

# Geochemistry, Geophysics, Geosystems



# **RESEARCH ARTICLE**

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#### **Key Points:**

- Blueschist and eclogite assemblages do not necessarily reflect equilibrium crystallization
- Exhumation following garnet growth must occur within 1 Ma to preserve compositional zoning
- The prograde subduction P-T path in the Cyclades is concave upward with initial shallow subduction followed by near isothermal loading

#### **Supporting Information:**

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

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# P-T Evolution of the Cyclades Blueschist Unit: Constraints on the Evolution of a Nascent Subduction System From Zr-In-Rutile (ZiR) and Quartz-In-Garnet (QuiG) Thermobarometry

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**Abstract** New results that employ Zr-in-rutile thermometry (ZiR) and quartz-inclusion-in-garnet (QuiG) barometry constrain the P–T conditions of garnet formation in blueschists and eclogites from the island of Syros, Greece. QuiG barometry reveals that garnet from different regions across the island formed at pressures ranging from 1.1 to 1.8 GPa and ZiR thermometry on rutile inclusions in garnet constrains the minimum temperature of garnet formation to have been 475–550°C. Most importantly, there is no systematic difference in the conditions of garnet formation from different regions across the island and these results are nearly identical to those obtained from the islands of Sifnos and Ios, Greece. A model is proposed whereby the rocks from all three islands were initially metamorphosed along a relatively shallow geotherm of around 11°C/km to a depth of around 45 km and were then subjected to metamorphism along a geotherm of around 7–8°C/km, which could have been caused by either an increase in the dip of the subduction zone or an increase in the rate of subduction. Garnet formed along this steeper geotherm was accompanied by the release of significant H<sub>2</sub>O from the breakdown of chlorite over a duration of 1 Ma or less based on thermal and diffusion modeling. It is concluded that rocks from Syros, Sifnos and Ios all followed a similar, roughly counter-clockwise prograde P–T path and that the present outcrop configuration is largely due to a complex exhumation history.

**Plain Language Summary** The metamorphism of rocks in subduction zones releases large quantities of  $H_2O$ , which ultimately helps flux melting in the overlying mantle leading to explosive island arc volcanism and provides a trigger for large earthquakes. One of the dominant processes that produce large amounts of  $H_2O$  is the formation of the mineral garnet. Here, we present results that constrain the pressure and temperature conditions for the formation of garnet from three islands in the Greek Cyclades: Syros, Sifnos, and Ios. Our results indicate that garnet formed in different rocks on all three islands in a similar subduction channel along a trajectory where the pressure increase was relatively rapid and the temperature remained nearly constant. The duration of garnet formation in the entire suite of samples is estimated to have occurred in 1 million years or less, during which time significant quantities of fluid are inferred to have been released and which most likely had a major impact on volcanism and seismicity in the region while subduction was active.

## 1. Introduction

The prograde P–T path of exhumed subduction complexes places first order constraints on the thermal structure of the subduction zone, the rate of subduction, the amount of shear heating along the subduction shear zone, and contributes to our understanding of the rates and magnitude of crustal material and volatile recycling into the mantle and the causes and frequency of subduction related earthquakes and island arc volcanism (e.g., Agard et al., 2018; Kohn et al., 2018; Peacock, 2020; Penniston-Dorland et al., 2015; van Keken & Wilson, 2023). Unfortunately, prograde P–T paths in these settings have been difficult to constrain. Studies of subduction P–T paths typically show the paths to be generally clockwise on a P–T diagram (e.g., Ernst, 1988; Ernst & Peacock, 1996; Gorce et al., 2021; Kotowski & Behr, 2019; Kotowski et al., 2022; Liou et al., 1998) to be consistent with thermal models of subduction (e.g., Gerya et al., 2002; Minear & Toksoz, 1970; Peacock, 2003; Syracuse et al., 2010) although the prograde part of these paths is typically either poorly constrained or not constrained at all

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by any quantitative data on the PT conditions. That is, quantitative P-T constraints on the prograde P-T path are generally lacking.

The Cyclades Blueschist Unit (CBU) that crops out on several islands in the Greek Cyclades provides an excellent natural laboratory for petrologic studies aimed at constraining the prograde P-T path during early Hellenic subduction. Numerous studies of the metamorphic evolution of the CBU have been published (e.g., Ashley et al., 2014; Avigad, 1993; Bröcker & Enders, 1999, 2001; Bröcker & Franz, 2000; Dixon, 1976; Dixon & Ridley, 1987; Dixon et al., 1987; Dragovic et al., 2012, 2015; Forster & Lister, 1999a, 1999b, 2005; Forster et al., 2020; Gorce et al., 2021; Hamlin et al., 2018; Hopfer & Schumacher, 1997; Huet et al., 2009; Kotowski & Behr, 2019; Kotowski et al., 2022; Lamont et al., 2020; Laurent et al., 2016, 2018; Lister & Raouzaios, 1996; Philippon et al., 2011; Putlitz et al., 2005; Ridley, 1984a; Ring & Layer, 2003; Schliestedt, 1986; Schumacher et al., 2008; Spear et al., 2006; Thomson et al., 2009; Tomaschek et al., 2003; Trotet, Jolivet, & Vidal, 2001; van der Maar & Jansen, 1983). Many of these studies have focused on blueschists on the islands of Syros, Sifnos, and Ios because these islands harbor the best-preserved blueschists in the Cyclades. Studies of rocks from these islands have concluded that the peak metamorphic conditions were between 1.2-2.2 GPa at temperatures of 450-550°C. These studies also assume prograde clockwise P-T paths along thermal gradients of around 7-9°/km. Many of these earlier studies utilized classical thermobarometry and phase diagram analysis using internally consistent thermodynamic data sets (e.g., pseudosections) to constrain the peak metamorphic conditions. More recent studies have employed trace element thermometry (e.g., zirconium-in-rutile or ZiR, Ti-in-quartz or TitaniQ) and inclusion barometry (e.g., quartz-in-garnet or QuiG) (e.g., Ashley et al., 2014; Behr et al., 2018; Castro & Spear, 2017; Cisneros et al., 2020; Gorce et al., 2021; Spear et al., 2006, 2023; Wolfe et al., 2023). Results of some of these more recent studies support the peak P-T conditions inferred from earlier studies for selected blueschist localities. In addition, and most importantly, the application of ZiR and QuiG thermobarometry has yielded details of aspects of the prograde P-T history that better constrain the prograde P-T path and are therefore of considerable value in understanding the tectonic evolution of the CBU (e.g., Spear et al., 2023).

