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Key Points:

- Na strongly affects the Si isotope fractionation between omphacite and garnet in eclogites
- The kyanite-bearing Dabie eclogite and the host quartz vein endured the same pressure-temperature condition during their formation
- The equilibrium Si isotope fractionation between zircon and granite at 1000 K is ∼0.45‰ for granite contains >70 wt% SiO_2

Supporting Information:

Supporting Information may be found in the online version of this article.

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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 Using our recently developed X-ray diffraction based *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. We find that Na strongly affects the Si isotope fractionation between omphacite and garnet. Our results have suggested that the omphacite and garnet in eclogite collected in the Dabie Mountain, as well as the kyanite and its host quartz veins, are isotopically in equilibrium, which further suggests that the Dabie Mountain eclogites and its host veins underwent the same high pressure-temperature condition during their formation. The Si isotope fractionation determined by our methods, together with published mass spectroscopy measurements, DFT-CIPW calculations and sigmoid fitting on various felsic granites, have suggested that the Si isotope fraction between zircon and whole rock “saturates” at ∼0.45‰ at 1000 K when the SiO_2 content in the granite is above ∼70 wt%.

Plain Language Summary The isotope fractionation of silicon is related to many geological phenomena. Using single crystal X-ray diffraction (XRD) technique and our new XRD *force constants* method, we have determined the equilibrium Si isotope fractionation between omphacite/garnet, quartz/kyanite and quartz/zircon. Our results suggest that incorporation of Na helps to enrich heavy Si into omphacite over garnet in eclogite. We found that the omphacite and pyrope garnet in Dabie Mountain eclogites, as well as the kyanite and its host quartz veins, are in equilibrium for Si isotopes, which suggests that the kyanite-bearing Dabie eclogite and the host quartz vein endured the same pressure-temperature condition during their formation. We also found that the Si isotope fractionation between zircon and granite saturates when the granite contains more than 70 wt% quartz, and the equilibrium Si isotope fractionation between zircon and granite at 1000 K is ∼0.45‰ for such granites.

1. Introduction

The isotope fractionation of silicon is involved in many geological processes, including the core-mantle segregation (Dauphas et al., 2015; Fitoussi & Bourdon, 2012; Georg et al., 2007; Savage et al., 2011; Shahar et al., 2009; Zambardi et al., 2013), the upper-lower mantle material transport (Huang et al., 2014; Wu et al., 2015), the rock-fluid interaction (Meheut & Schauble, 2014; Qin et al., 2016), global carbon cycle (Opfergelt & Delmelle, 2012; Opfergelt et al., 2012) and biogeochemical processes (Stamm et al., 2020). Silicon and oxygen are the two most abundant elements in the earth's lithosphere, and several studies have coupled both silicon and oxygen isotopes to constrain the fluid-rock interaction and chemical weathering of crustal materials (Qin et al., 2016; Trail et al., 2019). This two-elements investigation has the potential to separate low-temperature weathering contaminations from high temperature fractionations (Trail et al., 2019). Most recent studies use at least one of the two following approaches to quantify the silicon isotope fractionation in silicate minerals: mass spectroscopy (e.g., Guitreau et al., 2022; Y. Li et al., 2020; Trail et al., 2019) or density functional theory (DFT) calculations (e.g., Huang et al., 2014; Y. Li et al., 2019; Meheut & Schauble, 2014; Meheut et al., 2009; Qin et al., 2016), and these methods have their own advantages and disadvantages. Mass spectroscopy is a precise analytical method to constrain the isotope fractionation α-factor between two minerals in a sample. Since mass spectroscopy only measures the relative ratio of isotope abundances between minerals, it faces challenges to determine whether the equilibrium has been reached and whether kinetic processes are involved in the fractionation (Trail et al., 2019). On the other hand, DFT method computes the vibrational behavior of Si atoms in a

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crystalline mineral, and directly calculates the reduced partitioning function ratios (also known as the β-factor) from the phonon spectrum (Meheut et al., 2009; Qin et al., 2016). The equilibrium α-factor can be computed from the ratio between the β-factors of the two corresponding minerals. DFT is a versatile method that can be used in almost all mineral systems at various pressure and temperature conditions, yet the computation involves some approximations. Among the published DFT studies on the Si isotope fractionation in crust and mantle minerals, the crystal structure of each mineral was first relaxed at 0 GPa pressure and 0 K temperature (Huang et al., 2014; Y. Li et al., 2019; Meheut & Schauble, 2014; Meheut et al., 2009; Qin et al., 2016; Wentzcovitch, 1991; Wu et al., 2015), and the phonon spectrum were then calculated using DFT method based on the relaxed 0 K crystal structure. Several studies were able to investigate the pressure effect on the phonon spectrum by incorporating the thermal equation of states calculated from the quasi-harmonic Helmholtz free energy (Huang et al., 2014; Wu et al., 2015). The isotope fractionation β-factor at high temperatures and high pressures for each mineral was then calculated using the Urey equation and the phonon spectrum derived from the relaxed 0 K crystal structure (Huang et al., 2014; Y. Li et al., 2019; Meheut & Schauble, 2014; Meheut et al., 2009; Qin et al., 2016; Wu et al., 2015). Combining DFT and experimental data will generate a more accurate estimation on the isotope fractionation in minerals. Besides mass spectroscopy and DFT, there is nuclear resonant scattering (NRIXS) method that constrain the isotope fractionation of Fe, Sn, Eu and Dy through their partial phonon density of states (Dauphas et al., 2012; Polyakov et al., 2005), but this method doesn't work for Si as Si doesn't have any Mössbauer active isotope.

