Silicon isotope fractionation during the formation of (amorphous) hydroxyaluminosilicate (HAS) phases

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Motivation

- Weathering of silicate minerals is an important process on the Earth's surface
- Key Element: Silicon (Si)
- Critical Zone (Fig. 1):
  - Si is precipitated as short-range order **hydroxyaluminosilicate (HAS) solid phase, e.g., allophane (ALO) & hisingerite (HIS)**
- Experimental study of Si isotope fractionation between reactive fluids & HAS
- Investigation of kinetic & equilibrium Si isotope fractionation to understand mechanisms of HAS formation

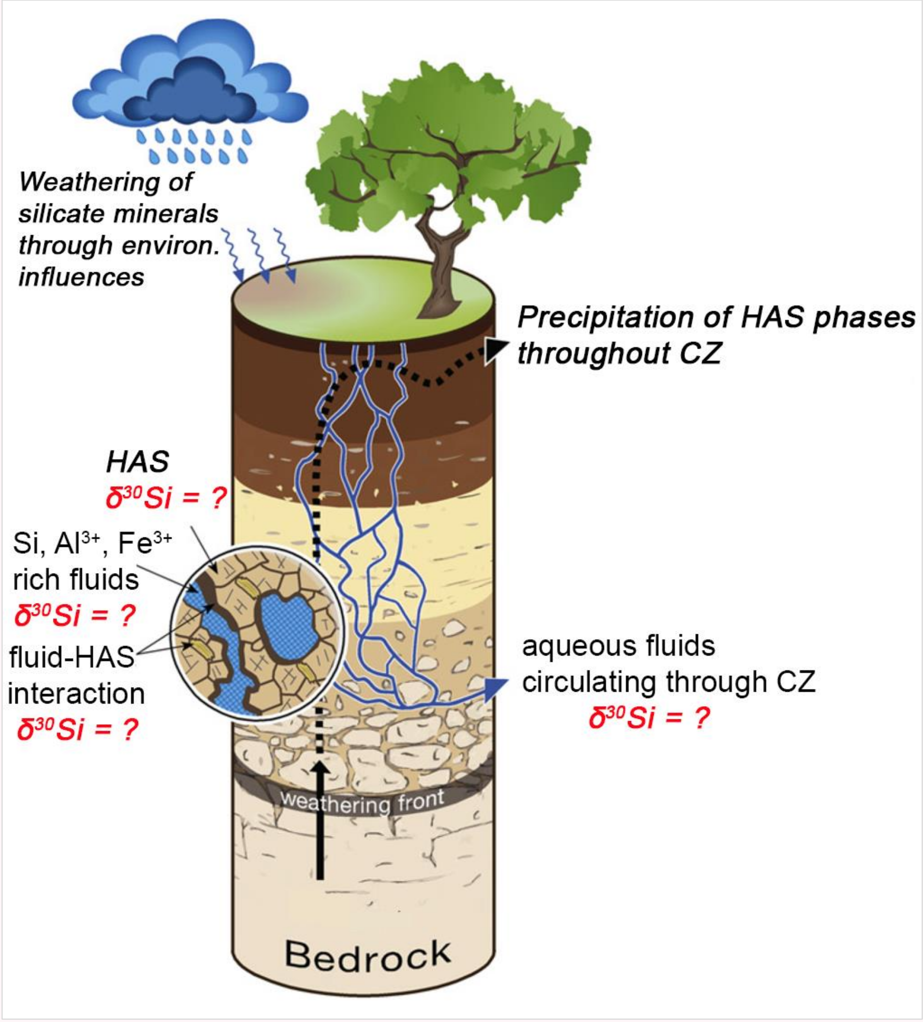

Fig. 1 Model of the Critical Zone (CZ) with processes and pathways leading to HAS formation (modified after v. Blanckenburg et al.[1])

Nomenclature & Theoretical Background

Si isotopic composition of a phase:

$$\delta\,^{30}Si(‰) = \left(\frac{(^{30}Si/^{28}Si)_{sample}}{(^{30}Si/^{28}Si)_{NBS-28}} - 1\right) \times 1000$$