The purpose of this contribution is to present new results from the application of ZiR and QuiG thermobarometry for the island of Syros, Greece, and to integrate these results with published studies from the islands of Sifnos and Ios into a new model for the prograde P-T evolution of the Cyclades subduction system. These prograde P-T paths are then used to place constraints on the temporal, thermal, and tectonic evolution of the paleo Hellenic subduction that resulted in the formation of the CBU.

# 2. Geologic Setting

The Attic-Cycladic Crystalline Massif (ACCM) is a complex of high-pressure metamorphic rocks that are part of an Alpine orogenic arc formed during Eurasia-African subduction that extends from mainland Greece to western Turkey (Figure 1) (Hopfer & Schumacher, 1997; Schumacher et al., 2008). The ACCM is exposed on several islands in the Aegean Sea and contains blueschist and eclogite facies rocks that are locally retrograded to greenschist facies assemblages. The ACCM is composed of three distinct structural units. The structurally lowest unit is composed of Hercynian basement gneisses and metagranites. This unit is overlain by highly deformed passive margin blueschist nappes thought to be derived from accretionary wedge material, volcanic and continental shelf sediment, and ocean floor basalt (Andriessen et al., 1987; Henjes-Kunst & Kreuzer, 1982; Maruyama et al., 1996). The highest structural unit is a mélange of Permian-Mesozoic sediment, Cretaceous greenschist facies rocks and ophiolite nappes.

Numerous studies have described the petrologic and tectonic evolution of various islands in the ACCM (e.g., Ashley et al., 2014; Avigad, 1993; Castro & Spear, 2017; Dixon & Ridley, 1987; Dixon et al., 1987; Forster & Lister, 2005; Gorce et al., 2021; Hopfer & Schumacher, 1997; Kotowski et al., 2022; Laurent et al., 2016, 2018; Ridley, 1984a, 1984b; Schliestedt, 1986; Schumacher et al., 2008; Trotet, Jolivet, & Vidal, 2001; Trotet, Vidal, & Jolivet, 2001 and references therein). The metamorphism of the ACCM has been broadly divided into several stages. (a) Pre-subduction metamorphism of the Hercynian basement complex; (b) ~45–50 Ma (Eocene) highpressure blueschist facies metamorphism associated with the Cycladic subduction system; (c) ~30-20 Ma (Oligocene to early Miocene) regional greenschist facies overprint; and (d) intrusion of Miocene-aged granitic bodies with local contact metamorphism (e.g., Lamont et al., 2020).

Some of the best-preserved exposures of high-pressure blueschists and eclogites occur on the islands of Syros, Sifnos and Ios. Although there is considerable variance in published accounts of the prograde subduction P-T

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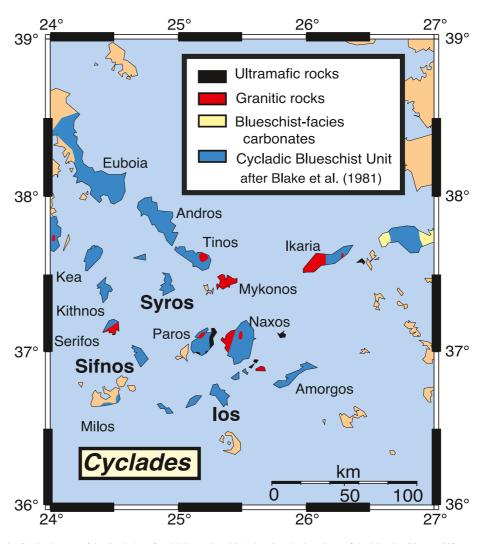


Figure 1. Geologic map of the Cyclades after Blake et al. (1981) showing the locations of the islands of Syros, Sifnos, and Ios as well as the distribution of rocks of the Cyclades Blueschist Unit.

paths of the various islands, it is generally accepted that the peak metamorphic conditions were on the order of 450–525°C at 1.8–2.2 GPa (e.g., Castro & Spear, 2017; Gorce et al., 2021; Hamlin et al., 2018; Kotowski et al., 2022; Laurent et al., 2018). Indeed, Laurent et al. (2018) have inferred that peak conditions and presumably the prograde P–T paths were similar for rocks on both Syros and Sifnos and a major goal of the present study is to further test this hypothesis using quartz-in-garnet and zirconium-in-rutile (QuiG and ZiR) thermobarometry. Proposed exhumation paths for rocks on various islands are quite variable (e.g., Kotowski et al., 2022; Laurent et al., 2018) and are not addressed in this study.

# 3. Methods

The methods utilized in this contribution include Zr-in-rutile (ZiR) geothermometry, quartz-in-garnet geobarometry (QuiG), phase diagram calculations (mineral assemblage diagrams or MADs; i.e., pseudosections), diffusion modeling, and thermal modeling. ZiR thermometry followed methods discussed in detail by Spear et al. (2006) and Wolfe et al. (2023), which yielded Zr analyses in rutile with precision of around 7–10 ppm. ZiR temperatures were calculated using the experimental calibration of Tomkins et al. (2007).

QuiG barometry followed methods outlined in Wolfe et al. (2021, 2023). Measurements were made using a Bruker Senterra Raman Spectrometer using a 100×, 0.9 N.A. Olympus objective with a 532 nm (green) laser and a 1,200 lines/mm diffraction grating in a fixed position. Peaks were located using the automated peak find routine

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in the OPUS software supplied by Brucker with the Senterra system. Spectra were accumulated for 30 s (three 10 s accumulations) on both quartz inclusions and standard materials. A grain of Herkimer quartz was analyzed daily to detect any instrument drift. Repeated measurements on Herkimer quartz over several years (2017–2022) displayed average values of  $465.0 \pm 0.151$ ,  $206.3 \pm 0.25$ , and  $128.5 \pm 0.15$  cm<sup>-1</sup> for the three major quartz Raman peaks. Matrix (unstrained) quartz was also measured on each thin section and values for the three quartz peaks were typically lower than those for Herkimer quartz by approximately 0.2, 0.4, and 0.2 cm<sup>-1</sup>, respectively. Matrix quartz values from each thin section were used as the standard reference material for the quartz inclusions, which resulted in a slightly larger Raman shift than had the values for Herkimer quartz been used. This translates to a difference in the calculated entrapment isomekes of approximately 0.04 GPa.

