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**Benita Putlitz · John W. Valley · Alan Matthews
Yaron Katzir**

Oxygen isotope thermometry of quartz–Al_2SiO_5 veins in high-grade metamorphic rocks on Naxos island (Greece)

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Abstract Diffusion models predict that peak metamorphic temperatures are best recorded by the oxygen isotope fractionation between minerals in a bi-mineralic rock in which a refractory accessory mineral with slow oxygen diffusion rate is modally minor to a mineral with a faster diffusion rate. This premise is demonstrated for high-grade metamorphism on the island of Naxos, Greece, where quartz–kyanite oxygen isotope thermometry from veins in high-grade metamorphic pelites gives temperatures of 635–690 °C. These temperatures are in excellent agreement with independent thermometry for the regional M2 peak metamorphic conditions and show that the vein minerals isotopically equilibrated at the peak of metamorphism. Quartz–sillimanite fractionations in the same veins give similar temperatures (680 ± 35 °C) and suggest that the veins grew near to the kyanite–sillimanite boundary, corresponding to pressures of 6.5 to 7.5 kbar for temperatures of 635–685 °C. By contrast, quartz–kyanite and quartz–biotite pairs in the host rocks yield lower temperature estimates than the veins (590–600 and 350–550 °C, respectively). These lower apparent temperatures are also predicted from calculations of diffusional resetting in the polyphase host-rock system. The data demonstrate that bimineralic vein assemblages can be used as accurate thermometers in high-temperature rocks whereas retrograde exchange remains a major problem in many polymineralic rocks.

B. Putlitz (✉) · A. Matthews
Institute of Earth Sciences,
Hebrew University of Jerusalem,
91904 Jerusalem, Israel
E-mail: benita.putlitz@img.uni.ch
Fax: +41-21-6924305

J.W. Valley · Y. Katzir
Department of Geology and Geophysics,
University of Wisconsin, Madison, WI 53706, USA

Present address: B. Putlitz
University of Lausanne,
Institute of Mineralogy and Geochemistry,
BFSH2, 1015 Lausanne,Switzerland

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Introduction

Quartz-rich veins can be important manifestations of fluid mobilization in metamorphic rocks. Their structure and geochemistry potentially record the kinematics and temperature interval over which the vein developed, and the sources and transport mechanism of fluids involved in vein formation. It has long been recognized that the oxygen isotope composition of veins in metamorphic rocks preserves a record of the fluid history. Less well recognized, however, is their potential for oxygen isotope thermometry, particularly in quartz-rich veins from high-grade metamorphic rocks. Quartz is intrinsically a high-diffusivity mineral susceptible to retrograde re-equilibration during cooling (see Giletti 1986; Eiler et al. 1993). Thus, in numerous instances of high-grade metamorphism (including Naxos) oxygen isotope thermometry of quartz-bearing mineral assemblages results in temperatures which are lower than those of peak metamorphism (e.g., Rye et al. 1976; Bowman and Ghent 1986). However, in quartz-rich metamorphic veins the modal dominance means that quartz will be the dominant oxygen 'reservoir' to the closed-system isotopic exchange system, and its $\delta^{18}O$ will not change during cooling (Ghent and Valley 1998). The oxygen isotope fractionation between quartz and refractory accessory minerals, which are resistant to retrograde re-equilibration (such as aluminum silicates and garnet), can potentially provide accurate thermometry of the event during which the vein formed. The theory and other aspects of Refractory Accessory Mineral (RAM) thermometry are reviewed by Valley (2001). High-grade metamorphic rocks frequently contain veins whose structural relations with the host rock indicate a syn-metamorphic origin, thus allowing the veins to record the temperature of metamorphism.

Previous oxygen isotope studies on the high-grade metamorphic rocks of the island of Naxos, Greece (Fig. 1) focused on unraveling the complex fluid-rock interaction history (e.g., Rye et al. 1976; Schuiling and Kreulen 1978; Kreulen 1980; Baker et al. 1989; Bickle and Baker 1990; Baker and Matthews 1994, 1995; Katzir et al. 2002). The pioneering study of Rye et al. (1976) presented oxygen isotope temperatures based on quartz–muscovite and quartz–biotite pairs. Their results showed that at higher metamorphic grades quartz-mica temperatures are systematically lower than predicted by phase equilibria, indicating that isotopic exchange has occurred during cooling. The present study explores the potential of oxygen isotope thermometry of veins in rocks near and above the sillimanite isograd (T = 620 °C) as means of determining the temperatures of high-grade metamorphism. The veins investigated contain the assemblage quartz + kyanite ± sillimanite ± muscovite, and their structural and mineralogical relations with the host rocks indicate a syn- (possibly peak) metamorphic origin. Laser fluorination techniques are particularly suitable for oxygen isotope analysis of refractory alumina-rich minerals, and in this work we study the isotopic variations of quartz, kyanite and sillimanite in veins.