Isotopic fractionation factor between two phases:

$$\Delta_{A-B} = \delta_A - \delta_B \approx 10^3 ln\alpha_{A-B}$$

Three isotope method (Fig. 2)[2,3]

- Determination of equilibrium isotope fractionation factors
- Precise determination of exchange reactions of small extent
- Monitoring of reaction kinetics
- Isotopic exchange between 2 phases:
  - *Phase A natural composition: plots on terrestrial fractionation line (TFL)*
  - *Phase B: enriched in ²⁹Si*
- Isotope exchange complete (100%) on secondary fractionation line (SFL)

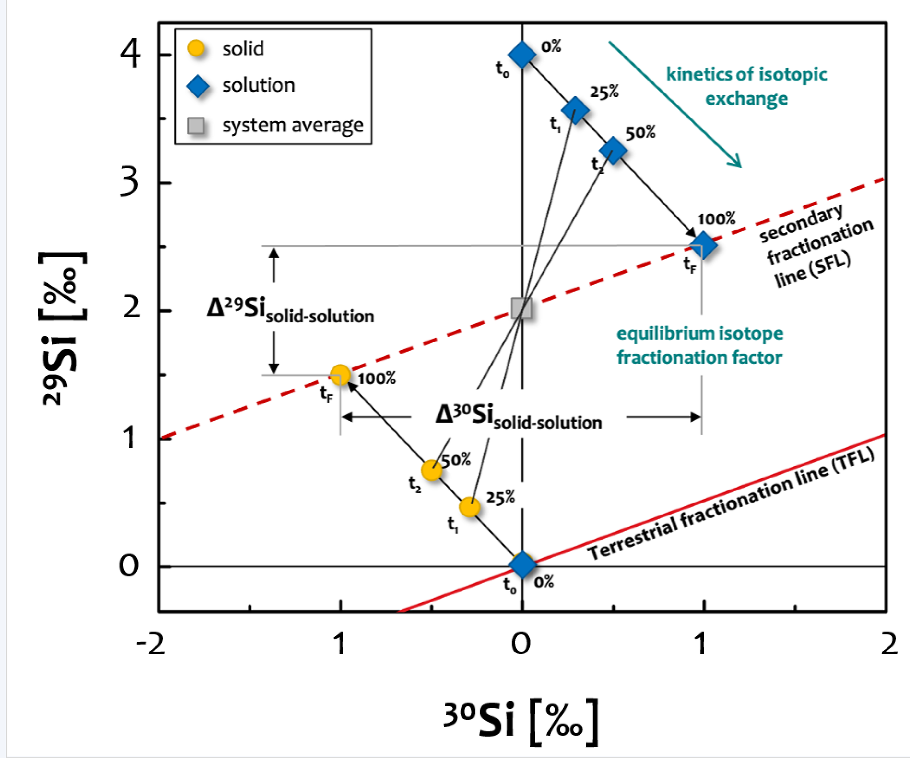

Fig. 2 Schematic diagramm of the three-isotope method applied to Si. modified after Stamm et al.[3]

Experimental Setup

Starting Solutions

- $Si(OH)_4$ rich solution prepared from $Na_2SiO_3 \cdot 5H_2O$ (pH ~13)
- Al^{3+} and Fe^{3+} solutions prepared from $AlCl_3 \cdot 6H_2O$ and $FeCl_3 \cdot 5H_2O$ (pH~2.7)