We have developed an X-ray diffraction (XRD) based *force constants* approach to constrain the Si isotope fractionation behavior in silicate minerals that contains four-coordinated Si (D. Z. Zhang et al., 2021). Our XRD *force constants* approach establishes a calibration between two kinds of force constants, namely resilience (N_r) and stiffness (N_s) (Hu et al., 2013; Leu & Sage, 2016), from XRD experiments and DFT calculations, respectively. Once we get the N_r of Si in a mineral from XRD at various temperatures, the N_r is estimated directly from our N_r/N_s calibration without further DFT calculations, and the Si β-factors in minerals is then approximated from N_s using expansions of Urey equation (Dauphas et al., 2018; Polyakov et al., 2005; D. Z. Zhang et al., 2021). Our XRD *force constants* approach addresses the elemental selectivity of NRIXS, and is faster and computational cheaper than *ab-initio* DFT calculations. Our approach is a promising complementary method besides DFT and mass spectroscopy to study the Si equilibrium isotope fractionation in crystalline silicate minerals.

Stable isotope fractionation between rock-forming minerals in igneous and metamorphic rocks provide crucial information about the geological processes in the crust and mantle. In igneous rocks, zircon is of special interest to geochemists because it's very resistant and provides information about the parent melts of the rock (Guitreau et al., 2022). However, the determination of equilibrium in zircon-related isotopic measurement is challenging (Trail et al., 2019), because diffusion is very sluggish in zircon (Cherniak & Watson, 2003). In metamorphic rocks, isotopic disequilibria are usually interpreted as a result of interaction with geofluids, because of the kinetic effect led by the fast diffusion in liquids (Bedard, 1989; Zheng et al., 2003). In this paper we focus on Dabie eclogite as an example for UHP metamorphic rocks, because it's from the world's biggest, most representative and most thoroughly-studied UHP metamorphic zone (R. Y. Zhang et al., 2009). Dabie eclogites have endured both UHP metamorphism and retrograde alternation (Yui et al., 1997; Zheng et al., 2003), so the geochemical equilibrium in Dabie eclogites reflects the typical interaction between subduction slabs and fluids. Hydrogen isotope disequilibria is observed in Dabie eclogites, and is associated with fluid-induced retrograde alternation (Zheng et al., 2003). Oxygen isotope disequilibria is also observed between omphacite and garnet in Dabie UHP eclogites which shows retrograde alternation (Zheng et al., 2003). On the other hand, it has been observed that the magnesium isotope is in equilibrium between omphacite and garnet in Dabie eclogites, even though fluid-induced retrograde alternation has been observed on the sample. One hypothesis to explain the observed hydrogen/oxygen isotope disequilibria and magnesium isotope equilibria in Dabie eclogite is that the eclogite (Yui et al., 1997) or its protolith (Zhao et al., 2007) have been interacted with meteoric water. If that's the case, we should expect to see a silicon isotope equilibria similar to magnesium isotope equilibria in Dabie eclogites, because meteoric water is expected to have a much larger isotope effect on oxygen than on silicon/magnesium (Yui et al., 1997). However, published DFT calculations and mass spectroscopy measurements have shown inconsistencies on the silicon isotope fractionation in Dabie eclogites. For example, DFT calculations have suggested that heavy silicon isotope tends to enrich in garnet over clinopyroxene (Huang et al., 2014), whereas mass spectroscopy measurement shows the opposite (Y. Li et al., 2020).

