Equilibrium silicon isotope fractionation in eclogites and granites constrained by single crystal X-ray diffraction and the force constants approach

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Abstract

We present a novel force constant approach that combines experimental and theoretical data to calibrate the β-factor of tetrahedrally coordinated silicon (^{IV}Si) in the crust and upper mantle minerals. We determine the resilience of ^{IV}Si from the Debye-Waller factor, which is derived from single crystal X-ray diffraction data collected at various temperatures, and calculate the stiffness of ^{IV}Si from the density-functional theory (DFT) studies. The relationship between the resilience and the stiffness is calibrated, and then the calibrated stiffness is further corrected with the effective coordination number of the SiO_4 tetrahedron. The corrected stiffness is used to calculate the equilibrium isotope fractionation β-factor of each mineral, and the $α_{Si30/28}$ factors is calculated by taking the ratio of β-factors of different minerals. We calculate the $α_{Si30/28}$ factors between minerals that contains SiO4 tetrahedra, and our results are consistent with DFT calculations and mass spectrometry results. Using our force constants approach, we have determined the equilibrium Si isotope fractionation between omphacite/garnet, quartz/kyanite, and quartz/zircon at temperatures relevant to the petrogenesis. Our results will be of interest to geochemists studying the silicon isotopic composition of minerals in ultra-high pressure metamorphism.

Background

Atomic force constant is the physical quantity that describes the restoring force that exerts on an atom when the atom is displaced from its equilibrium position. There are two different kinds of force constants, namely the resilience and the stiffness.

Resilience (Nr) is defined as:

$$N_r = \frac{k_B}{d\langle u^2\rangle/dT}$$

where k_B is the Boltzmann constant, $\langle u^2\rangle$ is the atomic mean square diplacement, which is measureable from single crsytal X-ray diffraction.

Stiffness (Ns) is defined as:

$$N_s = \int M\left(\frac{E}{\hbar}\right)^2 D(E)dE$$

where M is the atomic mass the isotope, ħ is the reduced Planck constant and D(E) is the partial phonon density of states.

Ns is used to calculate the isotope fractionation β-factor [Dauphas et al., 2018]:

$$ln\beta_{l/l^*} = \left(\frac{\hbar^2}{8k_B^2}\frac{N_s}{T^2} - \frac{5\hbar^4}{2016k_B^4 M}\frac{N_s^2}{T^4} + \frac{25\hbar^6}{326592k_B^6 M^2}\frac{N_s^3}{T^6}\right)\left(\frac{1}{M^*} - \frac{1}{M}\right)$$

In our earlier work [Zhang et al., 2021], we have established an empirical relationship between Ns and Nr for tetracoordinated Si in crust and mantle silicates:

$$\frac{N_r}{N_s} = 1.63\times10^{-3}N_r - 5.20\times10^{-3}$$

After calculating Ns from Nr using the calibration above, Ns will be further corrected by:

$$N_{sC} = N_s \times \frac{\text{ECoN}}{4}$$

where ECoN is the effective coordiation number. Using these equations, we can compute the isotope fractionation β-factor of Si from single crystal X-ray diffraction data collected from crust and mantle silicates at various temperatures.