Experiments @ 25°C

Step 1: Precipitation experiments

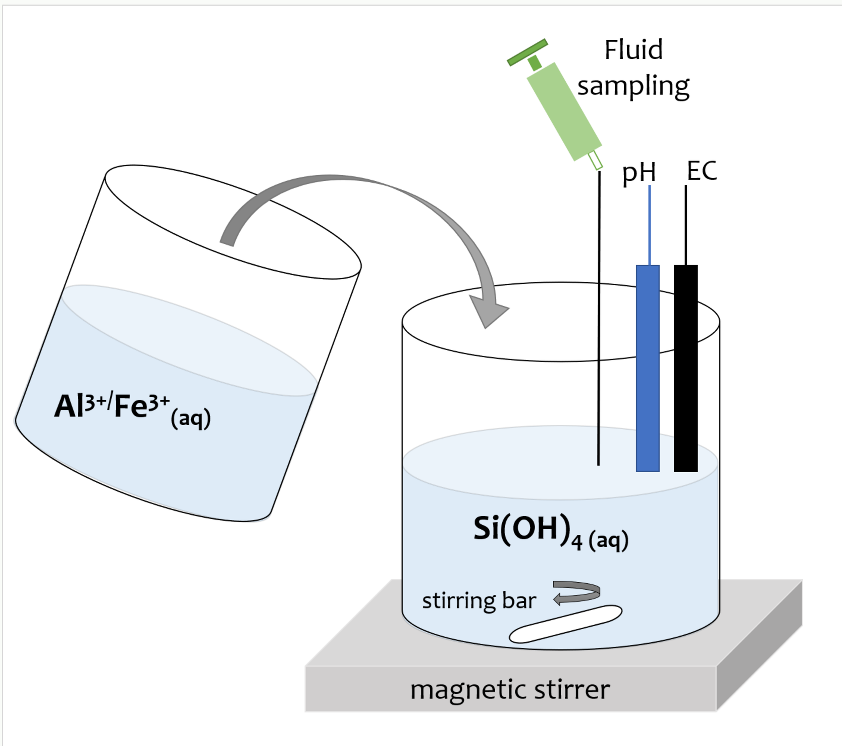

Fig. 3 Schematic diagramm of the precipitation experiments of two HAS phases: allophane and hisingerite (Al or Fe/Si 1:1; Ratz et al. [4])

- Time series sampling to monitor kinetic isotope effects during precipitation of allophane ($\sim Al_2^{3+}O_3(SiO_2)_{1.3-2} \cdot H_2O_{2.5-3}$; ALO) / hisingerite ($\sim Fe_2^{3+}Si_2O_5(OH)_4 \cdot 2H_2O$; HIS)

Step 2: Isotope exchange experiments

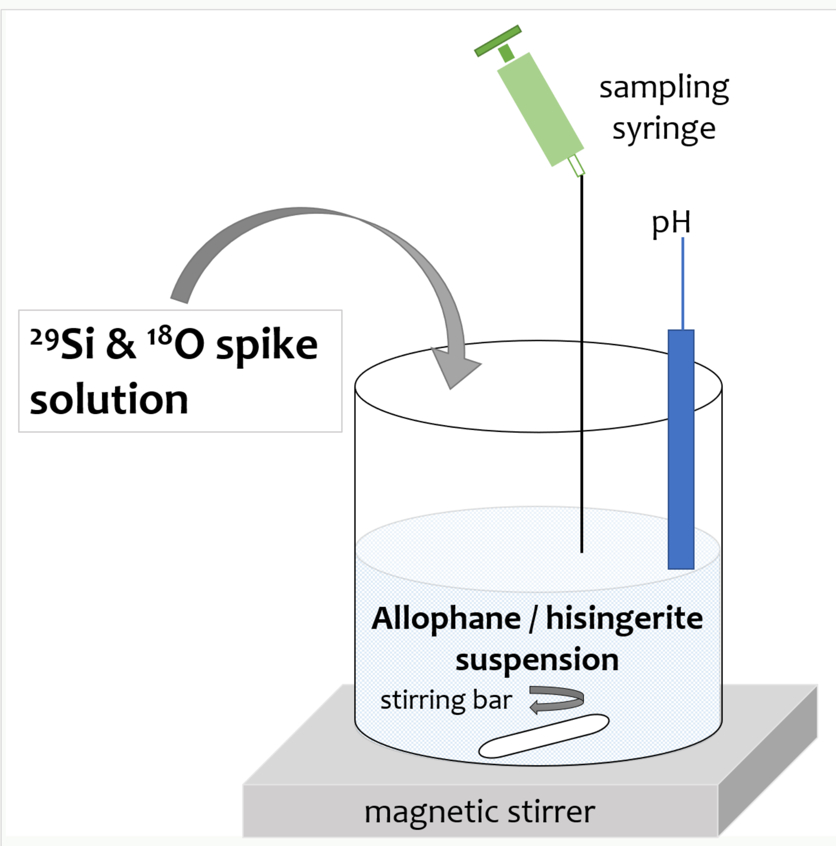

Fig. 4 Schematic diagram of isotope exchange experiments (modified from Ratz et al[4])