In the recent years there have been several new mass spectroscopic studies on the Si isotope fractionation between rock-forming minerals (e.g., zircon, kyanite, omphacite and garnet) in igneous and metamorphic rocks (Guitreau et al., 2022; Y. Li et al., 2020; Trail et al., 2019), and there have been discussions on whether the equilibrium has been reached in these rock samples. The determination of isotopic equilibrium is important for these rocks because disequilibrium is usually associated with metasomatism and extensive rock-fluid interaction (Jahn et al., 2005; Kwon et al., 2020). Several DFT calculations have been performed (Huang et al., 2014; Y. Li et al., 2019; Qin et al., 2016), and while they are largely consistent with the attainment of isotopic equilibrium in igneous and metamorphic rocks, some small discrepancies still remain. For example, the calculated equilibrium Si isotope fractionation between quartz and kyanite (Y. Li et al., 2019) is about 10% higher than the mass spectroscopy measurements in Dabie eclogitic veins (Y. Li et al., 2020), raising the question whether the vein is chemically altered after its formation. The purpose of this paper is to extend our XRD *force constants* approach to examine these rock-forming minerals in eclogites and granites, and assess whether the mismatch between mass spectroscopy and DFT results indicates an isotopic disequilibrium. Principles of our methodology is reviewed in Text S1 in Supporting Information S1. We have compiled high-T single crystal XRD data on these rock forming minerals published in the past 40 years, and have collected new XRD data when the minerals are not covered by previous studies (Text S2 in Supporting Information S1). From the high-T XRD data, we have fitted the N_r of Si in these minerals using linear regression (Table S1 in Supporting Information S1), and have estimated their isotope fractionation β-factors as well as corresponding uncertainties using our XRD *force constants* approach (D. Z. Zhang et al., 2021). We then compared our results with DFT calculations and Urey equation (Text S3 and Table S2 in Supporting Information S1), published nuclear resonance scattering data and Monte Carlo simulation (Text S4 and Figure S2 in Supporting Information S1), as well as mass spectroscopy measurements on natural samples (see sections below). We also compared our result with the ionic model derived from the Urey equation and crystallographic data (Young et al., 2015) and received consistent results (Text S6 in Supporting Information S1 and Figure 1). We use our results to interpret the Si isotope fractionation behaviors in these metamorphic and igneous rocks.

2. Si Isotope Fractionation Between Omphacite and Garnet

Eclogite is one of the most important metamorphic rocks that is commonly formed during the ultra-high-pressure (UHP) metamorphism, and is usually associated with the orogeny and subduction process (Jahn et al., 2005; Y. Li et al., 2020). Eclogites from the Dabie-Sulu orogen in east-central China is of special geologic interest because (a) the Dabie-Sulu orogen is the world's largest and most representative UHP metamorphic belt (R. Y. Zhang et al., 2009), (b) isotopic data set on the Dabie eclogite is the most complete and covers a wide range of elements (H, O, Mg, Si, etc., Zhao et al., 2007; Zheng et al., 2003), and (c) many Dabie eclogites endured fluid-related retrograde alternation, and are good candidates to study the geofluid-rock interaction (Y. Li et al., 2020; Zheng et al., 2003). Eclogite formation often involves interaction with various geofluids, leading to fluid-induced metasomatism and resultant geochemical disequilibria (Jahn et al., 2005; Kwon et al., 2020; W. Li et al., 2011; Y. Li et al., 2020; Zheng et al., 2003). Such disequilibria are commonly used as indicators to determine the origin and composition of geofluids (Jahn et al., 2005; Kwon et al., 2020; Yui et al., 1997). The two major mineral components in eclogite are pyrope-almandine garnet and omphacite (Coleman et al., 1965; McNamara, 2012), yet not all elements/isotopes seem to have reached chemical equilibria between garnet and omphacite in eclogites. For example, measurements on trace element distribution patterns, Rb-Sr isotope and Sm-Nd isotope have suggested that garnet and omphacite found in Dabie Mountain eclogites are out of chemical equilibrium (Jahn et al., 2005), yet Mg isotopes are in equilibrium between omphacite and garnet in the eclogite sample collected in the same region (Jahn et al., 2005; W. Li et al., 2011). Whether Si isotopes are in equilibrium between omphacite and garnet in Dabie Mountain eclogite is still an open question. First-principles calculations have suggested that at equilibrium, heavy Si isotope prefers pyrope garnet to diopside (the Ca-Mg endmember of omphacite, Huang et al., 2014), whereas recent MC-ICP mass spectroscopy measurements have suggested that heavy Si isotope tends to be enriched in the omphacite phase in Dabie Mountain eclogites (Y. Li et al., 2020). The discrepancy between first principles calculation and mass spectroscopy measurements poses questions on whether equilibrium has been reached in the Dabie Mountain eclogites, and whether metasomatism has changed the Si isotopic behavior during the metamorphism. In the meantime, Meheut and Schauble (2014) reported that low electronegativity cations lightens the Si isotope signature in the phyllosilicates, and Rabin et al. (2021, 2023) reported that local chemical composition (nature and number of second neighbor) around Si atoms is correlated with the Si β-factor. We also explore the effect of local chemical environment to the Si isotope fractionation in eclogite.

