Probing the silicon cycle with novel isotope systems

Kate Hendry
K.Hendry@bristol.ac.uk

With thanks to Morten Andersen (Cardiff) and Gregory de Souza (ETH Zurich)
Outline

• State of the art
  • Silicon isotopes in biogenic silica
    • Diatoms
    • Sponges
    • Other silicifiers
  • Trace metal isotope systems in biogenic opal
    • Germanium
    • Zinc
    • (Other solid phases)

• Challenges and outlook
  • Biological mechanisms of fractionation
  • Dissolution, diagenesis and exchange reactions
  • Whole ocean distributions and controls
Outline

• State of the art
  • Silicon isotopes in biogenic silica
    • Diatoms
    • Sponges
    • Other silicifiers
  • Trace metal isotope systems in biogenic opal
    • Germanium
    • Zinc
  • (Other solid phases)

• Challenges and outlook
  • Biological mechanisms of fractionation
  • Dissolution, diagenesis and exchange reactions
  • Whole ocean distributions and controls
The marine silicon cycle

[Diagram showing the marine silicon cycle with labeled steps: 1. Input of Dsi to seawater, 2. Upwelling waters, 3. Sinking Bsi, 4. Glacial ice/iceberg, and 5. Dust flow.]

Not to scale
SiO₂

Si

O

Zn  Ge  Fe  Al  Nd  B

C  N
Silicon isotopes

- Three stable isotopes of Si:
  - $^{28}\text{Si}$ (~92%)
  - $^{29}\text{Si}$ (~5%)
  - $^{30}\text{Si}$ (~3%)

- Variations expressed in standard delta notation

$$\delta^{30}\text{Si} = \left[\frac{(^{30}\text{Si}/^{28}\text{Si})_{\text{sample}}}{(^{30}\text{Si}/^{28}\text{Si})_{\text{standard}}} - 1\right] \times 1000$$

Frings et al., 2015
Some examples of... ... the use of silicon isotopes

Marine diatom productivity

After de la Rocha et al., 1997

\[ \delta^{30}\text{Si}(\text{per mil}) \]

\[ \delta^{30}\text{Si(OH)}_4 \]

\[ \delta^{30}\text{Si opal} \]
Some examples of...
... the use of silicon isotopes

Marine diatom productivity

After de la Rocha et al., 1997

Fractionation factor ($\varepsilon$)

\[ \delta^{30}\text{Si(OH)}_4 \]

\[ \delta^{30}\text{Si opal} \]
Some examples of...
... the use of silicon isotopes

Marine diatom productivity

Can we really assume a constant fractionation factor?

Compilation of laboratory cultures, field studies and sediment core work

Updated from Hendry & Brzezinski, 2014
Some examples of...
... the use of silicon isotopes

Marine diatom productivity

After de la Rocha et al., 1997
Some examples of...  
...the use of silicon isotopes

Diatoms as palaeoproxies

After de la Rocha et al., 1997

\[ \delta^{30}\text{Si(OH)}_4 \]
\[ \delta^{30}\text{Si opal} \]
Some examples of...

... the use of silicon isotopes

Diatoms as palaeoproxies

Horn et al., 2011
Some examples of... ... the use of silicon isotopes

Diatoms as palaeoproxies

Horn et al., 2011
Some examples of...
... the use of silicon isotopes

Sponges as palaeoproxies

Hendry & Robinson, 2012
Some examples of...
... the use of silicon isotopes

Sponges as palaeoproxies

Hendry & Robinson, 2012
Hendry et al., 2016
\text{SiO}_2

\text{Si} \quad \text{O}

[Blue circle]

\text{Zn} \quad \text{Ge} \quad \text{Fe} \quad \text{Al} \quad \text{Nd} \quad \text{B}

\text{C} \quad \text{N}
Germanium isotopes in diatoms

- Ge is important potential proxy for weathering
- Lighter Ge isotopes incorporated into diatom soft tissues
- No apparent Ge isotope fractionation into diatom opal

Germanium isotopes in sponges

Fractionation factor of $-0.87 \pm 0.37 \text{‰}$
Zinc isotopes in diatoms

Andersen et al., 2011; Zhao et al., 2014

• Zn incorporation into diatom opal linked with productivity
• BUT $\delta^{66}$Zn of diatom opal heavy and not reflected in seawater $\delta^{66}$Zn
  • Isotopically heavy due to adsorption? (concentration dependent?!)  
  • Only free Zn$^{2+}$ is taken up into opal? (but should scale with ligand binding strength, estimated at close to 0 ‰, Köbberich & Vance 2017, 2018)  
  • Some other biomediated fractionation during precipitation?  
• Very low proportion of Zn taken up by diatoms is incorporated into opal  

Andersen et al., 2011; Zhao et al., 2014
Zinc isotopes in sponges

- Hexactinellid sponges reflect seawater (potential proxy for the past oceanic Zn cycle?)
- Demosponges more variable, due to diet?

Hendry and Anderson, 2013
Outline

• State of the art
  • Silicon isotopes in biogenic silica
    • Diatoms
    • Sponges
    • Other silicifiers
  • Trace metal isotope systems in biogenic opal
    • Germanium
    • Zinc
    • (Other solid phases)

• Challenges and outlook
  • Biological mechanisms of fractionation
  • Dissolution, diagenesis and exchange reactions
  • Whole ocean distributions and controls
Outline

• State of the art
  • Silicon isotopes in biogenic silica
    • Diatoms
    • Sponges
    • Other silicifiers
  • Trace metal isotope systems in biogenic opal
    • Germanium
    • Zinc
  • (Other solid phases)

• Challenges and outlook
  • Biological mechanisms of fractionation
  • Dissolution, diagenesis and exchange reactions
  • Whole ocean distributions and controls
A lot is unknown about **biomineralization processes**...
What is the biochemical pathway responsible?

- Silicon Transporters (SiTS)
- Silicon polymerisation

*Javaheri et al., 2014; Tesson et al., 2017*
A lot is unknown about **biomineralization processes**... What is the biochemical pathway responsible? Take sponges as an example...

Some spicule types are enigmatic...
A. Desmas from carnivorous sponges (*Aspestopluma* sp.);
B. Giant spicules from the Western Pacific (*Monoraphis* sp.);
C. Hypersilicified/fused hexactinellid sponges.

Strange biomineralization $\rightarrow$ strange isotopic signatures!

*Cassarino et al., 2018; Hendry, Cassarino et al., in prep*
A lot is unknown about **biomineralization processes**... 
... and what about all the other silicifiers?
What’s the impact of **dissolution and diagenesis** on opal isotopic composition?

- Implications for global budgets via sediment fluxes
- Implications for use of proxies

---

**Dissolution**

- Si isotopes

**Demarest et al., 2009; Michalopoulos & Aller, 2004**
Whole ocean distribution

- Understanding the role of silicifiers in whole ocean distributions and isotopic behaviour
- Understanding the implications for interpreting geochemical archives
- Are they a control or an archive?? Or a bit of both...

Schematic of the global ocean biogeochemical cycling of Si in EMIC cGENIE, together with the structure of the sediment system.

Ridgwell et al., 2002
Perspectives

- GEOTRACES data
  → help understand modern distribution (e.g. Zn isotopes)
  → help understand dissolution and diagenesis reactions
  → help understand links between isotope systems that can be combined in palaeoceanographic applications (e.g. Si, Zn, Ge, Fe)

- Activities should encourage cross-discipline research (surface chemistry, biochemistry) and continuing modelling efforts