Doctoral Thesis

Geochemistry of stable silicon isotopes measured by high-resolution multi-collector inductively-coupled-plasma mass-spectrometry (HR-MC-ICP-MS)

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Geochemistry of Stable Silicon Isotopes measured by High-Resolution Multi-Collector Inductively-Coupled-Plasma Mass-Spectrometry (HR-MC-ICP-MS)

A dissertation submitted to the
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## Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>CONTENTS</td>
<td>3</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>6</td>
</tr>
<tr>
<td>KURZFASSUNG</td>
<td>10</td>
</tr>
<tr>
<td>CHAPTER 1: INTRODUCTION</td>
<td>14</td>
</tr>
<tr>
<td>1. INTRODUCTION</td>
<td>15</td>
</tr>
<tr>
<td>1.1 The global Si cycle</td>
<td>15</td>
</tr>
<tr>
<td>1.2 Motivation for this study</td>
<td>16</td>
</tr>
<tr>
<td>1.3 Background on stable Si isotopes</td>
<td>17</td>
</tr>
<tr>
<td>1.3.1 Stable isotope fractionation</td>
<td>17</td>
</tr>
<tr>
<td>1.3.2 Stable isotopes of Si</td>
<td>19</td>
</tr>
<tr>
<td>1.3.3 Silicon isotope variations in terrestrial samples</td>
<td>20</td>
</tr>
<tr>
<td>1.3.4 Silicon isotope fractionation during in-situ formation of clays</td>
<td>22</td>
</tr>
<tr>
<td>1.3.6 Silicon isotopes in groundwater</td>
<td>23</td>
</tr>
<tr>
<td>1.4 Mass-spectrometry: MC-ICP-MS</td>
<td>24</td>
</tr>
<tr>
<td>1.4.1 Principles of MC-ICP-MS</td>
<td>24</td>
</tr>
<tr>
<td>1.4.2 High-resolution MC-ICP-MS: the Nu1700</td>
<td>28</td>
</tr>
<tr>
<td>1.4.3 Mass-dependent Si isotope fractionation</td>
<td>31</td>
</tr>
<tr>
<td>1.4.4 MC-ICP-MS and Si isotopes</td>
<td>32</td>
</tr>
<tr>
<td>1.5 Outline of this thesis</td>
<td>35</td>
</tr>
<tr>
<td>CHAPTER 2: NEW SAMPLE PREPARATION TECHNIQUES FOR THE DETERMINATION OF SI ISOTOPIC COMPOSITIONS USING MC-ICP-MS</td>
<td>37</td>
</tr>
<tr>
<td>ABSTRACT:</td>
<td>38</td>
</tr>
<tr>
<td>2.1 Introduction</td>
<td>39</td>
</tr>
<tr>
<td>2.2 Experiments</td>
<td>40</td>
</tr>
<tr>
<td>2.2.1 Instrumentation</td>
<td>40</td>
</tr>
<tr>
<td>2.2.2 Reagents and samples</td>
<td>41</td>
</tr>
<tr>
<td>2.2.3 Alkaline fusion of silicates using solid NaOH</td>
<td>42</td>
</tr>
<tr>
<td>2.2.4 Chromatographic separation of Si</td>
<td>43</td>
</tr>
<tr>
<td>2.2.5 Mass-spectrometry</td>
<td>44</td>
</tr>
<tr>
<td>2.3 Results and discussion</td>
<td>46</td>
</tr>
<tr>
<td>2.3.1 Silicon recovery and elution profile</td>
<td>46</td>
</tr>
<tr>
<td>2.3.2 Silicon background and sensitivity</td>
<td>48</td>
</tr>
<tr>
<td>2.3.3 Reproducibility, precision and accuracy</td>
<td>50</td>
</tr>
<tr>
<td>2.5 Conclusion</td>
<td>52</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>53</td>
</tr>
</tbody>
</table>
# CHAPTER 5: RE-ASSESSMENT OF SILICON ISOTOPE REFERENCE MATERIALS USING HIGH-RESOLUTION MULTI-COLLECTOR ICP-MS

## ABSTRACT

**5.1 Introduction**  
**5.2 Methodology**  
**5.3 Results**  
**5.4 Discussion**  
**5.5 Conclusions**

## CHAPTER 6: SILICON ISOTOPE VARIATIONS DURING HIGH-TEMPERATURE PROCESSES

### 6.1 Introduction

### 6.2 Methodology

### 6.3 Case study 1: I- and S-type granites

#### 6.3.1 Results

#### 6.3.2 Discussion

### 6.4 Case study 2: Silicon isotope fractionation during contact metamorphism

#### 6.4.1 Results

#### 6.4.2 Discussion

### 6.5 Conclusions and Outlook

## SUMMARY

## REFERENCES

## DANKSAGUNG

## CURRICULUM VITAE
Abstract

This thesis deals with the use of stable silicon (Si) isotopes measured by high-resolution multiple collector inductively-coupled plasma mass spectrometry (HR-MC-ICPMS). Silicon constitutes 15% of the Earth and is overwhelmingly concentrated in the crust and mantle in the form of silica and silicates. Silicon is also a major nutrient within the marine environment. The primary bio-productivity of the world’s oceans depends amongst other things on the availability of Si. The cycling of Si though the processes of erosion and biogenic uptake is therefore of great interest because of the close connection to the global carbon cycle. The major input of Si into the ocean is via continental riverine pathways and nearly 85% of the Si supplied to the oceans is maintained through continental runoff. Like other dissolved components Si is released into the rivers by chemical weathering of the continental crust. The ability to weather makes the continental crust the major nutrient source for marine organisms, such as diatoms, that convert atmospheric CO2 into organic Corg. The other important link between the global cycles of C and Si is also in connection with continental weathering. The breakdown of Ca- and Mg-bearing silicates liberates those species into the dissolved load of rivers and finally into the oceans where they react with HCO3-, derived from atmospheric CO2, to form Ca/Mg carbonates. This process is thought to regulate the atmospheric CO2 content and thus to control the global climate on a long timescale. Understanding the rates of weathering of continental crust is thus crucial to the modelling of long-term climatic changes, and to gain understanding of how the climate changed throughout earth’s history and how it might change in the future. Since Si is, beside O, the major constituent of the continental crust it might be useful to tap this information for the calculation of weathering rates. However, many different processes govern Si, primarily the formation of secondary products, so that these processes bias the riverine Si concentration and make this pool of information unemployable for calculating weathering rates. Silicon isotopes might be used to distinguish between different processes that control the Si budget of rivers, providing a proxy for silicate weathering.

Silicon isotope ratios of natural samples have been analysed since the 1950s. However, the analytical protocols deployed were complicated, time consuming and hazardous. Furthermore, precision achieved was insufficient to resolve small variations in the Si isotope composition of natural samples. The advent of HR-MC-ICPMS should help to overcome complicated and time-consuming analytical protocols, whilst providing highly precise Si
isotope ratio measurements. However, it has been found that previously used methods did not meet the demands for MC-ICPMS. Therefore, a primary focus of this PhD project was to develop a new chemical protocol that allows the fast and precise determination of Si isotope ratios from a variety of natural sample types.

The result of this development stage was a new separation method that allows the simple and rapid determination of Si isotope ratios in a variety of different natural samples, such as river waters and silicate minerals / rocks to a limiting precision never achieved before. The second focus of this PhD project therefore was the application of the newly-developed method to questions in the geosciences. With this method it has become possible to detect even small variations in the Si isotope composition of natural samples, such as the seasonal variability of the Si isotope composition of river waters; something that has never been found before. A systematic investigation of changes in Si isotope composition and hydrochemistry from four different streams in Switzerland made it possible to assess in particular cases those processes controlling the Si isotope composition and thus the Si budget in these rivers. It appeared that the isotope composition of some rivers reflects mixing between different sources or pools of Sis, such as ground / soil waters and superficial runoffs. The relative contributions depend on discharge and runoff events. The picture gets more complicated as the amount of carbonate rocks and cultivated landscapes within a catchment increases. Here it is not possible to trace the origin of the dissolved Si by the use of its isotopic composition. In general it appears that a lower $\delta^{30}\text{Si}$ is usually indicative of higher silicate weathering rates. River water data obtained from 20 different rivers from Iceland confirm this relation between Si isotope composition and weathering intensity. Moreover, the Icelandic data set shows that on average 51-54% of all released Si is trapped in secondary weathering products. The associated Si isotope fractionation produces a wide range of riverine Si isotope compositions and can be modelled either as an open or closed system fractionation behaviour, depending on hydrological parameters. Interestingly, the age of the bedrock does not seem to impact on the Si isotope composition and ultimately on the weathering rates. However, glacial cover appears to have some influence, since the average Si isotope composition of rivers from glaciated catchments is significantly lighter compared to non-glaciated catchments.

The discovery of seasonal variations in the riverine Si isotope composition due to weathering style points out that the isotopic composition of the inputs into the oceans might have varied throughout earth’s history. Significant changes might occur across glacial-
interglacial transitions, where the weathering style might have changed on a global scale due to the retreat and build-up of vast ice shields. This is important to consider if Si isotopes are used as a bioproductivity proxy in marine studies, where changes of the initial Si isotope composition can compromise the results obtained from the analyses of biogenic opal. Recently, mass-balance calculations have been done to assess that problem but did not consider variations in the Si isotopic input into the oceans. Extending this mass-balance by adding variable Si isotopic inputs into the ocean shows that the oceanic Si isotope composition is more liable to fluctuations of the Si isotopic input into the oceans than to the amount of Si being delivered into the oceans. This thesis thus suggests that isotopic variations of the continental derived Si should be taken into account when interpreting marine palaeoproductivity records.

Beside low-temperature geochemistry, the newly developed method has found applications in solving other geochemical issues. It was possible to produce the first real long-term standard data record to re-assess the calibrations of the European Si reference material IRMM-018 against the international Si reference material NBS-28. The results show that both materials are not similar, as recently claimed. Since the advent of MC-ICPMS makes it relatively easy to acquire Si isotope data quite efficiently, it is necessary to have a reliable calibration on different standard materials in order to make sure that data obtained in different laboratories can be compared.

With the new method, and the high-precision measurements it provides, it was also possible to undertake the first systematic investigations of the fractionation behaviour of Si isotopes during high-temperature processes, such as magma crystallisation and contact metamorphism. In general the data obtained confirm predictions that a $^{30}$Si-enrichment might be associated with increasing SiO$_2$ concentrations, being a matter of the polymerisation degree of SiO$_4$$^4$ tetrahedra in silicate melts. However, the isotope effects found are an order of magnitude lower that predicted on a theoretical basis. The analysis of I- and S-type granites implies that Si isotopes can be used to trace different magma sources. Here it seems to be a matter of the Si source rather than SiO$_2$ concentration. The S-type granite has a lighter Si isotope composition, certainly due to a clay derived component within the host melt, although the SiO$_2$-wt% is higher than the I-type granite.
Silicon isotope data obtained from silicate minerals of a contact-metamorphic suite show that Si isotopes might be used to trace the path of fluids being involved in such processes. Furthermore, there appears to be an equilibrium isotope effect between orthosilicates and parasilicates, such as garnets-clinopyroxene and zircon-quartz. The differences found between quartz and zircon stemming from the same parent magma is interesting, since it implies that the Si isotope composition of zircons can be used as a robust tool to gather information about the composition and origin of the melt it derived from. It appears that Si isotopic compositions of zircons are not easily reset.
Kurzfassung


Die Isotopenzusammensetzung von Si in natürlichen Proben wird bereits seit den 1950er Jahren bestimmt. Jedoch sind die angewendeten analytischen Methoden zeitaufwendig, kompliziert und auch gefährlich, zudem ist die errichte Präzision nicht hoch genug, um kleine


Silizium Isotopenmessungen an unterschiedlichen Graniten und deren Mineralparagenesen zeigte, dass eine Anreichung in $^{30}$Si mit steigendem SiO$_2$-Gehalt in der Schmelze einhergeht. Diese Resultate bestätigen frühere Annahmen, dass der Grad der Polymerisierung von SiO$_4^{4-}$ Tetraedern Einfluss auf Si Isotopenfraktionierung in Silikatschmelzen hat. Untersuchungen an kontaktmetamorphen Mineralparagenesen zeigen systematische Fraktionierungseffekte zwischen Ortho- und Parasilikaten, so hat z.B. Granat eine leichtere Si Isotopie als co-existierender Klinopyroxen, ähnliche Effekte wurden auch in Zirkon-Quarz Paragenesen entdeckt. Diese Beobachtung bedeutet, dass die Si Isotopie von Zirkonen verwendet werden kann, um Rückschlüsse auf die Isotopie der Stammschmelze zu
schliessen. Es konnte keine Rückstellung der Si Isotopie in den untersuchten Proben beobachtet werden. Es ist also davon auszugehen, dass Zirkone die Si Isotopie auch durch extreme Prozesse hinweg beibehalten können und somit eine robuste Informationsquelle darstellen können.
Chapter 1: Introduction
1. Introduction

1.1 The global Si cycle

Silicon is the second most abundant element on earth after oxygen. The earth’s crust and mantle are composed mainly of silicate minerals and rocks, which make about 2/3 of the mass of the entire earth. The continental silicate crust is exposed to the atmosphere and hydrosphere and thus to the physical and chemical disintegrative processes of weathering. The weathering of silicate rocks contributes solutes and particles to the load of rivers and finally to the world's oceans. About 90% of the annual material flux into the oceans is transported by rivers as dissolved and suspended materials (Wollast and Mackenzie, 1983). Nearly 85% of the oceanic Si content is directly maintained via these continental riverine pathways with the remainder being derived from atmospheric deposition and low-temperature alteration of sea-floor basalt (Elderfield and Schultz, 1996; Tréguer et al., 1995). On its way from the weathering site to the river and finally to the oceans Si is involved in several biochemical and geochemical processes, such as the precipitation of weathering products, e.g. clays, opal phases and biogenic silica, e.g. in phytoliths and lacustrine diatom frustules. Once reaching the oceans, Si represents a major nutrient for planktonic diatoms and is thus essential for marine primary bio-productivity. Therefore, the global Si cycle is closely linked to the global carbon cycle because the marine primary production of organic carbon by diatoms is directly related to the availability of Si (Tréguer et al., 1995).

The linkage between the global Si and C cycle is of fundamental importance for global climate as it regulates the content of the atmospheric greenhouse gas CO$_2$ on two sites: (1) Primary production within the ocean converts inorganic atmospheric CO$_2$ into organic carbon (C$_{org}$). By subsequent transport of C$_{org}$ to the deep sea and final burial it lowers the alkalinity of the surface ocean and therefore atmospheric CO$_2$ (Ragueneau et al., 2000). (2) The weathering of Ca- and Mg-bearing silicate minerals / rocks liberates these species into the rivers and oceans where both react with HCO$_3^-$ to form Ca- and Mg-bearing carbonates. This combination of silicate weathering and carbonate precipitation provokes consumption of atmospheric CO$_2$ and so gives a controlling influence on the atmospheric CO$_2$ budget and finally on the global climate (Walker et al., 1981). The relation between weathering of silicate rocks and biologically-mediated CO$_2$ pumping within the oceans represents a vivid example of a close interaction between the biosphere and the global environment.
1.2 Motivation for this study

Nowadays geoscientists pay a lot of attention to the interactions between the biosphere and the global environment to gain a better understanding of how these systems influence the global climate. A thorough understanding of these interactions can help decipher how climate evolved throughout earth’s history and to predict how it might evolve in future (Ragueneau et al., 2000). For these purposes it is absolutely crucial to understand how global element cycles, such as the Si cycle, work and how they might change through time. The marine Si cycle has been the subject of intense research during the last two decades and a good review is given in (Ragueneau et al., 2000) and references therein.

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<thead>
<tr>
<th>Approach</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Elemental</td>
<td>ALEXANDRE et al., 1997; ANDERSON et al., 2000; ANDERSON et al., 2003; BICKLE et al., 2003; BICKLE et al., 2005; BLUM et al., 1998; DALAI et al., 2002; DARMODY et al., 2000; DESSERT et al., 2003; DREVER and ZOBRIST, 1992; FURMAN et al., 1998; GAILLARDET et al., 1999a; GAILLARDET et al., 1999b; GALLY and FRANCE-LANORD, 1999; GISLASON et al., 1996; HILL and APLIN, 2001; LASAGA et al., 1994; MILLOT et al., 2002; QUADE et al., 2003; RAYMO et al., 1988; RIEBE et al., 2003; TIPPER et al., 2006a; WHITE and BLUM, 1995</td>
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<td>chemistry</td>
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<td>Radiogenic</td>
<td>ANDERSSON et al., 2001; AUBERT et al., 2001; BICKLE et al., 2003; BICKLE et al., 2005; BURTON and VANCE, 2000; GALLY et al., 1999; JACOBSON et al., 2003; JACOBSON and BLUM, 2000; JACOBSON et al., 2002; KRISHNASWAMI et al., 1992; OLIVER et al., 2003; PANDE et al., 1994; RIOTTE et al., 2003; SHARMA and WASSERBURG, 1997</td>
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<tr>
<td>Isotopes</td>
<td></td>
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<tr>
<td>Stable Isotopes</td>
<td>HUH et al., 2001; KISAKOREK et al., 2005; PISTNER and HENDERSON, 2003; TIPPER et al., 2006; VILLIERS et al., 2005</td>
</tr>
</tbody>
</table>

Table 1.1: List of references related to weathering studies.

Continental rivers provide the major pathways of all weathering products, such as Si, to the oceans. The most common way of estimating weathering derived fluxes and rates is by considering the changes in riverine aqueous chemistry. Many different approaches have been used to model weathering rates and related processes, such as mass-balance estimates based on the elemental load of rivers, radiogenic isotopes of Sr, Nd, Pb and Os and stable isotopes of Mg, Ca, Li (Table 1.1). Understanding the chemical evolution and variations in rivers is the key to trace changes in continental weathering rates and better constraints on climate models.

As mentioned before, Si is the second most abundant element in the earth’s crust. It is virtually omnipresent within the continental environment. Despite being a major constituent
of silicate rocks, Si usually is ignored when calculating weathering fluxes because of the complication of the formation of secondary products, such as clays and biogenic silica. The complexity of biochemical and geochemical cycles makes it difficult to discern the behaviour of Si during weathering. Biology can modify the riverine Si budget, such that the role of weathering becomes unclear. Stable Si isotopes may represent a new tool that can help to constrain the origin of dissolved riverine Si, and further reconcile those processes that control the mass budget of riverine dissolved Si and thus rates of silicate weathering. Only a few studies so far have tried to apply Si isotopes to weathering processes but these were not able to show how variations in weathering rates might impact the riverine Si isotope composition (DE LA ROCHA et al., 2000; ZIEGLER et al., 2005a; ZIEGLER et al., 2005b). De la Rocha et al (2000) were the first to recognise a positive relationship between the concentration of dissolved Si in rivers and its isotope composition. This relationship was subsequently interpreted as the result of enhanced silicate weathering (ALLEMAN et al., 2005). More recent data from the Yangtze River in China show a negative correlation between the concentration of dissolved Si and its isotope composition, which has been interpreted to be the result of biological utilisation of Si (DING et al., 2004). The river data already published are presented and discussed in isolation from hydrological and hydrochemical background data (ALLEMAN et al., 2005; DE LA ROCHA et al., 2000; DING et al., 2004; ZIEGLER et al., 2005a). This makes it difficult to evaluate and interpret the Si isotope data in an appropriate manner.

1.3 Background on stable Si isotopes

1.3.1 Stable isotope fractionation

Isotopes are atoms of the same element that differ in the number of their neutrons but have equal numbers of protons and electrons. Stable isotopes experience neither a radioactive decay nor a radiogenic growth. Because isotopes differ in mass, atoms of different isotopes react at different rates, although all isotopes of one element take part in the same chemical reaction. Lighter isotopes and molecules containing light isotopes of one element react faster then heavy isotopes or isotopically heavy molecules. This mass dependent process is commonly known as isotope fractionation. The fractionation of isotopes during chemical reactions is thus a matter of reactions kinetics and not of different chemical properties. The chemical properties of isotopes of one element should be rather similar, given that the number of protons and electrons, and the configuration in the electron shell define the chemical properties. Isotope fractionation can be described by kinetic and thermodynamic functions.
In general there are two main types of isotope fractionation; (i) kinetic and (ii) equilibrium isotope fractionation. Kinetic isotope fractionation is usually associated with fast and incomplete chemical reactions, such as diffusion and evaporation (Hoefs, 1997; Melander and Saunders, 1980). Kinetic isotope fractionation usually requires that those phases involved in a chemical reaction are not in equilibrium, meaning simply that the chemical reaction is unidirectional (in one direction), e.g. the product formed does not react with the residual phase (reactant). One example is the evaporation of water molecules from the ocean into the atmosphere. Water molecules that contain the heavier isotopes $^{18}\text{O}$ and $^2\text{H}$ move slower than molecules comprising the light isotopes $^{16}\text{O}$ and $^1\text{H}$. Due to the higher velocity lighter molecules/isotopes cross phase boundaries (e.g. liquid to vapour) at higher rates than the heavier molecules/isotopes. Due to these different reaction rates the vapour is enriched in isotopically lighter water molecules. Kinetic isotope fractionation is often associated with low-temperature chemical processes, such as evaporation of liquids, biologically mediated reactions, diffusion and dissociation processes (Hoefs, 1997; Melander and Saunders, 1980). The associated isotope fractionations are larger for the kinetic reactions than for the equilibrium reactions. Equilibrium fractionation requires that chemical reactions are maintained in equilibrium. Those reactions are usually slow and bidirectional (working in two directions), meaning that the products formed can react with the reactant. An equilibrium fractionation is mainly based on the physical properties of isotopes, as the heavy isotopes and molecules containing heavy isotopes are usually more abundant in that phase with the lower energy state. One example of an equilibrium fractionation is given by the opposite of evaporation: the condensation of water from a vapour phase. During the condensation process the liquid phase represents the phase with the lower energy state, whereas the vapour has a higher energy state. As a consequence isotopically heavy water molecules tend to be more abundant in the liquid phase. These fractionation effects make rainwater isotopically heavy when compared to the clouds it condensed from.

The variations of stable isotope exchange decrease with higher atomic masses, because the relative mass difference between isotopes gets smaller with increasing atomic mass. For example, $^{18}\text{O}$ is 12.5% heavier than $^{16}\text{O}$, whilst $^{208}\text{Pb}$ is only 0.9% heavier than $^{206}\text{Pb}$. Variations of stable isotopes are usually expressed as deviations of ratios of the heavier to the lighter isotope (e.g. $^{30}\text{Si}/^{28}\text{Si}$) relative to the same ratio of a reference material. Those variations are usually small and are thus expressed in parts per thousand ($\permil$) to derive a convenient scale:
\[ \delta^{30}\text{Si} = \left[ \frac{\left( ^{30}\text{Si}/^{28}\text{Si} \right)_{\text{sample}} - \left( ^{30}\text{Si}/^{28}\text{Si} \right)_{\text{NBS-28}}}{\left( ^{30}\text{Si}/^{28}\text{Si} \right)_{\text{NBS-28}}} \right] \times 1000 \]

Where \( \left( ^{30}\text{Si}/^{28}\text{Si} \right)_{\text{sample}} \) is the ratio of \(^{30}\text{Si}\) to \(^{28}\text{Si}\) of the sample of interest and \( \left( ^{30}\text{Si}/^{28}\text{Si} \right)_{\text{NBS-28}} \) the corresponding ratio of heavy to light Si of the standard reference material, which is NBS-28. A \( \delta \)-value greater than 0 means that the sample is isotopically heavier than the reference material, i.e. it has a higher \(^{30}\text{Si}/^{28}\text{Si}\). Analogue, a \( \delta \)-value lower then 0 means that the sample is isotopically lighter than the reference material, i.e. it has a lower \(^{30}\text{Si}/^{28}\text{Si}\). This delta notation is the common way to express isotope variations of light elements, such as H, Li, O, C, N, Mg, Si, S, Ca and Fe.

1.3.2 Stable isotopes of Si

Silicon has three stable isotopes with the masses 28, 29 and 30. The average natural abundances are \(^{28}\text{Si}=92.229\%\), \(^{29}\text{Si}=4.683\%\) and \(^{30}\text{Si}=3.087\%\) with relative mass differences of 7.1\% \( (^{30}\text{Si},^{28}\text{Si}) \) greater than 3.5\% \( (^{29}\text{Si},^{28}\text{Si}) \). Isotopic variations are expressed using the \( \delta \)-notation as \( \delta^{30}\text{Si} \) and \( \delta^{29}\text{Si} \) in parts per thousands (‰) relative to the international standard NBS-28. The first instrumental studies on the Si isotopic composition of natural samples go back to the 1950s (Allenby, 1954; Reynolds and Verhoogen, 1953; Tilles, 1961), followed by extensive work on lunar samples and meteorites in the 1970s (Epstein and Taylor, 1970; Epstein and Taylor, 1973; Taylor and Epstein, 1970; Taylor and Epstein, 1973; Yeh and Epstein, 1978). Probably the two most cited publications on terrestrial samples that were published, are a publication from 1982 (Douthitt, 1982) and a book from 1996 (Ding et al., 1996). Both still serve as important references in recent publications. However, the Si isotope data in Douthitt (1982), and in most papers before 1982, are represented as relative deviations from the CalTech Rose Quartz standard (RQS) and not to the, nowadays used, international standard NBS-28. Molini-Velsko (1986) estimated the \( \delta^{30}\text{Si} \) of the CalTech RQS to be 0.28±0.18‰ lighter relative to NBS-28. However, the offset between RQS and NBS-28 has recently been estimated to in fact be of opposite sign viz. +0.24±0.15‰ (Robert and Chausidon, 2006). We have not measured RQS, so it is not possible to resolve the discrepancies between the two estimates of the RQS/NBS-28 calibration attempts. As a conservative estimate we assume both standards to be isotopically similar.
1.3.4 Silicon isotope variations in terrestrial samples

A compilation of Si isotope data that have been published within the last 25 years is given in figure 1.1. Compiling the extensive data from Douthitt (1982) and Ding et al. (1996) shows that igneous rocks have an average δ³⁰Si value of -0.3‰ ranging from -1.1 to about +0.2‰, where in general the δ³⁰Si is lower for rocks with less than 55 wt-% of SiO₂. More recently Ziegler et al. (2005a,b) published Si isotope data for basaltic and granitic rocks that are in good agreement with previous studies by Douthitt (1982) and Ding et al. (1996). The Si isotope composition of clastic sediments, such as sandstones, is quite similar to that of igneous rocks. This is not surprising since purely physical disintegration of silicate minerals/rocks would not yield any Si isotope effects. However, clays, as the products of the chemical weathering of silicates, indicate significant Si isotope effects, with a range observed in δ³⁰Si for clays between -2.3 and 1.5‰, with the majority of clays being lighter that the average of igneous rocks (De La Rocha et al., 2000; Ding et al., 1996; Douthitt, 1982; Ziegler et al., 2005a; Ziegler et al., 2005b). Biogenic silica spans the largest range of δ³⁰Si observed in nature. Common to the formation of biogenic silica is the discrimination against heavy Si isotopes during Si utilisation. The product of biological Si utilisation is always isotopically lighter then the composition of the source it originated from (Allemán et al., 2005; Cardinal et al., 2005; De La Rocha, 2003; De La Rocha et al., 1997; Ding et al., 2005a; Ding et al., 2003; Opfergelt et al., 2006a; Opfergelt et al., 2006b; Reynolds et al., 2006a; Varela et al., 2004). The isotopic composition of dissolved Si in fresh water (lakes and rivers) and seawater shows enrichment in heavy Si. The δ³⁰Si of seawater ranges between 0.4 and 3.1‰ (Cardinal et al., 2005; De La Rocha et al., 2000; Reynolds et al., 2006a; Varela et al., 2004) and that of rivers between 0.4 and 3.4‰ (Allemán et al., 2005; De La Rocha et al., 2000; Ding et al., 2004; Georg et al., 2006a; Ziegler et al., 2005a). More recently is has been suggested that low-temperature quartz of silcretes that formed in aquifers may represent a strongly ³⁰/²⁹Si-depleted pool with a mean δ³⁰Si value of -3.8‰ (Basile-Doelsch et al., 2005). However, unpublished Si isotope data of silcretes found in silicified soils in Portugal show unexceptional and in fact positive δ³⁰Si values (preliminary results of an ongoing cooperation between Georg and Dr. Sauer, Uni Hohenheim, Germany). From the same studies however it has become apparent that coexisting soil solutions contain very ³⁰Si-depleted dissolved Si. The observed fractionation causes ³⁰/²⁹Si-enrichment within the solid silcrete phase that is exactly opposite to that reported in the work by Basile-Doelsch et al. (2005). Unfortunately, the study by Basile-Doelsch et al. (2005) lacks the analysis of
concomitant groundwater and therefore the opportunity to compare the dissolved Si with the Si in silcretes. More work is definitely required to verify that Si isotope fractionation during the precipitation of silcretes in different environments, e.g. aquifers and soils, especially since it appears to be an important fractionation process occurring in low-temperature environments.