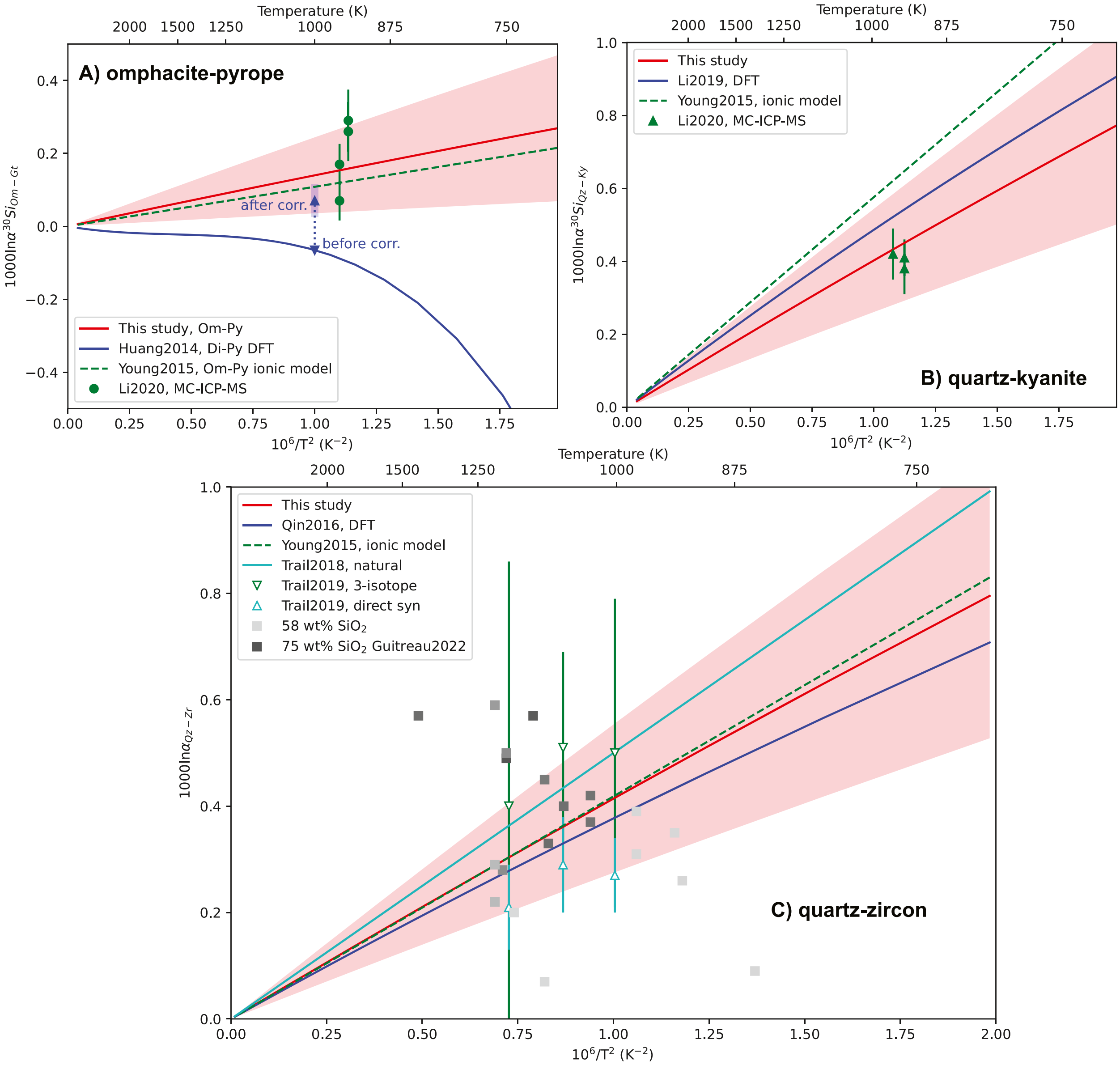

Figure 1. Equilibrium Si isotope fractionation between (a) omphacite and pyrope, (b) quartz and kyanite and (c) quartz and zircon. Red curves: X-ray diffraction (XRD) *force constants* approach. Red shaded regions: uncertainty range of the XRD *force constants* approach, determined following the Text S3 in Supporting Information S1. Blue curves: density functional theory (DFT) calculations. Green dashed lines: estimation using the ionic model (Young et al., 2015). Symbols: mass spectroscopy measurements. Blue triangles in panel (a): DFT calculated Si isotope fractionation lnα between Na-free diopside and pyrope (reversed, Huang et al. (2014)) and lnα between Na-bearing omphacite and pyrope (normal) corrected using the empirical relation between lnα and average Si-O bond length (Qin et al., 2016). Blue rectangle denotes the uncertainty of the correction. In panel (c), cyan curve: estimation from mass spectroscopy measurements on natural sample (Trail et al., 2018). Gray 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%).