Numerous quartz inclusions were measured in each sample, with the number of grains analyzed ranging from as few as three to over 40, depending on the sample. Shifts of the 464, 206, and  $128 \, \mathrm{cm}^{-1}$  peaks were calculated based on repeated measurements of matrix quartz as discussed above. All samples displayed a range of Raman shifts. For example, a typical sample might display a range of shifts of the 464 cm<sup>-1</sup> quartz peak  $1-2 \, \mathrm{cm}^{-1}$  (e.g., shifts of  $5-7 \, \mathrm{cm}^{-1}$ ). Based on the assumption that it is possible to decrease the amount of strain on a quartz inclusion by fracturing or inelastic deformation of the host garnet but not possible to increase the amount of strain, the grain displaying the largest Raman shift in each sample was used for calculation of the isomekes and these values are tabulated in Table S3 in Supporting Information S1. Most importantly, no systematic variation of Raman shift with position within the garnet was observed, similar to the findings of Wolfe et al. (2021, 2023) (see Figure S1 in Supporting Information S1). The overall uncertainty for the QuiG barometry is believed to be better than  $\pm 0.1 \, \mathrm{GPa}$ .

Pressures of quartz entrapment in garnet were calculated using both the so-called "hydrostatic" method that utilizes only the shift of the 464 cm<sup>-1</sup> Raman peak in quartz and the elastic strain method (e.g., Angel et al., 2019; Murri et al., 2018) which utilizes the 128, 206, and 464 cm<sup>-1</sup> peaks with pressures calculated using program EntraPT (Mazzuchelli et al., 2021). Thermodynamic calculations were made using program Gibbs (Spear & Wolfe, 2022: supplemental material; Spear, 2024c) using the SPaC thermodynamic dataset (Spear & Pyle, 2010).

Diffusion modeling was performed to constrain the time required for relaxation of an Mn zoning profile in garnet. This was accomplished using the explicit finite difference Fortran program GarDiff (Spear, 2024a) following methods detailed in Spear (2014) and utilizing the Mn diffusivities of Chakraborty and Ganguly (1992). Thermal modeling was performed to loosely constrain subduction parameters and to examine the plausibility of the proposed P–T path for the Cycladic blueschists. Thermal modeling was done using program ThrustNHeat (e.g., Spear, 2004, 2024b). The program is designed to calculate the 2-D thermal evolution of rocks situated in a body that is undergoing some combination of overthrusting, underthrusting, tectonic denudation, erosion, or igneous intrusion (cf., Spear, 2004). Details of the program are presented in the supplemental materials.

# 4. Summary of P-T Results

Samples discussed in this contribution are from the islands of Syros, Sifnos, and Ios, which display some of the best-preserved examples of the CBU (Figure 1). Results from Syros have not been previously published and are presented below. The Syros results are then integrated with published results from Sifnos and Ios (e.g., Castro & Spear, 2017; Spear et al., 2006, 2023; Wolfe et al., 2023) into a model for the prograde metamorphic evolution of the CBU.

# 4.1. Syros

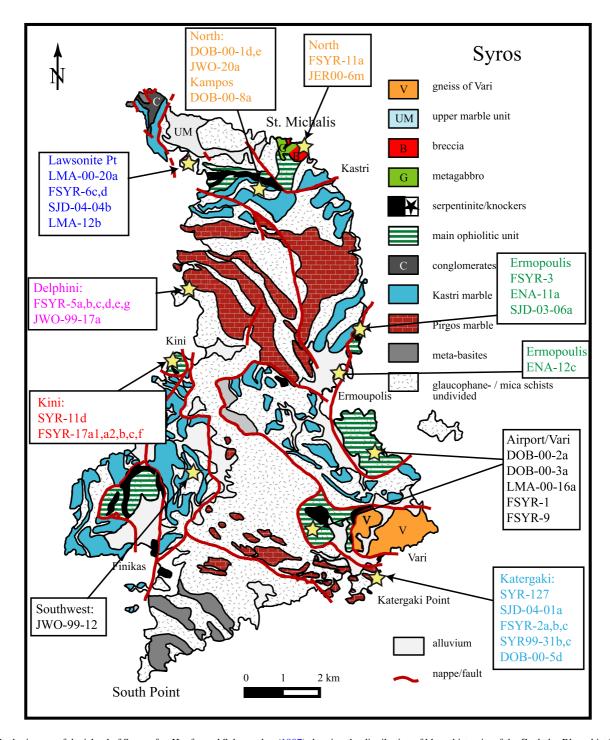
Figure 2 displays a map of the island of Syros showing the generalized geologic features and the locations of samples reported in this study. Samples have been grouped into 8 different areas from which at least one sample has been examined using ZiR and QuiG thermobarometry. Sample location, minerals present, bulk compositions, QuiG and ZiR data are given in Tables S1–S3 in Supporting Information S1.

Figure 3 shows the results of the QuiG and ZiR thermobarometry on samples from Syros. The ZiR thermometry ranges from around 475 to 525°C (at ca. 1.5 GPa). All samples record similar ZiR temperatures and there are no observed differences in the zirconium concentrations of rutile crystals in the matrix versus rutile inclusions inside of garnet. The results from the ZiR thermometry are interpreted to reflect the temperature of rutile formation, as has been concluded by Spear et al. (2023). It should be noted that all of the ZiR results shown in Figure 3 include

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**Figure 2.** Geologic map of the island of Syros after Hopfer and Schumacher (1997) showing the distribution of blueschist units of the Cyclades Blueschist Unit and the locations of samples reported in this study. Map corner coordinates are 35.527, 25.015 (upper right) and 37.357, 24.847 (lower left).

measurements from rutile inclusions in garnet and, as such, represent a lower bound on the temperature of garnet formation.

