Theoretical silicon isotope fractionation between aqueous and solid silica species

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Previous work has indicated the potential for silicon isotopes to be used as a paleo-pH proxy. The core of this potential is a 1-3‰ fractionation between H_4SiO_4 and its conjugate base $H_3SiO_4^-$. Combining this fractionation with aqueous silica speciation, predicts a pH dependent shift in the silicon isotope compostion of solids grown from solutions with pH > ~8.5. The purpose of this study is to provide new calculations of silicon isotope fractionation between H_4SiO_4, $H_3SiO_4^-$ and $H_2SiO_4^{2-}$ as well as the dimer $H_6Si_2O_7$ which is significant in solutions with higher silica concentrations (e.g. in equlibrium with amorphous silica). In addition to aqueous phase equlibrium, silicon and oxygen isotope fractionation factors are calculated for the three most common crystaline silica species formed at low temperatures, low-cristobalite, low-tridymite and quartz. Explicit hydration models of isotope fractionation between H_4SiO_4 and $H_3SiO_4^-$ which implement a free inner shell and a complete frozen second shell of hydrating water ($n_{H2O}=68$) are found to well reproduce experimental results. This model form closely mimics the methodology used for cluster model calculations of solids. The best matches to experiments are models utilizing the B3LYP, TPSSh, M11L and PBE0 functionals. Silicon isotope fractionation between $H_6Si_2O_7$ and H_4SiO_4 is found to be very close to unity. Significant differences in equlibrium silicon-30 isotope fractionations are predicted between the all three modeled crystaline phases with tridymite predicted to be ~1.2‰ heavier than quartz and cristobalite ~0.5‰ lighter than quartz at 25°C. The growth of cristobalite and tridymite in surface environments soely as a mixture in the form of opal-CT largely negates these small differences with a 50-50 ratio opal-CT predicted to have a silicon isotope compostion ~0.5‰ heavier than quartz. Similarly to silicon isotopes, equlibrium oxygen-18 fractionation between opal-CT and quartz is predicted to be ~0.4‰ at 25°C with a negligible difference in $\Delta^{17}O$. The results of this study provides additional modelling constraints on equlibrium silicon and oxygen isotope fractionations for pure silica phases in aqueous environments.