Although the existing database of Si isotope compositions in natural systems is rather limited it shows that dissolved Si in superficial waters is $^{30}$Si-enriched compared to igneous rocks, and Si precipitated in secondary products, such as biogenic silica and clays, is on average $^{30}$Si-depleted. The evolution of isotopically negative crustal Si to isotopically positive dissolved Si in superficial waters indicates that Si isotopes are fractionated during the breakdown of silicate rocks and the release of Si into continental runoff. De la Rocha et al. (2000) concluded that riverine Si isotope compositions result from fractionation processes such as biological utilisation of Si and the formation of clays.

**Figure 1.1:** The range observed for Si isotope variation in terrestrial materials is approximately from $-3.5 \text{ to } +3.5\%$ ($\delta^{30}\text{Si}$). Igneous materials average $-0.3\%$, superficial waters like sea, lake and river water are $^{30}\text{Si}$-enriched. This is supposed to be counterbalanced by $^{30}\text{Si}$-depleted secondary phases, such as clays and biogenic silica.
1.3.5 Silicon isotope fractionation during in-situ formation of clays

De la Rocha et al. (2000) proposed that weathering of igneous silicate minerals may fractionate Si isotopes, but no study has yet shown a direct Si isotope fractionation between coexisting primary igneous and secondary clay mineral phases. In order to evaluate whether this is indeed the case a small research study was made in cooperation with Chen Zhu (University of Indiana, USA) and was presented at the AGU fall meeting 2005 in San Francisco (GEORG et al., 2005).

To show the stable Si isotope fractionation occurs during in situ feldspar dissolution and formation of secondary clay minerals, the Navajo Sandstone, Black Mesa, Arizona was studied. The Jurassic Navajo Sandstone is composed of about 94% quartz and 2-4% K-feldspar. The K-feldspar grains are covered with kaolinite, and both quartz and feldspars are coated with a mantle of smectite (Fig 1.2). Petrographic studies demonstrate that the clay minerals formed in situ as alteration products of feldspar, and the smectite is a low-temperature variety (ZHU, 2005). Therefore, the Si isotope fractionation at low temperature (15-35°C) can be evaluated - something that is difficult to replicate in the laboratory. For the Si isotope analyses we used 20-30 mg of 5 separated clay samples, and 0.36 mg of hand picked feldspars. The silicates were fused with an alkaline flux and dissolved in a weak HCl acid. The dissolved Si was then separated by ion-exchange chromatography (see Chapter 2).

![Figure 1.2: (A) SEM image of a K-feldspar grain covered with a smectie mantle as the result of low-temperature in-situ alteration. (B) δ³⁰Si and δ²⁹Si data of the Navajo bulk rock, the feldspar fraction and 5 clay samples. All samples plot on the equilibrium mass fractionation line for Si with a slope of β = 0.5178. The three isotope plott shows that the majority of the clays is lighter compared to the host feldspar minerals.](image-url)
Chapter 1 - Introduction

R.B. Georg

The bulk rock and separated feldspar fractions have quite similar Si isotope compositions of -0.09±0.04‰ and -0.15±0.04‰ (± 95%SEM) δ³⁰Si, respectively (Table 1.2). The clay samples have δ³⁰Si values of -0.24±0.05‰, -0.16±0.04‰, -0.30±0.04‰, -0.42±0.04‰ and -0.52±0.04‰ (± 95%SEM) (Fig 1.3b and Table 1.2). These Si isotope analyses reveal that the majority of the clay separates are isotopically lighter by up to 0.4‰ compared to precursor feldspars. The results demonstrate for the first time that Si isotopes are indeed fractionated during the breakdown of feldspar minerals and the subsequent formation of isotopically lighter Si in clays.

1.3.6 Silicon isotopes in groundwater

In addition to the mineral separates from the Navajo sandstone groundwater samples from the same aquifer were analysed. From mass-balance considerations, circulating fluids should have higher δ³⁰Si values, however the analysis of groundwater samples show variations of δ³⁰Si values between +0.43 and -1.43‰ representing the most negative dissolved Si isotope composition so far found. The δ³⁰Si values of the dissolved Si in these groundwater samples seems to change with aquifer depth, as the shallow groundwater displays positive δ³⁰Si values, whereas the deeper groundwater displays negative δ³⁰Si values. The positive Si isotope composition in the shallow aquifer can of course be best explained by isotope counterbalance with isotopically negative clays. However, the positive counterpart for the negative Si isotope composition of the deeper aquifer is still missing. Basile-Doelsch et al. (2005) proposed that silcretes formed in aquifers represent a significant ³⁰Si-depleted pool, we found however, isotopically positive silcrete and concomitant negative soil solution in silicified soils from Portugal. In combination with the negative Si isotope composition of the groundwater from the deep Navajo aquifer it appears that the dissolved pool in aquifers is the major ³⁰Si-depleted Si pool and not necessarily the silcretes as proposed by Basile-Doelsch et al. (2005). As groundwater constitutes 98% of the global fresh water (excluding ice), the global Si biogeochemical cycle must include groundwater as an important component that is often overlooked. The fractionation behaviour of Si isotopes in groundwater systems is still unclear and more work is required to shed light upon this topic.

<table>
<thead>
<tr>
<th>Sample</th>
<th>δ³⁰Si (%)</th>
<th>95%SEM (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nav_bulk</td>
<td>-0.09</td>
<td>0.04</td>
</tr>
<tr>
<td>Nav_fsp</td>
<td>-0.15</td>
<td>0.04</td>
</tr>
<tr>
<td>Clays:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MSE - 4 (85.3 - 85.8)</td>
<td>-0.24</td>
<td>0.05</td>
</tr>
<tr>
<td>MSE - 1 (135.6)</td>
<td>-0.16</td>
<td>0.04</td>
</tr>
<tr>
<td>MSE - 6 (147-147.4)</td>
<td>-0.42</td>
<td>0.04</td>
</tr>
<tr>
<td>MSE - 3 (127-127.5)</td>
<td>-0.30</td>
<td>0.04</td>
</tr>
<tr>
<td>MSE - 1 (114.5)</td>
<td>-0.52</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Table 1.2: Si isotope data of the bulk rock, the feldspar and the clay fractions
1.4 Mass-spectrometry: MC-ICP-MS

One main concern of this thesis was to develop methods that allow for Si isotope measurements by high-resolution multi-collector inductively-coupled-plasma mass-spectrometry (from now on referred to as HR-MC-ICP-MS). This paragraph is complementary to Chapter 2 and is supposed to provide some information about the determination of Si isotope ratios using MC-ICP-MS, and the problems associated with previous used methods.

1.4.1 Principles of MC-ICP-MS

The MC-ICP-MS devices utilised for this thesis are the unique high-resolution MC-ICP-MS the Nu1700 built for ETH Zurich by Nu Instruments (Wrexham, UK) and a standard NuPlasma MC-ICP-MS also built by Nu Instruments. In principle both types of MC-ICP-MS are similar with notable exceptions. Both types consist mainly of four parts; (1) the sample introduction system, (2) the ion source, (3) the mass analyser and (4) the detection unit (Figure 1.3):

1. Samples are typically introduced into the ion source as an aerosol formed during aspiration and desolvation of an aqueous, usually mildly acidic solution. The desolvating unit mainly used for this thesis was the DSN-100 (Nu Instruments) equipped with self-aspirating 6mm micro-flow PFA nebulisers (Elemental Scientific Inc.) running with various sample uptake rates, typically between 60 and 80μl min⁻¹. The sample solution is taken up by the nebuliser, which converts the solution into a fine aerosol and aspirates it into the heated spray-chamber (110°C) of the DSN-100. The droplet size of the aerosol is important, since it is thought to influence the conditions of the plasma ion-source and thus the stability of the mass spectrometer. Generally speaking, the droplets of the aerosol should be small and the droplet size distribution narrow. The main functions of the spray-chamber are to heat the aerosol causing the evaporation of the solvent, which is usually mainly water. This has two main effects; (i) by evaporating the solvent a finer aerosol particle size and a narrower size distribution are achieved and (ii) the solvent gets separated from the analyte. In a next step the heated aerosol is then transferred into the also heated (110°C) desolvation membrane, which consists of hydrophobic and semi-porous PTFE Teflon. The membrane separates the sample aerosol from a hot counter flow, usually Ar gas. Due to the high temperature the solvent is mostly gaseous and can freely pass the membrane, whereas the analyte, still in droplet form, cannot due to the hydrophobic nature of the membrane. The
Chapter 1 - Introduction

R.B. Georg

The function of the counter flow (sweep gas) is to assimilate and transport the solvent molecules, e.g. water, which passed the membrane, away from the aerosol to maintain a concentration gradient that supports the movement of the solvent molecules through the membrane. This desolvation process can reduce the amount of the solvent by up to 99%. The analyte stays within the aerosol and exits the DSN-100 towards the mass-spectrometer. The reduction of solvent molecules lowers the ratio of solvent to analyte within the sample aerosol, which improves the sensitivity of the mass spectrometer for a given analyte concentration and reduces the amount of isobaric interferences derived from the solvent molecules, e.g. oxides and hydroxides. Once the aerosol has been formed and “dried” within the DSN-100 it is injected through the plasma torch into the plasma, where the ionisation occurs.

2. The ion-source of an ICP-MS comprises the inductively coupled Ar plasma operating at high temperatures (>5000 K). The Ar plasma can be described as an excited Ar gas that is partially ionised. The plasma is formed within an Ar stream (~15 l min⁻¹) at the end of the plasma torch, where the Ar meets a high frequency (27 MHz) electro-magnetic field. The electro-magnetic field is induced by a high frequency oscillating current within the RF coil controlled by the RF generator, which has an output power of about 1300W. A high-voltage ignition spark is applied to the Ar gas and causes electrons to be stripped off some Ar atoms. Where free electrons are available they get accelerated within the inducted electro-magnetic field and initiate a chain reaction by colliding in turn with other Ar atoms and causing electrons to be stripped away. The energy required to ionise Ar atoms (~15.8 eV) is high enough to ionise most elements of the periodic table. The plasma sustains this energy state as long as energy is induced in the plasma via the RF coil. The sample aerosol is injected into the plasma and experiences different physical and chemical alteration steps depending on the position within the plasma and the ambient plasma temperature. The reaction path includes: (droplet) desolvation - (particle) vaporization - (gas) atomisation - (atom) ionisation - (ion). The ions are transferred through the interface region where they get separated from the plasma and accelerated into the mass spectrometer. The interface consists of two nickel cones (sampler and skimmer cone) the main purpose of which is to extract the ions from the plasma (atmospheric pressure) into the mass-spectrometer (low pressure ~3-4 x 10⁻⁹ bar). This extraction is usually associated with a loss of ions, so that on average more than 99% of the material entering the plasma will not make it into the mass-spectrometer. Several potentials accelerate those ions that make it into the mass-
spectrometer and the ion-beam is focused and aligned by several optical lenses. The first acceleration potential of the Nu1700 is about 6kV and about 4kV for the standard NuPlasma.

Figure 1.3: Schematic overview of a Nu-Instrument NuPlasma mass spectrometer, with (1) sample introduction system DSN-100, (2) Ar-plasma ion source, (3) mass analyser consisting of ESA and magnet, and (4) detection unit consisting of 12 (fixed, standard NuPlasma) and 16 (10 fixed, 6 moveable, Nu1700) Faraday detectors, plus ion-counter systems for low level measurements.

3. The mass-analyser is the heart of a mass-spectrometer and splits the ion-beam into the mass spectrum of the ions it contains. The mass separation is achieved within a magnetic field, where ions are deflected (Lorenz force) due to the ratio m/z, of their mass (m) and their charge (z). The mass separation due to the m/z ratio requires that all ions have the same kinetic energy, which is a function of the velocity of the ions, for a given mass and charge. However, plasma ion sources produce ion beams with large energy spreads (depending on the type of instrument, but typically 0.5 to 5 eV for the NuPlasma), meaning that ions with the same m/z ratio have different kinetic energies/velocities and thus use different trajectories within the mass spectrometer. This would cause two ions, with similar m/z ratios but with different kinetic energies, to follow different trajectories before and after the mass separation. The mass spectrometer would measure two ions with different masses, although they have the same mass and charge. Any analyses were erroneous in this case. In
order to get around these obstacles it is necessary to correct for this energy spread. The mass analyser of the NuPlasma mass-spectrometers is therefore a double-focusing unit, which means that the ion beam is focused in terms of energy and the mass of the ions. Double focusing is achieved by a combination of electrostatic analyser (ESA) and the magnet (Fig. 1.4). The ESA deflects the ions as a function of their kinetic energy, such that slow ions with a lower kinetic energy are more deflected than faster ions. The magnet acts in the opposite sense but with the same magnitude, as it deflects faster ions more than slower ions. Generally speaking, the ESA and magnet have the same magnitude of focus but in opposite directions, ions are thus focused due to mass and energy. The result is that the initial energy spread of the ion source does not compromise the mass separation anymore. The double focusing feature is furthermore the fundamental basis for high mass resolutions and convenient peak shapes.

4. Once the ion-beam is focused and the masses are separated it needs to be detected. For this purpose the NuPlasma mass spectrometers are equipped with Faraday cups as well as discrete dynode electron multiplier ion-counting systems. Electron multipliers with ion-counting can count single ions and are designed for low-level measurements, they saturate at more than a few $\times$ 100,000 counts per second however. Faraday cups can detect very larger currents and are designed for measurements of higher analyte concentrations. However, they have an intrinsic noise that limits their use below an ion current of about $10^{-5}$ amps. A Faraday cup is a small metal bucket that contains an electrode at ground potential attached to a resistor (by default $10^{11}\Omega$). If the ion beam enters the Faraday cup
the positively charged ions are neutralised by inducing a flow of electrons (a current) through the resistor, which can be registered as a change in voltage. Use of a large but low noise resistor such as $10^{11}\Omega$ enables a typical ion beam of say $10^{12}$ A to be read and digitised as 100 mV. The ion-beam generated by ICP-sources is liable to fluctuations of its intensity. Since the beam intensity is the direct measure for the analyte concentration, fluctuations can affect the result and thus limit the precision of the analysis. In order to get around these limitations and to achieve high precision isotope ratio measurements, multiple collector arrays are used. Multiple collector arrays allow the detection of multiple ion beams of adjacent isotope masses simultaneously thus cancelling out beam fluctuations. The fact that different isotopes of the same element can be measured simultaneously improves significantly the precision of isotopic ratio measurements. The collectors of the NuPlasma mass-spectrometers are configured in a fixed array. The ion beams are focused on to the detectors by an array of zoom-lenses, which is positioned between the magnet and the collectors. This has one main advantage over mechanical collector arrays, as peak-jumping over larger mass-ranges can be much faster using electromagnetic zooming than with mechanical cup movement. The Nu1700 has 10 fixed Faraday collectors and 6 moveable, 3 to each, the low and the high mass side.

1.4.2 High-resolution MC-ICP-MS: the Nu1700

The main advantage of the ICP mass-spectrometer, namely the high ionization efficiency, is at the same time the biggest disadvantage; the plasma can ionise virtually all elements of the periodic table. Put simply, everything that enters the plasma will become ionised and will be transferred into the mass spectrometer. This can cause mass interferences within the spectrum one is interested in. One appropriate way to get around this problem is simply to remove all those compounds (the element matrix) that are not to be analysed from the sample. This is usually achieved with chemical purification protocols, such as ion-chromatography. With careful attention to artefacts and blanks, the risk of isobaric interferences can be reduced or even eliminated.

There are, however, interferences that cannot be eliminated by chemical purification. These interferences are usually molecular species derived from reactions within the plasma, such as Ar-oxides (e.g. $^{40}\text{Ar}^{16}\text{O}^+$ interfering with $^{56}\text{Fe}$) or simply from gaseous species dissolved within the sample solution, such as $^{14}\text{N}^{14}\text{N}^+$ and $^{12}\text{C}^{16}\text{O}^+$ ($^{28}\text{Si}$), $^{14}\text{N}^{15}\text{N}^+$ ($^{29}\text{Si}$) and $^{14}\text{N}^{16}\text{O}^+$ ($^{30}\text{Si}$). This kind of interference needs to be resolved by achieving a higher mass
resolution within the mass spectrometer. The Nu1700 offers such high-resolution capacity (Fig. 1.5). Basically the Nu1700 is a scaled-up version of the standard NuPlasma but has significant modifications and features that make it unique on the market for commercially available mass-spectrometers. The Nu1700 gains its high-resolution capability mainly from three features: (i) the large geometry, (ii) the fully adjustable source-defining slit and (iii) the fully adjustable collector slits.

Simply having a larger geometry increases mass resolution because a greater physical distance separates the ion beams by the time they reach the collectors at the focal plane. Scaling up the geometry from that of the NuPlasma to that of the larger radius of the Nu1700 increases the mass resolution from roughly 400 to roughly 1,000. To achieve a higher mass resolution it is necessary to reduce the width of the ion beam before it enters the mass analyser. This is usually achieved by physically cutting the outermost sides of the beam by two metal plates of the source-defining slit (Fig. 1.5a,b,c). Reducing the width of the beam is, however, associated with a loss in transmission and hence overall sensitivity. The Nu1700 has a fully adjustable source-defining slit, which provides the freedom to narrow the beam size only to the degree that is needed to attain the best compromise between narrowing the beam and maintaining a desirable sensitivity. The principle behind narrowing the beam is that one achieves a more complete mass-separation within the mass-analyser, simply because two adjacent beams in a mass spectrum appear as two beams, if they are narrower than the distance between them (Fig. 1.5b,c). A similar approach is taken with other types of MC-ICP-MS that are still too small to achieve full separation. This is sometimes called ‘pseudo’ high-resolution. A collector entrance slit wider than the distance between two beams would image both beams simultaneously and the ion peak would appear as one, although the mass-resolution is ‘pseudo’ high (Fig. 1.5b). However, one side of the peak is free of interfering beams and the signal can be measured without disturbing species even though the two beams appear not to be fully resolved. This resolution mode is best suitable to resolve interferences to the high-mass side of a peak, which is actually fine since most interfering species appear prominently on this side of the peak. Interferences on low the low mass side, such as doubly charged species ($^{56}$Fe$^{2+}$ on $^{28}$Si), can be resolved but the peak shape would not allow for measuring the actual beam anymore.

The Nu1700 has fully adjustable collector entrance slits unlike small geometry pseudo hi-res instruments. Each collector entrance slit can be closed. When the collector slit is narrower
than the distance of both beams, only one beam fits completely into the collector at once (Fig. 1.5c). In this case interfering beam and the one of interest will appear to be fully resolved from each other. The interference and beam of interest are recorded as two separated peaks.

The determination of Si isotope ratios via MC-ICP-MS requires high resolution since all three Si beams ($^{28}\text{Si}$, $^{29}\text{Si}$ and $^{30}\text{Si}$) are affected by polyatomic interferences. However, the effect of these interferences is less problematic for $^{28}\text{Si}$ and $^{29}\text{Si}$ but is considerable for $^{30}\text{Si}$. Silicon isotope data acquired on a low-resolution MC-ICP-MS are thus only reported as deviations of the $^{29}\text{Si}/^{28}\text{Si}$ ratio (Alleman et al., 2005; Andre et al., 2006; Cardinal et al., 2003; Cardinal et al., 2005; Opfergelt et al., 2006a; Opfergelt et al., 2006b). Missing the opportunity to measure all three Si isotopes represents an important lack of knowledge that can be drawn from the fractionation behaviour of these isotopes, e.g. it can not be proven, if all data follow a mass-dependent fractionation array within a three-isotope space.

Figure 1.5 a-c: The high-resolution capacity of the Nu1700 MC-ICP-MS; The default width of the source slit and thus the ion-beam is 0.3mm (A). The beam of interest (red) overlaps with an interfering beam (blue) and it is not possible to achieve an appropriate mass separation within the magnet, unless the beam width is reduced. The collector detects one beam and overlapping interferences compromise the measurement (red and blue mixed). The peak scan shows poor peak flatness. Reducing the width of the source-defining slit and thus the width of the ion beam will yield an appropriate mass-separation within the magnet. As a result two separated beams (red and blue) will enter the collector cup (B). If the collector entrance slit is wider than the distance of both adjacent beams they will simultaneous enter the collector. The peak scan will show a pseudo high-resolution, where the one side of the peak is free of the interference and a flat-topped section (red) is achieved, sufficient for high precision isotope ratio measurements. The true high-resolution of the Nu1700 is achieved by closing the collector entrance slits below the distance between the two beams (C). As a result only one of both beams is collected at the same time. A peak scan would show both flat-topped peaks being fully separated from each other.
1.4.3 Mass-dependent Si isotope fractionation

A common practice in isotope science is to describe stable isotope variations in terms of mass-dependent fractionation laws represented within the three-isotope space, which would be for Si a plot of $\delta^{29}\text{Si}$ vs. $\delta^{30}\text{Si}$. The idea behind this is that stable isotope fractionation is supposed to be dependent on only the masses of the isotopes. In this case the isotope data should fit onto a straight line within the three-isotope space. Any deviations from this trend might be related non-mass dependent isotope effects (CLAYTON, 1993; CLAYTON et al., 1973; FARQUHAR et al., 2000; MILLER, 2002; THIEMENS et al., 2001). So far there are no mass-independent Si isotope effects found in terrestrial materials, but extraterrestrial SiC grains can show large mass-independent $^{30}\text{Si}$ enrichments and do not fit on to the terrestrial mass-dependent Si isotope fractionation array (STONE et al., 1991). Such Si isotope anomalies are thought to be derived from presolar nucleosynthesis and can be find as inherited anomalies in SiC grains in meteorites (ZINNER et al., 1989).

Beside assessing isotope anomalies, mass fractionation lines can be also used as an indicator for data quality; if interferences are not sufficient resolved they might cause isotope ratios to be shifted away from a mass-dependent fractionation line. Assuming that all terrestrial data, e.g. water and rock samples, should follow a mass-dependent fractionation array, any shift can be related to analytical artefacts, such as interferences. The slope of this fractionation array depends on the fractionation process, e.g. either kinetic or equilibrium fractionation. Following (YOUNG et al., 2002) these slopes $\beta$ can be calculated using the exact atomic masses of the three Si isotopes ($^{28}\text{Si}: 27.97693, ^{29}\text{Si}: 28.97649, ^{30}\text{Si}: 29.97377$):

$$\beta = \left( \frac{1}{m_1} - \frac{1}{m_2} \right)$$

**equilibrium fractionation**

$$\beta = \frac{\ln \left( \frac{1}{m_2} \right)}{\ln \left( \frac{1}{m_3} \right)}$$

**kinetic fractionation**
Where \( m_1, m_2, \) and \( m_3 \) equal atomic masses of \(^{28}\text{Si}, ^{29}\text{Si},\) and \(^{30}\text{Si},\) respectively, the slopes for Si are \( \beta_{\text{kin}} = 0.5092 \) and \( \beta_{\text{equi}} = 0.5178. \) However, the slope \( \beta_{\text{kin}} \) can change due to different speciations, as it would be rather 0.5 for \( \text{SiO}_2 \) molecules. For Si both slopes are close together, and since Si isotope variations are usually small, the current precision is insufficient to resolve differences between kinetic or equilibrium isotope fractionation (Figure 1.6). So, in the course of this thesis the principle of mass-dependent fractionation will be used as a data quality indicator rather than to assess fractionation behaviour.

1.4.4 MC-ICP-MS and Si isotopes

Until 2002 most Si isotope studies were carried out utilising gas-source mass-spectrometry\(^1\) but this changed with the advent of MC-ICP-MS. De la Rocha (2002) and Cardinal et al. (2003) were the first to show that MC-ICP-MS can be utilized to obtain accurate and precise Si isotope ratios. Both studies used a similar NuPlasma MC-ICP-MS device but equipped with different sample introduction setups; De la Rocha (2002) used a sample introduction system based on a cyclonic PP spray-chamber fed by a PFA nebuliser, whereas Cardinal et al. (2003) used a CETAC ARIDUS desolvating system also fed by a PFA nebuliser. Both run solutions containing HCl-HF. The wet-plasma assembly used by De la Rocha (2002) was characterised by low a sensitivity (~0.45V/ppm Si with an uptake rate of ~0.29 ml/min), long washout times (15min) and thus high memory effects with blanks in the

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\(^1\) Other techniques, such as SIMS or nano-SIMS were used as well. But due to the inferior precision these applications were rarely used in terrestrial geochemistry (Basile-Doelsch et al. 2005).
order of 100mV on mass $^{28}\text{Si}$. The dry-plasma approach of Cardinal et al. (2003), yield a higher sensitivity ($\sim$6V/ppm Si with an uptake of $\sim$0.09ml/min) and fast washout times ($\sim$5min) associated with relatively low Si backgrounds (30-65mV on mass $^{28}\text{Si}$). Both groups demonstrated the accurate and precise determination of Si isotope ratios via MC-ICP-MS using pure silica samples. These silica samples, such as standard materials and pre-cleaned biogenic diatom and sponge samples, were digested using either a weak HF (De La Rocha, 2002; De La Rocha et al., 1996) or HCl-HF solutions (Cardinal et al., 2003). Dissolved samples were diluted with deionised water and introduced into the MC-ICP-MS. The concentration of HF was kept low in order to avoid the formation and the loss of volatile SiF$_4$. The use of HF, however, demands the use of special HF-resistant equipment and has a negative effects on the measurement reproducibility using a MC-ICP-MS. Furthermore, the presence of F$^-$ ions seem to result in a depression of the ionization efficiency of Si within the plasma and certainly causes a loss of Si as volatile SiF$_4$ through the membrane of the desolvating unit. In summary, the presence of HF causes severe problems and limits the reproducibility and the mass-spectrometer sensitivity. In order to achieve better sensitivity and reproducibility is was necessary to remove HF from the sample processing and to obtain HF-free solutions for the analysis via MC-ICP-MS.

Natural water and rock samples contain a chemical matrix that needs to be separated in order to obtain a pure Si enriched solution prior to the mass-spectrometric analyses. The only published method was the so-called ‘TEAmoly’ method and was basically designed for Si isotope ratio determination using gas-source mass spectrometer. With this method, modified after (De La Rocha et al., 1996) Si is separated from an aqueous solution by precipitation as silicomolybdate complexes. The most important advantage of this method is the near complete separation of Si from the ambient medium. In a first step, yellow aqueous silicomolybdate complexes are formed under acidic conditions by adding an ammoniumolybdate tetrahydrate salt, as utilised in spectrophotometric determinations of monosilicic acid concentrations. In a second step, this complex is precipitated by adding an organic counter ion such as a triethylene amine compound (De La Rocha et al., 1996). The resulting ‘TEAmoly’ precipitate is insoluble in water and can be separated by filtration through a 0.45$\mu$m filter paper. The removal of dissolved Si from an aqueous ion medium during the precipitation found to be very effective and quantitative with yields $>99.6\%$ for Si concentrations above 1ppm. However, for the analyses of seawater it was found that the ‘TEAmoly’ precipitation is inefficient and some pre-concentration of Si is required (Cardinal...
et al., 2005). The combined precipitate and filter paper is then dried in Pt crucibles, and combusted in a furnace in order to burn-off the paper, organic compounds and the excess Mo. A subsequent dissolution with an HCl-HF acid allows for the dissolution of the SiO₂ from the used Pt crucibles. After dissolution samples are diluted for Si isotope measurements on a MC-ICP-MS.

We found huge variations of the Si yields (between 80 and 96 %) during the latter combustion and re-dissolution steps, and that Mo was not completely removed. Silicon recovery yields of over 90 % have been reported (De La Rocha et al., 1996), with losses attributed to mechanical loss due to spillage, adhesion of ‘TEAmoly’ precipitate to the reaction bottle or passage of precipitate through the 0.45µm filter paper. Using FEP bottles as reaction vessels, instead of polypropylene bottles, can further minimize the loss due to adhesion. Even using FEP bottles Si yields were not above 96 %. We are unable to exclude possible Si loss during the ashing stage, due to the formation of volatile Si species with traces of F⁻ and/or Cl⁻ ions, which would result in Si isotope fractionation.