Pressures of quartz entrapment in garnet range from around 1.1 to 1.8 GPa (at ca.  $500^{\circ}$ C). Several localities (e.g., Delphini, North & St. Michalis, Ermopolis) contain quartz inclusions with isomekes that are, within error, identical (e.g., around  $\pm$  0.1 GPa). However, for some localities (e.g., Airport & Vari and Katergaki), the range of QuiG pressures for different samples exceeds the analytical uncertainty. It is important to note that samples

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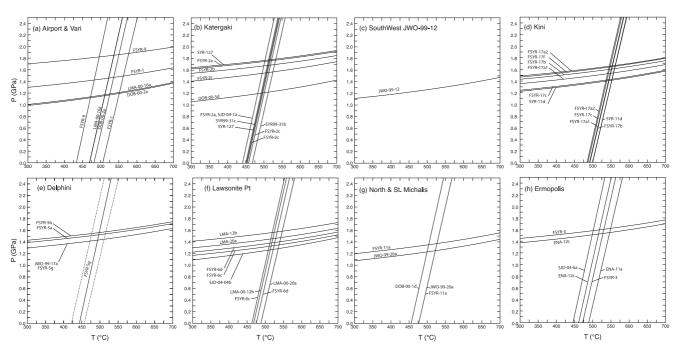


Figure 3. P-T diagram showing the results of QuiG and ZiR thermobarometry on rocks from the different study areas on Syros.

collected from the same locality must have gone through the same P–T history, so this observation places tight restrictions on the possible prograde P–T path, as will be discussed in detail below. A summary of the QuiG and ZiR results for the island of Syros is presented in Figure 4a.

As noted above, most analyzed rutile crystals and all analyzed quartz inclusions occur within garnet. Therefore, unless post-entrapment modification has occurred, garnet must have formed at P–T conditions along the QuiG isomekes and above the temperatures recorded by ZiR thermometry. That is, on the order of 525–550°C at pressures that range from around 1.1 to 1.8 GPa. It is also important to note that these P–T conditions are not necessarily the peak metamorphic conditions, but rather simply the P–T conditions where garnet formed. Similar to the findings of Castro and Spear (2017), Spear et al. (2023), Wolfe and Spear (2018, 2020), and Wolfe et al. (2023), the available data suggest that the growth of garnet occurred nearly isothermally and isobarically

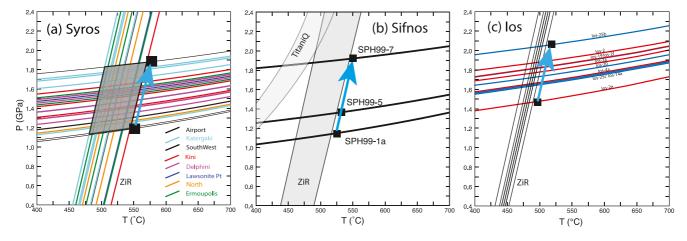


Figure 4. P-T diagram summarizing the results of QuiG and ZiR thermobarometry on rocks from (a) Syros (this study); (b) Sifnos (Spear et al., 2023); and (c) Ios (Wolfe et al., 2023). Near horizontal lines represent isomekes from QuiG barometry. Lines with steep positive slopes are the results of ZiR thermometry. "TitaniQ" (in panel b) shows the results of Ti-in-quartz thermometry. Red isomekes (in panel c) are for samples from the hanging wall blueschist unit on Ios and blue isomekes are for samples from the footwall unit. Black squares show the minimum temperatures of garnet formation constrained to lie along the QuiG isomeke. Blue arrows show the simplest hypothesized P-T path that can account for the array of garnet formation conditions.

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### 4.2. Summary of Results From Syros, Sifnos, and Ios

The results of QuiG barometry and ZiR thermometry for the islands of Syros (this study), Sifnos (Castro & Spear, 2017; Spear et al., 2023), and Ios (Wolfe et al., 2023) are shown in Figure 4. Temperatures from ZiR thermometry are remarkably similar for all three islands and, inasmuch as analyzed rutile crystals are inclusions inside of garnet, these place a lower limit on the temperature of garnet formation of 500-550°C, depending on the pressure. QuiG barometry also yields remarkably similar results with isomekes spanning the range from around 1.1 to 2.0 GPa (at 500°C).

conditions or that the P-T conditions of garnet growth are the peak metamorphic conditions.

Other estimates of metamorphic pressures using QuiG barometry are consistent with the results reported here. Ashley et al. (2014) report pressures based on QuiG barometry of 1.9–2.0 GPa for a sample from Sifnos entirely consistent with the highest pressure determined by Castro and Spear (2017) for the same area (Figure 4b). Behr et al. (2018) report pressures of 1.25-1.55 GPa for samples from the Kini area on Syros similar to the results reported here (Figure 3d). Gorce et al. (2021) report peak conditions from the Katergaki locality of 1.7–2.1 GPa, which is slightly higher but overlaps with the maximum pressure reported here of 1.8 GPa (e.g., Figures 3b) and Cisneros et al. (2020) report similar quartz-in-garnet isomekes for samples from three areas on Syros (corresponding to Airport & Vari, Kini, and Delphini) that indicate garnet formation pressures of 1.4-1.7 GPa, again consistent with the results of this study.

# 4.3. Discussion of Peak Metamorphic Conditions

It is important to reemphasize that the ZiR thermometry and QuiG barometry do not record the peak metamorphic conditions but rather the conditions of garnet formation. Peak metamorphic conditions must be at least as high as the maximum pressure conditions of garnet formation at any given locality. For example, the peak P-T conditions on Syros for the Katergaki locality (Figure 3b) must be at least 530°C and 1.8 GPa and those for the Kini locality (Figure 3d) must be at least as high as 560°C at 1.7 GPa.

Peak metamorphic conditions for blueschists and eclogites from Syros, Sifnos and Ios have been reported by a number of researchers (see excellent summary in Kotowski et al., 2022; Uunk et al., 2022). For example, Laurent et al. (2018) have estimated peak metamorphic conditions on Syros to be  $2.2 \pm 0.2$  GPa and  $530 \pm 30^{\circ}$ C, which is similar to the peak conditions reported by Trotet, Jolivet, and Vidal (2001). Other studies such as Schumacher et al. (2008) and Kotowski et al. (2022) have inferred lower peak pressures of around 1.6-1.7 GPa. It is important to point out that estimates of peak metamorphic conditions cannot be directly compared to pressures of garnet formation determined from QuiG barometry unless it is universally true that garnet nucleated and grew only at the peak conditions. The variation of QuiG pressures from a single locality (e.g., Katergaki: Figure 3b) clearly indicates that garnet nucleates and grows at different pressures in rocks of different bulk compositions.

