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Key Points:

- Debye model is used to fit the resilience of minerals from cryogenic crystallographic data
- Low temperature resilience is extrapolated to mantle temperatures to predict the Si isotope fractionation
- Fluid-rock interaction in Dabie and Alps orogens maintained the Si isotope signature

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Si Isotope Fractionation in Metamorphic Rocks From Cryogenic Temperature Crystallographic Data and Quantum Phonon Model

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Abstract In this study, we demonstrate that it is possible to fit the resilience at the high temperature limit using only the atomic mean square displacement determined from cryogenic temperature single crystal diffraction data. Our method introduces the Debye phonon model, under which the atomic mean square displacement displays quantum behavior at cryogenic temperatures and deviates from a linear temperature dependence. From the resilience of Si extrapolated from cryogenic temperature X-ray diffraction data, one can calculate the Si isotope fractionation using our recently developed force constants approach. We applied our method to epidote and coesite, which are common minerals in ultra-high pressure metamorphic rocks, and our predicted Si isotope fractionation $\ln\alpha_{\text{Si30/28}}$ are consistent with mass spectroscopy observations of $\Delta^{30}\text{Si}$ in Dabie eclogite and Alps whiteschist. Our results indicate that the geofluid involved in the fluid-rock interaction in Dabie and Alps orogens doesn't significantly alter the Si-isotope composition of ultrahigh pressure metamorphism. Our manuscript presents a novel experimental methodology to determine the high-temperature resilience and equilibrium isotope fractionation factors of silicon in minerals, which can be applied to the metastable upper mantle silicates that are non-quenchable at high temperatures and room pressure.

Plain Language Summary This study revisited the published low temperature X-ray and neutron diffraction data of epidote and coesite. By fitting the temperature dependence of atomic mean-square displacement to the quantum Debye phonon model, we could estimate the resilience of the Si atoms in epidote and coesite at temperatures higher than 600 K. The best-fit high temperature resilience of Si is used to estimate the Si isotope fractionation with the recent-developed force constants approach and is consistent with mass spectroscopy measurements on ultrahigh pressure metamorphic rocks. Our results suggest that the epidote and quartz in Dabie eclogitic veins, as well as the coesite and pyrope in Alps whiteschists are in equilibrium from a Si-isotope fractionation perspective. Our results also indicate that the geofluid involved in the fluid-rock interaction in Dabie and Alps orogens doesn't significantly alter the Si-isotope composition of ultrahigh pressure metamorphism.

1. Introduction

Stable isotope fractionation has been a central topic of interest in the geochemistry community. Among all elements, the isotope fractionation of Si is of special interest to geochemists studying metamorphism, because Si and O are the two most abundant elements in the earth's lithosphere, and Si isotope fractionation has been used to study the fluid-rock interaction (Li et al., 2020; Qin et al., 2016), metasomatism (Yu et al., 2024) and chemical weathering (Trail et al., 2018, 2019). Fluid-rock interaction plays an important role in crust-mantle mass exchange and is prevailing in ultra-high pressure (UHP) metamorphism and orogens (Li et al., 2020; Yu et al., 2024), while most studies on the Si isotope fingerprint of fluid-rock interaction focus on the low temperature region ($T < 500$ K). It is believed that during seawater-rock interaction, heavy Si isotope tends to fractionation into the fluid while the light Si isotope tends to incorporate into the precipitated minerals (Li et al., 2020; Trail et al., 2019; Yu et al., 2024). Such water-rock interaction is known to affect the O isotope fingerprint of UHP metamorphic rocks (Trail et al., 2018; Zheng et al., 2003), yet studies have indicated that the Si isotope fingerprint of the UHP metamorphic rocks hasn't been changed from their protolith (Li et al., 2020; Yu et al., 2024). Knowledge on the Si isotope fractionation of UHP eclogites will provide insight on the fluid composition

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(Li et al., 2020), amount of fluid and timing of fluid-rock interaction (Zheng et al., 2003) during the UHP metamorphic process.

For equilibrium isotope fractionation in crystalline solids, it has been demonstrated that the interatomic force constants play an important role, and have been successfully used to constrain the equilibrium isotope fractionation in elements like Fe (Blanchard et al., 2009; Dauphas et al., 2012; Polyakov & Mineev, 2000; Rabin et al., 2021; Sossi & O'Neill, 2017), Sn (Dauphas et al., 2018; Polyakov et al., 2005) and Si (Meheut et al., 2009; Meheut & Schauble, 2014; Qin et al., 2016; Zhang et al., 2021). There have been multiple ways to directly measure the interatomic force constants using spectroscopic methods such as nuclear resonant scattering (Dauphas et al., 2012, 2018; Polyakov et al., 2005) and single crystal diffraction (Zhang et al., 2021, 2025). These spectroscopic methods are mature, and over the past few decades a lot of spectroscopic data have been accumulated on various minerals, many of which are potential candidates to constrain the isotope fractionation in earth and planetary materials. However, since most of these spectroscopic data set were collected for different purposes (e.g., to study thermal expansion (Gatta et al., 2012), phase transition and diagram (Gatta et al., 2010), and chemical bonding (Smyth et al., 1987)), the data were not collected at the mantle conditions ($T > 600$ K). Some high pressure minerals (e.g., coesite) are metastable at ambient P-T condition, yet the crystals will not survive high temperatures because they will transform to stable low pressure phases during heating. As a result, cryogenic temperature single crystal diffraction provides the only variable-temperature crystallographic data for those metastable minerals. Extrapolation from cryogenic temperature experimental condition ($T < 200$ K) to mantle condition ($T > 600$ K) is necessary to study the isotopic behaviors in igneous and metamorphic rocks.