We have compiled the force constants of omphacite and pyrope garnet from our high-T single crystal XRD data and published results (Table S1 in Supporting Information S1). We found that the N_r of garnet clustered around 57 N/m, while the N_r of omphacite scatters between 31 N/m and 43 N/m. We report the Si isotope fractionation between pyrope and omphacite using their average N_r (58 ± 5 N/m for pyrope, 37 ± 4 N/m for omphacite). Our calculation has suggested that the heavy Si isotope prefers to fractioning into omphacite at high temperature conditions (Figure 1a), which is consistent with the MC-ICP-MS measurements (Y. Li et al., 2020). We notice that the DFT calculation suggests that heavy Si isotope tends to enrich in garnet phase over Na-free diopside (Huang et al., 2014), and we suspect that the incorporation of Na in clinopyroxenes may affect the Si isotope fractionation. It has been found that the average Si-O bond length has a negative correlation with the isotope fractionation beta factor (Qin et al., 2016). We've examined the Si-O average bond lengths in diopside ($CaMgSi_2O_6$, Cameron et al. (1973) and Qin et al. (2016), average Si-O bond length = 1.636 ± 0.001 Å), jadeite ($NaAlSi_2O_6$, Cameron et al. (1973), average Si-O bond length = 1.625 ± 0.001 Å), and omphacite ($[Ca_{0.5}Na_{0.5}][Mg_{0.5}Al_{0.5}]Si_2O_6$, Pavese et al., 2000; D. Z. Zhang et al., 2016, average Si-O bond length = 1.630 ± 0.001 Å). We noticed that the average Si-O bond length decreases with Na-content in the mineral, so Na-bearing omphacite is expected to have a larger β-factor than Na-free diopside.

We estimate the effect of Na on the Si isotope fractionation between clinopyroxenes and pyrope in the following way. Qin et al. (2016) has estimated that the $^{30}Si/^{28}Si$ fractionation factor at 1000 K has an empirical relationship for all silicates except zircon and olivine: $\ln\beta_{Si} = -22.657 \times d(Si\text{-}O) + 44.543$ (unit: ‰). Using the average Si-O bond length in Na-bearing omphacite (1.630 ± 0.001 Å), the $\ln\beta_{Si}$ for omphacite would increase by 0.136 ± 0.045‰ compared to Na-free diopside (average Si-O bond length 1.636 ± 0.001 Å). Huang et al. (2014) provided the Si isotope fraction $\ln\alpha_{Si}$ between Na-free diopside and garnet at 1000 K $\ln\alpha_{SiDi\text{-}Gt} = -0.066$‰. When we apply the correction of 0.136 ± 0.045‰, the corresponding $\ln\alpha_{SiOm\text{-}Gt}$ at 1000 K would increase to 0.070‰, which suggest that heavy Si isotope prefers omphacite to garnet, and is consistent with the results from our *force constants* approach and mass spectroscopy measurements on the natural sample (Figure 1a). Our result also confirms that the omphacite and garnet in the UHP eclogite sample collected from Dabie Mountain on average is in equilibrium for Si isotopes. Our result indicates that, even if there is fluid-induced metasomatism involved in the formation of the Dabie Mountain eclogite sample, it is unlikely that the fluid would significantly change the Si isotopic composition in eclogite. Since Si (this study) and Mg (W. Li et al., 2011) isotope compositions are all in equilibrium in eclogites, whereas isotopic disequilibrium is observed for trace elements (Jahn et al., 2005) and aqueous elements (H and O, Yui et al., 1997; Zheng et al., 2003), we conclude that the fluid-induced metasomatism in Dabie-Sulu orogen does not significantly affect the isotopic composition of Si and Mg in eclogites, while it has a strong effect on the isotopic composition of trace and aqueous elements. Our results also demonstrate that Na significantly affects the Si isotope fractionation between omphacite and garnet. Considering the fact that DFT calculations on solid solutions are significantly more expensive than endmembers because the necessity to expand unit cell to supercells (Wang et al., 2020), this example also demonstrates the advantage to combine both experimental and computational results over pure computational/experimental approaches.