Samples processed by the TEAmoly showed in general a reproducibility not much better than ±0.3‰ for δ³⁰Si and ±0.2‰ for δ²⁹Si on the 2σSD level for multiple consecutive measurements, as demonstrated by repeated measurements of four aliquots of one river water sample (Figure 1.7). It is not quite clear what was the main cause for this poor reproducibility, but mass scans revealed significant amounts of matrix components, especially Mo and diverse metals, such as Pb and Pt, probably derived from the used crucibles. It is thus likely that these levels of impurities might cause non-reproducible matrix effects and finally a poor reproducibility between different aliquots of the same sample. In general the ‘TEAmoly’ technique is well proven and its functionality has been demonstrated in various studies (De La Rocha et al., 1996; De La Rocha et al., 1997; De La Rocha et al., 2000; De La Rocha et al., 1998). All these studies applied gas-source based mass spectrometric analyses, where Si is extracted and measured as SiF₃ gas. Potential impurities are thus less significant, as they are “separated” from the Si during the fluorination procedure and do not enter the mass spectrometer. The situation is different for ICP-based mass spectrometric analyses, where impurities have a significant effect on the ionisation behaviour and thus on the mass bias of the mass spectrometer.
Figure 1.7: Four aliquots of the same river water sample have been prepared, using (a) the 'TEAmoly' method and (b) the ion-exchange chemistry (see Chapter 2). The reproducibility of the data for the aliquots using ion-exchange is twice as good as the reproducibility of the data of the 'TEAmoly' aliquots.

In summary, four significant problems were encountered with the use of this technique in our laboratory: (1) the Si yields during were not close enough to 100% in order to fully exclude any Si isotope loss and fractionation, (2) Mo is not completely removed even at 1000°C for 6 hours, (3) a long preparation time of several days is required per sample, and (4) one has to use HF. Due to these obstacles it became necessary to develop a new and more reliable chemical separation method for Si.

1.5 Outline of this thesis

The determination of Si isotope ratios via MC-ICP-MS requires high purity sample solutions and has special demands. Previously used methods optimised to prepare samples for Si isotope determination via gas-source-mass-spectrometry do not really meet the demands of MC-ICP-MS. It was thus necessary to develop a new preparation method for natural samples prior to the Si isotope measurement on MC-ICP-MS instruments. The results of the development are given in Chapter 2.

Chapter 3 & 4 deal with the systematic investigation of the Si isotope composition of the dissolved load of rivers draining different catchments within the Swiss Alps and Iceland. The Si isotope data are discussed in relation to hydrological and hydrochemical data, which makes it possible to draw important conclusion from these surveys.

The advent of MC-ICP-MS makes it possible to obtain relatively effortless precise Si isotope ratios on comparable low time demands. It is thus not surprising that Si isotopes has experienced an increasing use during the last couple of years. However, with increasing use it is getting more and more vital to have well known and characterised international standards that allow the user to verify the accuracy and precision of the acquired Si isotope data and to compare data acquired on different analytical setups in different isotope laboratories. The
international Si isotope ‘zero’ point is given by the reference material NBS-28 (NIST RM#8546), which is a pure SiO₂ silica sand provided by the National Institute of Standards and Technology (NIST), Gaithersburg, USA. A second standard that has been used is the European silica standard IRMM-018 provided by the Institute for Reference Materials and Measurements, Geel, Belgium. However, recent publications on the calibration of both standards show different results. The observed discrepancy is significant and needs to be addressed and verified. Based on the new measuring techniques described in Chapter 2 it was possible to present the first long-term measurement series on a Si reference material. The results of this campaign are given in Chapter 5.

Chapter 6 represents first results from an ongoing cooperation with John W. Valley (University of Wisconsin, Madison, USA). The aim of this chapter is to evaluate the use of Si isotopes in high-temperature geochemistry. The suite of samples was chosen to observe Si isotope effects during contact metamorphism.
Chapter 2: New sample preparation techniques for the
determination of Si isotopic compositions using MC-ICP-MS

Published as

New sample preparation techniques for the determination of Si isotopic compositions using MC-ICP-MS

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In press, Chemical Geology
Abstract:

Techniques for the purification of Si for the determination of its natural stable isotopic composition have in the past been based on the requirements for gas-source mass-spectrometry, rather than MC-ICP-MS. For high precision analyses by MC-ICP-MS it is essential to have very pure solutions and in this paper a new technique is presented for the separation and purification of Si from natural samples to improve the determination of isotope ratios. A method has been optimised based on alkaline fusion followed by ion-exchange chromatography. The application to natural samples, such as river water samples and silicate mineral/rock samples is demonstrated. Alkali fusion avoids the use of hydrofluoric acid (HF), which introduces difficulties for the determination of Si isotope ratios using MC-ICP-MS. By eliminating HF a 30-40% increase in sensitivity is achieved as well as a marked enhancement of mass bias stability leading to a factor of 2 improvement in reproducibility. The cation-exchange method enables processing of very small samples (3.6 μg Si) and a rapid and effective separation of Si from other cationic species. The overall recovery of Si during the entire procedure is better than 98% and no Si isotope fractionation is generated. Matrix tests demonstrate that this method is suitable for silicates, and that typical sulphate and nitrate abundances of river waters have no effect on measured Si isotope composition. The latter aspect is vital for analysis of river waters since the technique does not separate dissolved Si (silicic acid) from ambient anionic species. Overall, the new method presents a faster, safer and more reliable way to measure Si isotopes via MC-ICP-MS.
2.1 Introduction

Most studies published so far on silicon (Si) isotopes have been carried out using gas source mass spectrometry (GS-MS) (De La Rocha et al., 1996; De La Rocha et al., 1997; De La Rocha et al., 2000; De La Rocha et al., 1998; Ding et al., 2005a; Ding et al., 2003; Ding et al., 2004; Douthitt, 1982; Varela et al., 2004). The determination of Si isotope ratios by GS-MS requires the fluorination of silicon as mass-ratios are measured as SiF$_3^+$ ions. Fluorination occurs within a vacuum line, either as the direct fluorination of purified SiO$_2$ (Allenby, 1954) or by the thermal decomposition of Ba$_2$SiF$_2$ (Reynolds and Verhoogen, 1953). Sample preparation is complicated and time consuming, and requires the use of hazardous chemicals such as BrF$_5$ or F$_2$ (De La Rocha et al., 1996; Ding, 2004b). With the advent of multi-collector inductively coupled plasma mass-spectrometry (MC-ICP-MS) these problems can be avoided, facilitating the establishment of Si isotopes as a standard method in isotope geology and biogeochemistry. However, Si must be introduced to the plasma as an aerosol, so the sample preparation has to produce pure solutions (typically mildly acidic) of silicic acid rather than purified SiO$_2$ or Ba$_2$SiF$_2$. Indeed, the purity requirements in order to avoid 'matrix' problems during mass-spectrometric analysis are probably more acute for analysis using MC-ICP-MS.

It has been shown that MC-ICP-MS can be used to determine accurate and precise Si-isotope ratios (Cardinal et al., 2003; De La Rocha, 2002). The ability to replicate measurements easily leads to higher precision and confidence concerning the measured isotope ratios. Unfortunately, the analysis of Si isotopes via MC-ICP-MS has a major analytical difficulty; it is hampered by polyatomic interferences of CO$^+$, N$_2^+$, NO$^+$ and SiH$^+$ in the Si mass spectrum. The large $^{14}$N$^{16}$O$^+$ interference on $^{30}$Si$^+$ at normal “low-resolution” prevents the measurement of all three stable Si isotopes, such that stable isotope variations can only be based on the $^{29}$Si/$^{28}$Si ratio. By using a high-resolution MC-ICP-MS, like the NuPlasma 1700 (built by Nu Instruments Ltd., UK for ETH Zürich), it is possible to resolve polyatomic interferences to both, the low and high mass side of the Si$^+$ peaks and to measure all three Si isotope masses simultaneous (Halliday et al., in press). Using the high-resolution capacity of the NuPlasma 1700 MC-ICP-MS and applying a standard-sample-standard bracketing technique we are able to determine relative Si isotope variations of samples with a long-term external reproducibility of ±0.14 %o (2$\sigma_{SD}$) for the $^{30}$Si/$^{28}$Si and better than ±0.10 %o (2$\sigma_{SD}$) for the $^{29}$Si/$^{28}$Si (Reynolds et al., 2006b).
Another problem with MC-ICP-MS measurements is that major difficulties are encountered with the use of hydrofluoric acid (HF). Published methods have so far introduced Si as the SiF$_6^{2-}$ (aq) ions, but the presence of excess fluoride ions impair the plasma ionisation, and can lead to loss of volatile SiF$_4$ during sample introduction. We found the presence of HF within the sample solutions is associated with a significant loss of beam intensity and mass-bias stability. Furthermore, the use of HF requires special safety considerations and the need for special HF-resistant sample introduction equipment. This paper presents a separation procedure for Si from waters and geological materials without the use of HF, making the measurement of Si isotopes safer, faster and more reliable.

By combining the advantages of modern high-resolution MC-ICP-MS and a simplified chemical preparation method, Si isotopes should be within reach of a broader scientific community. Thus, Si isotopes can become a powerful and widely used tool for diverse fields such as weathering studies and soil science, marine biology, oceanography, and plant physiology, leading to a significant improvement in our understanding of the global biogeochemical cycle of silicon.

### 2.2 Experiments

#### 2.2.1 Instrumentation

Elemental concentrations were measured using a Varian ICP-OES at the Institute of Terrestrial Ecology, Soil Chemistry of ETH Zürich. Silicon concentrations were measured colometrically by the molybdenum-blue method using a photospectrometer.

Silicon isotopic compositions were mainly determined using the NuPlasma 1700 high-resolution MC-ICP-MS with a Nu DSN-100 desolvating nebuliser introduction system (Nu Instruments, Wrexham, UK). Sample uptake was via a self-aspirating 6mm microflow PFA-nebuliser with variable uptake rates between 60 and 80 µl/min. In order to lower the background of Si to below 1 ppb, the dry aerosol was introduced into the plasma using a semi-demountable torch equipped with an alumina injector. In addition to the standard setup the consistency between different analytical approaches was evaluated with a conventional NuPlasma MC-ICP-MS at low mass resolution and a Cetac ARIDUS desolvating nebuliser. Table 2.1 gives an overview of the instrument operating conditions.
Chapter 2 - Methods

Table 2.1: Operating conditions for the used MC-ICP-MS instruments, Nu Plasma 1700 and Nu Plasma.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Nu Plasma 1700</th>
<th>Nu Plasma IGMR – Isotope Lab at ETH Zurich</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF power</td>
<td>1300 W</td>
<td></td>
</tr>
<tr>
<td>1st acceleration potential</td>
<td>6 kV</td>
<td>4 kV</td>
</tr>
<tr>
<td>Sampler cone</td>
<td>“experimental” WA cone (Nu Instruments)</td>
<td></td>
</tr>
<tr>
<td>Skimmer cone</td>
<td>“experimental” WA cone (Nu Instruments)</td>
<td></td>
</tr>
<tr>
<td>Coolant flow rate (Ar)</td>
<td>13 l/min</td>
<td></td>
</tr>
<tr>
<td>Auxiliary flow rate (Ar)</td>
<td>0.9 – 0.75 l/min</td>
<td>0.9 – 1.0 l/min</td>
</tr>
<tr>
<td>Nebulizer</td>
<td>Self-aspiring 6mm microflow PFA (Elemental Scientific Inc.)</td>
<td></td>
</tr>
<tr>
<td>Nebulizer uptake rate</td>
<td>60 – 80 μl/min</td>
<td>50 μl/min</td>
</tr>
<tr>
<td>Mass-resolution (10% valley)</td>
<td>~2000</td>
<td>~400</td>
</tr>
<tr>
<td>Cup configuration</td>
<td>L7 (27Al), L4 (28Si), L1 (29Si), H1 (28Si), H6 (30Si)</td>
<td>L5 (29Si), Ax (28Si), H6 (30Si)</td>
</tr>
<tr>
<td>Desolvating device</td>
<td>DSN-100 (Nu Instruments)</td>
<td>Cetac ARIDUS</td>
</tr>
</tbody>
</table>

2.2.2 Reagents and samples

All acids were distilled by sub-boiling in Savillex teflon elbows. Solutions were made up using deionised water from a MilliQ-element (Millipore), referred to here as “MQ-e” (18.5 MΩ cm⁻¹), and were stored in pre-cleaned PTFE bottles. Two silica (SiO₂) samples were used to check for Si yields during the different procedural steps and for accuracy of Si isotopic compositions. These were an in-house Si(IV) oxide powder and the IRMM-018 silica standard. The international silica standard NBS-28 was used as the international ‘zero-point’ reference material. In order to test sample matrix-effects, an in-house standard was doped with various metal oxide and carbonate powders to produce typical cation compositions of the following silicate minerals: almandine, albite, pyrope, K-feldspar and clinopyroxene (Table 2.2). All solid silica samples were first ground and powdered using a Si-free boron-carbide mortar and pestle prior to the alkaline fusion procedure.

River water samples were filtered through 0.45μm Millipore cellulose acetate filters directly at the sampling site and acidified with HCl to a pH of 2-3 the same day in the lab. Filtered and acidified samples were stored in pre-cleaned polyethylene canisters.

The fusion procedure required solid NaOH pellets and silver (Ag) crucibles. The NaOH (analytical grade, Merck) had a Si blank of about 5 ppm, which is insignificant compared to the amount of sample material used. The Ag crucibles were made in-house from 99.99% pure Ag sheet.
2.2.3 Alkaline fusion of silicates using solid NaOH

In order to avoid the use of HF, a key issue of this study, an alkaline fusion was used to dissolve silicates instead of attacking them with HF. The idea was to transform solid silicate samples into an aqueous and HF-free solution and process them through chemistry as if they were a water samples. To comply with these requirements a fusion procedure was deployed using a solid sodium hydroxide (NaOH) flux. Sodium hydroxide was preferred over other fluxes such as lithium metaborate and alkaline carbonates, because it provides the simplest composition and by neutralisation with HCl it just forms NaCl and H₂O.

Fusions with alkaline fluxes have a long tradition in analytical chemistry and are especially used when silicate minerals and rocks are analysed for their Si content. Prior to fusion the sample powder was mixed with the flux in a metal crucible, typically composed of Pt, Ag, Ni or Au. The crucible material depends on the flux used, with Ag being more resistant to NaOH dissolution. Above a certain temperature the flux melted and the sample powder dissolved completely. For example, silicate rocks, mineral separates and biogenic silica samples were totally dissolved. The resulting “fusion cake” was subsequently dissolved in a weakly acidic solution. This fusion procedure can be applied to a variety of silicate mineral and rock samples and is the standard method for preparation of silicate minerals for the determination of Si concentrations. An overview of different fusion procedures and their applications is given elsewhere (Potts, 1987). The application of alkaline fluxes prior to Si isotope ratio measurements has been considered in numerous studies (Douthitt, 1982; Reynolds and Verhoogen, 1953; Tilles, 1961; Yeh and Epstein, 1978), and so should not be regarded as a totally new technique.

For NaOH fusion (Riley, 1958; Walsh et al., 1981), we used 1-20 mg of the powdered silicate material and ~200 mg of the solid NaOH flux. Fusion was carried out in Ag crucibles.
for 10 min at 730°C in a muffle furnace. After slight cooling, the crucibles and fusion cake were dropped directly into 30 ml teflon vials containing 20 ml MQ-e water, in which the resulting fusion cake dissolves. To aid dissolution an ultrasonic probe was used to agitate the water for a few minutes. After 24 hrs, the crucible contents were washed through PTFE funnels into a weakly acidified solution with a molarity of 0.12 (HCl is typically used to avoid additional NO+ formation in the plasma, but HNO3 can be used as well). To ensure the fusion cake is completely transferred the crucibles are rinsed several times with water. The ratio of flux to acid is approximately 3.1 ml of a 10 N HCl or 2.2 ml of a 14 N HNO3 for 200mg NaOH flux. Final solutions of 0.5 to 1 l are stored in pre-cleaned FEP bottles, with Si concentrations between 1 and 20 ppm.

2.2.4 Chromatographic separation of Si

One way to separate Si from ambient ionic species is via chromatography using an anion-exchange resin, as initially demonstrated by Wickbold (1959) and used more recently for the purpose of Si isotope measurements (Engström et al., 2006). To make Si exchangeable with the anion resin it needs to be converted to the weak divalent acid H2SiF6 that dissociates to the exchangeable anionic species SiF6^2-. The Si recovery is in excess of 97% and Si becomes effectively separated from ambient ionic species. This method, however, requires the use of HF and thus does not meet with our requirements for an HF-free final solution.

The ion-chromatography presented here is instead based on a cation-exchange process. The prevailing species of dissolved Si in natural waters is essentially non-ionic monosilicic acid Si(OH)4, that is in equilibrium with the anionic silicate species H3SiO4^- for the pH range from 2 to 8. Cation-exchange columns will not retain either Si species. The Si separation and purification is achieved using the BioRad cation exchange resin DOWEX 50W-X12 (200-400 mesh) in H^+ form, filled to a 1.8ml resin bed in BioRad columns. The resin is pre-cleaned by rinsing it several times with HCl and HNO3 and MQ-e water, as detailed in Table 2.3. Before loading the sample on the resin, the eluting water is checked for neutral pH to ensure complete removal of any acids. Since the prevailing Si species do not bind to the resin the elute is simply MQ-e water. The cation exchange resin effectively retains all the ambient cationic species.
This chromatographic method allows relatively small amounts of sample to be processed. Per ion-exchange column only ~3.6 µg Si of the sample material are separated, so the sample volume loaded depends on the initial Si concentration, e.g. for river water samples with Si concentrations of 1-2 ppm, 1-2 ml of water are used. The amount of Si used is approximately 80 times less than the 300µg load used for the anion exchange approach (Engström et al., 2006). The elute volume depends on the loaded volume but should be at least once the resin bed volume, around ~2.0 ml. The total elute is typically diluted to 6 ml, so that the final solution has a Si concentration of 0.6 ppm (21 µM). An example of the separation scheme is given in Table 2.3. This separation scheme is used to process both fused solutions and acidified river water samples. The latter being directly loaded onto the resin as no pre-treatment is required prior to the chromatographic procedure. The preparation time is short, in that a set of river water samples can be completely processed through the columns within 4 hours, including pre-cleaning steps (see Table 2.3).

2.2.5 Mass-spectrometry

The direct measurement of all stable Si isotopes by MC-ICP-MS requires high-resolution mass-spectrometry in order to resolve Si⁺ ions from polyatomic interferences of similar mass, in particular ¹⁴N¹⁶O⁺ interferences on the ³⁰Si⁺ ion beam (Cardinal et al., 2003; De La Rocha, 2002). We have analysed Si isotopes using the high-resolution capacity of the NuPlasma 1700 (Nu Instruments, UK) MC-ICP-MS at ETH Zürich (Halliday et al., in press). A mass-resolution of 2000 (m/Δm at 10% peak valley) allows for a separation of the three Si⁺ ion beams from all major polyatomic interferences including ¹²C¹⁶O⁺, ¹⁴N¹⁴N⁺, ¹⁴N¹⁵N⁺,
$^{14}\text{N}^{14}\text{N}^{1}\text{H}^+$ and $^{14}\text{N}^{16}\text{O}^+$. The unique high resolving power of the NuPlasma 1700 allows for the isolation of interferences to both the high and low mass sides of the Si$^+$ peak while maintaining flat-topped peaks. Furthermore, SiH$^+$ and Fe$^{2+}$ interferences can be resolved. All three Si peaks are measured simultaneously in static mode with Faraday collectors equipped with $10^{11}\Omega$ resistors. The mass bias of the NuPlasma 1700 is very stable with a drift in $^{30}\text{Si}/^{28}\text{Si}$ of standard solutions of $<1\%$ over 60hrs. It is corrected for by standard-sample bracketing. Silicon isotope data are reported as deviations of $^{30}\text{Si}/^{28}\text{Si}$ and $^{29}\text{Si}/^{28}\text{Si}$ from the international standard NBS-28 in parts per thousand (the standard delta notation $\delta^{30}\text{Si}$ and $\delta^{29}\text{Si}$) as follows:

$$\delta^{30}\text{Si} = \left[ \frac{(^{30}\text{Si}/^{28}\text{Si})_{\text{sample}} - (^{30}\text{Si}/^{28}\text{Si})_{\text{NBS28}}}{(^{30}\text{Si}/^{28}\text{Si})_{\text{NBS28}}} \right] \times 1000$$

External mass bias correction using Mg isotopes (Cardinal et al., 2003; Engström et al., 2006) was evaluated and rejected due to the significant differential behaviour of Si and Mg isotopes within the plasma. The NuPlasma 1700 has an array of 16 Faraday detectors equipped with independently adjustable collector slits and achieves sufficient mass dispersion to measure the Si and Mg isotopes simultaneously at high resolution in static mode. However, variation in the Mg mass-bias does not correct adequately for variable Si mass-bias at the sub-permil level. Adding Mg produces a matrix-effect that causes instability in the mass bias with larger drift in Mg than Si.

In order to address whether the new preparation techniques can be easily applied to other MC-ICP-MS instruments, we compared two different analytical setups of MC-ICP-MS, attached with different desolvating units. Beside the standard combination of the NuPlasma 1700 attached to the DSN-100, a second setup used was a combination of a standard NuPlasma attached to a Cetac ARIDUS desolvating unit (also at the Zürich Radiogenic Isotope Geochemistry Laboratory). Different sets of sampler and skimmer cones were used with the same semi-demountable torch, equipped with an alumina injector. A PFA nebuliser with a lower uptake rate of only 50\(\mu\)l/min (as compared with a standard uptake rate of 60-80 \(\mu\)l/min), was used on the NuPlasma. Silicon isotope data could not be acquired at high resolution on the standard NuPlasma, although more recent versions of this instrument have some such capability. As a result the measurements are only based on deviations of the
\(^{29}\text{Si} / ^{28}\text{Si}\) ratios and noted as \(\delta^{29}\text{Si}\). Both MC-ICP-MS instruments are equipped with an 80 l/min rotary pump for evacuating the space between the sampler and skimmer cones, which enhances the machine sensitivity. Each sample is measured several times and the results reported are based on a dataset consisting of multiple \(\delta\)-values. One \(\delta\)-value consists, according to the standard-sample bracketing protocol, of one sample measurement normalised to the average of two adjacent standard measurements. One measurement represents 25 cycles with 8 seconds integration time for each cycle. The background from the Faraday detector noise is evaluated by deflecting the beam in the electrostatic analyzer for 30 seconds prior to each measurement.

2.3 Results and discussion

The new separation and purification technique for Si based on NaOH fusion and ion exchange chemistry avoids problems associated with the use of HF. We will show that this has two major advantages: (1) HF-free solutions are more stable with respect to instrumental mass-bias, enabling better reproducibility for standard-sample bracketing and thus higher precision, and (2) HF-free solutions gain 30 to 40 \% higher Si beam intensity compared to solutions with equivalent Si concentrations containing HF.

2.3.1 Silicon recovery and elution profile

The recovery of Si for the fusion procedure has been estimated using standard materials, natural pure quartz and garnet with a known proportion of SiO\(_2\) (Table 2.4). The recovery during the fusion procedure, estimated on these different silicate materials averages 99.4\(\pm\)2.6\% \((\pm1\sigma_{SD}, n=18)\). Given the uncertainties on the Si concentration, the initial sample weight and sample heterogeneities of \(\pm2\%\), this is consistent with fully quantitative recovery.

The prevailing Si species after fusion exhibit no affinity for cation exchange resin and thus Si is quantitatively recovered through the chromatographic procedure. The measured Si recovery through column separation (Table 2.4) is 100.1 \(\pm\) 1.6\% \((\pm1\sigma_{SD}, n=18)\), and the eluted sample is free of all major cations (Na, Ca, K, Mg, Al) and free of trace metals (Fe, Ni, Mo).
### Table 2.4: Si recovery (in %) for the fusion procedure and the column chromatography. Beside standard materials natural silicates, such as quartz and garnets were used to assess the Si recovery of the fusion. SiO₂ wt% data of the garnets represent ion-probe analyses and were taken from (Clechenko and Valley, 2003). The recovery of the column chromatography has been determined using standards and water samples.

<table>
<thead>
<tr>
<th>Material</th>
<th>Recovery (%)</th>
<th>Material</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBS-28</td>
<td>99.6</td>
<td>NBS-28</td>
<td>99.4</td>
</tr>
<tr>
<td>NBS-28</td>
<td>105.1</td>
<td>NBS-28</td>
<td>97.6</td>
</tr>
<tr>
<td>IRMM-018</td>
<td>105.0</td>
<td>NBS-28</td>
<td>100.2</td>
</tr>
<tr>
<td>IRMM-018</td>
<td>100.9</td>
<td>NBS-28</td>
<td>101.2</td>
</tr>
<tr>
<td>Quartz</td>
<td>99.2</td>
<td>NBS-28</td>
<td>102.0</td>
</tr>
<tr>
<td>Quartz</td>
<td>96.9</td>
<td>NBS-28</td>
<td>102.4</td>
</tr>
<tr>
<td>Quartz</td>
<td>97.1</td>
<td>NBS-28</td>
<td>102.2</td>
</tr>
<tr>
<td>Quartz</td>
<td>96.0</td>
<td>B_03/04 river</td>
<td>100.4</td>
</tr>
<tr>
<td>Quartz</td>
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<td>B_03/04 river</td>
<td>99.2</td>
</tr>
<tr>
<td>Quartz</td>
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<td>Coop H₂O</td>
<td>100.0</td>
</tr>
<tr>
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<td>Coop H₂O</td>
<td>97.1</td>
</tr>
<tr>
<td>Quartz</td>
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<td>Coop H₂O</td>
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<tr>
<td>Garnet</td>
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<td>Coop H₂O</td>
<td>100.0</td>
</tr>
<tr>
<td>Garnet</td>
<td>98.5</td>
<td>T_05/04 river</td>
<td>100.1</td>
</tr>
<tr>
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<td>T_05/04 river</td>
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<td>T_05/04 river</td>
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</tr>
<tr>
<td>Garnet</td>
<td>98.2</td>
<td>T_05/04 river</td>
<td>101.2</td>
</tr>
<tr>
<td>Garnet</td>
<td>98.1</td>
<td>T_05/04 river</td>
<td>99.5</td>
</tr>
<tr>
<td>AVE</td>
<td>99.4</td>
<td>AVE</td>
<td>100.1</td>
</tr>
<tr>
<td>STDEV</td>
<td>2.6</td>
<td>STDEV</td>
<td>1.6</td>
</tr>
</tbody>
</table>

The separation efficiency is demonstrated by the elution curves of two samples that were loaded onto the pre-cleaned cation exchange resin (Fig. 2.1); Si is not retained by the resin and migrates straight through the column and nearly 70% of the loaded Si is already recovered while the sample load is still infiltrating the resin bed. The last 30% is eluted with 2ml of MQ-e water. The elution scheme in Figure 2.1 also demonstrates that the subsequent 4ml of elution with MQ-e is free of Si and cations. The separation peak for Si is thus clearly delimited, with no breakthrough of any cations into the Si eluant. This demonstrates a complete separation of Si from the ambient cation matrix. The cationic species first start to migrate through the resin as soon as an acidic solution is used as the eluting matrix, such as 3N HCl as shown in Figure 2.1.

However, it is worth considering that the preparation technique does not separate Si from other anions, which would also pass directly through the cation-exchange column. These anions could potentially cause a matrix-effect during analysis by MC-ICP-MS. The elution scheme for the river water sample shown in Figure 2.1, demonstrates that aqueous anionic species, such as SO₄²⁻, are eluted with Si. We tested whether the presence of sulphates or nitrates has an impact on the accuracy of the Si isotope measurements. An aliquot of NBS-28 was taken and doped with a sulphate solution, made up to be 50 ppm in SO₄²⁻ and processed through the chromatographic procedure. The doped NBS-28 solution yielded a δ³⁰Si value of −0.04 ± 0.15‰ (±2σSD, n=11), demonstrating no significant isotopic offset for a solution with a SO₄²⁻/Si molar ratio of ~14.4. We also tested for matrix-effects from nitrates by doping a NBS-28 aliquot with 0.1N HNO₃ (much higher than the natural NO₃⁻ content of river waters).
Figure 2.1: Elution curves for an acidified river water sample using the BioRad DOWEX 50W-X12 cation exchange resin. Silicon is quantitatively recovered during the load step and the first elution step using MQ-e water. The Si elution is quite delimited and there is no tailing from any cation peak as long as MQ-e water is used as the eluting matrix. Cations start to move through the resin when an acidic elution matrix is used. The elution scheme is similar for silicate samples, only the interfering \(\text{SO}_4^{2-}\) is not present.

This test revealed a \(\delta^{30}\text{Si} \) of \(-0.03 \pm 0.07\%_\text{o} (\pm 2 \sigma_{\text{SD}}, n=6)\) and shows that excess \(\text{NO}_3^-\) does not impact on the Si isotope composition. That low anion contents, excluding \(\text{F}^-\), do not introduce significant matrix effects is not surprising given that the amount of anions added during acidification is by far in excess of the original concentration of anions in river waters, which thus become negligible. However, for samples with higher concentrations of dissolved solids and corresponding higher contents of anions, such as seawater and brines, a pre-concentration step for Si prior to the chromatographic procedure is a more suitable approach to avoid possible matrix problems. We utilise a co-precipitation of Si on (oxy-) hydroxides in slightly alkali solutions. This procedure has been used to concentrate dissolved Si and P from seawater (Brzezinski et al., 2003; Karl and Tien, 1992), as the co-precipitate or adsorption is quantitative (Cardinal et al., 2005; Reynolds et al., 2006a).