In this manuscript, we would like to demonstrate the following: The cryogenic temperature crystallographic data show distinct behavior compared to the high temperature data, and produces interatomic force constants that are significantly different if the high temperature linear relationship between atomic mean-square displacement and temperature is used to fit the data; however, when cryogenic temperature data set is properly extrapolated to high temperature using a quantum Debye phonon model, the interatomic force constants from two different data sets converge, and the results are in agreement with the isotope fractionation behavior constrained by mass spectroscopy on samples of geological interest. Our crystallographic data set come from multiple studies published by different groups, which reduces the subjective bias of this methodology. Finally, we will use our result to interpret the Si isotope signature of UHP eclogites from Dabie and Alps orogens, which are two of the most representative UHP metamorphic zones.

2. Theoretical Background: Atomic Mean-Square Displacement, Force Constant and Debye Phonon Model

It is known that the atoms in minerals vibrates at finite temperatures (Trueblood et al., 1996). The amplitude of the atomic vibrations is described by the atomic mean-square displacement ($\langle u^2 \rangle$). One kind of force constant, the resilience (N_r), is determined by the temperature derivative of $\langle u^2 \rangle$ at the high temperature limit (Zaccai, 2000):

$$N_r = \frac{k_B}{d\langle u^2 \rangle/dT}, \quad (1)$$

where T is temperature and k_B is the Boltzmann constant.

The value of $\langle u^2 \rangle$ is a function of temperature. Although at temperatures relevant to the mantle ($T > 600$ K), the temperature dependence of $\langle u^2 \rangle$ approximates to a linear trend, at cryogenic temperatures ($T < 200$ K), the quantum effect deviates the temperature dependence of $\langle u^2 \rangle$ from the linear trend at high temperatures (Dunitz et al., 1988). In crystalline materials, the atomic vibrations are quantized as phonons (Dauphas et al., 2012; Polyakov et al., 2005), so we could use phonon models to describe the atomic vibrational behavior at various temperatures. In this paper we utilize the Debye phonon model, which properly describes the cryogenic temperature thermodynamic behavior in many crystalline solids, to study the cryogenic temperature atomic vibrations (Zhang et al., 2022). The Debye phonon model has the following phonon density of states (Zhang et al., 2022):

$$g(E) = \begin{cases} \frac{3E^2}{(k_B\theta)^3} & (E \leq k_B\theta) \\ 0 & (E > k_B\theta) \end{cases} \quad (2)$$

where E is the phonon energy, and the parameter θ is the material-specific Debye temperature. Under the Debye phonon model, the temperature dependence of $\langle u^2 \rangle$ approximates to (Zhang et al., 2022):

$$\langle u^2 \rangle = \frac{3\hbar^2}{Mk_B\theta} \left[\frac{1}{4} + \left(\frac{T}{\theta} \right)^2 \int_0^{\frac{\theta}{T}} \frac{x}{e^x - 1} dx \right] + \langle u_0^2 \rangle, \quad (3)$$

where $\hbar$ is the reduced Planck constant and M is the atomic mass. $\langle u_0^2 \rangle$ is the static disorder originating from the crystal defect, and doesn't change with temperature (Parak & Knapp, 1984). At high temperature limit ($T \rightarrow \infty$), $\langle u^2 \rangle \approx \frac{3\hbar^2 T}{Mk_B\theta^2} + \langle u_0^2 \rangle$, and $\langle u^2 \rangle$ is linearly dependent to temperature T . Under the Debye model, the resilience N_r approximates to the following equation when $E/k_B T$ is sufficiently small (Hu et al., 2013):

$$N_r = \frac{M}{\int \left(\frac{\hbar}{E} \right)^2 g(E) dE} = \frac{Mk_B^2\theta^2}{3\hbar^2}. \quad (4)$$

It is worth mentioning that, based on Equation 4, at the high temperature limit, we have the following temperature dependence of $\langle u^2 \rangle$ (Equation 5), which is equivalent to Equation 1. Equation 5 is usually used to calculate the resilience of minerals from high-temperature X-ray diffraction data.

