Silicon Isotopes

Quartz

Diatom

Radiolarian
Relative abundance of the most common elements in Earth’s continental crust

<table>
<thead>
<tr>
<th>Element</th>
<th>Approximate Percentage by Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen (O)</td>
<td>46.6</td>
</tr>
<tr>
<td>Silicon (Si)</td>
<td>27.7</td>
</tr>
<tr>
<td>Aluminum (Al)</td>
<td>8.1</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>5.0</td>
</tr>
<tr>
<td>Calcium (Ca)</td>
<td>3.6</td>
</tr>
<tr>
<td>Sodium (Na)</td>
<td>2.8</td>
</tr>
<tr>
<td>Potassium (K)</td>
<td>2.6</td>
</tr>
<tr>
<td>Magnesium (Mg)</td>
<td>2.1</td>
</tr>
<tr>
<td>All others</td>
<td>1.7</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
</tr>
</tbody>
</table>

Source: Data from Brian Mason.
## Common silicon-containing minerals

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Idealized Formula</th>
<th>Cleavage</th>
<th>Silicate Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olivine</td>
<td>(Mg, Fe)$_2$SiO$_4$</td>
<td>None</td>
<td>Single tetrahedron</td>
</tr>
<tr>
<td>Pyroxene group</td>
<td>(Mg, Fe)$_2$SiO$_5$</td>
<td>Two planes at right angles</td>
<td>Single chains</td>
</tr>
<tr>
<td>(Augite)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amphibole group</td>
<td>Ca$_2$(Fe, Mg)$_3$Si$_2$O$<em>5$(OH)$</em>	ext{4}$</td>
<td>Two planes at 60° and 120°</td>
<td>Double chains</td>
</tr>
<tr>
<td>(Hornblende)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Micas</td>
<td></td>
<td>One plane</td>
<td>Sheets</td>
</tr>
<tr>
<td>Biotite</td>
<td>K(Mg, Fe)$_2$AlSi$_3$O$<em>10$(OH)$</em>	ext{2}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Muscovite</td>
<td>KA$_2$(AlSi$_3$O$<em>9$)(OH)$</em>	ext{2}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feldspars</td>
<td></td>
<td></td>
<td>Three-dimensional networks</td>
</tr>
<tr>
<td>Orthoclase (Potassium feldspar)</td>
<td>KA$\text{Si}_3$O$_8$</td>
<td>Two planes at 90°</td>
<td></td>
</tr>
<tr>
<td>Plagioclase</td>
<td>(Ca, Na)Al$\text{Si}_3$O$_8$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quartz</td>
<td>Si$\text{O}_2$</td>
<td>None</td>
<td></td>
</tr>
</tbody>
</table>

- **Clays**: weathering of other silicate minerals
CYCLE of Si in Continental Environments

(Basile-Doelsch et al., 2005)

Fluxes: Tmoles/yr

**-Sources:** Weathering of rocks into soil and aquifers.

**-Sinks:**
- Inorganic precipitation (clays)
- Biologically-mediated precipitation (phytoliths and diatoms)
CYCLE of Si in the Oceans

**Sources:**
- Rivers
- Eolian
- Seafloor Erosion
- Hydrothermal fluids

**Sinks:**
- Biologically-mediated precipitation (diatoms, radiolarians, silicoflagellates, sponges)

(Tréguer et al., 1995)
Silicon Isotope Relative Abundance

- $^{28}\text{Si} = 92.22$ atom %
- $^{29}\text{Si} = 4.68$ atom %
- $^{30}\text{Si} = 3.08$ atom %
• Silicon isotopic ratios are expressed as:

$$\delta^{30}\text{Si} = \left[\frac{(^{30}\text{Si}/^{28}\text{Si})_{\text{sample}}}{(^{30}\text{Si}/^{28}\text{Si})_{\text{std}}} - 1\right] \times 10^3 \text{ (‰)}$$

Standard: NBS28 (quartz salt)
(Caltech Rose Quartz standard: in earlier studies)