In summary, our study does not provide information to refine estimates of the peak metamorphic conditions experienced by rocks from Syros, Sifnos, and Ios but does place constraints on the minimum conditions. It is entirely possible that all exposures of the CBU on these three islands have experienced nearly identical peak P-T conditions, as has been concluded by Kotowski et al. (2022) and Uunk et al. (2022), although the available data are also permissive of different regions on Syros having reached different peak pressures. What can be said is that the maximum observed values of garnet formation conditions are similar for all three islands (e.g., 1.8–2.0 GPa at 500-550°C: Figure 4). This suggests, but does not prove, that all three islands experienced similar subduction histories.

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# 4.4. Interpretation of P-T Paths

The main focus of this manuscript is to constrain the prograde P–T path for rocks of the CBU. Examination of the summary P–T conditions in Figure 4 reveals similar minimum temperature for garnet formation from ZiR thermometry and a range of garnet formation pressures. The blue arrows in Figure 4 are drawn to connect the pressures determined from the QuiG results with the minimum temperatures for garnet formation from ZiR thermometry. It is proposed that the blue arrows are the simplest prograde P–T paths that can explain all the observations on garnet formation.

Samples from Sifnos (Figure 4b) are all from the northern exposures of the CBU and garnet from different rocks from this locality formed at conditions ranging from around 1.1 GPa at 525°C to 1.9 GPa at 550°C. The only P–T path that can accommodate the garnet-formation conditions for all three samples is one of nearly isothermal loading (blue arrow). A similar argument can be made for the samples from Ios (Figure 4c) and for the Airport & Vari and Katergaki locations on Syros (Figures 3a and 3b). The other localities on Syros display an insufficient range of garnet-formation conditions to be conclusive, but the conditions that are recorded are entirely consistent with the blue arrow in Figure 4a. A possible subduction scenario to explain how these paths might have arisen is discussed below.

There are, of course, differences in the exhumation paths for different units on the three islands, which is to be expected as the rocks are now km apart and underwent different exhumation histories possibly at different times (e.g., Uunk et al., 2022). The exhumation history of the CBU has been addressed by numerous studies and will not be pursued here.

# 5. Constraints From Thermal Modeling

To evaluate the thermal and tectonic constraints imposed by the above P–T path, a series of 2-dimensional thermal models have been constructed (Figure 5). A detailed description of the thermal model program is provided in Supporting Information S1. In these models, it is assumed that subduction of the CBU occurs in a nascent subduction complex such that the thermal perturbation characteristic of mature subduction zones (e.g., Syracuse et al., 2010) is not yet established. Two different models were developed. First, the rate of subduction was chosen to be constant at 2 cm/year and the subduction zone dip changed from 20° at the surface to a depth of 48.4 km (1.3 GPa) to a dip of 45° below this threshold. In the second model, the dip of the subduction zone was kept constant at 20° and the rate of subduction was changed from an initial value of 2 cm/year to a rate of 10 cm/year when the surface of the slab reached a depth of 48.4 km (1.3 GPa).

Both models were able to reproduce the P–T paths shown in Figure 4 and only the first model is shown in Figure 5. It should be noted that the goal of the thermal modeling was not to argue for a particular subduction scenario or set of thermal parameters but rather to determine whether a plausible set of subduction parameters could account for the inferred P–T path and to establish a time frame over which the formation of garnet might have occurred. From Figure 5a, it is clear that the model parameters do, indeed, produce a P–T path that is similar to the blue arrows in Figure 4. In addition, as shown in Figures 5b and 5c, the overall time for the rocks to reach the peak metamorphic conditions is approximately 8–8.2 Ma. Most importantly, however, the time for the rocks to reach 1.3 GPa was on the order of 7.2 Ma and the time to go from 1.3 to 2.0 GPa was only on the order of 1 Ma. That is, the duration of subduction over which garnet formation and the associated dehydration and fluid release occurred is only around 1 Ma. Similar time scales were found in model 2 in which the rate of subduction was changed. Immediate exhumation (not modeled) is then required to ensure that the rocks do not heat beyond the peak temperature due to thermal relaxation.

# 6. Constraints From Diffusion Modeling

Chemical zoning in garnet crystals from selected samples displays sharp compositional changes, an example of which is shown in Figure 6. The Mn zoning profile was modeled using program GarDiff (Spear, 2014, 2017) assuming the initial profile was a step function (blue curve in Figure 6). Several different cooling rates were considered. The two simplest cooling histories involve (a) isothermal diffusional relaxation at 550°C for 1 Ma followed by rapid quenching (Figure 6b) and (b) constant cooling from 550°C at 40°C/Ma (Figure 6c). Both models give nearly identical fits to the observed profiles. In both cases, a time of around 1 million years is required

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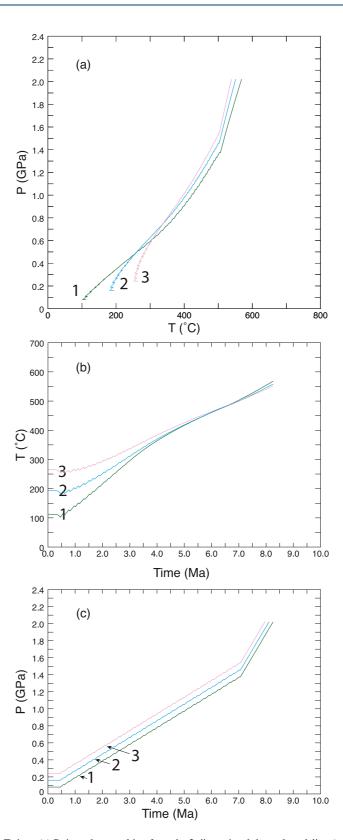


Figure 5. (a) P–T; (b) T-time; (c) P-time plots resulting from the 2-dimensional thermal modeling (see Supporting Information S1). The three models involve subduction at 2 cm/year with a slab dip of  $20^{\circ}$  down to 1.3 GPa (48.4 km) and a slab dip of  $45^{\circ}$  thereafter. The three rock paths are for rocks starting at 2, 6, and 9 km depth, respectively. The models were designed to mimic the shape of the postulated P–T paths shown in Figure 4.

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to match the zoning profile. Of course, if the initial temperature was higher or lower, the diffusional time would be shorter and longer, respectively.