$$\langle u^2 \rangle = \frac{k_B T}{N_r} + \langle u_0^2 \rangle. \quad (5)$$

Here we discuss how the uncertainty of resilience (dN_r) is estimated in this study. For each kind of mineral, there could be multiple Si sites and multiple measurements. Besides the error of each individual force constant measurement for each site ($\sigma_{N_{ij}}$), the values of force constants scatter among different sites and measurements. Therefore, we use pooled variance to estimate the uncertainty for the N_r of each mineral (Zhang et al., 2025).

$$dN_r = \sqrt{\frac{\sum_{i=1, j=1}^{i=M, j=N} (N_{ij}^2 + \sigma_{N_{ij}}^2)}{MN} - \frac{(\sum_{i=1, j=1}^{i=M, j=N} N_{ij})^2}{M^2 N^2}}, \quad (6)$$

where N_{ij} is the resilience from each individual measurement on each Si site, $\sigma_{N_{ij}}$ is the error of each individual measurement, M is the total number of measurements and N is the total number of Si sites in each mineral. In this study, the $\sigma_{N_{ij}}$ of each Si sites is fitted using the LMFIT software package (Newville et al., 2025) using Equations 3 and 4. We notice that some minerals investigated in this study suffers the “sparse data” problem, that is, when the total number of measurement $M = 1$, Equation 6 can't reflect the scatter of N_r among different measurements (Zhang et al., 2025). Hence for a mineral, if $M = 1$, we assign an overestimated $dN_r = 4 N/m$, so that the dN_r of that specific mineral is comparable with other minerals that have multiple diffraction measurements (Zhang et al., 2025).

3. From Cryogenic Temperature Crystallographic Data to the Force Constant of Epidote

Epidote is a silicate mineral, that is, commonly found in metamorphic basalts and gabbros that are associated with low grade metamorphism and hydrothermal events ($T \sim 600$ K, (Li et al., 2019; Li et al., 2020)). The ideal chemical formula of endmember epidote is $\text{Ca}_2(\text{Al}_2\text{Fe}^{3+})(\text{Si}_3\text{O}_{12})(\text{OH})$, and it has a $P2_1/m$ space group with three unique Si sites (usually labeled as Si1, Si2 and Si3 in crystallographic studies (Gatta et al., 2012)). High quality single crystal diffraction data have been obtained for epidote at temperatures ranging from 100 to 1000 K (Gatta et al., 2010, 2012). Moreover, a recent study has measured the Si isotope composition in eclogitic epidote using

high-precision mass spectroscopy (Li et al., 2020). Density Functional Theory (DFT) calculations have also been carried out on epidote to build a geothermometer (Li et al., 2019), allowing for theoretical equilibrium Si isotope fractionation to be compared with experimental result. Considering these aspects, epidote is an ideal candidate for the scope of this manuscript.

To date, two high-quality crystallographic data at various temperatures have been published on epidote, by the same group. Gatta et al. (2010) used single crystal neutron diffraction to study a natural epidote crystal between 293 and 1070 K. The crystal used in the 2010 study was from the intrusive metamorphic complex in Italian Alps and had a composition of $\text{Ca}_{1.925}(\text{Al}_{2.265}\text{Fe}_{0.745})(\text{Ti}_{0.004}\text{Si}_{3.037}\text{O}_{12})(\text{OH})$. In a later study, (Gatta et al., 2012) studied the cryogenic temperature behavior of the same natural epidote between 100 and 295 K using X-ray diffraction. In both studies, the crystal structure was well refined at each temperature. The atomic displacement parameter of Si has been well documented. Over the temperature range investigated, the epidote crystal demonstrated a chemical stability, and no dehydration or atomic diffusion were observed (Gatta et al., 2010, 2012).

The temperature dependences of the $\langle u^2 \rangle$ for the three Si sites in epidote (Si1, Si2 and Si3) are plotted in Figure 1. Si1, Si2 and Si3 sites each has its own N_r value because they have slightly different chemical environments, and in this study, the N_r of Si1, Si2 and Si3 sites are fitted individually using LMFIT package (Newville et al., 2025). Since the ratio of Si1, Si2 and Si3 sites in epidote is 1:1:1, the average N_r of the Si1, Si2 and Si3 sites are reported as N_r for the epidote mineral. To derive N_r from the temperature dependence of $\langle u^2 \rangle$, we utilized two methods. The first one is the linear-fit, which assumes that the temperature dependence of $\langle u^2 \rangle$ follows Equation 5, so that N_r is computed following Equation 1. Based on the theory mentioned above, the linear-fit is valid for data collected at high temperatures, so we fitted the high temperature neutron diffraction data using the linear-fit method.

