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Amorphous silica vs short-range ordered hydroxy-aluminosilicate formation – Reaction kinetics and Si isotope fractionation

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Amorphous silica (ASi) and short-range ordered hydroxy-aluminosilicates (SROAS) are highly reactive solid phases known as precursors for the formation of opal and clay minerals. The silicon isotope compositions of these in soils and sedimentary rocks are commonly used as environmental proxies to reconstruct their formation conditions and reaction pathways. The associated reaction kinetics and mechanisms as well as Si isotope fractionation are not yet sufficiently understood.

This study aims to decode the environmental controls on the formation pathways and Si isotopic fractionation underlying ASi and SROAS formation. A series of precipitation experiments with and without Al were performed at a high temporal resolution and ambient temperature. Elemental and Si isotope analyses of the fluid and solid revealed that the formation of ASi and SROAS follow different pathways, each with three distinct stages:

Stage 1: Slow ASi polymerisation over the course of three days vs. rapid SORAS precipitation within 15 seconds.

Stage 2: Within one day ASi begins to precipitate following classical first-order reaction kinetics vs. partial re-dissolution of SROAS.

Stage 3: ASi maturation vs. SROAS re-precipitation at slower rates.

The Al in the SROAS is present in [6] and [4] coordination with oxygen, where the level of $Si^{[4]}$ substitution depends on the Al/Si ratio. The formation of SROAS appears to proceed via a poorly-explored metastable transition phase that involves atomic-scale clustering of highly disordered octahedral template sheets, followed by Al substitution of $Si^{[4]}$ and Si polycondensation reactions with subsequent complex (de)polymerization during the reordering phase.

The Si isotope fractionation between the reactive fluid and ASi or SROAS is kinetically controlled, with the highest Si isotope fractionation ($1000\ln(\alpha_{SROAS\text{-}aq}) = -4.55‰$) measured in the SROAS after one day when the solid Si content in the ASi and the Si/Al ratio in the SROAS stabilized during in stage 3. Further, the Si isotope fractionation depends on the Si/Al ratio of the solid. Within 16 days, close to steady state conditions were reached, where the Si isotopic composition of the precipitates approached values typically found in allophanes and other clay minerals from both in laboratory experiments and field studies.