This simple diffusion calculation reveals that samples could not have resided at the peak temperature for longer than 1 Ma, if the diffusion was isothermal at 550°C. Alternatively, cooling must have been initiated immediately following attainment of the assumed peak temperature of 550°C, in which case the cooling must have been fairly rapid (e.g., 40°C/Ma). Of these two scenarios, the second seems more likely because if the sample had remained at the maximum depth for a period of 1 Ma, thermal diffusion from the overlying plate would have caused significant heating of the sample. It should also be noted that only the initial 50 degrees of cooling (from 550°C to 500°C) substantially modifies the compositional profile due to the sluggishness of diffusion in garnet below this temperature. It is required that the cooling rate decreases as the temperature decreases in order to match the inferred age of the greenschist facies overprint assumed to have occurred at 400–450°C at around 20–30 Ma (e.g., Brocker & Franz, 2000; Brocker et al., 2004; Skelton et al., 2019). Similar rapid cooling was concluded by Lister and Raouzaios (1996) and Forster et al. (2020) based on modeling argon retention in mica.

#### 7. Discussion

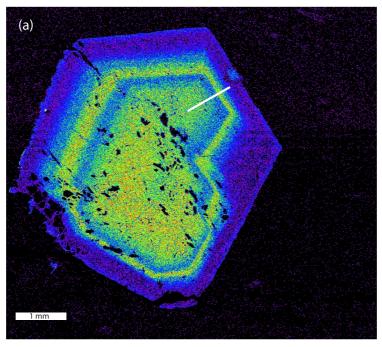
The proposed P–T model for the CBU is somewhat different from most published prograde P–T paths for the CBU (Figure 7). Peak P–T conditions for Syros, Sifnos, and Ios are generally concluded in most studies to be around 1.7–2.0 GPa (see discussion above). However, the prograde P–T paths are quite different. Previous studies have generally inferred clockwise P–T paths that are drawn indicative of "typical" prograde subduction paths. However, the results of the present study on garnet formation P–T conditions do not support such clockwise P–T paths because it is not possible for a single clockwise P–T path to encompass the range of garnet formation conditions determined for samples from individual areas such as the CBU unit of northern Sifnos, the upper and lower plates of the Ios assemblages, or the samples from the Airport & Vari and Katergaki localities on Syros. The only way a single clockwise path could encompass the garnet formation conditions is if garnet nucleated and grew on the exhumation portion of the path during cooling, and this is not believed to be likely.

A much simpler interpretation, and one that accommodates both the QuiG and ZiR data, is the one presented here whereby all rocks followed a similar prograde P–T path, as shown by the gray arrows in Figure 7. It is also not necessary to call upon multiple blueschist metamorphic "events" or complex P–T paths as has been done by several authors (e.g., Castro & Spear, 2017; Dragovic et al., 2015; Forster & Lister, 1999a, 2005; Gorce et al., 2021; Vidal, & Jolivet, 2001).

The short time scale for the metamorphic evolution of the CBU presented here (less than 1 Ma) is somewhat surprising but is consistent with some of the available chronology of garnet from Sifnos. For example, Dragovic et al. (2012) have reported Sm/Nd ages of garnet core, middle and rim of 46.50, 46.49, and 46.46 Ma, respectively. That is, within analytical error, the garnet grew instantaneously. This type of rapid garnet growth is consistent with inferences that garnet only nucleates after considerable overstepping and then grows nearly isothermally and isobarically (e.g., Castro & Spear, 2017). Two other studies of Sm/Nd dating of garnet conclude that there is a significant time difference between the growth of garnet cores and rims. Dragovic et al. (2015) report an age of a garnet core and rim from Sifnos of 53.4 and 44.96 Ma, respectively, and Gorce et al. (2021) report core-rim ages of 45.3 and 40.5 Ma, respectively. Absolute differences in bulk garnet ages have been addressed by Uunk et al. (2022) who conclude that different blueschist blocks on Syros and Sifnos reached similar peak metamorphic conditions but at different times. Differences in individual garnet core and rim ages of 5 Ma or more are more difficult to explain. While it is beyond the scope of the present paper to attempt to evaluate the robustness of these results, it is considered unlikely that a sample of blueschist could reside within a subduction zone for 5-8 million years at nearly constant pressure and temperature. Subduction zones are regions of active underthrusting and no simple mechanism exists for a rock to flounder at depth for extended periods of time. However, it is possible that the core ages represent an initial stage of garnet formation followed by recycling and resumed growth of garnet. Clearly, additional dating of garnet will help clarify the residence time of rocks in subduction complexes.

A further implication of the P–T path presented here is that the CBU is the result of relatively short-lived nascent subduction whereby the rocks were initially metamorphosed along a moderately shallow trajectory  $(10-11^{\circ}/\text{km})$  before significant thermal down-bowing had occurred. Otherwise, it is impossible to explain the Zr concentrations in rutile inclusions within garnet. This nascent subduction was either characterized by a change in the dip of

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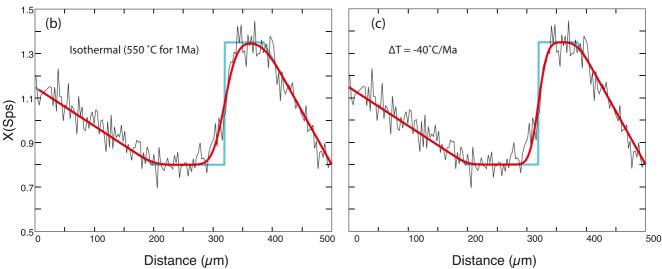


Figure 6. (a) Mn X-ray map of garnet from sample Syr-01 (Katergaki location). White line shows the location of traverse in panels (b) and (c). (b, c) Results of diffusion modeling. The black curve shows the measured composition, the blue line shows the assumed initial step function, and the red curve shows the result of the diffusion model. (b) Cooling history is 1 Ma at  $550^{\circ}$ C followed by quenching. (c) Cooling from  $550^{\circ}$ C at  $-40^{\circ}$ C/Ma. Both models fit the observed curve equally well.

subduction at a depth of 45–50 km or, alternatively, followed by a substantial increase in the rate of subduction (e.g., 2 cm/year to 10 cm/year). Exhumation must have occurred soon after the peak metamorphic conditions were reached to prevent significant heating of the rocks and homogenization of chemical zoning patterns. The present-day distribution of rocks in the CBU can then be explained as the result of complex post-subduction extension and exhumation.