We have also fitted the low-temperature X-ray diffraction data with the linear-fit method, yet we have noticed that the best-fit N_r by linearly fitting all the cryogenic temperature X-ray data (62 ± 9 N/m) is significantly higher than the best-fit N_r from the high temperature neutron data (39 ± 9 N/m). We propose that such deviation in linear-fit N_r is because the temperature dependence of $\langle u^2 \rangle$ is no longer linear at cryogenic temperatures. We have carried out two tests to examine our hypothesis. First, we fit the relatively higher temperature section (185–295 K) of the cryogenic temperature diffraction data, which gives a N_r of 48 ± 11 N/m, that is, closer to the high temperature neutron diffraction results. This indicates that the cryogenic temperature X-ray diffraction $\langle u^2 \rangle$ from Gatta et al. (2012) deviates from the linear trend at the high temperature limit (Equation 5). Then, we numerically fit the whole cryogenic temperature diffraction $\langle u^2 \rangle$ data set from Gatta et al. (2012) using a non-linear function (Equation 3) to get the best-fit θ , and further calculate N_r using Equation 4. The non-linear fitting resulted in a best-fit N_r of 42 ± 3 N/m, that is, consistent with the high temperature neutron diffraction data from (Gatta et al., 2010). All the best-fit N_r from different data sets and models are summarized in Table 1. One observation, that is, worth mentioning here is that N_r constrained from the $\langle u^2 \rangle$ measured by the X-ray diffraction at high temperature limits (42 ± 3 N/m) is consistent with N_r constrained from the $\langle u^2 \rangle$ measured by neutron diffraction (39 ± 9 N/m), although X-ray diffraction probes the electronic part of the atom while the neutron scattering probes the nuclei of the atom. This observation demonstrates the fact that high quality diffraction data, whether collected through X-ray diffraction or neutron diffraction, properly reflects the atomic vibrational properties in crystalline minerals. In conclusion, while a linear-fit to the relative higher temperature (185–295 K) subset of the cryogenic data yields a N_r (48 ± 11 N/m) that is compatible to the neutron diffraction value (39 ± 9 N/m), the Debye model fit to the entire low-temperature data set provides a N_r value (42 ± 3 N/m), that is, both more precise and accurate. This supports the superiority of the Debye model for extrapolation of N_r from low temperature data set of $\langle u^2 \rangle$ to high temperature.

Using the cryogenic temperature diffraction data set from Gatta et al. (2012), we are able to compare the coefficient of determination (R^2) from both the linear model and the Debye model, so as to assess the fitting quality for each model. R^2 is defined as (Newville et al., 2025):