1. Attainment of **chemical equilibrium**
2. Spiking of equilibrated solution with **²⁹Si & ¹⁸O**
3. Isotope exchange experiments
   1. Closed system
   2. Time-series sampling

Preliminary Results

Isotopic Exchange

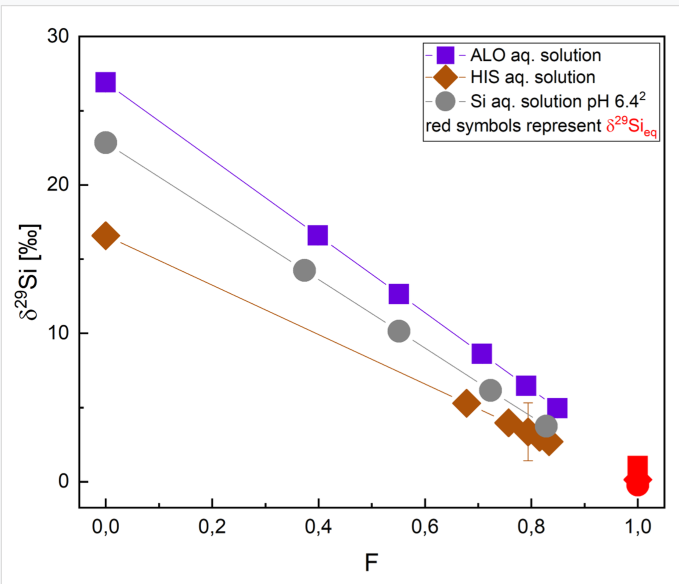

Fig. 5 Evolution of δ²⁹Si over the degree of isotopic exchange (F); 2SD shown within the symbols.

- Degree of isotopic exchange (F) determined for any reaction time t:

$$F = (\delta_t - \delta_i)/(\delta_e - \delta_i)$$

δ_t – δ at reaction time t of isotopic exchange
δ_i - initial δ of solution
δ_e - δ at equilibrium

- $\delta^{29}Si_{aq}$-F diagram shows fast depletion in δ²⁹Si in solution within 15 days
- Allophane (ALO) & hisingerite (HIS) show similar behaviour