3. Si Isotope Fractionation Between Quartz and Kyanite

Kyanite is a common mineral in blue schist and some eclogites, and is usually associated with high-pressure, low temperature metamorphism related to orogeny (Whitney et al., 2008). In many cases, kyanite-bearing high pressure rocks (blue schists and/or eclogite) form lenses embedded in host rocks that contain low pressure minerals such as quartz. The co-existence of the high pressure lenses and the low pressure host rock has two possible tectonic explanations (Cuthbert et al., 2000). It is either the whole rock sample experienced the high pressure, but only the high pressure lenses preserved while the host rocks degraded to low pressure facies, or the high pressure lenses are tectonically mixed with the host rocks that never experienced high pressures (Whitney et al., 2008). To elucidate between the two possibilities, one may examine the isotope fractionation between the high pressure (e.g., kyanite) and low pressure (e.g., quartz) minerals. If the isotopic disequilibrium is observed between the two minerals, it is likely that the high pressure lenses are mixed tectonically with the host rocks. For example, the tectonic mixing of sub-microscopic crustal inclusions in eclogitic garnet has led to the Sm-Nd isotopic disequilibrium in Himalayan and Alpine eclogites (Luais et al., 2001). To examine the possibility of disequilibrium, we need an accurate determination of the equilibrium Si isotope fractionation between quartz and kyanite. To our knowledge, only one study has constrained the equilibrium Si isotope fractionation between the two minerals using DFT calculations (Y. Li et al., 2019). The Si isotope fractionation between quartz and kyanite estimated through calculations is similar to the measurement obtained by mass spectroscopy on the eclogites and host veins from Dabie Mountain, albeit with a slight deviation. This small discrepancy between DFT calculation and mass spectroscopy measurement raised a question of whether the eclogite and the host veins have endured the same pressure-temperature path during their formation.

We have examined this question using our approach and published high temperature XRD data. Because the estimated sample temperature in Y. Li et al. (2020) lays in the stability field of β-quartz (Heaney & Veblen, 1991), we calculate the Si isotope fractionation using the N_r of β-quartz (27 ± 4 N/m), and its effective coordination number (ECoN) is fixed as 4 due to symmetry. We note here that the DFT calculation by Y. Li et al. (2019) used the crystal structure of α-quartz, which is expected to be unstable at temperatures between 850 and 1000 K. The N_r of kyanite is determined as 49 ± 4 N/m and the ECoN is determined as 3.995 (Winter & Ghose, 1979). Using these parameters, we calculate the Si isotope fractionation between kyanite and β-quartz at various temperatures (Figure 1b). Our $\ln\alpha$-$10^6/T^2$ curve is lower than its counterpart calculated by DFT, and our result is a close match to the mass spectroscopy measurements on the natural sample (Y. Li et al., 2020). Our result suggests that the eclogite sample and its host veins are in equilibrium from the Si isotope perspective. Our result is compatible with the scenario that both the Dabie Mountain eclogite and the host vein endured the same pressure-temperature condition during their formation.

4. Si Isotope Fractionation Between Quartz and Zircon

Zircon is a very resilient mineral that resists chemical and physical erosions. It is commonly found in continental crusts, especially in felsic granites (Guitreau et al., 2022; Trail et al., 2018). The Si isotope fractionation between quartz and zircon has been used to study the petrogenesis of different granites (Guitreau et al., 2022; Trail et al., 2019). There have been both computational (Qin et al., 2016) and experimental (Guitreau et al., 2022; Trail et al., 2019) studies on the isotope fractionation between quartz and zircon at high temperature conditions, yet the results are not always consistent. The diffusion of major and trace elements in zircon is known to be very sluggish (Cherniak & Watson, 2003), so it is very difficult to establish equilibrium between zircon and other minerals during high P-T experiment, which presents a technical challenge for experiments to reach equilibrium. For example, Trail et al. (2019) has observed that during a piston-cylinder experiment between 725 and 900°C and up to 1099 hr, only less than 35% of Si has exchanged between zircon and SiO_2, and as a result, two different analyses (direct synthesis and 3-isotope) on the same sample resulted in enormous error in the Si isotope fractionation ($\ln\alpha_{\text{3-isotope}} \approx 1.75 \ln\alpha_{\text{dir-syn}}$). Geochemists are interested in a property named the A-value in the granite-zircon system, which is defined as the slope of the derivative of Δ^{30}Si between whole rock and zircon over inverse-square of temperature ($10^6/T^2$): $A = \Delta^{30}\text{Si}_{\text{WR-zr}}/(10^6/T^2)$. The A-value has been used as a proxy to estimate the Si isotope fractionation of the whole igneous rock using measurements only zircon and quartz (Trail et al., 2019). Numerically, the A-value equals to the Si isotope fractionation between the felsic granite and zircon at 1000 K. DFT based calculation has suggested that the A-value between quartz-endmember and zircon is 0.37 (Qin et al., 2016), whereas the mass spectroscopy measurement based on 3-isotope approach has determined the A-value between quartz-endmember and zircon is 0.53 (Trail et al., 2019), 40% higher than the DFT result. Such a big variation in the A-value makes it challenging to assess its trend with the source magma composition (Guitreau et al., 2022). More measurements on the Si isotope fractionation between quartz and zircon will help reduce the uncertainties in the trend between A-value and the SiO_2 content in the whole granite.