$$R^2 = 1 - \frac{\sum_i (y_i - f_i)^2}{\sum_i (y_i - \bar{y})^2}, \quad (7)$$

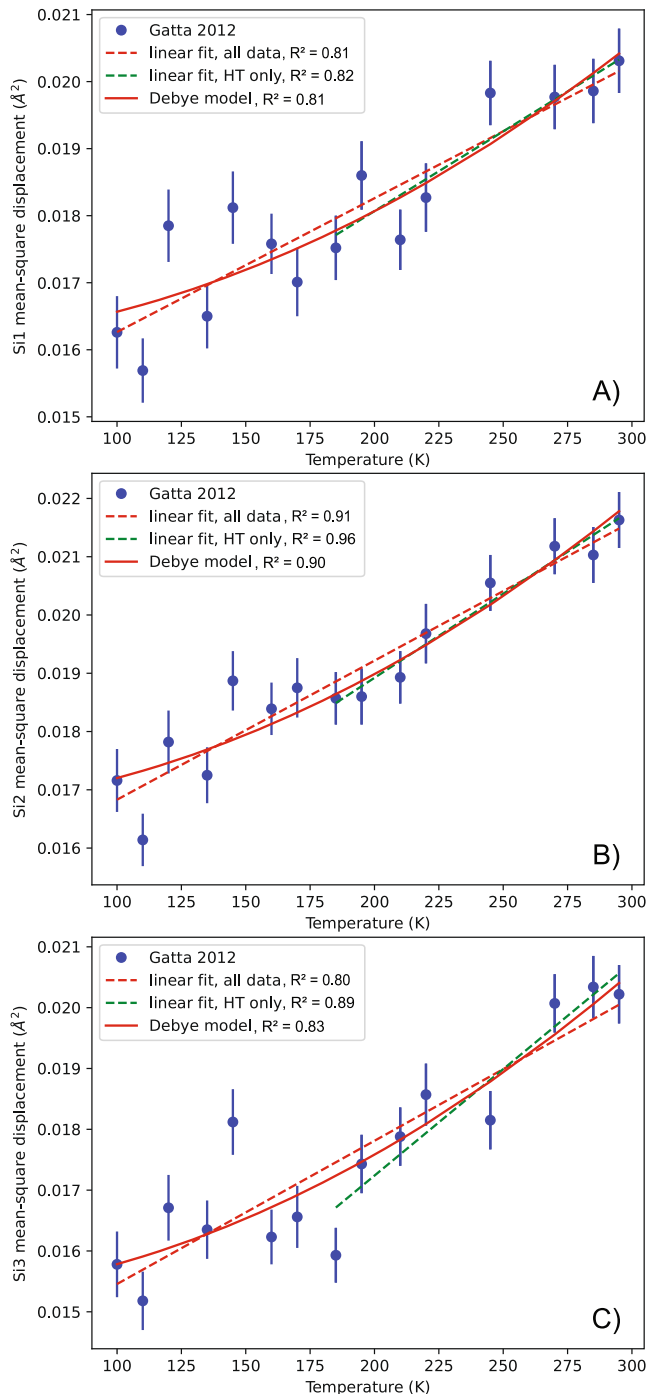


Figure 1. Atomic mean square displacement ($\langle u^2 \rangle$) for Si1 (a), Si2 (b) and Si3 (c) sites in epidote constrained by cryogenic temperature single crystal diffraction and their best-fit temperature dependence. Best-fit R^2 for each model is labeled. Blue circles with error bar: reported atomic mean-square displacement and its corresponding uncertainty from (Gatta et al., 2012). Red solid curves: best-fit temperature dependence to all experimental data based on Debye model. Red dashed line: best linear fit to all experimental data. Green dashed line: best linear-fit to experimental data between 185 and 295 K.

where y_i is each observed data, $\bar{y}$ is the mean of the observed data, and f_i is each modeled value. The larger the R^2 is, the better the model replicates the data set. Over the full temperature range (100–295 K) investigated by (Gatta et al., 2012), the linear model gives a best-fit $R^2 = 0.81$ for Si1 site, $R^2 = 0.91$ for Si2 site and $R^2 = 0.80$ for Si3 site, whereas the Debye model gives a best-fit $R^2 = 0.81$ for Si1 site, $R^2 = 0.90$ for Si2 site and $R^2 = 0.83$ for Si3 site. Statistically, the Debye model provides the same fitting quality in comparison with the linear regression. We note here that R^2 is only a good measure for fitting model with the same data set. Although linear regression with $T > 185$ K data (HT-only model in Table 1) generates better R^2 (Figure 1), because the HT-only model fits significantly smaller number of datapoints, the best-fit N_r from the HT-only model still has larger uncertainty (Table 1).

4. Force Constant of Si in Coesite: Handling the Sparse Data

Coesite is a common mineral indicator for ultrahigh pressure metamorphism. Yu et al. (2024) has measured the Si isotope fractionation between coesite and pyrope in Alps whiteschists and leucophyllites, and the authors found that the Si isotope composition of these metamorphic samples are inherited from their protoliths. The Alps whiteschist samples are estimated to be formed at $\sim 730^\circ$ C (1003 K) and ~ 4 GPa (Yu et al., 2024). However, as Yu et al. (2024) has pointed out, studies on the $\ln\beta$ of Si in coesite is lacking, because coesite has a much more complex structure than other common silica polymorph. Coesite crystal has a monoclinic C2/c space group, and its lattice parameters are $a \approx 7.14$ Å, $b \approx 12.38$ Å, $c \approx 7.18$ Å, and $\beta \approx 120.3^\circ$ (Smyth et al., 1987). Coesite has two independent Si sites, namely Si1 and Si2 (Smyth et al., 1987). It's very challenging to carry out high temperature single crystal diffraction on coesite, because it's a metastable phase at room pressure. So far, only one variable-temperature single crystal diffraction data set of coesite is available (Smyth et al., 1987), and the published diffraction data were measured at 15 and 292 K.

We attempt to extrapolate the Debye-Waller factor and resilience of coesite from 15 to 1003 K (Figure 2), and calculate the Si $\ln\beta$ using our force-constants approach (Zhang et al., 2021). For each Si site, only 2 data points of $\langle u^2 \rangle - T$ are available. Equation 3 has only two independent variables, namely the Debye temperature θ and the static disorder $\langle u_0^2 \rangle$, so it is possible to numerically solve θ and then calculate N_r using Equation 4. We found $\theta = 329$ K for Si1 site and 339 K for Si2 site in coesite, and their corresponding N_r are 29 N/m and 31 N/m, respectively. The average N_r for coesite based on Debye model is 30 N/m. Since coesite belongs to the “sparse data,” the uncertainty of N_r is estimated as $dN_r = 4$ N/m. We have also fitted the N_r using the linear model, and the estimated $N_r = 42$ N/m. Similar to epidote, the linear model over the full temperature range significantly overestimates N_r (Table 2). We would like to emphasize that, while the Debye model provides a physically more reasonable extrapolation than the linear model for coesite, the result is based on very sparse data and consequently carries a large uncertainty. The estimation of $dN_r = 4$ N/m is pragmatic and is based on our statistics of other tetracoordinated silicates (Zhang et al., 2025). Future studies with more low-temperature data points are needed to better constrain the resilience of coesite.