### 2.3.2 Silicon background and Sensitivity

Fusion blanks were assessed using 200 mg of solid NaOH in empty crucibles. The melt cakes were dissolved in 20 ml MQ-e and acidified with 3.1 ml of a 10 N HCl and diluted up to 45 ml. The Si concentration of these solutions was below 2 ppb. This low blank level
makes it possible to process small silicate samples with sizes of only 0.1-1 mg (Georg et al., 2005).

The very rapid washout performance of the DSN-100 meant that the Si blank on the mass-spectrometer could be reduced to below 20 mV prior to each measurement (corresponding to < 2 ppb Si in the analyte). A washout procedure of 150 seconds after measurement was sufficient to reduce the Si background to this adequate level. The ion beam to background ratio is on the order of 500, and no memory effects or build-up of Si background were observed even over several consecutive days of analysis (in fact background usually improved over time).

One major advantage of HF-free sample solutions is the enhanced sensitivity. Setting the NuPlasma 1700 MC-ICP-MS to a mass-resolution (m/Δm) of 2000 (10 % valley definition) is associated with a decrease in sensitivity of nearly 50%. This reduced sensitivity can be compensated by either higher analyte concentration or sample uptake rate. Our method shows an enhanced sensitivity and enables relatively low Si concentrations to be run. Compared to solutions containing HF we achieve between 30-40% higher sensitivity with a similar setup. The actual instrument sensitivity varies, but typical analyte concentrations of 500 to 600 ppb Si and uptake rate of 60-80 μl/min provides a total Si beam of ~8 V, whilst running in high-resolution mode. This sensitivity of ~13 V/ppm Si at 0.1 ml/min uptake is about 3 times higher than published results using a Neptune (Thermo Electron Corp., Bremen) MC-ICP-MS in similar high-resolution mode (Engström et al., 2006). The sensitivity at low-resolution mode on the standard Nu Plasma is naturally much higher (60 V/ppm Si at 0.1 ml/min uptake). This is > 60 times higher than achieved with a wet-plasma assembly (De La Rocha, 2002) and 5 times higher than for solutions containing HF running in dry-plasma mode (Cardinal et al., 2003) for the same type of MC-ICP-MS (a NuPlasma). It should be noted that the sensitivity also depends on the capacity of the turbo pump that evacuates the region between sampler and skimmer cone and the design of the used cones. Both, the Nu Instruments “experimental WA cones” and the 80 l/min pumps used in this study improve the overall machine sensitivity.
2.3.3 Reproducibility, precision and accuracy

In order to demonstrate the performance of our new method we have chosen the European Si Standard IRMM-018 and compared a sample prepared using the method described in this paper to a sample prepared by directly dissolution in HCl-HF acids following (Cardinal et al., 2003). The differences between the prepared aliquots are the acid matrix and the Si concentration. The HCl-HF aliquots had a Si concentration of 1ppm and an associated intensity of ~4.5V/ppm Si, whereas the HF-free aliquots had a concentration of 600ppb and an associated intensity of ~7.5V/ppm. Each IRMM-018 aliquot was measured on two different sessions (Fig. 2.2). The results display good agreement between the two preparation methods, with similar mean $\delta^{30}$Si values of -1.63 %o and -1.62 %. Hence, we conclude that there is no significant isotope fractionation effect induced during either the fusion or the column chemistry. The direct comparison between both sample preparation techniques shows that the HF-free solutions can be reproduced to a greater precision, as the HF-free solutions provides rather more stable measuring conditions for the MC-ICP-MS. By changing from HCl-HF solutions to HCl only we could improve the reproducibility by a factor of 2.

![Figure 2.2: Comparison of two IRMM-018 aliquots: one digested with HCl-HF (triangles) and one processed according to the combined fusion and ion chromatographic procedure (diamonds). Both aliquots yield the same Si isotope composition ($\delta^{30}$Si = -1.63 %o and -1.62 %o). The reproducibility of the HF-free solution is twice as good as the HCl-HF solution. Running conditions: HCL-HF solution: 1ppm Si, beam intensity: 4.5V/ppm – HF-free solution: 0.6ppm Si, beam intensity: 7.5V/ppm](image-url)
The long-term reproducibility of over 300 measurements of the IRMM-018 standard was ±0.14% (2σSD) for δ^{30}Si values and ±0.10% (2σSD) for δ^{29}Si values (Reynolds et al., 2006b) (see also Chapter 5). The standard data were acquired during 16 sessions between November 2004 and August 2005 and represent the first long-term evaluation of δ^{30}Si and δ^{29}Si data of a Si isotope reference material to be published. Since all standards were processed through the chemical separation procedure prior to each session, this standard reproducibility also includes the repeatability of the applied ion-chromatography procedure. Thus the ion-exchange chemistry is highly reproducible. The reproducibility of multiple sample measurements during a single session is usually better than ±0.10% for δ^{30}Si and ±0.07% for δ^{29}Si (2σSD). We are thus limited in our precision by our long-term standard reproducibility. Thus, our limiting precision (95% SEM) can be estimated from the number of replicates (n) using this long-term reproducibility (95% SEM = -2.5 SE for n = 7). For 11 repeated measurements our limiting precision is ±0.04 % on δ^{30}Si and ±0.03 % on δ^{29}Si ratios. This high precision facilitates the resolution of even small variations in the Si isotope composition of natural samples, such as the seasonal variation of the dissolved Si in river samples (GEORG et al., 2006a).

As there is no Si isotope rock standard yet available, in order to check the effects of sample matrix we doped our in-house Si standard to achieve artificial mineral matrixes and processed these through the entire procedure, including fusion and ion-chromatography. The results from the doped and pure samples all reproduce the δ^{30}Si composition of –0.51 ± 0.1 %.
Chapter 2 - Methods

(+2σSD, n=12) (Fig. 2.3), demonstrating that our method is suitable for natural silicate samples and does not introduce Si isotope fractionations.

![Figure 2.4](image)

Figure 2.4: The comparison between different analytical setups shows that the new method is highly reproducible and can be applied to different analytical setups. Aliquot 1 (triangles) and 2 (squares) measured on a standard NuPlasma attached to a Cetac ARIDUS, aliquot 3 (diamonds) was measured on the NuPlasma 1700 attached to the DSN-100. All measurements give a mean δ30Si of +0.34 % and a reproducibility of ±0.07 % (2σSD). Running conditions: NuPlasma, low resolution (~400): 250ppb Si, beam intensity: ~30V/ppm – NuPlasma 1700, high resolution (~2000): 0.6ppm Si, beam intensity: ~12.5V/ppm

A comparison of measurements obtained on different MC-ICP-MS instruments is limited by polyatomic interferences on mass 30Si on the standard NuPlasma. However, we can compare the 29Si/28Si ratios relative to the standard NBS-28. The results shown on Figure 2.4 demonstrate that the analyses of 3 different aliquots of the same sample (river water sample) are consistent between two distinct analytical set-ups. Thus, the sample preparation method described here is suitable for different types of MC-ICP-MS

2.5 Conclusion

The new method detailed here represents a robust, fast and reliable way to determine accurate and precise Si isotope ratios of natural samples using MC-ICP-MS. By avoiding the use of HF, it is possible to obtain higher sensitivity and mass-bias stability, which ultimately results in improved precision. Cations that introduce matrix-effects in the mass-spectrometer can be effectively removed using a cation exchange procedure. Indeed, this method is the
most effective way of excluding the potential problems of matrix-effects from additional cations. Anionic species that are not separated from Si and could represent a potential problem are shown to not affect our results for river water samples with natural sulphates and nitrates or for silicate samples. River waters contain these anionic species, though in extremely low abundances compared to the dominant anion in the analyte from acidifying our samples (~0.1 M Cl\(^{-}\)). For samples that contain higher concentration of anions, such as seawater and brines, a pre-concentration of Si prior to the cation exchange process can be easily completed using quantitative co-precipitation on MgOH. Since silicate minerals and rocks do generally not contain high amounts of anionic species, except sulphur rich samples, this new method is well suited for the determination of Si isotope ratios in natural materials.

Acknowledgements

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Chapter 3: Mechanisms Controlling the Silicon Isotopic Compositions of River Waters

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Mechanisms Controlling the Silicon Isotopic Compositions of River Waters

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Abstract

It has been proposed that silicon (Si) isotopes are fractionated during weathering and biological activity leading to heavy dissolved riverine compositions. In this study, the first seasonal variations of stable isotope compositions of dissolved riverine Si are reported and compared with concomitant changes in water chemistry. Four different rivers in Switzerland were sampled between March 2004 and July 2005. The unique high-resolution multi-collector ICP-MS Nu1700, has been used to provide simultaneous interference-free measurements of $^{28}\text{Si}$, $^{29}\text{Si}$ and $^{30}\text{Si}$ abundances with an average limiting precision of $\pm 0.04\%$ on $\delta^{30}\text{Si}$. This precision facilitates the clarification of small temporal variations in isotope composition. The average of all the data for the 40 samples is $\delta^{30}\text{Si} = +0.84\pm0.19\%$ (±1$\sigma_{SD}$). Despite significant differences in catchment lithologies, biomass, climate, total dissolved solids and weathering fluxes the averaged isotopic composition of dissolved Si in each river is strikingly similar with means of $+0.70\pm0.12\%$ for the Birs, $+0.95\pm0.22\%$ for the Saane, $+0.93\pm0.12\%$ for the Ticino and $+0.79\pm0.19\%$ for the Verzasca. However, the $\delta^{30}\text{Si}$ undergoes seasonal variations of up to 0.6%. Comparisons between $\delta^{30}\text{Si}$ and physico-chemical parameters, such as the concentration of dissolved Si and other cations, the discharge of the rivers, and the resulting weathering fluxes, permits an understanding of the processes that control the Si budget and the fate of dissolved Si within these rivers.

The main mechanism controlling the Si isotope composition of the mountainous Verzasca River appears to be a two component mixing between the seepage of soil/ground waters, with heavier Si produced by clay formation and superficial runoff and lighter Si associated with high discharge events. A biologically-mediated fractionation can be excluded in this particular river system. The other rivers display increasing complexity with increases in the proportion of forested and cultivated landscapes as well as carbonate rocks in the catchment. In these instances it is impossible to resolve the extent of the isotopic fractionation and contributed flux of Si contributed by biological processes as opposed to abiotic weathering.

The presence of seasonal variations in Si isotope composition in mountainous rivers provides evidence that extreme changes in climate affect the overall composition of dissolved Si delivered to the oceans. The oceanic Si isotope composition is very sensitive to even small changes in the riverine Si isotope composition and this parameter appears to be more critical than plausible changes in the Si flux. Therefore, concurrent changes in weathering style may
need to be considered when using the Si isotopic compositions of diatoms, sponges and radiolaria as paleoproductivity proxies.

3.1 Introduction

Weathering of silicate minerals and rocks is a fundamental process that is thought to regulate global climate on long timescales as a result of the drawdown of atmospheric CO₂ (Berner et al., 1983; Moulton et al., 2000; Tréguer et al., 1995; Walker et al., 1981). During breakdown of silicate minerals chemical weathering consumes CO₂ and contributes species such as silicon (Si) to the dissolved load of rivers (Bluth and Kump, 1994). In order to model long-term weathering and CO₂ consumption, different approaches have been applied, such as mass balance calculations using major and minor elemental fluxes of rivers (Gaillardet et al., 1999; Huh and Edmond, 1999; Millot et al., 2002), and radiogenic and stable isotope proxies, such as strontium (Raymo et al., 1988) and lithium (Huh et al., 2001; Pistorner and Henderson, 2003). Despite being a major constituent of silicate minerals and the continental crust, Si is usually excluded from calculations of chemical weathering fluxes owing to the complication of biogenic silica formation (Millot et al., 2002). Silicon is released by weathering of silicate rocks and minerals and can be recycled by biological processes in soils before it finally reaches the rivers and leaves the catchments (Alexandre et al., 1997; Farmer et al., 2005; Meunier et al., 1999). Silicon isotopes should in principle provide a constraint on the origin and mass budget of riverine dissolved Si. Detailed investigations on riverine Si isotope compositions have not yet been undertaken, but are now tractable using MC-ICP-MS analyses (Halliday et al., in press).

It has been shown that rivers contain Si that is isotopically heavy relative to the continental crust (De La Rocha et al., 2000; Ding et al., 2004). In principle two fractionation processes can explain the observed heavy isotope compositions of dissolved Si in rivers: (i) weathering of igneous minerals, and (ii) biological utilisation of resulting silicic acid. Secondary clays are isotopically lighter and balanced by a corresponding enrichment of heavy Si in ambient fluids (De La Rocha et al., 2000; Douthitt, 1982; Georg et al., 2005; Ziegler et al., 2005a; Ziegler et al., 2005b). Organisms incorporate Si from ambient fluids and form biogenic silica, e.g. skeletal material (diatoms) and phytoliths (higher land plants). Various studies have shown that during the formation of biogenic silica organisms discriminate against heavier Si isotopes, resulting in a lighter isotope composition of biogenic
silica and a corresponding enrichment of heavier Si isotopes in coexisting ambient solutions (De La Rocha et al., 1997; De La Rocha et al., 1998; Ding et al., 2005a; Ding et al., 2003; Oppenberg et al., 2006a; Reynolds et al., 2006a; Varela et al., 2004). Therefore, both biogenic processes and weathering can generate heavy dissolved Si in river waters. In principle, both can affect the composition of Si in seawater, yet this is assumed to be constant when inferring paleoproductivity from diatom records (De La Rocha et al., 1998).

Little is known about the mechanisms controlling the Si isotope composition in rivers under different climatic conditions. In order to understand this and the role of biological processes versus weathering it is necessary to investigate whether the Si isotope composition of particular river systems varies with seasonality, weathering rates and lithology. To investigate the role of catchment lithology and relief, four rivers draining three different parts of the Swiss Alps have been sampled; the Birs in the north, the Saane in central Switzerland and the Verzasca and Ticino in the south. These rivers were sampled over an annual cycle, from March 2004 to July 2005. The concentration (or [Si]) and isotopic composition of dissolved Si were measured and compared with the cation composition in order to constrain the geochemistry of Si within these different catchments. A comparison of the Si isotope composition with physico-chemical parameters, such as river discharge, the water chemistry and the resulting weathering flux can help to constrain the processes that control the Si isotope composition of these catchments. A positive correlation between Si isotope composition and concentration of riverine Si was first recognised by De La Rocha et al. (2000) and interpreted as the result of enhanced weathering (higher $\delta^{30}$Si and higher [Si]) (De La Rocha et al., 2000). Biological processes in contrast remove Si from solution and therefore generate a negative correlation between isotopic composition and concentration of dissolved Si. Such a model may however be too simplistic, as explored in this paper.

3.2 Sampling and analytical methods

3.2.1 Sampling sites and geological setting

The location of the sampling sites and respective catchment areas are shown in Figure 3.1; some details on the geomorphology are given in Table 3.1. The Verzasca and the Ticino rivers are both located in the Tessin, and drain catchments dominated by the lithology of the Pennine units of the central Alps. The bedrocks are predominantly crystalline gneisses with some calcareous shists (Bündnerschiefer) and evaporites in the north of the Ticino catchment...
Chapter 3 - Swiss River

(Wenger and Steiger, 1990). The Verzasca is a high mountain river with small catchment (186 km²) that has eroded a narrow V-shaped valley into the crystalline bedrock. Bedrock outcrops and thin soil layers dominate the catchment's surface. In the Ticino catchment (1515 km²) the main valley consists of cultivated alluvial flood plains covered with extensive soil horizons, flanked on both sides by high mountains. The two other rivers, the Birs (catchment size of 911 km²) and the Saane (catchment size of 1861 km²), are located within the Helvetic unit of the Alps and represent meandering river systems. The land use in both catchments is mainly agriculture and forestry. The Birs is located in the northern part of Switzerland and mainly drains the Swiss Jura Mountains, where shallow marine carbonate deposits dominate over minor proportions of siliciclastic sediments. The catchment of the Saane covers a variety of different sedimentary lithologies, mainly marine siliciclastic rocks (Flysch and Molasse), but also carbonate-sandstones, mudstones and limestones.

3.2.2 Sampling

Each of the four rivers was sampled 10 times during 2004 and 2005. Sample locations were chosen to be near monitoring stations of the Swiss Federal Office for the Environment (FOEN), so that changes in discharge for each sampling point are well documented (Fig. 3.1). River water samples were filtered directly at the sampling site through 0.45μm Millipore cellulose acetate filters and acidified with suprapure HCl to a pH between 2 and 3. The [Si] was measured colometrically by the molybdenum blue method using a spectrophotometer at the laboratory at ETH Zürich one day later (Grasshoff, 1964). Cation concentration measurements for each sample were performed by ICP-MS at ACME Analytical Laboratories Ltd. in Vancouver, Canada.

3.2.3 Source of additional data

The hydrochemical parameters of Saane, Birs and Ticino were part of a long-term investigation of the NADUF (National programme for the long-term analytical investigation of Swiss rivers) monitoring program, in collaboration with the Swiss Federal Institute of Aquatic Science and Technology (EAWAG) (Binderheim-Bankay et al., 2000). The NADUF program provides a database for hydrochemical data, such as pH, temperature, major cation and anion composition, and covers periods beginning in 1978 to the late 1990s. The Verzasca has been monitored as part of an international program (Cooperative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes: ICP-waters), which has been established by the United Nations Economic Commission for Europe's Convention on
Long-Range Transboundary Air Pollution (LRTAP). We used these long-term datasets to constrain the basic water chemistry of the investigated rivers.

**Figure 3.1:** Map of Switzerland showing the four sample stations (white dots), the river courses (black lines) and catchment outlines (black pointed lines). Station 1 = Verzasca, Station 2 = Ticino, Station 3 = Saane, Station 4 = Birs. Rainwater composition was taken at stations in Chaumont, Payerne and Magadino (open black cycles).

The chemical composition of rainwater was taken from the NABEL (National Air Pollution Monitoring Network) program (2005). We have chosen three stations that are close to the studied catchments. The selected stations are Magadino (for Ticino and Verzasca), Payerne (for Saane) and Chaumont (for Birs) (Fig. 3.1). Annual average rainwater compositions are provided as concentration (mg/l) and as elemental flux (mg/m²/yr) for the year 2004 (Table 1). The rainwater compositions and the long-term chemistry data were used to calculate correction factors for wet depositional input, which were then applied to the cation composition of the river water samples in order to obtain weathering-derived dissolved fluxes.
### Table 3.1: Long-term average chemistry data of the studied rivers. The annual average composition of rainwater is used to calculate correction factors for wet depositional input. *pH value of the Birs is based on field measurements throughout 2004-2005.

<table>
<thead>
<tr>
<th>River</th>
<th>Station</th>
<th>AVE Catchment</th>
<th>Discharge m³/s</th>
<th>Temp °C</th>
<th>pH</th>
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<th>SO₄²⁻ mg/l</th>
<th>NO₃⁻ mg/l</th>
<th>Cl⁻ meq/l</th>
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<td></td>
<td></td>
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</tr>
</tbody>
</table>

**Average long-term data (additional sources, see section 2.3), uncorrected for wet depositional input.**

- **Magadino** (Ticino, Verzasca)
- **Payerne** (Saane)
- **Chaumont** (Birs)

<table>
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<th>Precipitation (mm)</th>
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<th>NO₃⁻</th>
<th>Cl⁻</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
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<td>0.03</td>
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</tr>
</tbody>
</table>

Annual average rainwater element fluxes in mg/m²/year:

- **Magadino** (Ticino, Verzasca)
- **Payerne** (Saane)
- **Chaumont** (Birs)

<table>
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<tr>
<th></th>
<th>SO₄²⁻</th>
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Correction factors for wet depositional input in %:

- **Birs**
- **Saane**
- **Ticino**
- **Verzasca**

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3.2.4 Correction for wet depositional input

In order to correct the dissolved riverine load for wet depositional contributions correction factors were calculated in two ways: first using the CI⁻ based method (STALLARD and EDMOND, 1981) and second using a volumetric approach comparing the wet depositional element flux per unit area per year with the riverine flux of the specific element. The CI⁻ correction yields negative riverine fluxes of NO₃⁻ and SO₄²⁻ for the Birs and Saane and negative riverine fluxes of NO₃⁻ for the Ticino. These negative fluxes show that the Cl⁻ load of these three rivers cannot only have been of atmospheric origin but that there must have been an additional input that probably originated from road salt and fertilizers. The volumetric approach uses the elemental flux in precipitation compared with the average annual riverine amount of the element dissolved. The correction factor represents the percentage of the rainwater contribution to the specific riverine element annual flux. This approach is not able to reconcile the high NO₃⁻ flux observed in the Verzasca. Both correction approaches are subject to errors as average rain compositions and precipitation data are deployed. In addition, the rainwater compositions were not directly measured within the catchment introducing possible geographical biases. The volumetric approach yields more consistent data so these correction factors were used to correct for wet depositional input (Table 3.1). No data exist for the Si concentrations of these rainwater pools, but the Si concentration of rain is usually very low, especially when compared to cation concentrations (DARMODY et al., 2000; STALLARD and EDMOND, 1981). Therefore, the Si contribution from rain is assumed to be insignificant compared to weathering Si fluxes.

3.2.5 Chemical preparation techniques

Silicon was separated from the water matrix and purified using a newly developed cation-exchange chemistry (HALLIDAY et al., in press). All acids used were distilled by sub-boiling in Savillex elbows. Dilutions used deionised water (MilliQ-element “MQ-e” (Millipore)). The Si blank in the reagents is below the detection limit (1 ppb) of the Molybdate-blue method using a spectrophotometer.

The new ion-exchange chromatographic separation and purification technique for Si is based on a cation-exchange process, whereby Si is separated from the entire cation matrix of the sample using ion exchange columns filled with a resin bed of 1.8 ml DOWEX 50W-X12 (200-400 mesh). The ion-chromatography separates 3.6 µg Si from the cationic species and the purified sample solutions were diluted to 0.6 mg/l Si (21 µmolar) for mass spectrometric
measurement. The Si recovery for the separation procedure is 100% and no column induced Si isotope fractionation has been found using standard solutions. The eluted sample is effectively free of all cationic species including trace metals (Halliday et al., in press).

3.2.6 Mass spectrometry

The direct measurement of Si isotopes by MC-ICP-MS requires high-resolution mass-spectrometry in order to resolve Si+ ions from polyatomic interferences of similar mass, in particular \(^{14}\text{N}^{16}\text{O}^+\) interferences on the \(^{30}\text{Si}^+\) ion beam (Cardinal et al., 2003; De La Rocha, 2002). We have analysed Si isotopes using the high-resolution capacity of the Nu1700 (Nu Instruments, UK) multiple collector-ICP-MS at ETH Zürich (Halliday et al., in press). A true high mass resolution of 2000 (m/Δm at 10% peak valley) allows for a separation of the three Si+ ion beams from all major polyatomic interferences including \(^{12}\text{C}^{16}\text{O}^+\), \(^{14}\text{N}^{14}\text{N}^+\), \(^{14}\text{N}^{15}\text{N}^+\), \(^{14}\text{N}^{14}\text{N}^{1}H^+\) and \(^{14}\text{N}^{16}\text{O}^+\). Samples are introduced to the plasma via a DSN-100 desolvating nebuliser system (Nu Instruments, UK) using a 6mm PFA nebuliser (Elemental Scientific Inc.) with a variable uptake rate of between 60 and 80 μl/min. All three Si peaks are measured simultaneously in static mode with Faraday collectors equipped with 10 MΩ resistors. The mass bias of the Nu1700 is very stable with a drift in \(^{30}\text{Si}/^{28}\text{Si}\) of standard solutions of < 1% over 60hrs. It is corrected for by a standard-sample bracketing protocol. In order to minimise analytical blanks the dry aerosol is introduced to the plasma through a semi-demountable torch equipped with an alumina injector. Silicon isotope data are reported as deviations of \(^{30}\text{Si}/^{28}\text{Si}\) and \(^{29}\text{Si}/^{28}\text{Si}\) from the international standard NBS-28 in parts per thousand (the standard delta notation \(\delta\) for \(^{30}\text{Si}\) and \(\delta\) for \(^{29}\text{Si}\), with \(X = 30\) or 29) as follows:

\[
\delta^X\text{Si} = \left[ \frac{\left(\frac{X\text{Si}}{28\text{Si}}\right)_{\text{sample}} - \left(\frac{X\text{Si}}{28\text{Si}}\right)_{\text{NBS28}}}{\left(\frac{X\text{Si}}{28\text{Si}}\right)_{\text{NBS28}}} \right] \times 1000
\]

The long-term reproducibility of over 300 measurements of the IRMM-018 standard was ±0.14‰ (2σ SD) for \(\delta^{30}\text{Si}\) values and ±0.10‰ (2σ SD) for \(\delta^{29}\text{Si}\) values (Reynolds et al., 2006b). The standard data were acquired during 16 sessions between November 2004 and August 2005. Since all standards and samples were processed through the chemical separation procedure prior to each session this standard reproducibility also includes the repeatability of the applied chemical separation procedure. The silicon isotope composition of the river samples was reproducible during different measuring sessions with a similar average of
0.13% (2σSD) for δ³⁰Si and 0.08% (2σSD) for δ²⁹Si. The precision given as standard error of the mean for over 12 duplicate analyses is thus limited to ±0.04% for δ³⁰Si values and ±0.03% for δ²⁹Si values at the 95% confidence level by our long-term reproducibility.

The sensitivity of the analytical setup varies but is typically ~10⁻¹⁰ A/ppm Si while running at high mass-resolution with an uptake rate of ~80μl/min. Due to the very rapid washout performance of the DSN-100 the Si blank was reduced to below 2x10⁻¹³ A on mass ²⁸Si within 150 seconds of each measurement, which is equivalent to a ~ 1ppb Si blank.

### 3.3 Results

#### 3.3.1 Major element chemistry

The collected data, such as compositional long-term averages of the studied rivers and precipitation and the cation data for our samples are given in Table 3.1 and Table 3.2, respectively. We used the long-term data in Table 3.1 to constrain major element chemistry. The examined rivers have total dissolved solid “TDS” concentrations (calculated as the sum of cation, anion and Si concentrations in ppm) ranging from 16 mg/l (Verzasca) to about 410 mg/l (Birs). In the Saane and Ticino the TDS was 330 and 180 mg/l, respectively. All rivers show strong seasonal gradients regarding the mean water temperature ranging between about 2 and 5°C during the winter months (November to April) to ~14-17°C during the summer months (May to October). The Verzasca, Ticino and the Saane have fairly stable pH values of 6.7, 7.8 and 8.2, respectively, with variations of 0.1-0.2 (1σSD). There is no long-term pH record for the Birs available but our measurements indicate lightly alkaline pH values around 8.2.

The rainwater contribution of major cations constitutes less than 5 % of the riverine major cation fluxes of the Birs, Saane and Ticino. However, for the Verzasca, the estimated rainwater contribution is higher, between 5 and 14 %. The input-corrected cation data of the collected samples were used to calculate a weathering flux (g/s), computed as the product of the measured discharge given in m³ s⁻¹ and the base cation concentration (sum of Ca²⁺, Mg²⁺, K⁺ and Na⁺ in mg/l).
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Table 3.2: Discharge, compositional cation data (+2σ, not corrected for wet depositional input) and Si isotope data for each sample taken throughout 2004-2005.
On a molar basis, Ca\(^{2+}\) is the most abundant cation in most rivers; [Ca\(^{2+}\)] > [Mg\(^{2+}\)] > [K\(^{+}\)+Na\(^{+}\)] > [Si]. The Verzasca shows a different composition of decreasing abundance: [Ca\(^{2+}\)] > [Si] > [K\(^{+}\)+Na\(^{+}\)] > [Mg\(^{2+}\)], documenting the importance of silicate-derived dissolved load in this river. The anionic species are dominated by [HCO\(_3^-\)] > [SO\(_4^{2-}\)] > [Cl\(^-\)+NO\(_3^-\)]. Noteworthy are high [SO\(_4^{2-}\)] in the Ticino and Verzasca, and high [NO\(_3^-\)] in the Verzasca (Fig. 3.2). The high [SO\(_4^{2-}\)] is lithogenic, and is derived from the leaching of Mesozoic evaporites such as CaSO\(_4\) that occur in the northern part of the Ticino valley (Pastorelli et al., 2001). An atmospheric origin is unlikely since both correction approaches do not eliminate the [SO\(_4^{2-}\)] in these rivers. The high [NO\(_3^-\)] in the Verzasca is probably derived from atmospheric inputs, as the Cl- approach eliminates this anomalous flux. Although Ticino and Verzasca drain the same gneissose lithology, the rivers show quite distinct chemical compositions, with a higher carbonate-derived component in the Ticino, based on higher Ca/Na and Mg/Na ratios (Gaillardet et al., 1999). Considering that all [SO\(_4^{2-}\)] is derived from the dissolution of CaSO\(_4\), the high Ca/Na ratios do overestimate the contribution from carbonate weathering. Assuming all SO\(_4^{2-}\) is derived from leaching of CaSO\(_4\) the rainwater corrected riverine Ca\(^{2+}\) content can be calculated as follows:

\[
\text{Ca}_{\text{cor}} = \text{Ca}^* - \text{SO}_4^* \times 0.42
\]

Note that Ca\(^*\) and SO\(_4^*\) are the measured riverine concentrations after correction for wet depositional input and 0.42 is the theoretical anhydrite molar [Ca\(^{2+}\)]/[SO\(_4^{2-}\)] ratio. The anhydrite correction shows that nearly 70% of the dissolved [Ca\(^{2+}\)] is contributed by evaporites. The associated Ca/Na ratios change from 16.9 to 5.3 after the anhydrite correction. The higher Mg/Na ratios of the Ticino can be related to dolomitic marbles that occur in the northern part of the Ticino valley. The larger catchment of the Ticino contains a larger diversity of different rocks, which are exposed to weathering and contribute to the dissolved load of the Ticino.