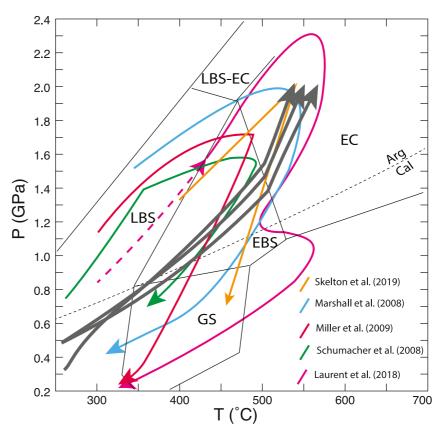
# 7.1. Fluid Evolution

The P–T paths shown in Figure 4 are constrained based on the conditions of formation of garnet resulting from QuiG and ZiR analyses. The nucleation and growth of garnet typically generates considerable amounts of  $H_2O$  due to the breakdown of chlorite and has been proposed as a source of fluids responsible for processes such as arc magmatism and seismicity (Baxter & Caddick, 2013). The present dataset permits calculation of the amount of

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**Figure 7.** P-T diagram showing postulated prograde metamorphic paths for blueschists from Syros, Sifnos, and Ios (gray lines). The steep parts of the gray paths are constrained by the QuiG and ZiR thermobarometry (Figure 4). The lower temperature parts of the gray paths are from the thermal modeling. Colored paths are from Marschall et al. (2008—blue), Miller et al. (2009—red), Schumacher et al. (2008—green), Skelton et al. (2019—orange), and Laurent et al. (2018—magenta). Facies fields are after Peacock (1993): GS = greenschist; LBS = lawsonite blueschist; EBS = epidote blueschist; EC = eclogite.

water released by garnet formation by comparing the  $\rm H_2O$  content of a rock before and after the growth of garnet. This has been done for several samples in the current study set and the results are presented in Table 1. For these calculations, it was assumed that the pre-garnet (i.e., garnet-absent) assemblage was the calculated equilibrium assemblage with garnet removed from consideration (all calculations were done using Program Gibbs and the SPaC thermodynamic dataset; Spear & Wolfe, 2022). Invariably, these pre-garnet assemblages contained chlorite. It was also assumed that garnet nucleation and growth took place isothermally and isobarically at the P-T

**Table 1**Estimates of H<sub>2</sub>O Released During Garnet Formation

| T   | P                          | $\Delta$ moles/kg rock                                      | $\Delta$ moles/m <sup>3</sup> rock <sup>a</sup>  | kg H <sub>2</sub> O/m <sup>3</sup> rock <sup>b</sup>  | $m^3 H_2O/m^3 rock$   | $m^3 H_2O/km^3 rock$   |
|-----|----------------------------|---|--|---|---|--|
| 500 | 1.6                        | 0.0173  | 52   | 0.94  | 0.000850  | 850,255  |
| 556 | 1.41                       | 0.7239  | 2,172  | 39.09   | 0.035537  | 35,536,909   |
| 524 | 1.14                       | 0.0217  | 65   | 1.17  | 0.001065  | 1,065,273  |
| 530 | 1.36                       | 0.0084  | 25   | 0.45  | 0.000412  | 412,364  |
| 534 | 1.9                        | 0.0660  | 198  | 3.56  | 0.003240  | 3,240,000  |
| 508 | 1.9                        | 0.4663  | 1,399  | 25.18   | 0.022891  | 22,891,091   |
| 534 | 1.9                        | 0.3801  | 1,140  | 20.53   | 0.018659  | 18,659,455   |
|     |                            | Average   | 722  | 12.99   | 0.011808  | 11,807,906   |
| 5:  | 00<br>56<br>24<br>30<br>34 | 00 1.6<br>56 1.41<br>24 1.14<br>30 1.36<br>34 1.9<br>08 1.9 | 00 1.6 0.0173<br>56 1.41 0.7239<br>24 1.14 0.0217<br>30 1.36 0.0084<br>34 1.9 0.0660<br>08 1.9 0.4663<br>34 1.9 0.3801 | 00     1.6     0.0173     52       56     1.41     0.7239     2,172       24     1.14     0.0217     65       30     1.36     0.0084     25       34     1.9     0.0660     198       08     1.9     0.4663     1,399       34     1.9     0.3801     1,140 | 00     1.6     0.0173     52     0.94       56     1.41     0.7239     2,172     39.09       24     1.14     0.0217     65     1.17       30     1.36     0.0084     25     0.45       34     1.9     0.0660     198     3.56       08     1.9     0.4663     1,399     25.18       34     1.9     0.3801     1,140     20.53 | 00     1.6     0.0173     52     0.94     0.000850       56     1.41     0.7239     2,172     39.09     0.035537       24     1.14     0.0217     65     1.17     0.001065       30     1.36     0.0084     25     0.45     0.000412       34     1.9     0.0660     198     3.56     0.003240       08     1.9     0.4663     1,399     25.18     0.022891       34     1.9     0.3801     1,140     20.53     0.018659 |

<sup>&</sup>lt;sup>a</sup>Assumes density of rock = 3,000 kg/m<sup>3</sup>. <sup>b</sup>Assumes an average density of H<sub>2</sub>O of 1,100 kg/m<sup>3</sup>.

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conditions constrained by QuiG and ZiR thermobarometry. The moles of  $H_2O$  released per kilogram of rock were converted to moles or mass of  $H_2O$  per cubic meter or rock assuming an average rock density of 3,000 kg/m<sup>3</sup> and an average  $H_2O$  density of 1,100 kg/m<sup>3</sup>.

The calculated moles of  $H_2O$  released per cubic meter of rock ranged from 25 to 2,172 and the mass of  $H_2O$  released ranged from 0.45 to 39 kg/m<sup>3</sup> of rock. The large range of values reflects the differences in bulk composition of the sample and, most importantly, the amount of chlorite present. It should be noted that this is not the total amount of water released by a subducting rock but rather the amount that is released as a result of the formation of garnet. What is most important is that this water is released over the steep part of the P–T paths where the rocks are subducting from around 48 km to around 75 km over a period of around 1 Ma (from Figure 5). Using the average fluid amounts from Table 1 of 722 mol or 13 kg  $H_2O/m^3$  of rock, these values thus correlate to fluid release rates/Ma.