Experiments

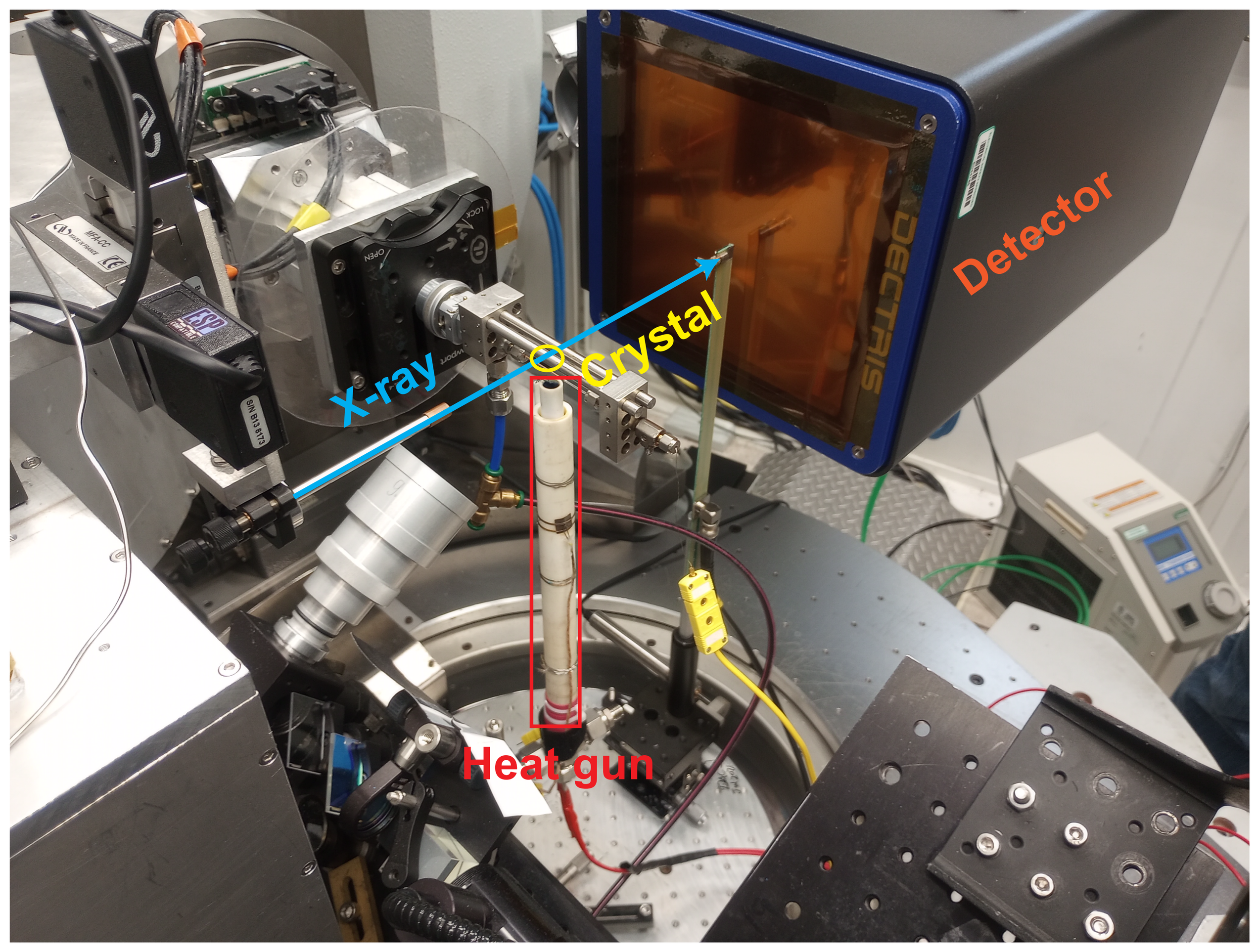

Figure 1: High temperature single crystal X-ray diffraction setup at APS 13-BM-C.