Table 1

Resilience (N_r) of Each Si Site and Their Average Computed From Different Crystallographic Data Sets of Epidote

Reference	Condition	Resilience, N_r (N/m)			
		Si1 site	Si2 site	Si3 site	Average
Gatta et al. (2010)	Neutron, 293–1070 K, linear fit	38(4)	45(11)	35(7)	39(9)
Gatta et al. (2012), all data	XRD, 100–295 K, linear fit	69(8)	58(5)	59(7)	62(9)
Gatta et al. (2012), HT only	XRD, 185–295 K, linear fit	58(11)	49(6)	39(5)	48(11)
Gatta et al. (2012)	XRD, 100–295 K, Debye model	46(2)	41(1)	40(2)	42(3)

Note. The averaged resilience from Debye model (highlighted in bold) is used to calculate the Si isotope fractionation. Numbers in the parenthesis are the uncertainty to the last significant digit determined using the methodology described in Section 2.

5. Si Isotope Fractionation in Metamorphic Rocks and Geochemical Implications

The purpose of determining N_r of Si atoms in epidote and coesite is to constrain the equilibrium Si isotope fractionation in epidote-bearing rocks using the recently developed force constants approach (Zhang et al., 2021). The procedures to constrain the Si isotope fractionation β -factor in epidote are briefly outlined here. We first convert resilience N_r to stiffness N_s using our established empirical calibration:

$$N_s = \frac{N_r}{C_s} = \frac{N_r}{A \times N_r + B}, \quad (8)$$

where A and B are best-fit calibration coefficients. Tetrahedral Si has been calibrated with best-fit $A = 1.63(6) \times 10^{-3}$ m/N and $B = -5.20(2) \times 10^{-3}$ (Zhang et al., 2021). The N_s is then further corrected for crystal distortion:

$$N_{sC} = N_s \times \frac{\text{ECoN}}{4}, \quad (9)$$

where ECoN is the effective coordination number (3.965 for epidote and 3.997 for coesite, (Gatta et al., 2012; Smyth et al., 1987)). Finally, the corrected N_{sC} is used to compute the Si isotope fractionation β -factor using the following equation:

$$\ln \beta_{l/l^*} = \left(\frac{1}{M^*} - \frac{1}{M} \right) \left(\frac{\hbar^2}{8k_B^2} \frac{N_{sC}}{T^2} - \frac{5\hbar^4}{2016k_B^4 M} \frac{N_{sC}^2}{T^4} + \frac{25\hbar^6}{326592k_B^6 M^2} \frac{N_{sC}^3}{T^6} \right), \quad (10)$$

where M and M^* are the atomic masses of isotopes l and l^* .

We estimate the uncertainty of $\ln \beta_{l/l^*}$ using the following approach. Once the N_r and its pooled variance dN_r is determined from XRD experiment (see Section 2), N_s is then derived from Equation 8, and its uncertainty is estimated from the differential of Equation 8:

$$dN_s = \frac{|B|dN_r}{(AN_r + B)^2}, \quad (11)$$

where A and B are the best-fit calibration coefficients in Equation 8. The uncertainty range of the corresponding isotope fractionation $\ln \beta$ is estimated by:

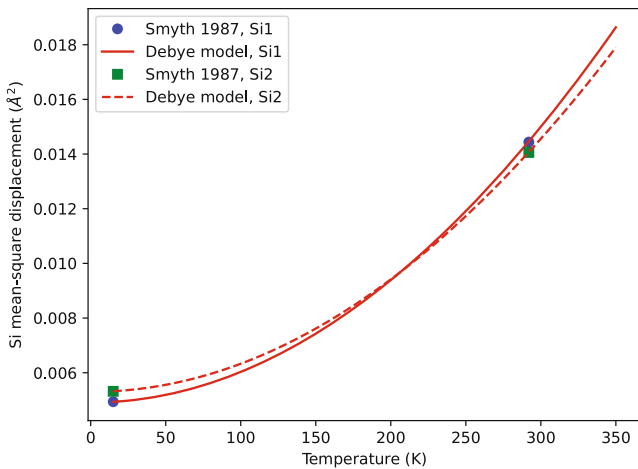


Figure 2. Atomic mean square displacement ($\langle u^2 \rangle$) for Si1 (blue circle) and Si2 (green square) sites in coesite constrained by cryogenic temperature single crystal diffraction. The temperature dependence based on the Debye phonon model for Si1 (red solid curve) and Si2 (red dashed curve) is solved using Equation 3.

Table 2

Resilience (N_r) of Each Si Site and Their Average of Coesite Computed From Linear Model and Debye Model

Reference	Condition	Resilience, N_r (N/m)		
		Si1 site	Si2 site	Average
Smyth et al. (1987)	Neutron, 15 and 292 K, linear model	40	44	42
	Neutron, 15 and 292 K, Debye model	29	31	30

Note. Neutron diffraction data is retrieved from Smyth et al. (1987). The fitting error of N_r is 0 and $R^2 = 1$ because there are only two $\langle u^2 \rangle - T$ data points and each model has two free variables. The reported uncertainty of average N_r of Si in coesite is estimated to be ± 4 N/m so as to be consistent with other minerals with sparse data points (Zhang et al., 2025).