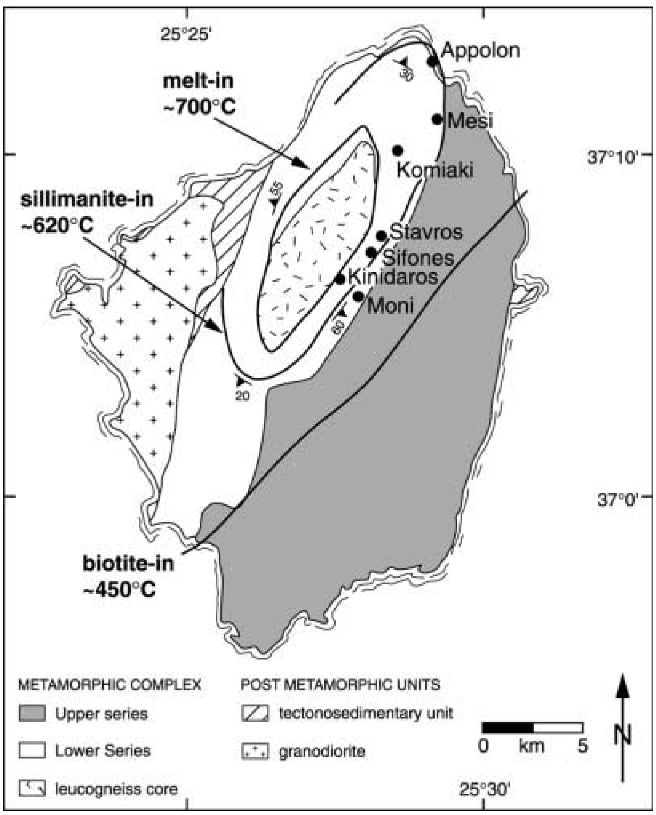


Fig. 1. Simplified geological map of Naxos (after Jansen 1977; Buick 1988; Baker and Matthews 1995) showing the sample sites of the veins studied in this work. With the exception of the Moni locality, all sites are located between the sillimanite-in isograd (620 °C) and the melt-in line (700 °C). The veins from Moni are sampled outside, but near the sillimanite-in isograd. The temperatures of the isograds are based on the work of Jansen and Schuiling (1976), Buick (1988), and Baker and Matthews (1995)

Geological setting

The island of Naxos (Fig. 1) is situated in Greece in the central part of the Aegean Sea, about 200 km southeast of Athens, and geologically it forms part of the Attic-Cycladic Massif. The Attic-Cycladic Massif has undergone intense deformation and metamorphism of Alpine age, whereby early Tertiary eclogite facies metamorphism (M1) has been variably overprinted by a greenschist-amphibolite facies event (M2) of Miocene age. Locally, on Naxos, this overprint reached upper amphibolite grade. The main part of Naxos island is formed by a polymetamorphic complex, which has been subdivided into three main units (Fig. 1). The lowermost of these, the pre-Alpine basement or leucogneiss core (Buick 1988), is dominated by migmatitic gneisses and pelitic rocks, some of which have undergone partial melting during the M2 metamorphism. The leucogneiss core is overlain by the "Lower Series" schists and marbles (Jansen and Schuiling 1976; Buick 1988). The structurally highest unit in the metamorphic complex, the "Upper Series" (Jansen and Schuiling 1976), is dominated by marbles. The metamorphic complex takes the form of a late NNE–SSW trending structural dome with a series of isograds (Fig. 1) increasing in grade towards the leucogneiss core. Peak M2 metamorphic conditions have been estimated as 6 ± 2 kbar, with temperatures increasing from below 450 °C (in SE Naxos) to 700 °C in the leucogneiss core (Jansen and Schuiling 1976; Buick and Holland 1989; Katzir et al. 1999). M1 high-pressure metamorphic assemblages are only preserved in the southeastern part of the island (Avigad 1998).

The quartz–Al_2SiO_5 veins occur within Lower Series schists and gneisses. Seven localities were studied at Stavros, Kinidaros, Komiaki, Sifones, Appolon, Mesi and Moni (Fig. 1; more details of the sample localities are given in Table 1). With the exception of the Moni locality, these sites are all located between the sillimanite-in and melt-in isograds mapped by Jansen (1977). The veins from the Moni site were sampled just below the sillimanite-in isograd, but within kyanite-bearing host rock (Fig. 1). Quartz + kyanite ± sillimanite ± white mica form the vein assemblages, and host rocks are pelitic and quartzo-feldspathic schists and gneisses. Temperatures in the range 620–700 °C are expected due to the positions of the sillimanite-in isograd at around 620 °C and the melt-in line at around 700 °C (Jansen and Schuiling 1976; Buick 1988). Garnet–biotite exchange thermometry (Buick 1988) yields mean temperatures of 615 to 630 °C for samples taken close to the sillimanite-in isograd. The temperatures calculated for migmatitic gneisses vary between 640 and 680 °C, and agree well with the estimate of 670 °C made by Jansen and Schuiling (1976) for the beginning of melting. The regional