Birs and Saane have similar Ca/Na ratios (14.2±5.4 and 16.6±4.1, respectively), indicating a carbonate-dominated chemistry (Gaillardet et al., 1999). According to the geological map (Cavalli et al., 1998) the catchment of the Saane also contains evaporites within the source area, so that the anhydrite correction should also be applied to correct the [Ca\(^{2+}\)] concentration of the Saane. The correction shows that the dissolution of CaSO\(_4\) might contribute up to 20%
to the dissolved Ca load. The associated Ca/Na ratio changes to 13.2±3.6. The abundance of carbonate rocks within the catchment explains the overall carbonate-derived solute load within a mainly siliciclastic catchment. Although dolomites are exposed in the Swiss Jurassic Mountains, an average Mg/Na ratio of only 0.7 does not indicate significant contributions from dolomite weathering.

Figure 3.2: Ternary diagrams showing the major cation and major anion composition of the studied rivers (uncorrected for wet depositional input and anhydrite contribution).

We used the long-term averages given in Table 3.1 and the software PhreeqC to calculate saturation states of the waters sampled here relative to primary and secondary minerals (Parkhurst and Appelo, 1999). The calculation shows that all rivers are saturated with respect to kaolinite, thus this phase is one potential secondary mineral that might form within the catchment. Birs and Saane are saturated with respect to calcite but undersaturated with respect to quartz, reflecting the carbonate influence on the solute load. Ticino and Verzasca are undersaturated with respect to calcite and quartz. All rivers are undersaturated with respect to amorphous silica and primary silicates, such as anorthite, albite and K-feldspar.
3.3.2 Silicon concentrations and isotopic compositions

The measured Si isotope composition, the [Si] and cation concentration data and discharges for each sample are given in Table 3.2. All Si isotope measurements agree with the mass-dependent equilibrium fractionation line of Si, documenting the elimination of all molecular interferences ($\delta^{29}\text{Si} = 0.5178 \times \delta^{30}\text{Si}, R^2 = 0.96$), as shown in Figure 3.3.

All rivers carry a positive value of $\delta^{30}\text{Si}$ in the dissolved Si, consistent with previous conclusions that weathering and/or biological processes offset the composition of Si added to the oceans away from an average igneous $\delta^{30}\text{Si}$ range of -0.3 to 0.3‰ (Ding et al., 1996; Douthitt, 1982) toward heavy values (De la Rocha et al., 2000; Ding et al., 2004). The average $\delta^{30}\text{Si}$ of the Ticino (+0.93±0.12‰, ±1σSD) and the Saane (+0.95±0.22‰) are slightly heavier than the average of all data (+0.84±0.19‰); the average Birs composition is slightly lighter (+0.70±0.12‰) and Verzasca is similar (+0.79±0.19‰) to the mean Si isotope composition of all four rivers. A striking observation is the overall uniformity of these high precision data. Despite seasonal variations, the observed average Si isotope composition for each river is about the same and no systematic relationship exists between the Si isotopic composition of the river and the source lithology, TDS content or calculated weathering flux.

The high precision of the measurements facilitates the resolution of small seasonal variations in the Si isotope composition of the studied rivers (Table 3.2). Our results demonstrate for the first time that the Si isotope compositions of the rivers can undergo seasonal variations of 0.6‰ in $\delta^{30}\text{Si}$ (Fig. 3.4). Noteworthy is the seasonal co-variation between the $\delta^{30}\text{Si}$ and the [Si] of the Verzasca, which is not shown in the other three rivers (Fig. 3.4).
3.4 Discussion

In order to constrain the processes that control the Si isotope composition we assess the relationships between Si isotope variability, water chemistry and weathering flux.

3.4.1 Verzasca

For the mountainous Verzasca river the pronounced direct correlation between [Si] and Si isotope composition ($R^2 \approx 0.85$) over the sampling period (Fig. 3.5a) indicates a relatively simple process controlling the Si chemistry in these waters. A positive relationship between the concentration and isotopic composition of dissolved riverine Si was first recognised by De la Rocha et al. (2000) and interpreted as the result of enhanced weathering (yielding higher $\delta^{30}Si$ and higher [Si]) (DE LA ROCHA et al., 2000). However, the total cation flux is dominated
by the discharge (Fig. 3.5c) and actually decreases with Si isotopic composition (Fig. 3.5b (note log scale)). Therefore, the weathering flux is inversely related to the \( \delta^{30}\text{Si} \) composition of the riverine dissolved Si.

\[
\delta^{30}\text{Si} = 0.36x - 0.03 \\
R^2 = 0.85
\]

\[
y = -0.4x + 1.35 \\
r = 0.87
\]

\[
y = 0.28x - 1.5 \\
R^2 = 0.95
\]

\[
\delta^{30}\text{Si} = 0.36x - 0.03 \\
R^2 = 0.85
\]

\[
y = -0.4x + 1.35 \\
r = 0.87
\]

\[
y = 0.28x - 1.5 \\
R^2 = 0.95
\]

**Figure 3.5:** Relationship between (a) \( \delta^{30}\text{Si} \) and [Si], (b) \( \delta^{30}\text{Si} \) and weathering flux (as base cation flux), (c) discharge and weathering flux and (d) \( \delta^{30}\text{Si} \) and Al/Si ratios for the Verzasca. Uncertainties on \( \delta^{30}\text{Si} \) ratios are given as 95% SEM, on discharge and fluxes are \( \sim 10\% \).

The formation of clays is considered to be the key fractionation process during weathering. Clay formation should remove Al relative to Si, whilst leading to Si isotope fractionation, thus resulting fluids should have low Al/Si ratios correlated to high \( \delta^{30}\text{Si} \) values, as shown to be the case in Figure 3.5d. Given that clay formation is a key fractionation process, the upper intercept at \( \sim +1\% \) in Figure 3.5d might represent a limit for clay-induced fractionation, reflecting exhaustion of the finite reservoirs of dissolved Al and the highest measured \( \delta^{30}\text{Si} \). The removal of Al during clay formation should dominate dissolved Si/Al ratios, and other cation to Al ratios, such as Ca/Al. This is exactly as observed for the
Verzasca, and it is found that $\delta^{30}\text{Si}$ varies with Si/Al and Ca/Al (Fig. 3.6), implicating Si isotope fractionation during clay formation. However, processes dominated simply by clay formation cannot readily explain the observed co-variations between discharge, weathering flux and $\delta^{30}\text{Si}$ (Fig. 3.5b and c).

The speciation of Al in fresh water is considered to be either predominately dissolved as Al(OH)$_4^-$ (Hassan et al., 2006) or associated in colloidal / particulate forms (Upadhyay et al., 2002). Therefore, elevated Al concentrations might reflect alumosilicate species (e.g. ultra-fine clays, <0.45μm) or their leachates following acidification of the filtered samples. However, using the Al:Si ratios for clays of 1:2 and 1:1, the slope in Figure 3.5d ($y = -11.74 x + 0.96$) would imply a $\delta^{30}\text{Si}$ value of the alumosilicate to be between -5% and -11%. Such an extremely low $\delta^{30}\text{Si}$ value, given that the observed $\delta^{30}\text{Si}$ range for clays is between -2.3 and +0.1% (De La Rocha et al., 2000; Ding et al., 1996), implies that the observed trend in Figure 5d is not due to the incorporation of fine clay particles, and that Al is instead a truly dissolved and reactive species.

In order to explain the correlation between $\delta^{30}\text{Si}$ and discharge, the relationship between Si isotopic composition and water chemistry can more readily be interpreted in terms of mixing between two components ($A$ and $B$), representing different solute pools with distinct Si isotopic and chemical compositions (Fig. 3.6). These two components can be used to characterise different facets of the weathering process. Component $B$, with the heaviest Si, low discharge and low solute fluxes, corresponds with low weathering fluxes, although the solute concentration is high. Clay formation appears active within the soil horizons and/or on in-situ sites within the host rock, as indicated by highly fractionated Si isotopes and the relative removal of Al. On this basis, Component $B$ represents basal flow conditions, where the river discharge is mainly maintained through seepage from soil and/or ground waters. Component $A$ is characterised by lower $\delta^{30}\text{Si}$ values, higher Al abundances and higher solute fluxes, indicating higher mineral dissolution rates and less effective clay formation. There are two potential sources of lighter Si isotopes and Al; (i) dissolution of clays and (ii) enhanced dissolution of primary silicates. The dissolution of clays is likely to contribute at least to some extent because the rainwater is undersaturated with respect to kaolinite and thus strong precipitation could cause clay dissolution. The enhanced solute flux reflected in the discharge would be consistent with this (Fig. 3.5c). The dissolution of both primary and secondary
minerals releases Al and lighter Si isotopes into the river. This example shows that the Si isotope composition is inversely correlated with the silicate derived weathering flux, which is at its highest when the riverine $\delta^{30}\text{Si}$ is low.

![Figure 3.6: The relationship of the $\delta^{30}\text{Si}$ composition and the water chemistry of the Verzasca can be described in a simple system using Si/Al vs. Ca/Al (black circles and line) and $\delta^{30}\text{Si}$ vs. Ca/Al (grey triangles). The system varies between two components A and B and is governed by the riverine discharge. Component B is likely to be basal flow; component A represents high superficial runoff.](image)

The proposed association of component B with clay formation is consistent with previous work that has shown that $\delta^{30}\text{Si}$ of soil solutions and groundwater can be positive due to the dissolution of igneous minerals and the subsequent formation of secondary clay minerals (Georg et al., 2005; Ziegler et al., 2005a). It should be mentioned, however, that plants producing phytoliths utilise Al as well as Si and other macronutrients (Bartoli and Wilding, 1980; Carnelli et al., 2001; Carnelli et al., 2002; Carnelli et al., 2004; Hodson and Sangster, 1999; Wüst and Bustin, 2003). The related Si isotope fractionation and Al depletion might therefore be expected to be similar. However, estimates of Si/Al in phytoliths range from about 8-20 to 100-4000 (after (Bartoli, 1985)), and considering the sparse
vegetation within the Verzasca valley, the biological uptake of Al should be negligible compared to the storage of Al in clays.

By excluding a significant biological storage of Si, the Si weathering flux thus corresponds to the chemical denudation rate of Si. Normalising the elemental flux to the catchment area, the chemical weathering of Si is on average about 2.9 tons km\(^{-2}\) yr\(^{-1}\), compared to an average base cation derived weathering flux of 6.3 tons km\(^{-2}\) yr\(^{-1}\) which results in a total flux of 9.2 tons km\(^{-2}\) yr\(^{-1}\). This is about 5 times higher than the chemical denudation rate of other granitoid-dominated catchments in northern climates, but still lower than the chemical denudation rate of tropical granitoid catchments (Millot et al., 2002). The silica weathering flux of ~6 tons km\(^{-2}\) yr\(^{-1}\) is less than a value obtained for glaciated catchments within the Swiss Alps of ~10 tons km\(^{-2}\) yr\(^{-1}\) (West et al., 2005).

3.4.2 Ticino

Although the Ticino drains a catchment lithology similar to the Verzasca, the basic water chemistry is quite different, apparently because of a contribution from carbonate and evaporite-derived weathering. There is no correlation between [Si] and Si isotope composition, but there are trends between Si isotope composition and discharge (R\(^2\)=0.54) and the base cation flux (R\(^2\)=0.51) (Fig. 3.7). The relationship is similar to the mixing trend of the Verzasca discussed above although not as pronounced, probably because of this additional complexity in dissolved source components (Fig. 3.8). Another important distinction between the Ticino and the Verzasca catchments is the presence of extensive soils and agriculture in the Ticino valley. Widespread, well-developed soils and agriculture provide extensive opportunities for Si to be biologically-utilised. The biological influence on the Si flux should thus be higher than in the Verzasca. The slightly higher average \(^{30}\)Si composition compared to the Verzasca would be consistent with this.

3.4.3 Birs & Saane

As with the Ticino, both the Birs and Saane do not show an overall correlation between [Si] and Si isotope composition. Again, the processes controlling the Si isotope composition within these rivers are complex. Neither river displays a relationship between Si isotope composition and discharge or weathering flux. It appears that the Si isotope composition is completely decoupled from the weathering flux in both rivers because of the contributions from carbonate to the dissolved load.
Figure 3.7: Relationship between $\delta^{30}$Si and (a) discharge and (b) base cation flux for the Ticino.

Figure 3.8: The relationship between $\delta^{30}$Si and base cation flux (grey triangle) and Si/Al ratios (black circles) for the Ticino.
The Si isotope composition of the Saane, however, shows a weak trend with Ca/Na ($R^2=0.33$) and Mg/Na ($R^2=0.35$) ratios, where lower $\delta^{30}$Si values are related to higher Ca/Na and Mg/Na ratios and vice versa. The sample from May 2004 shows the highest $\delta^{30}$Si composition among the entire data set and, considering a potential clay fractionation limit of $\sim+1\%$ (see section 3.4.1.) this value might be the result of biological fractionation. Excluding this sample improves the correlations between $\delta^{30}$Si and Ca/Na and Mg/Na significantly ($R^2=0.70$ and 0.83, respectively) (Fig. 9a,b). As the catchment of the Saane is made up of silicate and carbonate rocks the correlation between Si isotope composition and Ca/Na and Mg/Na may indicate relative changes in the weathering intensity of both lithologies. The long-term dataset of the Saane shows that the Ca/Na ratio scales with the discharge (Fig 3.9c), i.e. high discharge gives higher Ca/Na ratios. This relationship shows an enhanced release of Ca due to the favoured dissolution of highly soluble carbonates during high discharge periods. In fact, this means that the carbonate weathering rate is higher during high discharges. The Si isotope composition is, however, lower during this time, indicating an indirect relationship between Si isotope composition and discharge. As discussed in the previous sections, a lighter Si isotope composition is associated with an enhanced breakdown of silicate mineral phases and thus an increase in silicate weathering intensity. The changes in Ca/Na ratios with discharge result from an increase of carbonate weathering relative to silicate weathering during high discharge. The Si isotope composition decreases and thus also indicates an increase of primary silicate weathering. This is consistent with an increase of the total weathering (silicate + carbonate weathering) with discharge.

The carbonate-dominated Birs has the lowest average $\delta^{30}$Si composition of all four studied rivers and the Ca/Na ratio also scales with discharge ($R^2=0.64$). The relation between $\delta^{30}$Si and Ca/Na shows a similar trend, however, it is not as pronounced ($R^2=0.14$) as within the Saane. The weathering flux of the Birs is always dominated by carbonate dissolution and changes in weathering intensity do not influence Si isotope composition, which seems to be buffered by other processes. The [Si] of the Birs is not significantly lower than that of the other rivers, despite the fact that silicate rocks are of only minor importance. It has been shown for forested catchments that the Si flux derived from the recycling of biogenic silica can be in excess of the weathering-derived Si flux (Alexandre et al., 1997; Carnelli et al., 2001; Carnelli et al., 2004; Conley, 2002; Farmer et al., 2005). Therefore, a biogenic
origin for the Si in the Birs is plausible and consistent with the lower average $\delta^{30}\text{Si}$, reflecting dissolution of lighter biogenic silica.

![Graphs](image)

Figure 3.9: Relationship between $\delta^{30}\text{Si}$ and (a) Ca/Na and (b) Mg/Na, excluding sample May 2004 (grey square), and between (c) discharge and Ca/Na for the Saane.

3.4.4 Implications for the global silicon budget

The average $\delta^{30}\text{Si}$ value of 40 samples from the Swiss rivers is $+0.84\pm0.19\%$o ($\pm1\sigma_{SD}$) and in good agreement with some previous studies (De La Rocha et al., 2000; Ziegler et al., 2005a). No river-water studies yield $\delta^{30}\text{Si}$ values as high as $+2.13\pm0.74\%$o reported for the Yangtze River in China (Ding et al., 2004), the reason for which is unclear. It has been suggested that stable continental shields with older and deeply weathered soils have lower
average $\delta^{30}\text{Si}$ because of (i) weak present-day weathering and (ii) the dissolution of minerals that are mainly secondary in origin (ZIEGLER et al., 2005a). In contrast, tectonically-active mountain belts expose unaltered primary minerals and achieve high weathering rates leading to elevated $\delta^{30}\text{Si}$ in rivers. However, such models are not supported by the data presented here. Weathering regimes can be complex and many parameters, such as climate and topography, contribute to a regime that can be either (chemical) weathering- or transport-limited (JACOBSON et al., 2003). For example, if a watershed is weathering-limited due to its topography and climate (e.g. steep slopes, high precipitation), the soil formation is limited by intense physical erosion. Under these circumstances weathering favours the dissolution of highly soluble minerals, such as carbonates, silicate weathering is incomplete and the formation of soils and clays is limited due to high erosion rates. Under these conditions one would expect rivers to have generally low $\delta^{30}\text{Si}$ values due to ineffective clay induced fractionation. In turn, a transport limited watershed, where soil development and silicate weathering prevail should yield higher $\delta^{30}\text{Si}$ values in the water because of more clay formation, unless the main Si source is secondary in origin (ZIEGLER et al., 2005a).

The high altitude watersheds of the Alps certainly represent weathering limited regimes (WEST et al., 2005), like the Verzasca valley, where the presence of steep slopes limits the development of soil by erosion (DREVER and ZOBRISt, 1992). Most of the Birs and Saane catchments have a low relief and in contrast to Verzasca soil formation prevails. The Si isotope composition of the studied alpine rivers is in good agreement with reported Si isotope compositions from transport-limited watersheds, e.g. Amazon and Congo river (DE LA ROCHA et al., 2000). Our data indicate that the influence of different weathering regimes on the Si isotope composition is not as clear nor pronounced as previously proposed (ZIEGLER et al., 2005a).

Despite the similarity in general tectonic environment between the European Alps and the Himalayas the results presented here are in stark contrast to the data recently reported for Chinese Rivers (DING et al., 2004). In both cases the effects should be dominated by a tectonically active mountain belt where fresh rock surfaces and young soils are exposed as a consequence of the last glaciation. Yet the Swiss rivers do not yield the extremely heavy $\delta^{30}\text{Si}$ values that are reported for the Chinese rivers. Based on the $\delta^{30}\text{Si}$ systematics of the Swiss rivers it seems to be unlikely that weathering of primary silicates and the formation of clays
can produce dissolved riverine Si with δ³⁰Si values as high as +2.13‰. The δ³⁰Si of the Yangtze River is elevated where wetland and seasonally flooded rice fields start to appear (DING et al., 2004), and it has been shown that the growth of rice plants is associated with a large Si isotope fractionation, and thus could account for the very high average δ³⁰Si of the Yangtze River (DING et al., 2005a). However, recycling of organic matter from plants, which results in high biogenically-derived Si fluxes (ALEXANDRE et al., 1997; CARNELLI et al., 2001; CARNELLI et al., 2004; CONLEY, 2002; FARMER et al., 2005) should counterbalance the effect of biogenic Si isotope fractionation and limit δ³⁰Si to more normal values. Therefore, the reasons for these differences are unclear. It is however possible that there are systematic analytical offsets in reported δ³⁰Si values, as indicated by recent publications on the assessment of standard materials (DING et al., 2005b; REYNOLDS et al., 2006b).

3.4.5 Glacial-interglacial variations in seawater δ³⁰Si

The seasonal δ³⁰Si variations reported here can be used to assess the impact on the global oceanic Si isotope composition of glacial-interglacial cycles. The sensitivity of the average Si isotope composition of the oceans has been recently addressed by De La Rocha and Bickle (DE LA ROCHA and BICKLE, 2005), who used a two box model with a constant δ³⁰Si value for the continental Si flux to the oceans of +0.8‰. This value represents a mass-balance between a 85% riverine input with an average δ³⁰Si of +1.0‰ and a 15% contribution of a non-riverine source with an average δ³⁰Si of -0.3‰ (after ELDERFIELD and SCHULTZ, 1996; TRÉGUER et al., 1995) in (DE LA ROCHA and BICKLE, 2005)).

De La Rocha and Bickle argue that the Si flux must decrease by more than 50% of present day in order to change the input into the ocean significantly. However, the effects of glacial-interglacial changes in riverine δ³⁰Si are not considered. The average continental riverine discharge during the Last Glacial Maximum (LGM) was very similar to

<table>
<thead>
<tr>
<th>riverine δ³⁰Si</th>
<th>Change in riverine δ³⁰Si</th>
<th>initial Si Flux</th>
<th>+10% Si Flux</th>
<th>-10% Si Flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>+0.2</td>
<td>+0.64</td>
<td>+0.65</td>
<td>+0.62</td>
</tr>
<tr>
<td>1.2</td>
<td>+0.2</td>
<td>+0.98</td>
<td>+0.99</td>
<td>+0.95</td>
</tr>
</tbody>
</table>

Table 3.3: Applying small offsets of ±0.2‰ to the riverine δ³⁰Si composition results in a significant shift of the continental δ³⁰Si input to the ocean. The δ³⁰Si composition of the ocean is thus more sensitive to variations of the riverine δ³⁰Si composition than to changes of the riverine Si flux. *Data taken from (DE LA ROCHA and BICKLE, 2005).
the present day value (Munhoven, 2002), as the global Si flux to the oceans would not have changed by a significant amount (~10%) compared to the present day value during glacial-interglacial cycles (Jones et al., 2002). However, our results indicate that the $\delta^{30}$Si composition of rivers can undergo large variations that relate to weathering style. Small offsets in average riverine $\delta^{30}$Si from $+1.0\%$ to $+1.2\%$ and $+0.8\%$, result in the average continental input changing from $+0.8\%$ to $+0.98\%$ and $+0.64\%$, respectively (Table 3.3), and thus significantly change the Si isotopic input into the oceans. Extending the published mass-balance calculations (De La Rocha and Bickle, 2005) it is apparent that the average isotopic composition of dissolved continental Si that is transferred to the oceans is much more significant than changes in the total Si flux (Fig. 3.10). Variable continental $\delta^{30}$Si inputs need to be considered in future applications of Si isotopes as a proxy for marine palaeoproductivity and past Si utilization.

![Figure 3.10](image)

**Figure 3.10:** Variations in the $\delta^{30}$Si values of the continental input to the ocean due to variations in the riverine Si flux and the initial riverine $\delta^{30}$Si composition. The model shows that the continental input into the oceans is more sensitive to changes in the riverine $\delta^{30}$Si composition than to changes in the riverine Si flux. The grey box indicates changes in riverine Si flux of $\pm10\%$. 

78
3.5 Conclusions

The average Si isotopic compositions of 4 Alpine rivers are very similar despite a range of weathering styles, climate, erosion flux and biomass. This is hard to reconcile with quite variable values reported for the Yangtze. However, the isotopic composition of dissolved Si varies significantly on a seasonal timescale with an amplitude of up to 0.6 %. Using variations in discharge, water chemistry and weathering flux the mechanisms controlling the sources of dissolved riverine Si can be constrained. The Si isotope composition of a high mountainous catchment reflects the mixing of soil / groundwater and high discharge waters originating from precipitation and snow melt. The underlying dominant mass fractionation process is the formation of clay, which incorporates lighter Si isotopes. The coupling between weathering flux and Si isotope composition implies that biological effects on dissolved Si are unimportant and can be neglected in high mountainous catchments. Catchments with higher proportions of carbonate rocks, cultivated soils and forests show a progressive decoupling of the Si isotope composition from the weathering flux. It appears to be common that an enhanced total weathering flux (carbonate + silicate weathering) is associated with lighter $\delta^{30}$Si, even though carbonate dissolution dominates the solute load. The mechanisms controlling the Si isotope composition in lowland rivers are complex and cannot be distinguished unambiguously, but are likely a combination of Si derived from silicate weathering and recycling of biogenic silica. Overall, there appear to be regionally distinct mechanisms controlling the Si geochemical budget of river waters, namely; in high mountainous catchments Si is controlled by weathering of primary minerals and precipitation of clays, whilst is lowland areas the main control on the $\delta^{30}$Si value and Si continental weathering flux may be biological utilization.

The continental input of Si into the oceans may have had variable $\delta^{30}$Si values on short time-scales. Mass balance calculations show that the input into the ocean is more sensitive to variations of the riverine $\delta^{30}$Si composition than to changes of the Si flux, and can lead to a change in the average $\delta^{30}$Si value of the global ocean.
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Chapter 4: Silicon isotope variations during basalt weathering on Iceland

To be published as

Silicon isotope variations during basalt weathering on Iceland


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Abstract:

This study presents the dissolved Si isotope compositions of twenty rivers from across Iceland. The high-resolution Nu Plasma 1700 MC-ICPMS was used to provide interference-free $^{30}\text{Si}/^{28}\text{Si}$ ratios with an average limiting precision of $\pm 0.04\% \delta^{30}\text{Si}$. The Si isotope composition ranges from $-0.08\%$ to $+1.42\% \delta^{30}\text{Si}$, averaging of $0.63\pm0.38\%$ ($\pm 1\sigma_{\text{SD}}$). This is only slightly lighter than the recently reported mean of $+0.84\pm0.19\%$ for high precision measurements of Swiss rivers but is significantly lighter than the compositions that have been reported from other parts of the world. The Si isotope composition varies slightly with the amount of glacial cover, which provides evidence that the continental Si input into the oceans would be climatically controlled and varies over glacial-interglacial cycles. A trend of $\delta^{30}\text{Si}$ vs. Ca/Si, after correction for the dissolution of trace amounts of calcite in one region, is consistent with the measured basaltic composition and indicates isotopic fractionation during Si removal from the dissolved phase. By calculating the fraction of Si that is removed from the dissolved phase into secondary phases it becomes possible to use the riverine Si flux (Si denudation rate) to calculate the initial dissolution rate of Si within these catchments. The results show that $\sim 50\%$ of the initially dissolved Si from primary weathering is released into the rivers and contributed to denudation. Using the Si isotope composition and the Si fraction removed, it is possible to model the Si isotope fractionation as either a Rayleigh-type fractionation or a steady-state system. Both yield similar fractionation factors of about $-1.5\% \delta^{30}\text{Si}$, implying only one underlying fractionation process that varies in form due to external parameters, such as runoff. Furthermore, rivers, which follow a steady-state system fractionation, are associated with higher Si dissolution rates and lower $\delta^{30}\text{Si}$ values, leading to an inverse relationship between weathering rates and dissolved riverine Si isotope composition.
1. Introduction

The weathering of silicate rocks and the associated consumption of atmospheric CO₂ are thought to be part of a major feedback loop or module that has a regulating influence on the global climate (BERNER et al., 1983; WALKER et al., 1981) (BERNER et al., 1983; WALKER et al., 1981). The modelling of long-term weathering rates is thus of particular interest for the reconstruction of the global CO₂ cycle throughout the earth’s history. Diverse isotopic systems show a distinct sensitivity to weathering processes, including radiogenic isotopes like those of Sr and Nd (ANDERSSON et al., 2001; BURTON and VANCE, 2000; RAYMO et al., 1988) and stable isotope fractionations, such as those of Li and Mg (HUH et al., 2001; KISAKÜREK et al., 2005; VILLIERS et al., 2005). The stable isotopes of silicon (Si) represent a relatively new tool that has been increasingly used as a bio-productivity proxy during the last decade (CARDINAL et al., 2005; DE LA ROCHA et al., 1997; DE LA ROCHA et al., 1998; DING et al., 2005a; OPFERGELT et al., 2006a; REYNOLDS et al., 2006a). The potential use of Si isotopes for weathering studies has only been explored in a few studies (DE LA ROCHA et al., 2000; GEORG et al., 2006a; ZIEGLER et al., 2005a; ZIEGLER et al., 2005b). The rather complicated geochemistry of Si and the affinity for both biological and abiotic fractionation processes renders as complex the behaviour of Si isotopes during weathering. The processes controlling the Si budget and finally the Si isotope composition of river waters are often numerous and can typically only be deciphered by relationships to the water chemistry (GEORG et al., 2006a).