• Many chemical and physical processes have significant isotopic fractionation → enrichment or depletion of the heavy isotope.
• Fractionation occurs during silica biomineralization and also during weathering and clay formation.
MEASUREMENT of Si ISOTOPE NATURAL ABUNDANCE

- **Gas Isotope Mass Spectrometry**
  - Pure SiO$_2$ loaded into a vacuum line
  - Reacted via laser-heating with a purified F$_2$ gas $\rightarrow$ SiF$_4$ gas
  - SiF$_4$: cryogenically purified and analyzed by MS

- **Multicollector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS)** (De La Rocha, 2002)
  - SiO$_2$: dissolved in HF
  - Sample solution measured by MC-ICP-MS
Methods

Si as biogenic silica or dissolved silicic acid is chemically converted to pure SiO$_2$ and fluorourinated to SiF$_4$ for isotopic analysis at masses 85, 86, 87.
Fluorination Vacuum Line

Producing pure F₂
A CO₂ laser is used to heat SiO₂ in the presence of F₂ to produce SiF₄, O₂, HF
SiF₄ is isolated using cryogenics
Yield is measured and sample sealed for mass spectrometry
• Measurement introduced in 1950s: little work since then due to hazardous methodology

• 1960-1970s: Studies on lunar samples and meteorites

• 1980: First comprehensive study of terrestrial samples. No applications were apparent, thus Si isotope studies were no pursued

• 1988: Ding and colleagues revised methodology and investigated wide range of terrestrial samples

• 1996: Book by Ding and colleagues on “Silicon Isotope Geochemistry”. Applications were emerging

• 1996: De La Rocha et al. developed technique to measure Si isotopes in marine diatoms and dissolved silicon. Oceanic studies started
**$\delta^{30}$Si values of marine and terrestrial samples**

*Figure 1.8: A summary figure indicating the observed range of $\delta^{30}$Si values in terrestrial materials (from Reynolds, 2011).*
APPLICATIONS of STABLE Si ISOTOPIC RATIOS

- Tool to:
  - Studies of the Si cycle
  - Determine the contribution of oceanic and terrestrial ecosystems to the global Si cycle

- Tracer for:
  - Temporal and spatial variations in Si utilization and biogenic silica production (diatoms) in today’s oceans
  - Glacial-interglacial variations in Si utilization and diatom production in the oceans
  - Past biogeochemical conditions in the oceans
  - Formation conditions of clay minerals and siliceous rocks
  - Formation and evolutionary history of igneous and metamorphic rocks
  - Geochemical evolutionary history of the atmosphere and hydrosphere

- Potential tracer for:
  - Weathering intensity of terrestrial rocks
  - Age of soil clays
Applications in Oceanography

* Biological fractionation of silicon isotopes in Southern Ocean surface waters

Varela, Pride and Brzezinski, 2004, GBC
Marine diatoms fractionate Si isotopes during opal deposition in their cell walls ...

\[ \text{Si(OH)}_4 \]

\[ \delta^{30}\text{Si} (\text{‰}) \]

Fraction of dissolved silicon remaining, \( f \)

Rayleigh model

\[ \varepsilon = 1.1 \text{ ‰} \]

(De La Rocha et al., 1997)
Diatom Fractionation Factor

\[ ^{30}\alpha = 0.9989 \]
\[ \varepsilon = -1.1 \]

Fractionation independent of:

- temperature (12-22°C)
- species (3)
- growth rate
- dissolution?

(De La Rocha et al. 1997)
Experimental Determination of $\varepsilon$

<table>
<thead>
<tr>
<th>Species</th>
<th>$T$ (°C)</th>
<th>$\alpha$</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Skeletonema</em></td>
<td>15</td>
<td>0.9990 ± 0.0004</td>
<td>4</td>
</tr>
<tr>
<td><em>costatum</em></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Thalassiosira</em></td>
<td>12</td>
<td>0.9991 ± 0.0002</td>
<td>5</td>
</tr>
<tr>
<td><em>weissflogii</em></td>
<td>15</td>
<td>0.9989 ± 0.0004</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>22</td>
<td>0.9991 ± 0.0004</td>
<td>6</td>
</tr>
<tr>
<td><em>Thalassiosira</em> sp.</td>
<td>15</td>
<td>0.9989 ± 0.0004</td>
<td>5</td>
</tr>
</tbody>
</table>

De La Rocha et al. 1997
Rayleigh Distillation

Increases in relative nutrient use results in more positive, i.e. heavier, values.