We have determined the Si isotope fractionation between quartz and zircon using our XRD *force constants* approach (Figure 1c). Since the temperature of granite petrogenesis is around 1000 K, which lies in the stability field of β-quartz, we use the N_r of β-quartz to calculate the Si isotope fractionation. Our calculation has shown that the Δ^{30}Si - $10^6/T^2$ curve for quartz/zircon system lies between the Δ^{30}Si and $10^6/T^2$ relations determined by DFT calculations (Qin et al., 2016) and 3-isotope measurements on high P-T synthetic samples (Trail et al., 2019), while its uncertainty range covers both results. At 1000 K, our calculation results in a $\Delta^{30}\text{Si}_{\text{qz-zr}}$ (numerical equivalent to the A-value) of 0.42 ± 0.09‰, which overlaps with the 3-isotope measurement (0.50 ± 0.29‰) and the Si isotope fractionation between felsic granite that contains 58–72 wt% SiO_2 and zircon (Guitreau et al., 2022) (Figure 1c).

We also investigated the A-value as a function of SiO_2 content in the whole granite by comparing our data with published mass spectroscopy measurements (Figure 2). Guitreau et al. (2022) tentatively assumed a linear trend between the A-value and the SiO_2 content in the whole rock, while Trail et al. (2019) suggested that the trend is likely non-linear. According to Dauphas et al. (2014) and Rabin et al. (2021), the stiffness and isotope fractionation ratios of Fe and Si in silicates should be a sigmoid function with respect to SiO_2 content. Therefore, we have used a sigmoid function with the following formula to fit the Guitreau et al. (2022) data.

$$A = \frac{L}{1 + e^{-k(x-x_0)}} + b,$$

where A is the A-value of the rock sample, x is the SiO_2 content of the rock, and L, b, k and x_0 are the fitting parameters. Our best-fit gave $L = 0.36 \pm 0.11$, $x_0 = 61.7 \pm 3.6$, $k = 0.25 \pm 0.20$ and $b = 0.14 \pm 0.06$. Figure 2