This study presents Si isotope data for the dissolved load of 20 rivers draining predominantly basaltic watersheds on Iceland. The consistent basaltic character of these catchments makes it possible to eliminate lithological variability permitting investigation of the Si isotope fractionation during weathering processes. The sparse vegetation and relative constant climate also help in this respect. Therefore, this study contrasts with a previous study on Si isotope fractionation during basalt weathering on Hawaii (ZIEGLER et al., 2005a), by reporting riverine Si isotope compositions under oceanic boreal climatic conditions without significant biological influence.

2. Climate and Geology

Only a brief overview of the geology and climate will be given below. Both can be found described in more detailed elsewhere (EYTHORSSON and SIGTRYGGSSON, 1971; GISLASON et
al., 1996; SAEMUNDSSON, 1979). The general climate of Iceland is of a maritime character. The warm waters of the North Atlantic Current maintain a relatively mild climate considering that Iceland is located north of 60°N and close to the Arctic cycle. The annual temperatures are fairly constant with a mean of 4°C and low amplitude of seasonal variation of approximately 15°C. In order to constrain climatic differences between the sampling areas we compiled climate data obtained from the Icelandic Meteorological Office (IMO). We have chosen 10 weather stations that together contain around 6000 monthly averages of climatic parameters since the 1960s from the eastern and western sides of Iceland. The average temperatures on both sides of Iceland are similar (~4°C), however, the precipitation is twice as high on the eastern side (1355 mm) of Iceland than on the western side (776 mm).

The glaciers cover about 11% of the total land area and reached their present size about 8000 years ago. The largest glacier is the Vatnajökull (8300 km²) in SE Iceland (GISLASON et al., 1996). The rivers east of the main rift show a hydrological affinity to the local glaciers and can be considered as glacially-fed river systems.

The lithology on Iceland is predominately of basaltic composition (80-85%), followed by intermediate and silicic volcanics and volcanicalstic sediments. The age of the rocks increases with distance from the central rift zone, the oldest exposed rocks being ~ 13 Ma (MOORBATH et al., 1968).

### 3. Sampling and analytical methods

#### 3.1. Sample preparation

The isotopic composition of the dissolved Si was determined for 20 streams located all over Iceland (Fig. 4.1), with catchment sizes ranging from 46 to 5100 km². The sampling procedure and techniques for the chemical analyses of cation and anion concentrations are described elsewhere (GANNOUN et al., 2006; VIGIER et al., 2006). The bedrocks of the studied catchments range between 0.2 and 11.2 Ma in age and the glacial cover varies in extent between 0 and 100% (GANNOUN et al., 2006). Silicon was separated from the water matrix and purified using a recently developed cation-exchange chemistry (GEORG et al., 2006a; GEORG et al., 2006b).
3.2. Correction for wet depositional and hydrothermal inputs

The riverine solute load has been corrected for airborne derived wet depositional input assuming all Cl' in the rivers is derived from rain with a known or estimated chemical composition (Stallard and Edmond, 1981). The approximate chemical composition of the rain has been estimated from two collected snow samples from the Langjökull glacier field W-Iceland. The X/Cl molar ratios for Mg, Na, K, Ca, Sr are 0.093, 0.9, 0.003, 0.02, 0.0002, respectively, typical of an oceanic origin (Gannoun et al., 2006). The Si concentration of these snow samples was below detection limit of ICP-OES, although the average Si concentration for Icelandic rain has been estimated to be about 0.5 µg/l SiO₂ or 0.23 ppb Si (Gislason et al., 1996). This is a negligible contribution to the riverine Si concentrations of >1 ppm Si.

![Figure 4.1: Map of Iceland showing the sampling locations as well as the average age of the catchment rocks.](image)

3.3 Silicon isotope measurement by MC-ICP-MS

We have analysed Si isotopes using the high-resolution capacity of the NuPlasma 1700 (Nu Instruments, UK) multiple collector-ICP-MS at ETH Zürich following the protocols
detailed elsewhere (Georg et al., 2006a; Halliday et al., in press). The mass bias is corrected for by a standard-sample bracketing protocol. Silicon isotope data are reported as deviations of $^{30}\text{Si}/^{28}\text{Si}$ and $^{29}\text{Si}/^{28}\text{Si}$ from the international standard NBS28 in parts per thousand (the standard delta notation $\delta^{x}\text{Si}$, $x = 30$ or 29) as follows:

$$\delta^{x}\text{Si} = \left( \frac{(x/28)_{\text{sample}}}{(x/28)_{\text{NBS28}}} \right) \times 1000$$

The long-term reproducibility of over 300 measurements of the IRMM-018 standard was $\pm 0.14\%$ (2σSD) for $\delta^{30}\text{Si}$ values and $\pm 0.10\%$ (2σSD) for $\delta^{29}\text{Si}$ values (Reynolds et al., 2006b). The silicon isotope composition of the Icelandic river samples was reproducible during different measuring sessions with an average of 0.11% (2σSD) for $\delta^{30}\text{Si}$ and 0.08% (2σSD) for $\delta^{29}\text{Si}$. The precision given as standard error of the mean for over 12 duplicate analyses is thus limited to $\pm 0.04\%$ for $\delta^{30}\text{Si}$ values and $\pm 0.03\%$ for $\delta^{29}\text{Si}$ values at the 95% confidence level by our long-term reproducibility. The accuracy of the Si isotope ratios during runs was checked using the IRMM-018 standard.

4. Results

Two host rocks samples were analysed for the Si isotope composition. Both, the bulk basalt (from Heimaey) and a scoria sample (from Skjaldbreiður) yield a $\delta^{30}\text{Si}$ of -0.35±0.1% (±2σSD) (Tab 4.1, Fig 4.2a).

4.1. Riverine aqueous chemistry

The compositional data of the sampled rivers is given in Table 4.1. On a molar basis the anions decrease from $[\text{HCO}_3^-] > [\text{Cl}^-] > [\text{SO}_4^{2-}]$ and cations (including Si) decrease from [Si] > [Na$^+$+K$^+$] > [Ca$^{2+}$] > [Mg$^{2+}$]. The composition of the solute load reflects basalt weathering and agrees well with the relative level of weathering derived elemental fluxes (Gislason et al., 1996). The concentration of the dissolved major cations and Si does not vary with the degree of glacial cover or with the age of the associated bedrock.
The PHREEQC software (PARKHURST and APPELO, 1999) and the chemical data from Table 4.1 were used to calculate the saturation states of the collected samples regarding (a) the main basaltic primary minerals, such as anorthite, diopside, forsterite and (b) kaolinite as an example of secondary weathering products. The river waters are undersaturated with respect to the primary basaltic minerals and glass and oversaturated with respect to secondary minerals, such as gibbsite and kaolinite. Among the primary minerals olivine and clinopyroxene are the most undersaturated phases whereas anorthite and basaltic glass are close to saturation, which means that the riverine dissolved load is mainly derived from the latter phases. The secondary phases are over saturate and might be potential weathering products within the studied catchments.

4.2. Isotope composition of the dissolved riverine Si

The mean $\delta^{30}\text{Si}$ value of the river waters is $+0.63\%_\text{o}$ ranging from $-0.08$ to $+1.42\%_\text{o}$ (Table 4.1). All Si isotope measurements agree with the mass-dependent equilibrium fractionation line of Si (Fig. 4.2a), documenting the elimination of all molecular interferences ($\delta^{29}\text{Si} = 0.5178 \times \delta^{30}\text{Si}, R^2 = 0.99$). All rivers, except for IS-23, carry a positive value of $\delta^{30}\text{Si}$ in the dissolved Si. The age of the host rock appears to have no influence on the riverine Si isotope composition. The average $\delta^{30}\text{Si}$ of $0.63\pm0.38\%_\text{o}$ ($\pm1\sigma_{\text{SD}}$) is lower than previously published values for rivers although in some instances, such as the Swiss rivers, this difference is statistically insignificant (ALLEMAN et al., 2005; DE LA ROCHA et al., 2000; DING et al., 2004; GEORG et al., 2006a; ZIEGLER et al., 2005a). There are however, differences between the rivers E' and W' of the main rift; the riverine $\delta^{30}\text{Si}$ composition of the W' rivers has a higher average of $0.91\pm0.44\%_\text{o}$ compared to $0.46\pm0.20\%_\text{o}$ on the E' side. There also seems to be some dependence of the $\delta^{30}\text{Si}$ values on the amount of glacial cover in the catchment (Fig 4.2b) since none of the rivers from glaciated catchment have $\delta^{30}\text{Si}$ values above $+0.8\%_\text{o}$, whereas four out of seven rivers from non-glaciated catchments have $\delta^{30}\text{Si}$ vales above $+0.8\%_\text{o}$. 
Figure 4.2a-b: (a) All water samples (black dots) and rock samples (grey diamonds) fit onto a mass-dependent fractionation array, with a slope of 0.5178, documenting the interference-free determination of all three Si isotopes via HR-MC-ICP-MS. (b) None of the glaciated catchments yields $\delta^{30}\text{Si}$ values greater than $+0.8\%o$. 
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<th>Discharge Time of sampling</th>
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<th>T</th>
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<th>Cl⁻</th>
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<td>0.3</td>
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<td>0.04</td>
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Table 4.1: Hydrological, compositional and isotopic data of the analysed water samples as well as Si isotope data for two rock samples. n.a. = not analysed. All data, except Si isotope data were taken from (GANNOUN et al., 2006). The Si isotope composition of sample IS 01 was also analysed after ultrafiltration (10KD). The <10KD aliquot (italic letters) is within errors identical to the <0.2μm aliquot.
5. Discussion

The $\delta^{30}$Si of the studied rivers shows a wide range from $-0.08\%$o to $+1.46\%$o, with no obvious relation to Si concentration. As Iceland has a virtually mono-lithological geology, mild maritime climate and sparse vegetation cover, we can assume that the major source for the dissolved load for those rivers is basalt and that biology and seasonal climate has only minor influences on the dissolved solute pool. However, such large variations imply there are considerable differences in the behaviour of weathering between the watersheds. We will first consider the elemental composition of the rivers before reconsidering the highly variable Si isotope compositions.

5.1. Assessing the silicate derived weathering flux.

In order to evaluate the release of ions during weathering be will first look at the Ca/Si ratio because after Si, Al and Fe, Ca is the most abundant cation in basalts (Gislason and Hans P. Eugster, 1987), but only Ca has a similar relative mobility to Si, whereas Al and Fe(III) are not readily soluble and thus have a mobility during weathering which is between two and three orders lower than Ca or Si (Gislason et al., 1996). The similar mobility means that basaltic weathering should yield relatively constant riverine Ca/Si. Any extreme changes of the riverine Ca/Si should be either related to weathering not directly from the basaltic rocks or to the removal of Ca and/or Si into secondary phases, such as clays.

There are four samples (IS 16, 17, 22, 23) that are not consistent with a Ca/Si molar ratio below 0.75. One explanation for this shift towards a higher Ca/Si ratio might be an insufficient correction regarding the Ca input from precipitation. The Ca/Cl ratios of the Icelandic rain are not uniform, and the Ca correction can be underestimated for Cl-concentrations below 7ppm (Gislason et al., 1996). A poor correction of the rainwater Ca contribution to sample IS 16 might be likely as the Ca/Si molar ratio is only just above 0.75. Such an explanation cannot be applied to the other samples given the much higher Ca/Si ratios. Alongside elevated Ca/Si, low Na/Ca and Mg/Ca attest Ca enrichment. There are mainly two important sources that could mix into the riverine runoff: (i) atmospheric deposition, either direct as rain or indirect over the meltdown of ice and snow and (ii) geothermal fluids. A direct or indirect contribution from atmospheric deposition or from geothermal waters is highly unlikely, since geothermal fluids, rain and melts waters all have
relatively high Na contents compared to Ca (GANNOUN et al., 2006; GISLASON and EUGSTER, 1987), which would be inconsistent with the observed high Ca/Na ratios.

A study of the glacial runoff from the Fjallsjökull glacier, which belongs to the eastern Vatnajökull ice field, came to the conclusion that the dissolution of calcite could have an impact on the solute load of the glacial runoff even though the abundance of calcite within the subglacial host rocks is ≤ 3% (RAISWELL and THOMAS, 1984). Those rivers with significant Ca enrichment are associated with the glacial runoff from the Vatnajökull ice field and the relative high proportion of Ca relative to Mg, Na and Si in these rivers can thus be simply explained by the subglacial erosion of carbonate minerals. Such weathering would have no effect on the Si isotope composition. The contribution from the dissolution of calcite can be corrected for by estimating the Ca input from the silicate fraction only ($Ca_{sil}$), using the approach of (QUADE et al., 2003), modified from (GALY and FRANCE-LANORD, 1999):

$$Ca_{sil} = (Ca/Na)_{sil} \times Na_{sil}$$

where $Na_{sil}$ is the riverine Na concentration corrected for atmospheric and geothermal inputs and $(Ca/Na)_{sil}$ is the average Ca/Na ratio of carbonate-free rivers. We have taken the catchments from the eastern side of Iceland to represent carbonate-free rivers and estimated $(Ca/Na)_{sil} = 0.67 \pm 0.17$. The $Ca_{sil}$ correction implies that ~46% (IS 16), ~73% (IS 17), and ~81% (IS 22) of the Ca is derived from carbonate dissolution. The associated Ca/Si ratios change from 1.08 (IS 16), 2.49 (IS 17) and 6.74 (IS 22) to 0.61, 0.68 and 1.28, respectively.

A relative Ca enrichment is not the only distinctive feature of sample IS 23, as the Al and Fe concentrations are an order of magnitude (299.7 and 494.1 µg/l, respectively) higher compared to the other rivers. The resulting molar riverine Si/Al and Si/Fe ratios are 8.6 and 10.8, respectively, and are close to the corresponding basaltic rock ratios of 6.8 and 4.0, respectively. The molar Mg/Si ratio (~0.14) of the river is also close to the Mg/Si of the basaltic host rocks (~0.17). These ratios indicate that the dissolved load of IS 23 is quite close to both the basaltic rock composition and further, the negative $\delta^{30}$Si ratio is also close to the basaltic Si isotope composition. The elemental ratios, particular the high Al concentration and the igneous like $\delta^{30}$Si value, indicate that the solute load of IS 23 is close to the basaltic composition, indicating that formation of secondary weathering products has not yet taken
place to a degree that would result in alteration of relative element mobilities or significant Si isotope fractionation. The formation of secondary weathering products reduces Al concentrations and causes Si isotope fractionation (Georg et al., 2006a). The relatively Ca enrichment may still be due to the dissolution of a calcite component. As sample IS 23 shows such distinct chemical features, it will be excluded in the following discussions.

5.2. Variations of the elemental load and $\delta^{30}\text{Si}$

The removal of Si into secondary clay minerals should lead to both higher Ca/Si ratios and higher dissolved $\delta^{30}\text{Si}$ values, as the clay preferentially incorporates lighter Si isotopes. This hypothesis can be tested by comparing $\delta^{30}\text{Si}$ values to riverine Ca/Si ratios, as shown in Figure 4.3. Most of the investigated rivers follow a positive trend ($r^2=0.77$) with fairly stable Ca/Si weight ratios between ~0.3 and ~0.8 and changes in $\delta^{30}\text{Si}$ between 0.19% and 1.46%. The observed trend is consistent with the Ca/Si ratio (0.33) (Crovisier et al., 1992; Gislason and Hans P. Eugster, 1987) and measured $\delta^{30}\text{Si}$ of -0.35% for the Icelandic basalt. The results clearly support the hypothesis that the riverine dissolved Si is derived from the direct dissolution of basalt and fractionation of Si during the formation of secondary clay minerals.

Figure 4.3a,b: (a) The riverine Ca/Si ratios scale with the riverine $\delta^{30}\text{Si}$ composition. This trend is also consistent with the basaltic composition of Ca/Si = 0.33 and $\delta^{30}\text{Si} = -0.35\pm0.1\%$, indicating the basalt derived solute load. However, 4 samples do show a Ca enrichment that is derived from weathering of trace calcite. Plot b shows the carbonate corrected Ca/Si ratios.
5.3. Estimating Si removal

The carbonate corrected Ca/Si ratios of all samples seems to have evolved from the basaltic end-member (Ca/Si ~0.33, δ30Si -0.35‰) and the overall positive correlation between Ca/Si and δ30Si shows that Si removal causes mass-fractionation. Therefore, changes in riverine Ca/Si ratios during isotope fractionation can be compared with basaltic Ca/Si to calculate the degree of Si loss. Here we assume that any biogenically-mediated Si storage is negligible compared to storage in secondary weathering products. For the first instance we also assume that no Ca loss has occurred, even though the uptake of Ca by secondary weathering products has been estimated to be between 10 and 30% (Crovisier et al., 1992; Moulton et al., 2000; Stefansson and Gislason, 2001). The fraction left in the dissolved pool is from now referred to as $f_{Si}$ and is defined as:

$$f_{Si} = \frac{(Ca/Si)_{rock}}{(Ca/Si)_{river}}$$

where $(Ca/Si)_{rock}$ is the basaltic Ca/Si weight ratio (0.33) and $(Ca/Si)_{river}$ is the riverine Ca/Si weight ratio, corrected for wet depositional and carbonate derived inputs. The percentage of Si being removed ($Si_{loss}$) is thus given by:

$$Si_{loss} = (1 - f_{Si}) \times 100$$

Calculations for each river result in $f_{Si}$ values between 0.3 and 0.75, averaging 0.49, yielding an average $Si_{loss}$ of 51% of the primary weathered Si stored in secondary phases. This percentage is in good agreement with previous estimates (Crovisier et al., 1992; Stefansson and Gislason, 2001). The $f_{Si}$ correlates with the δ30Si (Fig. 4.4a). In general higher losses of Si are associated with higher fractionated riverine Si isotope compositions. The two different trends in figure 4.4a suggest that the Si fractionation is the result of more than one type of process.
Figure 4.4a-c: The relation between $f_{Si}$ and $\delta^{30}Si$ can be described in the $\ln f_{Si}$ / $\delta^{30}Si$ space. The slopes give an estimate of the associated fractionation factor $\varepsilon$. (a) As given in the Ca/Si / $\delta^{30}Si$ space, two main trends can be recognised. However, it has to be considered that Ca might have been lost from the dissolved phase by sequestering into secondary phases. Such a case would compromise the calculation of $f_{Si}$ obtained from the Ca/Si ratio. Inverse modelling can assess the effect of Ca loss; a loss of Ca by X-% can be evaluated by adding X-% Ca to the riverine Ca concentration and using the adjusted Ca/Si ratios to recalculate $f_{Si}$. It appears from plot b and c that a 5% Ca loss seems to be reasonable since this would be still consistent to the basaltic end-member. A loss of Ca by 10% would already result in inconsistency to the basaltic end-member, a loss of Ca by 20% is definitely unreasonable. Considering a loss of maximum 5% Ca results in a 2% change of the average Si loss.

5.4. Rayleigh-type vs. steady-state isotope fractionation

Following the approach of (SIGMAN et al., 1999) and modifying the equations it is possible to model the Si isotope fractionation for steady-state and Rayleigh-type kinetics as follows:

**Steady-state:**

$$\delta^{X}Si_{\text{dis}} = \delta^{X}Si_{\text{initial}} - \varepsilon \left(1 - f_{Si}\right)$$

$$\delta^{X}Si_{\text{product}} = \delta^{X}Si_{\text{initial}} + \varepsilon \cdot f_{Si}$$

**Rayleigh type:**

$$\delta^{X}Si_{\text{dis}} = \delta^{X}Si_{\text{initial}} + \varepsilon \left(\ln f_{Si}\right)$$

$$\delta^{X}Si_{\text{product}} = \delta^{X}Si_{\text{initial}} + \varepsilon$$
where $\delta^{Si}_{dis}$ is the Si isotope composition of the dissolved phase (riverine Si isotope composition), $\delta^{Si}_{product}$ is the Si isotope composition of the formed product, $\delta^{Si}_{initial}$ is the initial Si isotope composition, which we set to be the basaltic $\delta^{30}Si$ value of -0.35‰, and $f_{Si}$ is the fraction of Si remaining within the dissolved phase. The fractionation factor ($\varepsilon$) is assumed to be a constant. We can thus expect linear trends in either $\delta^{30}Si - \ln f_{Si}$ space, or $\delta^{30}Si - f_{Si}$ space. The fractionation factor has been set to be $\varepsilon = -1.5$ given by the slopes in figure 4.4a.

To decipher a linkage between the Si removal and the Si isotope fractionation the data are plotted in the $\delta^{30}Si - \ln f_{Si}$ space (fig 4.4). The plot shows two different arrays; samples mostly collected on the western coast area of Iceland follow a linear array indicating a Rayleigh-type fractionation trend where the slope gives an estimate for the underlying fractionation factor, $\varepsilon = 1.52$ ($r^2 0.98$). Rivers on the eastern side and central Iceland follow a curved array, indicating a system that operates at steady-state. Both trends are consistent with a basaltic end-member even to the 1σSD level of the isotopic composition of the basalt, which suggests that Ca removal was not very significant. A simple inverse model can assess the effect of Ca loss, where different degrees of Ca loss are assumed to have occurred in all rivers. We increased the measured riverine Ca concentration by a fixed percentage and repeated the calculation of $f_{Si}$ based on the new Ca/Si ratios (Fig. 4.4 b,c). A sensitivity analyses revealed that the Ca loss must be between 0 and 5%, with an associated Si loss between 51 and 54%. Above 5% Ca loss, the trends observed in figure 4.4 b,c would be inconsistent with the measured basaltic composition. The average Si loss of ~52% is in good agreement with a previous estimate (Crovisier et al., 1992), however, the loss of Ca (0-5%) is significantly lower than compared to previous estimates (Crovisier et al., 1992; Moulton et al., 2000; Stefansson and Gislason, 2001).

Looking at the data in $\delta^{30}Si - f_{Si}$ space, the rivers from eastern and central parts of Iceland, which previously plotted along a curve array, now plot along a linear array, indicating fractionation in a steady-state system ($\varepsilon = -1.52$, $r^2 0.76$) (fig. 4.5). The similar fractionation factor for both systems supports the view that a single fractionation process operated, but that this varies between behaviour as a steady-state and Rayleigh-type system. Regardless of the fractionation processes the steady-state system implies that the products form under a constant Si supply, allowing a constant re-equilibration between the product and the fluid. The
drawdown of Si is intense (up to 75%) but the isotope effect is comparatively low ($\delta^{30}\text{Si}_{\text{max}} = 0.77\%$) and is limited by external processes. In general this steady-state system is characterised by higher dynamics and in order to achieve a steady Si supply the associated Si fluxes through the system must be high. However, the different system behaviour also raises the question if this is the result of different fractionation processes, e.g. biotic vs. abiotic Si isotope fractionation.

**Figure 4.5**: The relation between the riverine Si isotope composition and $f_{\text{Si}}$, computed using the Ca/Si ratios, can be described by an open and closed system fractionation behaviour. It appears that rivers collected on the western part of Iceland (triangles) follow rather a Rayleigh-type model, whereas rivers collected on eastern and central Iceland (black dots) follow a steady-state system fractionation kinetics. Calcium losses are assumed to be max 5% for the Rayleigh-type model and 0% for the steady-state system, following the best fit obtained in figure 4.4 b,c.

### 5.5. Biotic vs. abiotic fractionation

As potential biologically mediated fractionation processes we have to consider Si isotope fractionation by land plants and freshwater organisms, such as diatoms. Fractionation factors obtained for Si isotope fractionation in land plants are $\varepsilon \geq -1.0\%$ (Ding et al., 2005a; Ding et al., 2003; Oppergelt et al., 2006b; Ziegler et al., 2005a) and are close to isotopic effects observed during diatom growth in marine and freshwater diatoms (Alleman et al., 2005; De La Rocha et al., 1997; Varela et al., 2004). However, the database is rather limited and there is no fresh water diatom record available for cold environments. But based on the existing database, a fractionation factor of $\varepsilon = -1.5$ is inconsistent with a biologically mediated Si isotope fractionation. Therefore, it is unlikely that biological fractionation has a significant
influence on the Si isotope composition and thus on the Si budget within the rivers studied here.

The only estimate for a fractionation factor by clay formation is given in De la Rocha et al. (De La Rocha et al., 2000) with a fractionation factor of $\varepsilon = -1.1\%$. The fractionation factor ($\varepsilon = -1.5$) obtained here seems to be reasonable given the wide range observed for clays ($\delta^{28}$Si -2.5 to 0.1 %) (De La Rocha et al., 2000; Ding et al., 1996; Ziegler et al., 2005a). The association between the fractionation behaviour and the runoff/precipitation rate should have an influence on the clay induced Si isotope fractionation, as it controls the residence time of the dissolved Si within the weathering horizons; lower runoff/precipitation results in stagnant water bodies within soils and thus increases the time for water-rock interactions but limits the available solute supply. The logical consequence would be that any isotope fractionation follows a Rayleigh-type fractionation. High runoff/precipitation, on the other hand, would lead to a dynamic system where the time for water-rock interactions is limited but a more steady solute supply is achieved. In this case isotope fractionation will rather follow a steady-state system. Taking the hydrological association into account it is very likely that the two different fractionation scenarios observed here display weathering based fractionation processes occurring during the formation of clay minerals. The drawdown of Si can be directly linked to the storage of Si into secondary weathering products.

5.6. Implications for weathering fluxes

Since all Si is derived from the dissolution of basalt, Si fluxes are a function of primary weathering and the open system is thus characterized by high chemical weathering rates. The products forming under Rayleigh-type kinetics have more time to evolve but experience to some extent a Si limitation. This limitation indicates that the Si supply derived from the dissolution of primary material is not as constant and steady as within the steady-state system and the overall weathering derived Si flux through the system is lower. This actually means that the overall chemical weathering intensity is lower compared to the steady-state system. The main question thus has to be, which parameter controls whether chemical weathering is in steady state or is rather limited in terms of Si supplies.

One parameter controlling the magnitude of the weathering derived Si fluxes is the runoff within the catchments, as given by the positive correlation between the chemical denudation rate and runoff for Icelandic catchments (Gislason et al., 1996). The most important climatic
difference between those catchments on the eastern side (steady-state fractionation) and western side (Rayleigh-type fractionation) on Iceland is the precipitation rate and runoff, which is on average 50% lower on the western side compared to the eastern side. The glaciers on the western side should enhance seasonality, with higher discharge during the glacier ablation season. This could explain the weak affinity of the summertime Si isotope composition to the glacial extent. The glacial cover might also provide fine-grained material, which should have high susceptibility to chemical weathering and thus has an enhancing effect on chemical weathering fluxes. The hydrological parameters obviously promote the differences in water-rock interaction leading to either the steady-state (high precipitation, runoff and weathering derived Si fluxes) or the Rayleigh-type system (lower precipitation, runoff and weathering derived Si fluxes), and seem to be the prime control on chemical weathering rates.

It appears, however, that other parameters like age of the rocks in the catchment, does not control chemical weathering rates of major mineral phases supplying the base-cations (e.g. plagioclase, olivine, etc.), as proposed in several other studies (Gislason et al., 1996; Gislason and Hans P. Eugster, 1987; Stefansson and Gislason, 2001) and more recently by (Vigier et al., 2006). It has been proposed that younger rocks show higher dissolution rates due to a higher abundance of glassy components that show a greater susceptibility to dissolution. This would be associated with a near congruent dissolution of the basaltic glass (Vigier et al., 2006). Our modelling using the Ca/Si ratios shows neither congruent dissolution nor a relation to the age of the host rocks. The amount of Si being stored in secondary phases is independent from the age of the host rocks and only hydrological parameters, such as precipitation and runoff appear to have a controlling influence on the chemical weathering rates.