Note *relative* use not absolute depletion.
U.S. JGOFS-AESOPS and SOFeX Cruises to the Pacific Sector of the Southern Ocean

AESOPS

Oct - Nov 97 (Survey I)
Dec - Jan 97/98 (Process I)
Jan - Feb 98 (Survey II)
Feb - Mar 98 (Process II)

SOFeX

Jan-Feb 02 (Transect 1)
Feb 02 (Transect 2)
An Intense Diatom Bloom Consumes $>40 \ \mu M \ Si(OH)_4$
Strong meridional gradient in $[\text{Si(OH)}_4]$]. Bloom consumed 40-50 $\mu$M Si(OH)$_4$ pushing gradient 500 km southward.

Silicon isotopes show expected inverse relationship with $[\text{Si(OH)}_4]$, but are confounded by water mass and mixing events.

SOFeX data from transits along 170°W fours years after AESOPS.
Relationship between $\delta^{30}\text{Si}$ of Surface Silicon and Silicic Acid Concentration

$\varepsilon = 1.1 \, \%$

$\text{Rayleigh Model}$

Dissolved silicon
Instant biogenic silica
Accumulating biogenic silica

$\delta^{30}\text{Si} (‰)$

Fraction of dissolved silicon remaining, $f$

$\ln [\text{Si(OH)}_4] \, (\text{of } \mu\text{M})$

$ r^2 = 0.9$

$ r^2 = 0.8$

AESOPS - Dec 97
AESOPS - Jan 98
SOFeX - Jan/Feb 02
SOFeX - Feb 02

Dissolved Si

Biogenic Si
Antiphasing of N and Si Isotopes Persists Through 3 Glacial Cycles

Southern Ocean sediment core
(53° 53' S; 4° 56' W; 2,677 m)

- δ³⁰Si signals may be used as an indicator of past silicic acid use and diatom productivity

- When combined with other sedimentary tracers (e.g. δ¹⁵N), δ³⁰Si signals may be used to reconstruct biogeochemical conditions and assess the influence of nutrient dynamics to climate change on glacial time scales

**(Brzezinski et al., 2002)**

- Interglacial periods
  - High utilization of Si(OH)₄
  - Low utilization of NO₃⁻
  - Si/NO₃⁻ utilization > 4

- Glacial periods
  - Low utilization of Si(OH)₄
  - High utilization of NO₃⁻
  - Si/NO₃⁻ utilization < 2
Si(OH)$_4$:NO$_3^-$
2:1 uptake ratio

Holocene

PF
NO$_3^-$
Si Depletion NO$_3^-$ Excess

SACCF
4:1 uptake ratio

Glacial

PF
Si(OH)$_4$
NO$_3$ Depletion Si Excess

SACCF
1:1 uptake ratio

Si(OH)$_4$:NO$_3^-$
2:1
The fractionation of silicon (Si) stable isotopes by biological activity in the surface ocean makes the stable isotope composition of silicon (d30Si) dissolved in seawater a sensitive tracer of the oceanic biogeochemical Si cycle.

strong meridional and smaller, but resolvable, vertical d30Si gradients

The basin-scale deep Atlantic d30Si gradient thus owes its existence to the interaction of the physical circulation with biological nutrient uptake at high southern latitudes, which fractionates Si isotopes between the abyssal and intermediate/mode waters formed in the Southern Ocean.

de Souza et al., 2012
It has been suggested that stable continental shields with older and deeply weathered soils have lower average $\delta^{30}$Si because of (i) weak present-day weathering and (ii) the dissolution of minerals that are mainly secondary in origin. In contrast, tectonically-active mountain belts expose unaltered primary minerals and achieve high weathering rates leading to elevated $\delta^{30}$Si in rivers. More complicated... (climate, topography, vegetation, weathering type)