Fluids released from subducting slabs have been implicated in the melting of the overlying mantle, resulting in the development of arc volcanism. This is not a reasonable inference for the present calculations inasmuch as the typical arc magmatism is not observed until the slab reaches around 100 km depth although the range of depths extends from 72 to 173 km (e.g., England et al., 2004; Syracuse & Abers, 2006). However, depths of 48–75 km have been cited as the range where decoupling of the slab and the overlying mantle occurs and the slab interface becomes relatively aseismic (e.g., Abers et al., 2006; Kohn et al., 2018; Syracuse et al., 2010). A possible explanation of this decoupling is the formation of serpentinite in the overlying mantle. It takes two mol of H<sub>2</sub>O to convert 1 mol of forsterite into 1 mol of antigorite, so every cubic meter of dehydrating slab rock could potentially produce 0.03 m<sup>3</sup> of antigorite. If the mantle rock contains 50% olivine, then around 15 m<sup>3</sup> of dehydrating slab rock is required to convert the olivine in 1 m<sup>3</sup> of mantle rock into serpentine (i.e., 50% serpentine). Furthermore, the dehydration of a 1 km column of slab rock could potentially hydrate around 63 m of the overlying mantle to 50% serpentinite. A value of 50% serpentinite is entirely consistent with estimates of mantle hydration inferred from studies of VP/Vs in active subduction zones (e.g., Comte et al., 2016).

#### 8. Conclusions

The application of quartz-in-garnet and Zr-in-rutile thermobarometry reveals aspects of the evolution of blueschists and eclogites that are not readily apparent from either classical thermobarometry or equilibrium thermodynamic calculations. There are a number of implications from the results of this study:

- 1. Blueschist and eclogite assemblages in subduction complexes do not necessarily reflect equilibrium crystal-lization. Garnet clearly nucleates and grows at conditions well above the equilibrium garnet-in reaction (e.g., Castro & Spear, 2017) and it is quite possible that other common porphyroblastic phases (e.g., chloritoid, pyroxene, amphibole, lawsonite, epidote) also do not form in conformance with equilibrium calculations. Therefore, interpretation of P-T histories based on sequences of mineral growth as compared with the predicted sequence from equilibrium calculations may not yield a correct interpretation, as was concluded by Waters and Lovegrove (2002).
- 2. Constraints imposed by QuiG barometry and ZiR thermometry suggest that the initial prograde subduction geotherm in the Cyclades was relatively shallow (e.g., around 10–11°/km) but then increased due to either an increase in the rate of subduction or an increase in the angle of subduction.
- 3. The preservation of sharp chemical zoning boundaries such as those observed in Mn zoning in garnet reveal that times at peak temperature must be relatively short and exhumation must occur relatively soon after peak conditions are reached. Importantly, this implies that prolonged residence of rocks in subduction channels is not likely. This result, coupled with constraints imposed by the thermal modeling, suggests that most garnets from the CBU probably grew over time scales shorter than 1 Ma (e.g., Dragovic et al., 2012) and that samples that display differences in garnet core and rim ages (e.g., Dragovic et al., 2015; Gorce et al., 2021) are possibly the result of recycling of previously subducted material.

A final question concerns the tectonic processes that lead to the exhumation of subduction complexes. The peak of metamorphism is well-constrained to around 50–42 Ma based on  $^{40}$ Ar/ $^{39}$ Ar ages on micas and Sm/Nd and Lu/Hf ages on garnet (e.g., Dragovic et al., 2012, 2015; Gorce et al., 2021; Putlitz et al., 2005; Uunk et al., 2022). However, the initiation of subduction in the ACCM is not well constrained. It has been suggested that subduction could have commenced in the Cretaceous based on ca. 80 Ma zircon ages (e.g., Bröcker & Enders, 1999; Cheney et al., 2000), although Tomaschek et al. (2003) have interpreted these ages as magmatic. Regardless, the thermal

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models (Figure 5) constrain the duration of the prograde metamorphism to be on the order of 8 Ma. If the high-pressure rocks of Syros, Sifnos and Ios were incorporated into the subduction channel during nascent subduction, then the initiation of subduction must have occurred at around 55–60 Ma. Of course, there is no evidence that the subduction of these rocks began at the onset of subduction, but 50–60 Ma must provide a lower bound to the initiation of subduction.

The question remains as to the causes of exhumation of these and other blueschist terranes. Based on the results of the present study, the prograde P–T paths for rocks of Syros, Sifnos, and Ios all appear to be very similar. Additionally, the peak P–T conditions recorded by rocks from Sifnos, Ios, and several areas on Syros are quite similar at around 1.8 GPa,  $500-500^{\circ}$ C. It is not known whether all the blueschists from Syros experienced similar peak P–T conditions as suggested by Uunk et al. (2022), but nothing in our present dataset rules this out. This raises the intriguing possibility that metamorphic processes in the subducting slab are responsible for triggering exhumation. A plausible mechanism is the rapid and voluminous production of  $H_2$ O-rich fluids resulting from garnet growth, as discussed above. These fluids could potentially soften the overlying mantle and generate conditions conducive to exhumation.

It has also been pointed out that the P–T conditions recorded by rocks from subduction complexes are generally somewhat hotter than those predicted by models of mature subduction zones (e.g., Penniston-Dorland et al., 2015; Syracuse et al., 2010). Whereas it is possible that the thermal models have neglected to incorporate sufficient heat generation due to shear heating (e.g., Kohn et al., 2018), it is also possible that the dynamics of a subduction zone make it difficult or impossible for rocks in mature subduction zones to be exhumed and the exhumation of blueschists can only occur shortly after the initiation of subduction and if triggered by fluid-producing reactions such as the formation of abundant garnet. This is a fertile field for future study.

# **Data Availability Statement**

The zirconium in rutile concentration data (ZiR) and quartz-in-garnet (QuiG) are available at EarthChem (Spear et al., 2024). The software used in this publication (GarDiff, ThrustNHeat, and Gibbs) is available on GitHub at the following URLs: https://github.com/frankspear101/GarDiff95\_repo.git (Spear, 2024a); https://github.com/frankspear101/ThrustNHeat95\_repo.git (Spear, 2024b); https://github.com/frankspear101/Gibbs\_repo.git (Spear, 2024c).

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Acknowledgments

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