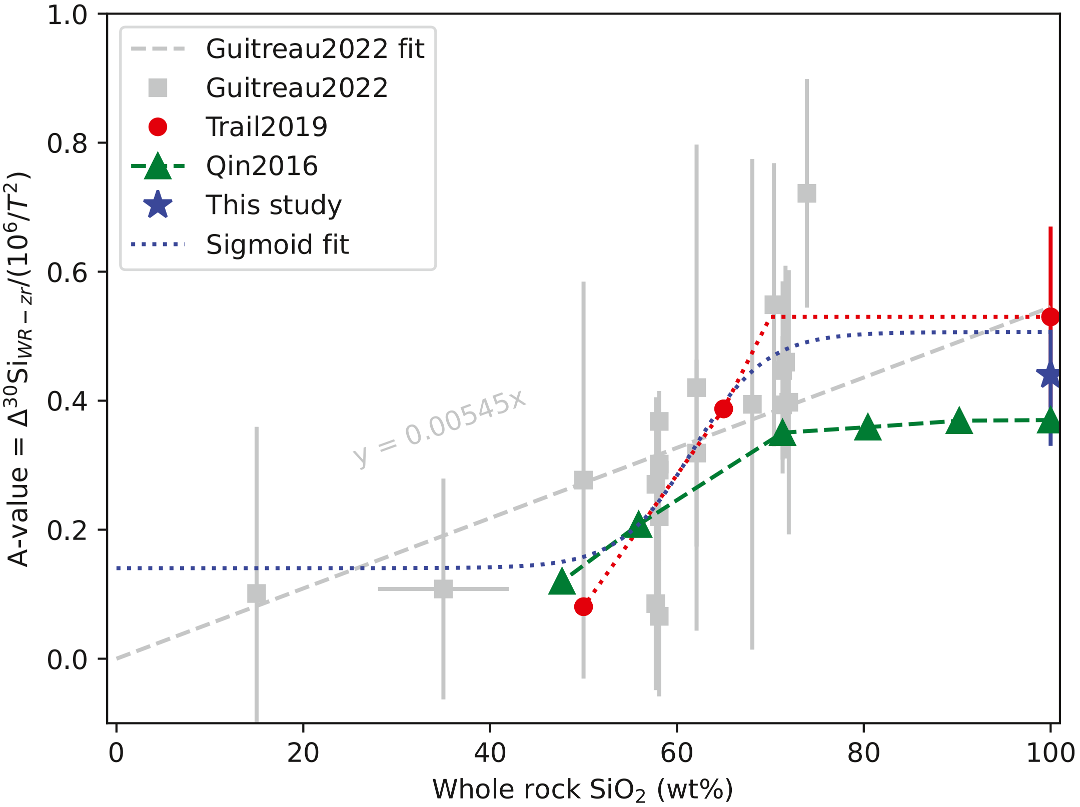

Figure 2. *A*-value as a function of whole rock SiO_2 content in natural igneous samples. Grey squares and dashed line: mass spectroscopy measurements on felsic granite and best linear fitting (Guitreau et al., 2022). Blue star: *A*-value determined from the Si isotope fractionation between quartz and zircon in this study (0.42 ± 0.09). Blue dotted curve: sigmoid fit to Guitreau et al. (2022) data. Green triangles: *A*-value of mineral assemblages calculated using density functional theory calculations and the CIPW worksheet provided by Qin et al. (2016). Red circles: mass spectroscopy measurements (Trail et al., 2019). Red dotted line: visual guideline for the "saturation" model using the Trail et al. (2019) data and assuming that the *A*-value plateaus when SiO_2 content in the granite reaches 70 wt%.

shows that the best-fit sigmoid function also shows a saturation at $A = 0.50 \pm 0.17$, which is coherent with our result (0.42 ± 0.09). We have also performed calculation based on the CIPW approach developed in Qin et al. (2016). This approach assumes bulk magma compositions, and then estimates normative mineral compositions of the whole rock using the CIPW worksheet (Qin et al., 2016, Supporting Information S1). The final silicon isotope fractionation between the whole rock and zircon is computed using the DFT-calculated β-factor of each mineral (Qin et al., 2016). We assumed magmas with different SiO_2 contents (basalt: 47.7 wt% SiO_2, Zambardi et al. (2014); andesite: 55.9 wt% SiO_2, Zambardi et al. (2014); granite: 71.3 wt% SiO_2, Qin et al. (2016); 70% granite + 30% quartz: 80.4 wt% SiO_2; 35% granite + 65% quartz: 90.2 wt% SiO_2), and the *A*-factors were calculated using the CIPW worksheet (Qin et al., 2016). The *A*-factors calculated by the CIPW approach show an obvious plateau when the magma SiO_2 content reaches 70 wt% (Figure 2, green triangles), and is consistent with our "saturation" hypothesis. By combining our data, the CIPW calculation and the mass spectroscopy measurements in the zircon/granite system, we conclude that the most probable *A*-value at "saturation" is ~0.45, which indicates that the equilibrium Si isotope fractionation Δ^{30}Si between zircon and the whole granite at 1000 K is ~0.45‰ for felsic granite whose SiO_2 content is above 70 wt%.

5. Concluding Remarks

In this paper we have applied the XRD *force constants* approach and our established calibration (D. Z. Zhang et al., 2021) to constrain the equilibrium Si isotope fractionation between common minerals (omphacite/pyrope, quartz/kyanite and quartz/zircon) in important metamorphic rocks (eclogite and schist) and granite, which are representative constituents in convergent continental margins and continental crusts. Compared to pure DFT calculations, our methodology has the advantages that it takes into account the experimental data at temperatures of relevant to the mantle and crust, and is expected to reflect the atomic dynamics which is usually non-processable by DFT simulations.

We applied our methods to the high-pressure to ultrahigh-pressure metamorphic eclogites and hosting veins collected in the Dabie Mountain region, and we noticed that Na strongly affect the Si isotope fractionation between omphacite and garnet. Our result suggests that the omphacite and garnet in Dabie Mountain eclogites are in equilibrium for Si isotopes. Combining our result with the observations on other elements (Jahn et al., 2005; W. Li et al., 2011; Yui et al., 1997; Zheng et al., 2003), we conclude that the fluid-induced metasomatism is unlikely to affect the isotopic composition of Mg and Si in Dabie Mountain eclogites. The Si isotope fractionation between quartz and kyanite also suggests that the eclogite and its surrounding veins are isotopically in equilibrium, implying that both the eclogite and the host vein likely endured the same pressure-temperature condition during their formation.

We have also investigated into the Si isotope fractionation between quartz and zircon, two common minerals in felsic granites. We found that the equilibrium Si isotope fractionation determined by the XRD *force constants* approach lies between the results of DFT calculations and high pressure-temperature synthesis experiments. By combining our results with published mass spectroscopy measurements on granites and DFT-CIPW calculations (Guitreau et al., 2022; Qin et al., 2016; Trail et al., 2019), we conclude that there is likely a threshold SiO_2 content (~70 wt%) for the granites, above which the A-value (slope between $\Delta^{30}\mathrm{Si}_{\mathrm{WR\text{-}zir}}$ and $10^6/T^2$) "saturates" at ~0.45. Our result indicates that the equilibrium Si isotope fractionation Δ^{30}Si between zircon and SiO_2-rich (>70 wt%) granite is around 0.45‰ at temperatures around 1000 K.

Data Availability Statement

The CIWP calculation workbooks to calculate the *A*-factors for different magma compositions (Figure 2) are available at D. Z. Zhang et al. (2024).

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