$$\ln \beta_{l/r} \pm = \left(\frac{1}{M^*} - \frac{1}{M} \right) \left(\frac{\hbar^2}{8k_B^2} \frac{N_{sC} \pm dN_s}{T^2} - \frac{5\hbar^4}{2016k_B^4 M} \frac{(N_{sC} \pm dN_s)^2}{T^4} + \frac{25\hbar^6}{326592k_B^6 M^2} \frac{(N_{sC} \pm dN_s)^3}{T^6} \right). \quad (12)$$

The uncertainty range of the corresponding isotope fractionation $\ln \alpha$ between two minerals A and B is estimated by:

$$\ln \alpha_{A-B,+} = \ln \beta_{A+} - \ln \beta_{B-} \quad (13)$$

$$\ln \alpha_{A-B,-} = \ln \beta_{A-} - \ln \beta_{B+}$$

We used the average N_r of Si from the non-linear fit of the cryogenic temperature XRD data from Gatta et al. (2012) (42 ± 3 N/m). N_r of Si for quartz is determined to be 27 ± 1 N/m (Zhang et al., 2025). Using these numbers, we have computed the Si equilibrium isotope fractionation α factor between quartz and epidote, and have compared it with both DFT calculations (Li et al., 2019) and mass spectroscopy measurements of $\Delta^{30}\text{Si}$ (Li et al., 2020; Figure 3). We found that the $\ln \alpha$ calculated by DFT from Li et al. (2019) is $\sim 30\%$ higher than the mass spectroscopy measurements and our force constants calculations at temperature of 950 K, which is expected to be

the vein crystallization temperature for the eclogitic magma estimated by self-consistent thermodynamic modeling (NCKFMASH, (Guo et al., 2012; Guo et al., 2015)). The NCKFMASH modeling has a precision of 30 K (Holland & Powell, 1998; Powell et al., 1998; White et al., 2001). The Si isotope geothermometer from Li et al. (2019) overestimated the equilibrium temperature by ~ 100 – 200 K, which the authors owed to kinetic processes such as chemical and thermal diffusion or experimental uncertainty. Our results on the Si isotope fractionation suggests that the quartz and epidote should be in chemical equilibrium in the mass spectroscopy-investigated Dabie eclogite host rock at its formation temperature of 950 K. Using normalization isocon diagram and mass balance calculations (Guo et al., 2009), the Dabie eclogite rock investigated by mass spectroscopy is estimated to have lost $20 \pm 10\%$ of Si in the bulk rock during the fluid-rock interaction (Guo et al., 2012, 2015), whereas our Si isotope fractionation model at 950 K still fits the measured $\Delta^{30}\text{Si}$ in Dabie eclogite. Therefore, we conclude that the lower temperature rock-fluid interaction didn't modify the Si isotopic signature. Our result supports the hypothesis that the fluid percolation did not significantly change the Si isotopic composition in Dabie eclogite, and the geofluid likely have a similar Si isotopic signature with the eclogite (Li et al., 2020).

We have also investigated the $\ln \alpha$ between coesite and pyrope (Figure 4). In our calculation, the N_r of Si in coesite is determined as 30 ± 4 N/m and the N_r of Si in pyrope is determined to be 58 ± 5 N/m (Zhang et al., 2025). Using the garnet-clinopyroxene-phengite thermometer based on self-consistent KCMASH thermodynamic modeling, the Alps whiteschist's formation

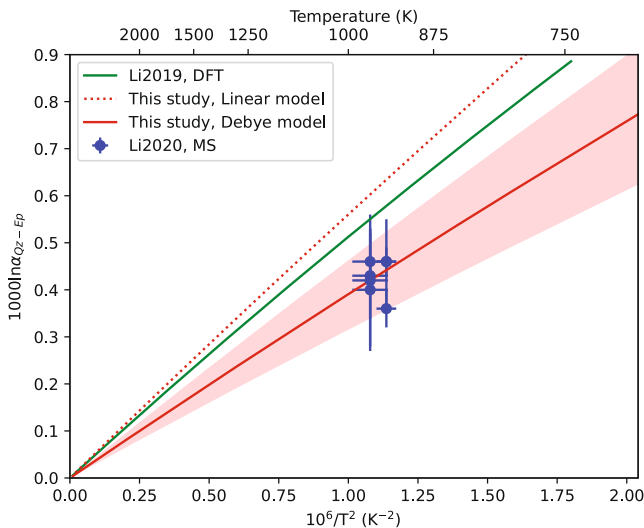


Figure 3. Calculated $\ln \alpha_{\text{Si30/28}}$ between quartz and epidote, compared to mass spectroscopy measurements on Dabie eclogitic veins (blue circles; Li et al., 2020). Green curve: DFT calculated $\ln \alpha_{\text{Si30/28}}$ (Li et al., 2019). Red solid curve: $\ln \alpha_{\text{Si30/28}}$ determined from the force constants approach and epidote resilience fitted using the Debye model ($N_r = 42$ N/m). Red dotted curve: $\ln \alpha_{\text{Si30/28}}$ when epidote resilience fitted using the linear model over the whole temperature range ($N_r = 62$ N/m). Red shaded region highlights the uncertainty estimated by Equation 13.