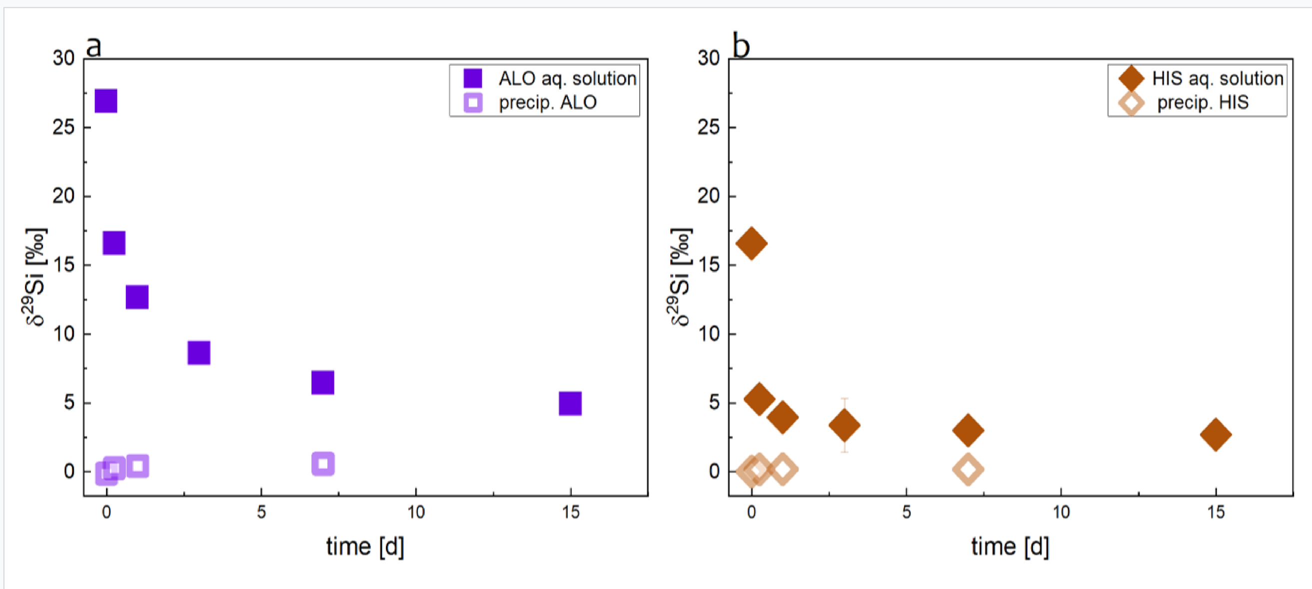

Fig. 6 Evolution of δ²⁹Si over time for the isotope exchange experiments with a) allophane (ALO) and b) hisingerite (HIS); 2SD if not shown, within the symbols

- Evolution of δ²⁹Si of the solid and reactive solution over reaction time throughout allophane (ALO) and hisingerite (HIS) formation
- $\Delta^{30}Si_{eq}$ over reaction time indicates clear and fast depletion of spiked element

Determination of $\Delta^{30}Si_{solid-Si(aq)}$

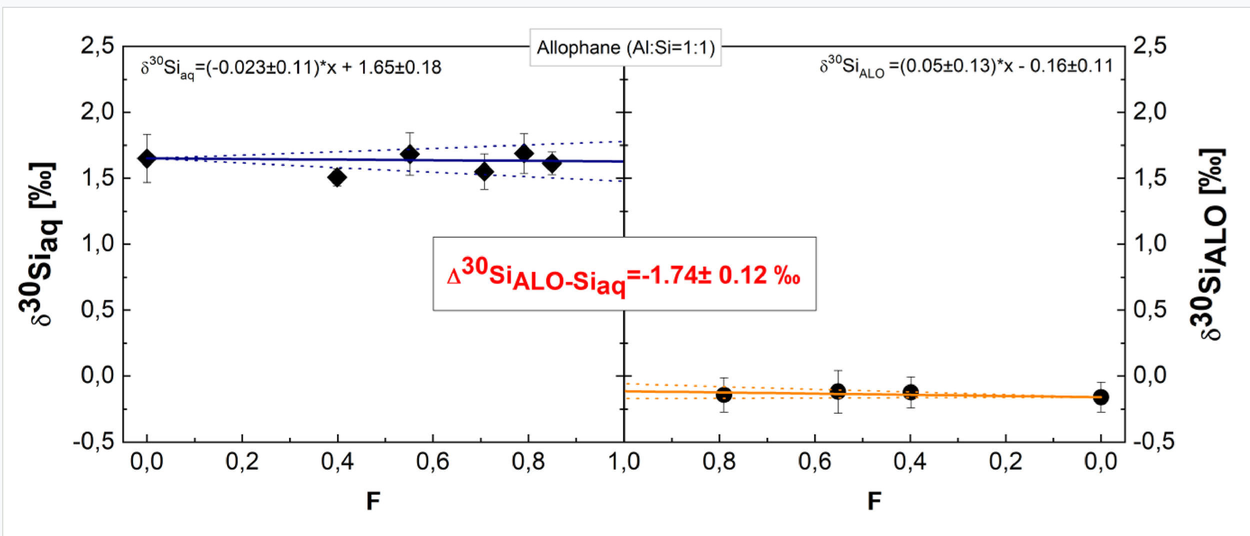

Fig. 7 Determination of the equilibrium fractionation factor ($\Delta^{30}Si_{ALO-Si_{aq}}$) between allophane and the reactive solution by extrapolation (dashed line 95% confidence interval).