Unique to the study presented here is the possibility to correct the riverine Si flux for Si loss and to estimate the average removal of Ca, both occur during the formation of secondary products. The average Si loss in the studied rivers here during secondary phase formation is between 28 and 74% averaging about 50%. The measured riverine Si concentration (ppm) and the discharge (annual mean in m³/s) can be multiplied to yield the riverine Si flux of each catchment (Table 4.2). The average annual area weighted Si flux of all catchments, based on these data is ~14.1 t/km²/yr (or ~30.2 t/km²/yr SiO₂), in good agreement to previous estimates (27.3 t/km²/yr SiO₂) for southwest Iceland (Gislason et al., 1996). Considering the average
Si loss for each catchment, the initial dissolution of basalt must release on average about 30 t/km²/yr of Si (or 64.2 t/km²/yr SiO₂) and scaled up to the size of Iceland (~103,000 km²) this would be about 3.0x10⁶ t/yr of Si (or 6.6x10⁶ t/yr of SiO₂). This exemplifies the difference between dissolution rates and denudation rates, as the latter excludes the removal of solutes into secondary products. The measured riverine Si fluxes thus significantly underestimate the real primary dissolution weathering rate. Furthermore, we can use the difference between the denudation rate of Si and the initial dissolution rate of Si for each catchment (both in t/km²/yr) to test the hypothesis that higher weathering derived Si fluxes take place when the Si isotope fractionation occurs as an open system (Fig. 4.6 and Table 4.2). Rivers from eastern Iceland, following an open system array (Fig. 4.6) are associated with a higher average Si dissolution rate (~35.9 t/km²/yr) compared to rivers from western Iceland (~21.9 t/km²/yr) that follow the closed system fractionation (Fig. 4.5). In both cases, higher initial Si dissolution rates are associated with lower δ³⁰Si values. Such an inverse relation between the δ³⁰Si composition, runoff and weathering derived Si fluxes is consistent to findings from a previous study on the riverine Si isotope composition of rivers draining the Swiss Alps (GEORG et al., 2006a).

Figure 4.6: Those catchments with rivers characterised by the steady-state system behaviour display a higher average initial dissolution rates for Si and thus higher average chemical weathering rates, compared to catchments with rivers fitting to the Rayleigh-type modelling.

The first study of Si isotope compositions of riverwater found a positive relationship between the concentration of dissolved Si and its isotope composition (DE LA ROCHA et al., 2000). This correlation was interpreted as the result of enhanced weathering (high δ³⁰Si, high
dissolved Si). A more detailed study on the seasonal variability of the riverine Si isotope composition has shown the opposite, as higher weathering fluxes (not simply Si concentrations) are associated with lower δ30Si values, reflecting the enhanced breakdown of silicate minerals (Georg et al., 2006a). The modelling data presented here further supports this observation, as a higher weathering-derived Si flux is associated with lower riverine δ30Si values with less incorporation of Si into secondary clay minerals.
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<td></td>
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<td>1.08</td>
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<td>-0.60</td>
<td>0.45</td>
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<td>-0.68</td>
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<td>0.67</td>
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<td>0.74</td>
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<td>0.78</td>
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<td>-0.89</td>
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<td>12.8</td>
<td>163.8</td>
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<tr>
<td>IS 21 F</td>
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<td>0.78</td>
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<td>0.33</td>
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</table>

Table 4.2: Ca/Si weight ratios (uncorrected and corrected for carbonate contribution), estimates for f/Si and Si removal (assuming 0% and 5% of Ca loss), Si* denotes the riverine Si concentration (ppm) corrected for Si loss. The mean annual discharge of each river is used to calculate the Si denudation rate (Si flux) as the product of discharge measured riverine Si concentration (see Table 4.1) and the initial Si dissolution rate as the product of the discharge and Si*. 
5.6. Relative weathering mobility of Si

The discrepancy between Si denudation rate (riverine Si flux) and initial chemical dissolution rate means that the relative weathering mobility of Si calculated through the riverine Si concentration would underestimate the mobility of Si during primary weathering. Gislason et al. (Gislason et al., 1996) computed the relative mobility of elements during the weathering of basalt based on the riverine elemental concentration and the elemental abundance in the basaltic host rock. The Si concentration has not been corrected for Si loss during the formation of secondary phases, which for the Icelandic streams in averages ~50%. The resulting mobility of Si relative to other elements is thus underestimated, since it does not take the amount of Si into account that has been initially released from the basaltic host rock but experienced a subsequent removal in secondary phases, even if this takes place at the mineral/water interface. In order to obtain a non-biased mobility for Si it is necessary to use the initial dissolution rates for Si and not the chemical denudation rate. The average annual area weighted chemical denudation rate for Si is 14.1 t/km²/yr, whereas the initial dissolution rate must be around 30 t/km²/yr. Considering the amount of other elements being stored in secondary phases is relatively small we assume that the riverine flux is equal to the initial dissolution rate of these elements. As with the Si fluxes it is possible to calculate the individual average area weighted base-cation fluxes (in t/km²/yr), such as Ca (10.9), Mg (3.7), K (1.0) and Na (14.3) and sum it up to the total base-cation flux of ~30 t/km²/yr. Including the riverine SiO₂ flux (uncorrected for Si loss) this gives a total chemical denudation rate (excluding bicarbonates) of about 60 t/km²/yr, which is in good agreement with previous estimates (Gislason et al., 1996). However, the total dissolution rate after correcting for SiO₂ dissolution is 94 t/km²/yr, with Mg/Si and Ca/Si ratios of 0.15 and 0.36, respectively. The values are strikingly similar to the Mg/Si and Ca/Si ratios of the basalts (0.15 and 0.33, respectively). These results demonstrate that all three elements (Si, Ca and Mg) appear to weather congruently. That is to say they have similar primary weathering mobilities, with Ca being released slightly faster compared to Mg and Si. Following Gislason et al. (Gislason et al., 1996), by using Na as a reference element it is possible to quantify the weathering mobility, Φ:

Φₓ = (X/Na)ₓriv / (X/Na)basalt

where (X/Na)ₓriv is the Na normalised ratio of the riverine load and (X/Na)basalt the basaltic ratio of the considered element normalised to Na. The (X/Na)ₓriv ratios are calculated from the
Chapter 4 – Icelandic Rivers

R.B. Georg

riverine elemental concentrations given in ppm. The associated basaltic ratios are 16.4 (Si/Na), 5.3 (Ca/Na) and 2.4 (Mg/Na). The average Na normalised weathering mobilities for Ca, Mg and Si\textsuperscript{2} are 0.12±0.03, 0.11±0.05 and 0.12±0.03 (±1\sigma_{SD}), respectively. This is in surprisingly good agreement with the results from Gislason et al. (Gislason et al., 1996), since the riverine Si data in the latter study have not been corrected for potential Si drawdown by secondary phases. One would expect the mobility for Si, based on the previous Si concentration data, to be 50% lower. This discrepancy appears to be due to a previous error in the calculations based on SiO\textsubscript{2}/Na riverine concentrations, but basaltic Si/Na ratios (Gislason et al., 1996)

5.7. Glacial-interglacial variations of riverine $\delta^{30}$Si

Silicon isotopes have been used as a palaeo-productivity proxy during the last decade (Cardinal et al., 2005; De La Rocha et al., 1998; Reynolds et al., 2006a) and variations of the continental riverine $\delta^{30}$Si input into the ocean might complicate interpretations of long-term (>15 kyr - residence time of Si within the ocean (Tréguer et al., 1995)) changes in biogenic or marine $\delta^{30}$Si values, particularly over glacial-interglacial cycles, when the build-up or retreat of large ice shields would significantly change terrestrial weathering. Although the Si isotope composition on Iceland appears to be controlled by only one process, the degree of fractionation depends largely on external factors providing different weathering regimes. The data presented here show that glaciation can have an effect on riverine $\delta^{30}$Si composition as the average riverine $\delta^{30}$Si composition as glacier-fed is 0.3‰ lower than non-glaciated catchments. On a global scale, the retreat of large ice-shields, with higher meltwater runoff are likely to cause higher weathering intensities and thus lower $\delta^{30}$Si values in the continental runoff, whilst the buildup of large ice-shields might provide rather high $\delta^{30}$Si values. Hence secular variations in marine $\delta^{30}$Si values should be expected from variations in continental weathering (Georg et al., 2006a).

6. Conclusions

Despite mono-lithological geology, mild climate and sparse vegetation, river waters in Iceland have very large variations in their dissolved Si isotope composition. The fractionation of the riverine Si isotope composition of the Icelandic rivers can be model as either a steady-

\textsuperscript{2} Si\textsuperscript{*} denotes the riverine Si concentration (in ppm) corrected for Si loss.
state or Rayleigh-type fractionation, both results give a consistent fractionation factor ($e = -1.5$). Rivers from western Iceland with higher runoff / precipitation follow a steady-state system, characterized by higher dissolution rates for Si and limited enrichment of heavy Si isotopes. The similar fractionation factor for both systems would imply that only one process fractionates the Si isotope composition within the rivers studied here and that the Si isotope composition of the Icelandic rivers studied are controlled by the degree of secondary clay formation after initial dissolution of the primary minerals. For the Iceland rivers there is a negative relationship between weathering rates and riverine $\delta^{30}$Si values, as was found in rivers from the Swiss Alps, despite different lithologies and climatic conditions (GEORG et al., 2006a).

Using the Si isotope data in combination with the basic water chemistry is was possible to calculate the amount of Si that has been removed from the dissolved phase into secondary weathering products. This allows us to calculate the difference between the chemical denudation rate for Si and the total dissolution rate for Si. This shows that an average of ~50% of the primary weathered Si is trapped and precipitated into secondary weathering products within the watersheds.

Acknowledgements

We wish to thank Josh West for insightful comments and Lousie Gall for providing hard rock samples. This work was founded by the Swiss National Fonds (Nr: 2000 20/101 780).
Chapter 5: Re-assessment of silicon isotope reference materials using high-resolution multi-collector ICP-MS

Published as

Re-assessment of silicon isotope reference materials using high-resolution multi-collector ICP-MS

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Abstract

Silicon isotope ratios can now be measured to very high precision using high-resolution multi-collector ICP-MS. Based on this technique we report that the Si isotope composition of IRMM-018 is significantly lighter than the NBS-28 standard, in direct contrast to previously published results. Our data are also inconsistent with recently published absolute Si isotope abundances for these standards by (Debievre et al., 1994) and (Ding et al., 2005b). Instead, our results are coherent with the certified values for NIST standard SRM990 that was used to determine the atomic weight of Si, with a $^{30}\text{Si}/^{28}\text{Si}$ ratio that is over 6 permil lower for the same atomic weight. In order to avoid problems with future assessments of stable Si isotope variations, the NBS-28 silica sand standard (RM8546) should remain the zero point. Therefore, an inter-laboratory calibration of NBS-28 and other references materials is recommended to solve the observed discrepancies and establish a reliable scale for reporting Si isotopes.
5.1 Introduction

The absolute silicon (Si) isotope abundances of NBS-28 (RM8546) has recently been determined in two studies with distinctly different results (Debievre et al., 1994; Ding et al., 2005b). The new values do not agree with previous estimates of the absolute isotope abundances (Coplen et al., 2002), that were based upon certified silicon isotope abundances of IRMM-017 (Debievre et al., 1994; Ding, 2004a). In terms of relative Si isotope composition, the $^{30}$Si/$^{28}$Si ratio of IRMM-018 has been published as both $+1.3$ and $+2.9$ permil higher than IRMM-017 (Coplen et al., 2002; Debievre et al., 1994), or $+0.0$ and $+1.6$ permil higher than NBS-28 (Debievre et al., 1994; Ding, 2004a). There is thus ambiguity in both the relative and absolute Si isotope composition of international standards, as shown in Table 1. In this paper we aim to address the relative and absolute isotope abundances using a new analytical technique of high-resolution multi-collector inductively-coupled-plasma mass-spectrometry (HR-MC-ICP-MS) in order to resolve these discrepancies and guarantee comparability of mass-dependent and mass-independent fractionations effects. Here we report the precise Si isotope composition of IRMM-018 relative to NBS-28, and can show an improved precision on the measurement of relative Si isotope composition. We will show that our data are not consistent with the published data (Coplen et al., 2002; Debievre et al., 1994; Ding, 2004a; Ding et al., 2005b), both in terms of relative differences between the standards and the absolute Si isotope abundances. However, our results are in agreement with the certified values for the NIST standard SRM990 that was used to determine the atomic weight of Si (Barnes et al., 1975; Deslattes, 1980).

The published absolute Si isotope compositions were measured using gas-source mass-spectrometry with the conversion of sample to SiF$_4$ gas. Estimation of the Si isotope atomic ratios and abundances from the measured ion current ratios has been achieved using gravimetrically controlled mixtures of chemically pure and highly enriched isotopes with known isotope composition to determine the conversion factor ($k_{res}$) used to account for instrumental mass-fraction due to the adsorption of viscous gases (Gonfiantini et al., 1997). The given conversion factors (Debievre et al., 1994; Ding et al., 2005b) indicate non mass-dependent fractionation during analyses of NBS-28 that may be related to analytical artefacts or addition instrumental mass-bias.
5.2 Methodology

The advancement of MC-ICP-MS now enables very small relative mass differences in natural samples to be assessed, although interferences and matrix effects can make Si isotopic measurements by MC-ICP-MS erroneous. The Nu Plasma 1700, built by Nu Instruments Ltd for ETH Zürich, is a large-geometry double focusing MC-ICP-MS instrument characterized by a large dispersion to (de)-magnification ratio of 1760mm : 0.8, which allows for high-resolution measurement of isotope ratios while still providing flat-topped peaks. Polyatomic isobaric interferences in the Si$^+$ ion spectrum include NO$^+$, CO$^+$, N$_2^+$, SiH$^+$, and N$_2$H$^+$. These species are sufficiently resolved from the Si masses at a mass resolution setting of $\sim$3,000 (as defined by a 10% valley convention), using a combination of reduced slit widths on the Faraday collectors and narrowing the source-defining aperture. Sample solutions are introduced to the plasma as a dry aerosol, aspirating $\sim$21 μM silicic acid solutions at about 80 μl/min via a nebulizer and de-solvating membrane. Preparation of silica standards uses alkali fusion and ion-exchange chromatography to avoid the use of hydrofluoric acid as SiF$_4$ is highly volatile. Chemical yields are 100% with no resulting mass-fractionation possible (HALLIDAY et al., in press). The solutions introduced to the plasma are made of dilute (0.002 M) hydrochloric acid and are highly pure with respect to trace metal contamination.

5.3 Results

We report the relative difference between IRMM-018 and NBS-28 based on more than 250 measurements of solutions prepared from two different initial dissolutions of each of the standard powders. The data shown in Figure 5.1 were acquired over an interval of one year with many different running conditions and yield a mean Si isotope composition of IRMM-018 relative to NBS-28 of:

$$\delta^{30}\text{Si} = -1.606 \pm 0.008 \, \%$$
$$\delta^{29}\text{Si} = -0.826 \pm 0.006 \, \%$$

where $\delta^i\text{Si}$ denotes the deviation in parts per thousand of the $^i\text{Si}/^{28}\text{Si}$ ratios of IRMM-018 from those of NBS-28, and the associated uncertainties refer to the standard error of the mean at the 95% confidence limit (external).
Figure. 5.1: Long term reproducibility of Si isotope composition of IRMM-018 relative to NBS-28. $\delta^{29}\text{Si}$ and $\delta^{30}\text{Si}$ are shown in open and closed circles, respectively, with values given for the mean and two standard deviations of the mean.

### Table 5.1: The published certified values (superscripts define reference) for the Si isotope abundances of international standards (with 95% confidence limits given in parentheses), and the relative isotope composition of these standards relative to NBS-28 measured in different laboratories, and expressed as $\delta^{30}\text{Si}^\ast$ and $\delta^{29}\text{Si}^\ast$ relative to $\text{Si}^{28}\text{Si} = 0.033532$ and $\text{Si}^{29}\text{Si} = 0.050804$, the values for NBS-28 given in Coplen et al. (2002). Values for IRMM-017 given as unpublished data in Coplen et al. (2002) are published in Ding (2004). Absolute values estimated here for IRMM-018 assume the atomic weight of NBS-28 to be equal to 28.08553.

<table>
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<tr>
<th>Certified Standard</th>
<th>Atomic weight g/mol</th>
<th>$^{30}\text{Si}/^{28}\text{Si}$</th>
<th>$^{29}\text{Si}/^{28}\text{Si}$</th>
<th>$^{30}\text{Si}/^{29}\text{Si}$</th>
<th>$\delta^{30}\text{Si}$</th>
<th>$\delta^{29}\text{Si}$</th>
<th>$\delta^{30}\text{Si}^\ast$</th>
<th>$\delta^{29}\text{Si}^\ast$</th>
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<td>Barnes et al. (1975)$^a$</td>
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</tr>
<tr>
<td>SRM990</td>
<td>28.085 526 (56)</td>
<td>0.033 621 (28)</td>
<td>0.050 633 (24)</td>
<td>0.664 02 (45)</td>
<td>-</td>
<td>-</td>
<td>2.7 (9)</td>
<td>-3.4 (5)</td>
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<td>DeBievre et al. (1994)$^a$</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IRMM-017</td>
<td>28.085 408 (15)</td>
<td>0.033 489 (8)</td>
<td>0.050 772 (7)</td>
<td>0.659 60 (6)</td>
<td>-</td>
<td>-</td>
<td>-1.28 (16)</td>
<td>-0.63 (20)</td>
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<td>IRMM-018</td>
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<tr>
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<td>28.085 408 (15)</td>
<td>0.033 499 (8)</td>
<td>0.050 772 (7)</td>
<td>0.659 60 (6)</td>
<td>-1.28 (36)$^b$</td>
<td>-0.63 (20)$^b$</td>
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<td>0.050 822 (2)</td>
<td>0.659 81 (5)</td>
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<td>0.050 827 (2)</td>
<td>0.659 73 (5)</td>
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<td>0.08 (12)</td>
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<td>Ding et al. (2005)$^a$</td>
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<td>0.050 745 (3)</td>
<td>0.672 91 (4)</td>
<td>-</td>
<td>-</td>
<td>+18.34 (9)</td>
<td>-1.16 (7)</td>
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<td>0.034 101 (2)</td>
<td>0.050 708 (3)</td>
<td>0.672 50 (4)</td>
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<td>-0.72 (3)</td>
<td>+10.17 (9)</td>
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</tr>
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<td>28.086 53 (13)</td>
<td>0.034 145 (2)</td>
<td>0.050 743 (3)</td>
<td>0.672 90 (4)</td>
<td>-0.05 (3)</td>
<td>-0.03 (3)</td>
<td>+18.28 (9)</td>
<td>-1.20 (7)</td>
</tr>
<tr>
<td>SRM990</td>
<td>28.086 38 (13)</td>
<td>0.034 167 (2)</td>
<td>0.050 760 (2)</td>
<td>0.673 10 (4)</td>
<td>-18.94 (9)</td>
<td>-0.86 (7)</td>
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</tr>
<tr>
<td>This study</td>
<td>28.085 40 (5)$^c$</td>
<td>0.033 59 (1)</td>
<td>0.050 54 (2)</td>
<td>0.664 6 (3)</td>
<td>-1.606 (8)</td>
<td>-0.826 (6)</td>
<td>-1.7 (4)</td>
<td>-5.1 (4)</td>
</tr>
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</table>

These results contrast sharply with published data, shown in Table 5.1, where the $\delta^{30}\text{Si}$ and $\delta^{29}\text{Si}$ value of IRMM-018 are given as essentially zero relative to NBS-28 (DING, 2004a; DING et al., 2005b). Since it has been shown that there is no systematic offset between gas-source and ICP-source mass-spectrometry for Si stable isotope variations (Cardinal et al.,
2003), such a large discrepancy between the results is difficult to explain. A recent publication (DEBIEVRE et al., 1994) refers to an IRMM-018a standard that has a $\delta^{30}$Si value of $+0.08 \pm 0.12 \%$ relative to NBS-28. Thus, the Si isotope composition of '018a' may or may not be distinct from '018' depending upon which results for '018' are used for comparison. As different preparation of the standard in our laboratory yielded identical results we do not believe the different results could be caused by heterogeneity of the standard. Our result and the possible discrepancy calls for confirmation by an inter-laboratory comparison.

5.4 Discussion

Variations in the natural abundances of stable isotopes are caused by kinetic and equilibrium reactions that fractionate the isotopes along theoretical mass-dependent fractionation (mdf) lines (Young et al., 2002), following the relationship:

$$\frac{(^{29}Si/^{28}Si)_{F}}{(^{29}Si/^{28}Si)_{O}} = \left(\frac{(^{29}Si/^{28}Si)_{F}}{(^{29}Si/^{28}Si)_{O}}\right)^{\delta}$$

where $\beta$ is a constant, and subscripts F and O refer to the fractionated and initial isotope ratios respectively. If this isotopic fractionation occurs under thermodynamic equilibrium, $\beta$ will have a value of 0.5178, whereas under kinetic isotopic fractionation $\beta$ of atomic Si will have a value of 0.5092. For larger molecules the kinetic isotope fractionation would have a $\beta$ value closer to 0.5, e.g. for SiO2 $\beta = 0.505$. The measured difference between the two standards has a mean $\beta$ value of 0.515 $\pm$ 0.003, which is in agreement with an equilibrium mdf, rather than a kinetic fractionation. If both of the standards represent natural terrestrial materials the fractionation between them thus appears to be controlled by isotope exchange between compounds with different zero-point energies (Young et al., 2002).

Naturally occurring stable isotope variations lead to a change in the atomic weight of Si by 2.83 ppm for a 1-permil change in the $^{30}$Si/$^{28}$Si ratio along the mdf line. Our results demonstrate that the atomic weights of NBS-28 and IRMM-018 differ by 4.5 ppm (or 0.00012 g/mol). This difference is larger than the estimated error on the atomic weights (Barnes et al., 1975). Unfortunately, as SRM-990 is no longer available we are unable to estimate the
absolute atomic weights of NBS-28 or IRMM-018 relative to the certified weight of SRM-990. It is somewhat surprising that the atomic weights of IRMM-018a and NBS-28 given by Valkiers et al. (2005) and SRM-990 all agree to within 0.15 ppm. Indeed, the good agreement in the atomic weight of NBS-28 and SRM990 suggests that these two NIST standards are isotopically equivalent, even though they are in the form of silica and silicon respectfully.

In terms of absolute Si isotope composition, it is impossible to fully correct for instrumental mass-bias in ICP-MS. Typical instrumental mass-bias results in a ~4%/amu increase in the $^{29}\text{Si}^{28}\text{Si}$ ratio, but significantly varies between measurement sessions due to variable conditions within the plasma and pressures in the ion introduction region. The short-term temporal variations in mass-bias are small, of the order of 0.2 % per hour. The instrumental mass-bias is a smooth function of mass, such that an instrumental mdf array can be established. The equation given above for mdf can be rearranged to give the following equation for a straight line:

$$\ln(\frac{^{29}\text{Si}}{^{28}\text{Si}})_F = \beta \ln(\frac{^{30}\text{Si}}{^{28}\text{Si}})_F + c,$$

where the constant $\beta$ is the gradient (and $c$ is a function of $\beta$ and the isotope composition of the standard). We can thus plot the observed Si isotope ratios to determine the instrumental mass-bias of the MC-ICP-MS. By direct comparison of measured Si isotope ratios using both standard solution introduction and laser ablation, we can demonstrate that there is no significant mass fractionation during sample preparation and introduction to the plasma. It has been shown for several elements including Mg (Galy et al., 2001) and Nd (Wombacher and Rehkämper, 2003) that the instrumental mass-bias for MC-ICP-MS lies between the kinetic and equilibrium conditions. Our data for individual measurement sessions also fall along a mdf array, with $\beta = 0.51$, which is in between the theoretical equilibrium and kinetic mdf lines. Slight offsets between the estimated instrumental mdf lines from different sessions possibly result from a variable combination of kinetic and equilibrium fractionation processes that occur in the plasma/high-vacuum interface.

The measured array of Si isotope ratios, as shown in Figure 5.2, is thus the result of kinetic and equilibrium fractionation during sample measurement of the original Si isotope composition of the standards. Using the published atomic weight (Ar) of Si in either IRMM-
018a, NBS-28 or SRM9907, with \( \text{Ar} = 28.08553 \text{ g/mol} \) (Table 5.1), we can estimate an original absolute Si isotope abundance, by applying an inverse model of possible instrumental mass-fractionation. As the instrument’s mdf lies between the kinetic and equilibrium mdf lines, we may take these lines as fully describing all possible extremes of instrumental mass-bias. Here we assume that there are no analytical artefacts that are non-mass dependent above the typical analytical precision of 0.1%. On Figure 5.2, lines of equal atomic weight are almost perpendicular to the mdf array. The estimated instrument mass-fractionation array, as shown in Figure 5.2, results in an estimate for the initial \( ^{30}\text{Si}/^{28}\text{Si} \) molar ratio of 0.03364 ± 1 and \( ^{29}\text{Si}/^{28}\text{Si} \) molar ratio of 0.05059 ± 2 for an atomic weight of 28.08553 g/mol. These Si isotope abundances are similar to the molar fractions estimated for the SRM990 Si standard (Fig. 5.2).

![Figure 5.2](image)

Figure 5.2 The measured array of Si isotope ratios (in logarithmic representation) are shown as black circles together with the theoretic mass-dependent fractionation lines (mdf) confining the data set. Data are from multiple measurement sessions spanning more that one year. In Figure 5.2b, measured ratios was fitted to an average \( \beta \) values of 0.51 shown in Black, and bounded by MDF lines with \( \beta = 0.5178 \) (upper grey line) for equilibrium fractionation, and \( \beta = 0.505 \) (lower grey line) for kinetic fractionation of SiO\(_2\). A kinetic fractionation of SiO\(_2\) rather than atomic Si is taken in order to more fully express all possible compositions of the unfractionated standard. In Figure 2a, these mdf lines intersect the thick black line representing an atomic weight of 28.085526 close to the certified isotope composition of the NIST SRM990 Si standard (black circle) Barnes et al., 1975.

A comparison of the Si isotope abundances given for the international standards is shown in Figure 5.3, using their \( ^{30}\text{Si}/^{28}\text{Si} \) and \( ^{29}\text{Si}/^{28}\text{Si} \) ratios. It is quite clear, that even though the atomic weights for the given Si standards are in general accord, the absolute molar abundances are not in agreement, that is to say they fit onto different mdf arrays. As for other light isotopes like O (Miller, 2002) and Mg (Galy et al., 2001), naturally occurring
terrestrial Si samples fall along a single mdf array (Young et al., 2002). The position of this terrestrial array for Si isotopes is thus controversial, with the $^{30}\text{Si}/^{29}\text{Si}$ ratios differing by over 6% between the calibration of IRMM (using IRMM-018 and NBS-28) (Debievre et al., 1994) and NIST (using SRM990) (Barnes et al., 1975), or over 13% for SRM990 between the calibration from Ding et al. (2005) and the NIST certified value (Barnes et al., 1975). The values we obtain are close to what would be predicted from SRM990, unlike either of the recently published composition for NBS-28 (Debievre et al., 1994; Ding et al., 2005b). Our high-resolution measurements are able to fully resolve isobaric interferences, such as SiH$^+$ that may offset the mdf array. However, we are unable to resolve the major discrepancy between our results and the recently published calibration of Si isotope molar masses (Debievre et al., 1994; Ding et al., 2005b).

Figure 5.3: The published certified values for the Si isotope abundances of international standards, given in terms of their $^{30}\text{Si}/^{28}\text{Si}$ and $^{29}\text{Si}/^{28}\text{Si}$ ratios, as presented in Table 5.1 (superscripts define reference). Our mdf array (grey band) is taken from Figure 5.2, its intersection with the black lines possibly defining the true Si isotope composition of NBS-28 or IRMM-018 (assuming that our instrumental mass fractionation is a mixture of theoretical kinetic and equilibrium mass-dependent fractionation processes).

3 Atmospheric oxygen has been found to lie off the terrestrial mdf array, due to mass independent fractionation by ozone decay in the stratosphere.
5.5 Conclusions

Clearly, future work is needed to resolve the discrepancies in the absolute stable isotope abundances of NBS-28, but it should remain the international standard for stable isotope comparison. Data published using other standards as the zero reference point, like IRMM-018 (Engström et al., 2006), cannot be compared to other published results whilst such large discrepancies between the standards exist. Slight differences between measurement techniques must be addressed by an interlaboratory calibration exercise, which is currently underway in more than 8 laboratories world-wide. The improved analytical precision shown here enables variations in the relative atomic weights of silicon to be resolved at the 0.02 ppm precision level (or 0.05 \( \delta^{30}\text{Si} \)). The use of such techniques may enable future improvement in the experimental determination of Avogadro’s constant.
Chapter 6: Silicon isotope variations during high-temperature processes
6.1 Introduction

This chapter deals with Si isotope variations during high-temperature processes, such as magma crystallisation and metamorphism and is intended as a reconnaissance study that may lead to new areas of research. Most of the data have been presented at international conferences in Vienna (EGU meeting) and Melbourne (Goldschmidt Conference 2006).

Little study has been made of Si isotope fractionations during high-temperature processes. This is mainly because the variations during such processes will be small and could not be unambiguously resolved with the inferior precision of previously used methodologies. However, within the course of this thesis it has been shown that the combination of high-resolution MC-ICP-MS with our newly developed separation method (Chapter 2) provides limiting precisions for multiple measurements in the range of ±0.04‰, which makes it possible to resolve even small seasonal variations of the Si isotope composition of river waters (Chapter 3). Although the main focus of this PhD project was on the low-temperature fractionation behaviour of Si isotopes associated with weathering processes, the newly developed method is ideally suited to silicate minerals and rocks, and provides the tools for undertaking the first systematic survey of the Si isotope fractionation behaviour during high-temperature processes.

