i^2}}$$

(B.1)
Appendix B                Results of the carrier-free $^{10}$Be-Measurements

The error of the weighted mean, $\sigma_R$, is calculated according to

$$\frac{1}{\sigma_R^2} = \sum_{i=1}^{N} \frac{1}{\sigma_i^2} \quad \text{(B.2)}$$

The table 10 summarises the $^{10}$Be/$^9$Be ratios measured in the crusts GMAT 14D, D11-1 and ROM96 with on one hand the ISOLAB-120 instrument and on the other the combination of $^{10}$Be AMS and ICP-MS. These are the ratios the Accelerator SIMS measurements were compared to in figures 32, 33 and 34 in chapter 5 and as published in (Ling et al., 1997; Frank et al., 1999; Frank et al., 2003b).

<table>
<thead>
<tr>
<th>GMAT 14D (ISOLAB-120)</th>
<th>D11-1 (ISOLAB-120)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depth [mm]</td>
<td>&lt;R&gt; [$\cdot 10^{-9}$]</td>
</tr>
<tr>
<td>0-1</td>
<td>115</td>
</tr>
<tr>
<td>7-8</td>
<td>80.5</td>
</tr>
<tr>
<td>14-16</td>
<td>58.8</td>
</tr>
<tr>
<td>26-28</td>
<td>32.3</td>
</tr>
<tr>
<td>36-38</td>
<td>20.9</td>
</tr>
<tr>
<td>49-51</td>
<td>12.3</td>
</tr>
<tr>
<td>61-67</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td>19.9-21.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ROM96 (AMS/ICP-MS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depth [mm]</td>
</tr>
<tr>
<td>0-0.2</td>
</tr>
<tr>
<td>2.0-2.5</td>
</tr>
<tr>
<td>6.0-7.0</td>
</tr>
<tr>
<td>9.5-10.5</td>
</tr>
<tr>
<td>14.0-15.0</td>
</tr>
<tr>
<td>18.0-19.0</td>
</tr>
</tbody>
</table>

**Table 10:** Summary of $^{10}$Be/$^9$Be ratios used for comparing Accelerator SIMS measurements to. The data was taken from (Ling et al., 1997; Frank et al., 1999; Frank et al., 2003b).
References


References


References


References


References


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