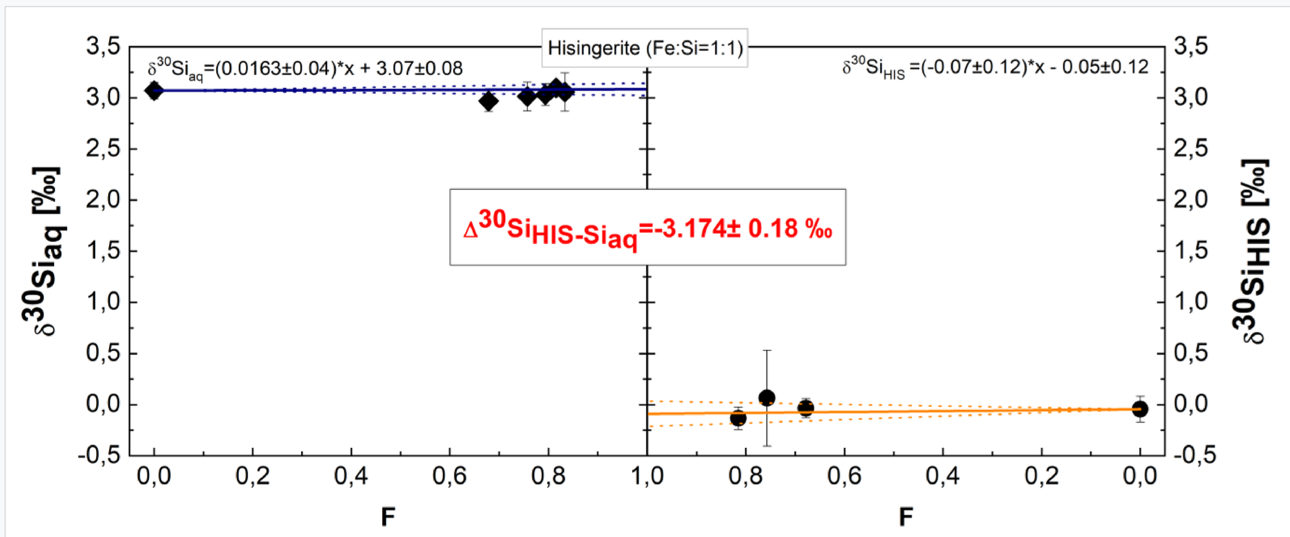

Fig. 8 Determination of the equilibrium fractionation factor ($\Delta^{30}Si_{HIS-Si_{aq}}$) between hisingerite and the reactive solution by extrapolation (dashed line 95% confidence interval).

- $\Delta^{30}Si_{eq}$ between solids (allophane/ hisingerite) and aqueous solutions determined by extrapolation of δ³⁰Si isotopic compositions of the two phases

Conclusions & Outlook

- Light isotopes are preferentially incorporated in the HAS precipitates
- Si isotope re-distribution between allophane/ hisingerite and reactive solutions occurs within days
  → highly dynamic exchange between solid and aqueous Si tetrahedrons
- Si isotope exchange kinetics slightly increase in the order of HIS>ALO & pure Si system
  → Polymerization steps more relevant than Me-O-Si for isotopic re-equilibration?

Outlook

- Study of the evolution of the isotopic composition during allophane & hisingerite precipitation
- O isotope exchange experiments to investigate coupling between Si and O isotope exchange reaction mechanisms
- Determination of Si and O isotope exchange kinetics and apparent/equilibrium fractionation factors
- Implications: assessment and monitoring of invers weathering scenarios by (coupled) Si and O isotope distribution between interstitial solutions and HAS precipitates in natural surroundings

References & Acknowledgements

[1] v. Blanckenburg et al. (2012) EPSL, **351-352**, 295-305; [2] Matsuhisa et al. (1978) GCA **42**, 173-182; [3] Stamm et al. (2019) GCA **255**, 49-68; [4] Ratz et al. *in prep.*

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