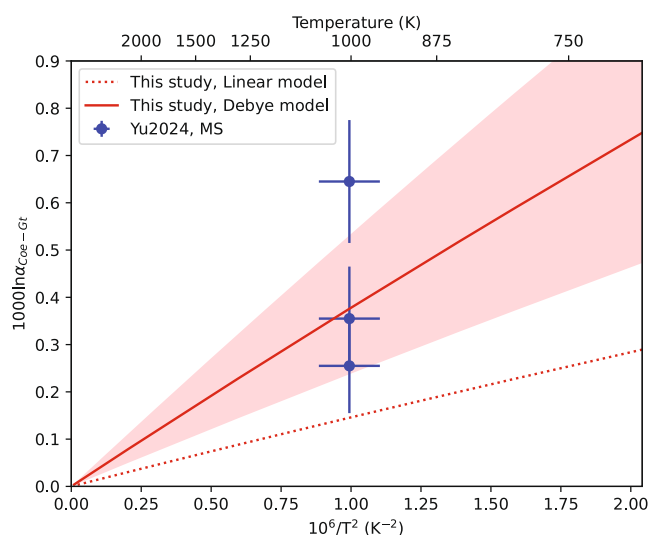


Figure 4. Calculated $\ln \alpha_{\text{Si30/28}}$ between coesite and pyrope, compared to mass spectroscopy measurements on Alps whiteschists (blue circles; Yu et al., 2024). Red solid curve: $\ln \alpha_{\text{Si30/28}}$ determined from the force constants approach and coesite resilience fitted using the Debye model ($N_r = 30$ N/m). Red dotted curve: $\ln \alpha_{\text{Si30/28}}$ when coesite resilience fitted using the linear model ($N_r = 42$ N/m). Red shaded region highlights the uncertainty estimated by Equation 13.

temperature is estimated to be 1003 ± 60 K ($730 \pm 60^\circ\text{C}$, Castelli et al. (2007), Krogh Ravna and Terry (2004), Yu et al. (2024)). Our modeled $\ln \alpha$ between coesite and pyrope at 1003 K is $0.38 \pm 0.14\%$, which is close to the average $\Delta^{30}\text{Si}_{\text{coe-gt}}$ measured by mass spectroscopy in Alps whiteschists ($0.42 \pm 0.16\%$, (Yu et al., 2024)). Our result indicates that the coesite and pyrope are in equilibrium for Si isotopes during the formation of Alps whiteschists. Similar to Dabie eclogite, this observed Si isotopic equilibria is an indicator that the geofluid involved in the metamorphic process doesn't significantly alter the Si-isotope composition, and as a result, the Si isotope signature of the metamorphic rocks preserves their protolith composition (Li et al., 2020; Yu et al., 2024). We also note that $\Delta^{30}\text{Si}_{\text{coe-gt}}$ in the Alps whiteschists have a huge variation in values, which likely comes from the pressure variation in the whiteschist formation (Huang et al., 2014). Due to the lack of high pressure data, we can't constrain the effect of pressure on $\ln \alpha_{\text{coe-gt}}$. It's possible that the pressure will affect the $\ln \beta$ of both coesite and pyrope, which leads to the variation in the observed $\ln \alpha_{\text{coe-gt}}$ (Yu et al., 2024).

6. Conclusions

In this study, we revisited the published X-ray and neutron diffraction data of epidote and coesite from 15 to 1070 K. The temperature dependence of $\langle u^2 \rangle$ collected at cryogenic temperatures ($T < 200$ K) allows to fit the quantum Debye phonon model, so that we could fit the N_r of the Si atoms in epidote and coesite at high temperatures ($T > 600$ K) more accurately.

Our methodology has demonstrated how to properly extrapolate the information extracted from low-temperature X-ray diffraction data sets to high temperatures. Considering that there are many commercially available diffractometers equipped with cryogenic temperature stages, while diffraction experiments around 1000 K are still challenging, our method should significantly reduce the difficulty to reliably measure resilience in crystalline minerals. Our results also show that, when one studies the atomic vibrational behaviors in crystals at temperatures below 200 K, the quantum Debye phonon model should be used, and this model can be extrapolated to mantle temperatures while still properly reflecting the atomic vibrational behaviors.

The best-fit high temperature N_r of Si is used to compute the Si isotope fractionation with our force constants approach. Our results suggest that the epidote and quartz in Dabie eclogitic veins, as well as the coesite and pyrope in Alps whiteschists are in equilibrium from a Si-isotope fractionation perspective. Our results also indicate that the geofluid involved in the fluid-rock interaction in Dabie and Alps orogens doesn't significantly alter the Si-isotope composition of ultrahigh pressure metamorphism. As a result, the Si isotope signature of the metamorphic rocks should preserve their protolith composition.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

All the crystallographic data analyzed in this paper has been published. The data files used in this paper are available at (Gatta et al., 2012; Smyth et al., 1987).

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