Two case studies were undertaken to investigate Si isotope fractionation in high-temperature processes. In the first case studied two granite samples; one classic I-type granite (G-38, from the Moonbi Monzogranite complex, Australia) and one classic S-type granite (VB-140, a two-mica granite, Koetong Suite, Wagga Batholith, Australia). These samples were provided as a part of a cooperation with Professor Bruce Chappell (Australian National University, Canberra). Besides whole rock samples complementary mineral separates were analysed as well to check for intra mineral Si isotope fractionation. A second case study focuses on the Si isotope fractionation behaviour during contact metamorphism. This is part of an ongoing cooperation with Professor John W. Valley (University of Wisconsin, Madison, USA). The main sample suite in this case comprises mineral separates from the mid-Proterozoic (Grenvillian) Adirondack Mountains, northern New York State, and consists of samples from the Marcy anorthosite intrusion, calc-silicate skarn minerals from the Willsboro and Oak Hill wollastonite mines as well as silicate minerals from the marble country rocks. This sample suite is designed to assess Si isotope fractionation during contact metamorphism and the effects of fluid flow on mineral isotopic compositions.
6.2 Methodology

All mineral and bulk rock samples were crushed and ground in a Si free boron-carbide mortar using also a boron-carbide pestle. The amount of sample varies but was typically between 1 and 20mg. Chemical processing was accomplished using the alkali fusion and ion-exchange procedure as well as the mass-spectrometric protocols described in Chapter 2. The Si yield was assessed by comparison to ion-probe data for garnets from the Willsboro Wollastonite Skarn (see also Table 2.4, Chapter 2). From that comparison the Si yield throughout the fusion procedure appears to be quantitative.

6.3 Case study 1: I- and S-type granites

Both granite samples are well characterised and the chemical as well as petrographic description can be found elsewhere (Chappell, 1999; Kent, 1994; Mustard, 2004). I-type granites are usually supposed to be derived from infracrustal sources, such as differentiated mantle melts. The source rock is assumed to be un-weathered and the chemical composition is unaltered and igneous. S-type granites have usually supracrustal sources and source rocks usually comprise weathered material with an altered chemical composition. This can be derived from partially molten sediments that were depleted in Na and Ca and enriched in Al and Si by weathering processes (Chappell, 1999). As seen in previous chapters, the weathering of crustal rocks does also alter the Si isotope composition in as much as clays can be strongly $^{30}\text{Si}$-depleted with low $\delta^{30}\text{Si}$ and $\delta^{29}\text{Si}$ ratios. Granites derived from a sedimentary source rock can be assumed to inherit a clay-derived Si isotope signature.

6.3.1 Results

The Si isotope data reveal a clear difference between sample G-38 (I-type) and sample VB-140 (S-type); Sample G-38 has a Si isotope composition of $\delta^{30}\text{Si} -0.04\pm0.04\%$o ($\pm$ 95%SEM, n=28), whereas VB-140 shows a lighter composition of $\delta^{30}\text{Si} -0.26\pm0.05\%$o, clearly distinct from the I-type granite (Table 6.1 and Figure 6.1). Mineral separates (quartz-Qtz, feldspar-Fsp, muscovite-Ms, biotite-Bt) obtained from both samples were also analysed. It appears for both samples that Qtz is slightly more positive in $\delta^{30}\text{Si}$ compared to the bulk composition, Fsp is slightly higher or equal to the bulk rock composition, that is indistinguishable from Ms. Biotite is in both cases lighter by ~ -0.28%o compared to the bulk rock, whereas the other mica, Ms, is similar to bulk rock.
6.3.2 Discussion

There appears a isotopic fractionation among those mineral phases, this $\delta^{30}\text{Si}$ values $\text{Bt} < \text{Ms/Fsp} = \text{bulk} < \text{Qtz}$. A similar fractionation sequence among coexisting mineral phases as well as a positive co-variation with $\delta^{18}\text{O}$ have been earlier proposed by others (Douthitt, 1982; Taylor and Epstein, 1970). Differential $^{30}\text{Si}$-enrichment$^4$ associated with an increase in $\text{SiO}_2$-wt% among coexisting mineral phases has been predicted based on theoretical constraints back in the 1950s (Grant, 1954). Grant proposed that the Si isotope fractionation in high-temperature processes, such as melt-crystal segregation depends on the degree of polymerisation of $\text{SiO}_4^4$ tetrahedra. A higher degree of polymerisation is usually provoked by higher $\text{SiO}_2$ contents. The $^{30}\text{Si}$ enrichment factors calculated ranged from 4% (at 1000°C) to 2% (at 1500°C) for a $\text{SiO}_2$-rich compared to a $\text{SiO}_2$-poor melt. He also predicted

$^4$ Grant (1954) used the term $^{30}\text{Si}$-enrichment. Given a mass-dependent fractionation, this is accompanied with an enrichment in $^{29}\text{Si}$ by ~50% of the $^{30}\text{Si}$-enrichment and means actually $^{30,29}\text{Si}$-enrichment.
$^{30}$Si-enrichment between orthosilicates and parasilicates. The following discussion uses the description of different silicate groups following the work of Grant (1954); All silicates that show SiO$_4^{4-}$ polymerisation, e.g. an O-bridge between adjacent SiO$_4^{4-}$ tetrahedra will be referred to as parasilicates. Nesosilicates, where isolated SiO$_4^{4-}$ tetrahedra occur are referred to as orthosilicates. For example, garnet, zircon, olivine and topaz represent orthosilicates, whereas quartz, clinopyroxenes and wollastonites are summed up as parasilicates. Grant (1954) predicted $^{30}$Si enrichment factors for the pair quartz-topaz range between 11%o (at 108°C) and 5%o (at 377°C). For example; Quartz is supposed to be 11%o enriched in $^{30}$Si over co-existing topaz, if formed at 108°C. Quantitatively these enrichment factors seem to be wrong, simply because they seem to be too large, and were not yet confirmed by later observations. However, the sign (or sense) of the theoretical fractionation has been confirmed by my observations and the work by Grant (1954) explains the observed relation between $\delta^{30}$Si and SiO$_2$-wt% of minerals. The same relation has been also observed for rocks with different SiO$_2$-wt% (Douthitt, 1982) and can be confirmed herein by comparing the higher $\delta^{30}$Si of the granites to the $\delta^{30}$Si value of the Icelandic basalt (Chapter 4). However, the S-type granite VB-140 has a SiO$_2$-wt% of 68.8 and is thus higher than the I-type granite G-38 (SiO$_2$-wt% of 61.6), but the $\delta^{30}$Si value is significantly lower by $\sim$0.2%. This example shows that the SiO$_2$-content is not the only important parameter influencing the Si isotope composition of the rocks. For the S-type granite this source is of sedimentary origin and the lighter value compared to the I-type granite probably reflects a light clay component. The overall positive relationship between SiO$_2$-wt% and $\delta^{30}$Si does exist, inasmuch that there are differences between mantle rocks, basalts and granitic rocks (Douthitt, 1982). Although no systematic difference between S- and I-types granites has been found before (Ding et al., 1996; Douthitt, 1982), the limited database of this work suggests that Si isotope might be used to distinguish between sources of different granitic melts within a batholith.

### 6.4 Case study 2: Silicon isotope fractionation during contact metamorphism

The Adirondack Mountains in northern New York, USA (Figure 6.2), provides a good opportunity to investigate Si isotope fractionation behaviour during contact metamorphism. The geological history and settings are described in detail elsewhere (Bohlen et al., 1985; Clechenko and Valley, 2003; Valley and O'Neil, 1984; Whitney and Olmsted, 1998). The Adirondack Mountains are part of the Mid-Proterozoic Grenville Orogen and show a
multi-stage metamorphic history. Contact metamorphism and skarn formation took place during the intrusion of the Marcy anorthosite massif at 1155±10 Ma at shallow levels in the crust (Clechenko and Valley, 2003; Valley and O’Neil, 1982). Peak metamorphism (granulite facies) that was accompanied by penetrative deformation and for many rocks recrystallization was reached around 100 Myrs later during the Ottawan phase of the Grenville Orogeny. In simple terms, the anorthosite intruded into marbles and the skarns were formed by concomitant marble devolatilization and formation of calc-silicate minerals, mainly wollastonite (Wo), clinopyroxene (Cpx) and garnet (Grt). The skarns have been mined at three localities in the NE Adirondacks, Willsboro, Lewis, and Oak-Hill Mines and wollastonite-rich rocks will be referred to as ores. In addition to the marbles, ores and anorthosite, some garnetites were sampled as well. Garnetites consist of garnet-rich (85% or higher) bands interlayered with the wollastonite ores.

Silicon isotope data for silicate minerals, including samples from the Marcy anorthosite, calc-silicates from the contact skarn and the marbles were obtained from drill cores. The skarns were sampled at Willsboro and Oak Hill wollastonite mines (Figure 6.2). These suites of samples allow examination of Si isotope variation caused by fluid interaction during contact metamorphism. To constrain the end-member Si isotope composition separated silicate mineral samples from the anorthosite and the marble were analysed. In addition, the silicate samples from the contact skarn zone were analysed to evaluate mixing between the two end-members. All silicates were processed and analysed following the protocols described in Chapter 2.
6.4.1 Results

Results are given in Table 6.2 and Figure 6.3. Silicon isotope analyses reveal two distinct end-members: 1) the anorthosite body with a typical igneous δ30Si of −0.16‰ and 2) meta-sediments with an average δ30Si of +0.8‰. Calc-silicates (Wo) of the skarns display intermediate δ30Si with an average of +0.4‰. The δ30Si values of the calc-silicates increase with distance from the igneous contact indicating mixing of Si between the igneous and sedimentary end-member during contact metamorphism. This relation is, in part, mirrored by δ18O, giving an end-member with high δ18O around +20.4‰ (VSMOW), typical for silicates in metamorphosed limestones and an igneous end-member with an average δ18O of +8.1‰ (Valley and O’Neil, 1984). Calc-silicates of the contact skarn, however, have low δ18O around +2.7‰ indicating the mixing of low-18O meteoric and intermediate δ18O magmatic waters (Valley and O’Neil, 1982) during contact metamorphism, in a manner that would not be expected to yield cause fractionation of Si isotopes.

Figure 6.3: The three-isotope plot shows the results of the Si isotope measurements of the Adirondack sample suite. The spread is exceptional for igneous minerals. All samples follow a mass-dependent fractionation array, documenting the interference-free determination of all three Si isotopes by HR-MC-ICP-MS.
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Willsboro

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<td>134° 4'</td>
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<td>-0.44</td>
<td>-0.25</td>
<td>0.27</td>
<td>0.25</td>
</tr>
<tr>
<td>185° 2'</td>
<td>Garnetite</td>
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<td>-0.26</td>
<td>-0.12</td>
<td>-0.72</td>
<td>15.5</td>
</tr>
<tr>
<td>205° 9' garnetite</td>
<td>Garnetite</td>
<td>37.28</td>
<td>-0.43</td>
<td>-0.23</td>
<td>1.68</td>
<td>21.77</td>
</tr>
<tr>
<td>215° 8'</td>
<td>Garnetite</td>
<td>38.16</td>
<td>-0.32</td>
<td>-0.15</td>
<td>2.57</td>
<td>24.79</td>
</tr>
<tr>
<td>103° 3'</td>
<td>Clinopyroxene</td>
<td>40.96</td>
<td>-0.01</td>
<td>-0.01</td>
<td>0.91</td>
<td>3.12</td>
</tr>
<tr>
<td>144° 6'</td>
<td>Clinopyroxene</td>
<td>49.3</td>
<td>-0.29</td>
<td>-0.14</td>
<td>1.32</td>
<td>3.35</td>
</tr>
<tr>
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<td>Clinopyroxene</td>
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<td>-0.14</td>
<td>-0.06</td>
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</tr>
<tr>
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<td>Clinopyroxene</td>
<td>50.74</td>
<td>0.06</td>
<td>0.02</td>
<td>-0.72</td>
<td>15.5</td>
</tr>
<tr>
<td>205° 9' garnetite</td>
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<td>49.07</td>
<td>-0.16</td>
<td>-0.11</td>
<td>1.68</td>
<td>21.77</td>
</tr>
</tbody>
</table>

Laurel Mt., Sierra Nevada

<table>
<thead>
<tr>
<th>Sample</th>
<th>phase</th>
<th>SiO₂ content</th>
<th>δ²⁹Si</th>
<th>δ²⁸Si</th>
<th>δ¹⁸O</th>
<th>Distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>655 zr</td>
<td>Zircon</td>
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<td>-0.15</td>
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<tr>
<td>655 qz</td>
<td>Qtz</td>
<td>0.03</td>
<td>0.02</td>
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</tr>
</tbody>
</table>

Table 6.2: Silicon and O isotope data for samples from the Adirondack Mountains. Errors are 0.04% for δ²⁹Si, 0.03% for δ²⁸Si and 0.2% for δ¹⁸O. Oxygen isotope data are compiled from Valley et al. 1982, 1984 and Clechenko 2001 (unpl. MSc. Thesis, University of Wisconsin, Madison, USA). Distance is given in meters and assigns distance of the sample from the last igneous anorthosite contact, according to the drill core. Qtz: quartz, Di: diopside, Tr: tremolite, Phi: phlogopite, Wo: wollastonite, Cpx: clinopyroxene, Grt: garnet, Zrc: zircon.
6.4.2 Discussion

Both end-members, the igneous and the sedimentary rocks, show a pronounced co-variation between $\delta^{30}$Si and $\delta^{18}$O ($r^2=0.9$) (Figure 6.4). The O isotope composition is typical for the rocks considered. The Si isotope composition for the igneous rocks is also typical, as discussed above. However, the very positive $\delta^{30}$Si values obtained for the silicates from meta-sediments are inconsistent with a clastic sedimentary origin. In clastic sediments one would expect $\delta^{30}$Si values closer to the igneous value. Modern marine sediments can have positive $\delta^{30}$Si values due to the biogenic silica derived from isotopically heavy seawater. However, a biological sink for Si was, at least to current knowledge, not present within the Proterozoic oceans. The main mechanisms sequestering Si from the Proterozoic oceans are assumed to be sorption of Si onto clays and the silicification of marine carbonates (Siever, 1992). It is very likely that the silicate minerals separated from the marbles had such a diagenetic Si source. Similar Si and O isotope data were acquired for Proterozoic meta-sediments from China (Zhang et al., 2003). It is thus evident that the high $\delta^{30}$Si composition of the marbles reflects a marine sedimentary Si source.

![Figure 6.4: Anorthosite and marble show distinct Si and O isotope bulk compositions. The average Si isotope composition for the bulk anorthosite is -0.16‰ and 0.8‰ for the marble and O is on average 9.1‰ and 20.4‰, respectively. However, these averages have been brought closer to each other as a result of mass transfer between the anorthosite and marble reservoirs.](image)

As mentioned above, the minerals from the contact skarn display low $\delta^{18}$O values around +2.7 indicating the evolvement of meteoric fluids during contact metamorphism and skarn formation (Valley and O’Neil, 1982) (Figure 6.5). The Si isotope compositions of wollastonite ores display clear relationships with distance from the igneous contact as determined from those samples that lie within 18 meters measured from drill core distances (Figure 6.6). There is no co-variation with $\delta^{18}$O.
The relation to distance is observed in both localities; Willsboro and Oak-Hills, and provides compelling evidence of mixing between Si derived from the anorthosite and the marbles, presumably transported via magmatic, meteoric and metamorphic fluids during and following igneous emplacement. Coexisting Grt as well as Cpx from the Oak-Hill drill core also follow the trend towards heavier Si isotope compositions with distance from the contact (up to 18 meters) (Figure 6.7). However, the absolute isotopic compositions indicate equilibrium fractionation between coexisting Wo-Cpx-Grt mineral assemblages.

Figure 6.6: The Si isotope composition of Wo scales in both localities with the distance from the igneous contact. However, the gradients at which the mixing occurred was distinct, probably reflecting different chemical compositions and/or properties of the fluids.

From this limited database we can estimate fractionation factors between coexisting minerals at high temperature that may or may not be equilibrium features of $\Delta^{30}\text{Si} \,(\text{Grt-Cpx})^5$:

$$\Delta^{30}\text{Si}(X-Y)$$ denotes the difference of the $\delta^{30}\text{Si}$ values of phase X and Y, where X has a lower $\delta^{30}\text{Si}$ value.

---

5 Where $\Delta^{30}\text{Si}(X-Y)$ denotes the difference of the $\delta^{30}\text{Si}$ values of phase X and Y, where X has a lower $\delta^{30}\text{Si}$ value.
0.3±0.1‰ (±1σSD) and Δ^30Si(Grt-Wo): 0.6±0.1‰, where Grt are isotopically lighter compared to either Wo and Cpx. These data are consistent with the idea of ^30Si-enrichment in parasilicates (Cpx / Wo) over orthosilicates (Grt). However, the difference Δ^30Si(Cpx-Wo): 0.3±0.2‰ between wollastonite and clinopyroxene cannot be readily explained by this hypothesis, as both phases have very similar silica contents of 48.7±1.5 and 49.8±0.7 (wt% SiO₂), and similar single chain silicate crystal structures. Hence, there are no obvious theoretical constraints for significant equilibrium fractionation between Wo and Cpx. We note however that the ionic radii of Fe and Mg are significantly smaller than that of Ca such that a fractionation effect is perhaps possible because of this.

Figure 6.7: Oak-Hill: Coexisting Grt and Cpx minerals from the wollastonite skarn show similar trends towards heavier Si isotope compositions like Wo samples. Garnetites have a rather igneous Si isotope composition and seem to be remnants of igneous rocks associated with the intrusion, such as sills or dykes. The skarn samples adjacent to the garnetite show evidence of mixing, imposing Si mixing with igneous Si derived from the garnetite and the marble.

It is possible that the drop in δ^30Si beyond 18 meters found in the garnetite reflects a hidden contact with the anorthosite in close proximity. Alternatively, it may be that this assemblage reflects a fundamentally different primary lithology. The garnetite mineral phases actually show δ^30Si values more like those expected from igneous rocks. There is no fractionation between clinopyroxene and wollastonite i.e. δ^30Si_Cpx ≈ δ^30Si_Wo. The fractionation between garnet and clinopyroxene persists at a similar level that was observed within the ores with Δ^30Si(Grt-Cpx) = 0.3‰. Again, consistent to the relationship found in parasilicates over orthosilicates. Therefore, the explanation for the difference between the level of mineral fractionation found between coexisting ore minerals on the one hand and coexisting garnetite minerals is best explained if the garnetite represents the remnant of igneous material, such as
a dyke or sill. If it were simply that there is an igneous contact close to the garnetite, which is just not covered by the drill core, it would be surprising that the garnetites do not show any mixing with the Si derived by devolatilization of the marbles, as is found with the ore minerals. The fact is that the garnetites have igneous Si isotope values similar to the anorthosite, and ore mineral assemblage, provides evidence of equilibrium fractionation between garnet and clinopyroxene/wollastonite with similar isotope composition for Wo and Cpx. Assuming that this is the case and the garnetite has an unaltered igneous $\delta^{30}\text{Si}$, it is noteworthy that the ore sample 215'8", which is about 3 meters away from the igneous-like garnetite shows a $^{30}\text{Si}$-enrichment for Wo and Grt that is just like two other ore samples at 103'3" and 144'6", which are about 3.1 and 3.3 meters distant from the igneous anorthosite contact. This observation supports the view that the garnetite itself was a source of igneous-like $^{30}\text{Si}$ values. The ore minerals of sample 215'8" crystallised under Si infiltration derived from the garnetite.

The ore Cpx and Grt have a similar difference in Si isotopic composition to that found in the garnetite ($\Delta^{30}\text{Si}(\text{Cpx-Wo})$ of 0.3%). Considering that the garnetite appears to display equilibrium fractionation between Cpx and Wo, the question arises as to why the ore Wo differs in its isotopic composition from that of the Cpx. It appears that Grt and Cpx are in isotope equilibrium but that the Wo of the ores is not in equilibrium with the Cpx and Grt. This could potentially mean that Wo crystallised from different fluid generations than Cpx / Grt, with distinct timing and / or compositions between them. As both fluid generations also show a progressive Si isotope mixing between igneous and sedimentary Si with increasing distance from the igneous contact, it might also reflect a change in fractionation with temperature. However, there is no systematic change in the fractionation with distance from the contact that one would expect, if the fractionation factor significantly varied with temperature.

Six zircons (Zrc) from Adirondack igneous rocks yield an average Si isotope composition of $-0.37\pm0.06\%$o ($\pm1\sigma_{\text{SD}}$), $\sim-0.2\%$o lighter than the average bulk anorthosite composition of $-0.16\pm0.03\%$. The Si isotope composition however appears with no evidence of resetting. Another zircon (Zrc)-quartz (Qz) pair from the Laurel Mt. pluton, Sierra Nevada, yields a $\Delta^{30}\text{Si}(\text{Zrc-Qtz})$ of 0.34%o (Table 6.2) suggesting a difference between coexisting Zrc-Qz mineral pairs of $\sim-0.3\%$, again consistent with the $^{30}\text{Si}$-enrichment theory mentioned earlier.
Although more work is needed, these preliminary data indicate that Zrc-Qz pairs show systematic differences in their Si isotope composition. Since zircons have the ability to resist alteration, such as metamorphism and low-temperature weathering, it is highly likely that zircons keep their Si isotope composition throughout these processes. The Si isotope composition of zircons is thus likely to be a robust source of information about the Si isotopic composition of the magma they crystallised from (and able us to determine sedimentary from igneous derived zircons).

6.5 Conclusions and Outlook

The methodological improvements described in Chapter 2 made it possible to undertake the first systematic investigations on the Si isotope fractionation behaviour during high-temperature processes. Previous findings, experimental and theoretical, proposed a relation between $\delta^{30}$Si and SiO$_2$-wt% as $^{30}$Si-enrichment occurs with higher degrees of SiO$_4^{4-}$ tetrahedral polymerisation. In principle, the data presented above confirm this prediction, although the observed isotope effects are roughly an order of magnitude smaller than predicted from theory. Beside the SiO$_2$ content, the inherited source of the Si seems to be an important factor, given by the comparison between I- and S-type granites. Silicon isotopes should be able to provide the ability to distinguish between different source regions within a batholith.

Silicon isotope data from the Adirondack Mountains show Si isotope mixing during contact metamorphism, between igneous-derived Si and Si derived from during devolatilization of the meta-sedimentary marble. There appears to be constant equilibrium fractionation between Grt and Cpx, whereas Wo only shows isotope equilibrium with Cpx and Grt in igneous like garnetites. The fact that Wo appears to be out of equilibrium within the ores suggests that Cpx/Grt were crystallised from a different fluid generation from the Wo. However, both fluid generations indicate progressive isotope mixing with increasing distance from the igneous contact. Silicon isotopes might have the ability to trace the extent of such fluid flow, if the end-members can be well constrained.

The Si isotope composition of zircons has been found to be rather constant with an average $\delta^{30}$Si of $-0.37\pm0.06$ (±1$\sigma_{SD}$) and is not reset. This is important information, since it implies that the Si isotope composition of zircons can be used to constrain the isotope composition of
the magma from which they formed. This could provide a robust source of information to constrain the origin of ancient magmas.

This chapter clearly shows that high precision Si isotope measurements can be used to detect small but systematic Si isotope effects during high-temperature processes.
Summary
This thesis presents the development and applications of a new method for a robust, fast and reliable way to determine accurate and precise Si isotope ratios of natural samples using MC-ICP-MS. By combining traditional and new technical approaches, it was possible to obtain higher sensitivity and mass-bias stability, which ultimately results in an improved precision. The acquisition of data of a reasonable quality has become quite simple and the Si isotope compositions of natural samples can now be measured down to a precision that allows resolution of even small temporal variations in river water samples.

The average Si isotopic compositions of 4 Alpine rivers are very similar despite a range of weathering styles, climate, erosion flux and biomass. The average $\delta^{30}$Si for all four rivers is $0.84 \pm 0.19\%$ (±1SD). However, the isotopic composition of dissolved Si varies significantly on a seasonal timescale with an amplitude of up to $0.6\%$. Comparing Si isotope data to changes in hydrochemical and hydrological parameters the mechanisms controlling the sources of dissolved riverine Si and its isotope composition can be constrained. The Si isotope composition of a high mountainous catchment reflects the mixing of soil / groundwater and high discharge waters originating from precipitation and snowmelt. The underlying dominant mass fractionation process is the formation of clay, which incorporates lighter Si isotopes. Catchments with higher proportions of carbonate rocks, cultivated soils and forests show a progressive decoupling of the Si isotope composition from the weathering flux. The mechanisms controlling the Si isotope composition in lowland rivers are complex and cannot be distinguished unambiguously, but are likely a combination of Si derived from silicate weathering and recycling of biogenic silica. However, it appears to be common to different river systems that an enhanced total weathering flux (carbonate + silicate weathering) is associated with lighter $\delta^{30}$Si, even though carbonate dissolution dominates the solute load. This relationship can be confirmed by a study on 20 different rivers on Iceland. The Si isotope composition of the Icelandic streams studied here can be assessed as a mixing between the basaltic host rocks and one fractionated Si pool, which is the result of the formation of secondary weathering products. The fractionation of the riverine Si isotope composition of the Icelandic rivers can be modelled in dependently of the weathering regime as either a steady-state or Rayleigh-type fractionation, with a similar fractionation factor of $\sim -1.5\%$.

Using the Si isotope data in combination with the basic water chemistry it was possible to calculate the amount of Si that is stored in secondary weathering products. From this the
difference between the chemical denudation rate for Si and the total dissolution rate for Si can be calculated. The results show that, on average, ~50% of the released Si is locked up in secondary weathering products.

The associations between riverine $\delta^{30}\text{Si}$ and the weathering regimes reported here, strengthen the argument that continent-derived Si isotope input into the oceans might vary as a function of the amount of glacial cover. Such variations should be considered in future work that utilise Si isotopes as a proxy of long term (>15Ky) palaeo-productivity changes. The continental input of Si into the oceans may have had variable $\delta^{30}\text{Si}$ values on short timescales. Mass balance calculations show that the input into the ocean is more sensitive to variations of the riverine $\delta^{30}\text{Si}$ composition than to changes of the Si flux, and can lead to a change in the average $\delta^{30}\text{Si}$ value of the global ocean.

The first long-term data record on standard measurements is presented here and shows that IRMM-018 is not similar in Si isotope composition to NBS-28, which should remain the international standard for stable isotope comparison. In contrast to recently published data the difference between NBS-28 and IRMM-018 is shown to be $-1.60\pm0.14\%$ ($\delta^{30}\text{Si}$) and $-0.83\pm0.1\%$ ($\delta^{29}\text{Si}$).

The methodological improvements described in this thesis made it possible to undertake the first systematic investigations on the Si isotope fractionation behaviour during high-temperature processes. Although such fractionation has already been predicted theoretically, the observed isotope effects are roughly an order of magnitude lower. The SiO$_2$ content appears to play a role but the source of the Si also seems to be an important factor in magmatic rocks, as demonstrated by the comparison between I- and S-type granites. Silicon isotopes therefore provide the ability to distinguish between different melts within a batholith complex.

Silicon isotope data from a contact metamorphic suite show Si isotope mixing during contact metamorphism, between igneous derived Si and Si released during de-volatilisation of the meta-sedimentary marble. There appears to be constant equilibrium fractionation between Grt and Cpx of 0.3\% ($\delta^{30}\text{Si}$), whereas Wo does only show isotope equilibrium to Cpx and Grt in pristine igneous like garnetites. The fact that Wo is out of equilibrium within the ores
suggests that Cpx/Grt were crystallised from a different fluid generation than the Wo. However, both fluid generations indicate progressive isotope mixing with increasing distance from the igneous contact. Silicon isotopes might have the ability to trace the extent of such fluid flows, if the end-members can be well constrained.

Next to Grt/Cpx another equilibrium fractionation has been found between Qz-Zrc pairs (~0.3% $\delta^{30}\text{Si}$), crystallised from the same parent magma. The Si isotope composition of zircons has been found to be rather constant and no obvious sign of resetting could have been identified. This important information implies that the Si isotope composition of zircons can be used to constrain the isotope composition of the magma they were formed from. This could provide a robust source of information to constrain the origin of ancient magmas.
References

R.B. Georg


References


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Well, I think its time to say a big „Thank you“ to a couple of people. However, I prefer to do this special task in my native tongue, which is German. But since many of you have been in Switzerland for quite a while, this little bit of German shouldn’t be a problem – I’ll keep it simple.

***


***

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Danke

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