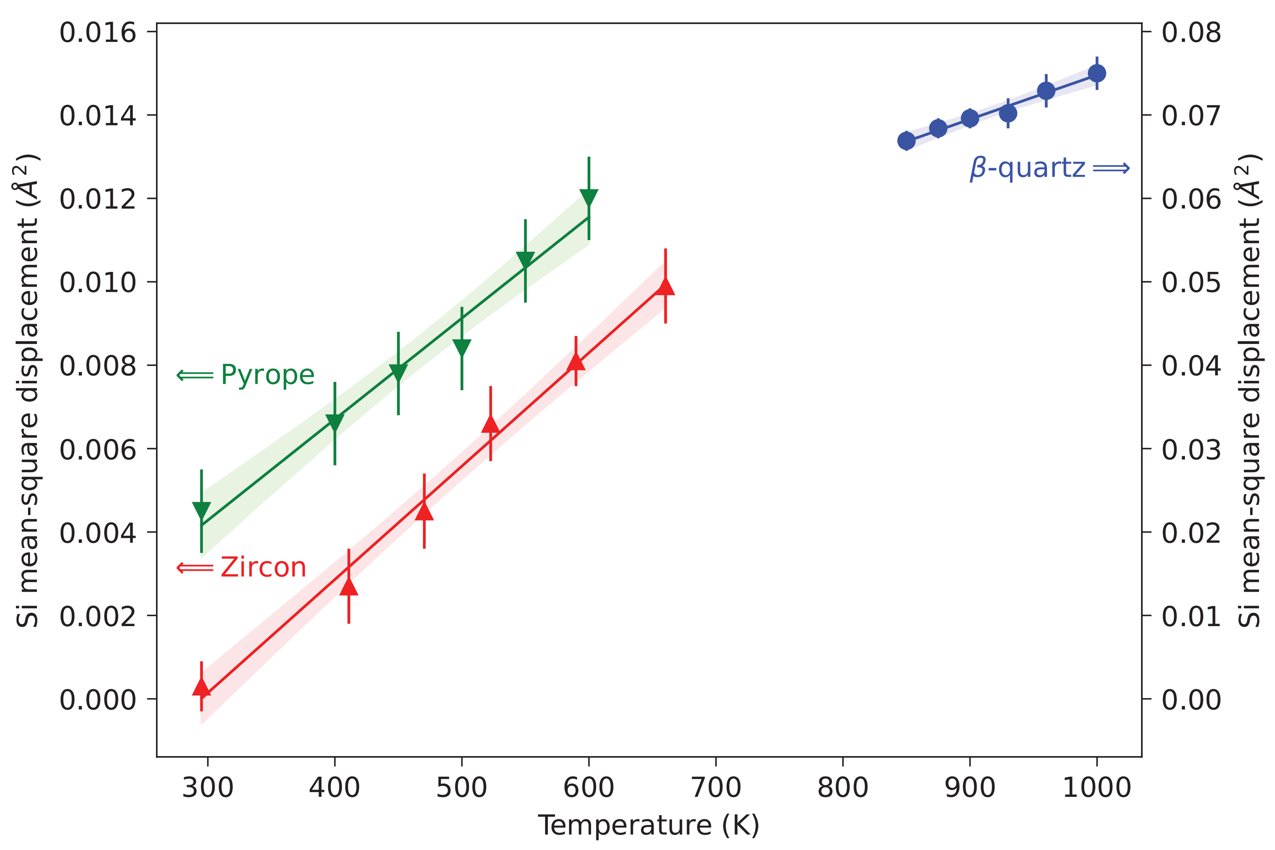

Figure 2: The Si atomic mean square displacement $\langle u^2\rangle$ as a function of temperature determined by the high-T XRD experiments from this study. Best linear fits and fitting error ranges are shown as the straight lines and shaded regions.

Table 1: Resilience and ECoN of minerals investigated in this study. Bold values are used in the calculation of isotope fractionation. a: fixed by symmetry. b: averaged over all Si sites.

Pyrope			Omphacite		
	Resilience (N/m)	ECoN		Resilience (N//m)	ECoN
This study	57(5)		*Cameron et al.* [1973], diopside	32(2)	3.90
Meagher [1975]	58(15)		*Pavese et al.* [2000]	41.7(7)	3.96 [b]
Pavese et al. [1995]	60(2)	4[a]	*Tribaudino et al.* [2005]	37(3)	3.95 [b]
Nakatsuka et al. [2011]	55.4(6)		*Tribaudino and Mantovani* [2014]	37(5)	3.95 [b]
Average	**58(5)**		**Average**	**37(4)**	3.94
β-quartz			Other minerals		
	Resilience (N/m)	ECoN		Resilience (N/m)	ECoN
This study	26(5)		**This study, zircon**	**51(3)**	4[a]
Kihara [1990]	28(3)	4[a]	***Winter and Ghose* [1979], kyanite**	**49(1)**	3.995 [b]
Average	**27(4)**				

Results

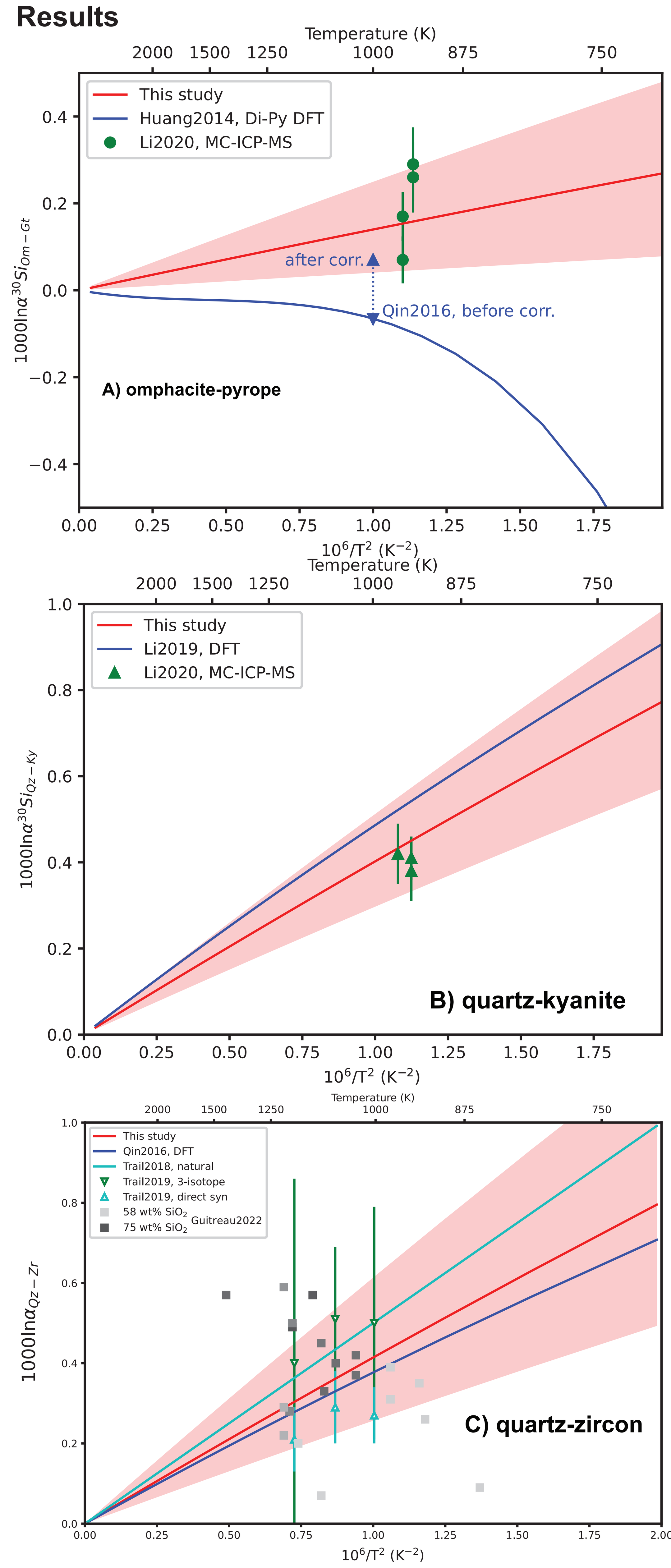

Figure 3: Equilibrium Si isotope fractionation between A) omphacite and pyrope, B) quartz and kyanite and C) quartz and zircon. Red curve: force constants approach. Red shaded region: uncertainty range of the force constants approach, determined from the distribution of the resiliences of the two minerals. Blue curve: DFT calculations. Green/cyan triangles: mass spectroscopy measurements. C) Cyan curve: estimation from mass spectroscopy measurements on natural sample [Trail et al., 2018]. Grey squares: Si isotope fractionation between natural zircon and host granite, [Guitreau et al., 2022]. The shades of grey indicate the SiO_2 content in the whole granite (58-75 wt%).

Conclusions

1. The Si isotope fractionation between omphacite and pyrope is strongly affected by the Na content in the pyroxene phase.
2. Retrograde alternation seems to have little effect on the Si isotope fractionation in UHP metamorphic rocks.
3. The Si isotope fractionation between quartz and zircon in granite is affected by the SiO_2 content in the rock, yet a potential "saturation" value exists.

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