Table 1. Oxygen isotope ratios from vein and host-rock samples and temperatures from Naxos island (Greece)

Sample		δ^{18}O SMOW (‰)													T (°C)[a]							
		Qtz	1σ (qtz)		Ky	1σ (ky)		Sill	1σ (sill)		Others	1σ (others)			Qtz–ky	σ(T)[b]	Qtz–sill	σ(T)[b]	Qtz–mica[a]	σ(T)[b]	Qtz–gt	σ(T)[b]
Kinidaros – near bridge at road from Moni to Kinidaros																						
Nk 301	X-cutting vein	9.65	±0.10	(1)	7.19	±0.10	(1)								690	±30						
Komiaki – near the village at path to Appollon																						
Nx 173	S-parallel vein	12.56	±0.07	(2)				9.82	±0.08	(2)							640	±20				
Nx 175	S-parallel vein	12.75	±0.01	(2)	10.27	±0.03	(2)								690	±10						
Nx 178	Veinlet in host	12.72	±0.02	(2)																		
Nx 180	Host rock				10.27	±0.06	(2)				5.38	±0.01	(2)	Bi								
Nx 181	Host rock				9.71	±0.08	(2)				6.33	±0.03	(2)	Bio								
Stavros – path from Stavros church to Kinidaros																						
Nx 16-1	X-cutting vein A	13.05	±0.10	(1)	10.40	±0.10	(1)								655	±25						
G 23	X-cutting vein B	13.12	±0.01	(2)	10.46	±0.05	(2)				10.66	±0.06	(2)	Mu	650	±10			560	±10		
G 24	X-cutting vein B	13.14	±0.08	(8)	10.48	±0.08	(5)	10.86	±0.19	(5)	11.33	±0.10	(1)	Mu	650	±20	730	±50	700	±35		
G 25	X-cutting vein B	13.10	±0.02	(2)	10.58	±0.07	(2)								680	±15						
G 26	X-cutting vein B	13.23	±0.10	(3)				10.87	±0.10	(1)							710	±30				
G 29	X-cutting vein C	13.51	±0.10	(3)	10.93	±0.01	(2)								670	±20						
G 21	X-cutting vein D	13.09	±0.03	(2)	10.44	±0.10	(1)	10.32	±0.06	(2)					650	±5	635	±10				
G 22	X-cutting vein D	13.09	±0.11	(3)	10.43	±0.10	(1)								650	±20						
G 27	Veinlet in host rock	13.08	±0.04	(2)																		
G 27	Host rock	13.86	±0.10	(1)	10.85	±0.03	(2)				7.18	±0.03	(2)	Bio	600	±15			350	±5		
G 28	Veinlet in host rock	13.17	±0.04	(2)																		
G 28	Host rock	13.86	±0.13	(2)	10.80	±0.11	(3)				6.19	±0.03	(2)	Bio	590	±25			310	±5		
Sifones – roadcut at the road to Stavros																						
Nx 98	X-cutting vein	13.35	±0.09	(2)	10.89	±0.02	(2)								690	±20						
Nx 104	Veinlet in host	13.59	±0.15	(2)																		
Nx 106	Host rock	13.16	±0.06	(2)							9.11	±0.04	(2)	Bio					530	±10	590	±10
											8.93	±0.05	(2)	Gt								

Mesi – ridge at the road from Mesi to Appollon																				
Nx 236	S-parallel vein	14.47	±0.02	(2)	11.70	±0.02					10.39	±0.10	(1)	Bio	635	±5			530	±10
Appolon – entrance to village																				
Nx 78	S-parallel vein	13.76	±0.09	(2)	11.00	±0.10	(1)								635	±15				
Nx 82	S-parallel vein	13.76	0.09	(2)				11.31	±0.05	(2)							690	±20		
Nx 76	Host rock	14.12	±0.05	(2)							9.82	±0.11	(2)	Bio					510	±10
Moni – near ultrabasic bodies E of Moni																				
Nx 30	X-cutting vein in bloc	10.78	±0.10	(1)	8.12	±0.10	(1)								650	±25				
Nx 31	X-cutting vein in bloc	10.84	±0.10	(1)	8.12	±0.10	(1)								640	±30				

G 24 ky with bluish core = 10.48‰ and whitish rim = 10.45‰ ± 0.10 (2); two analyses are unspecified with 10.51‰ ± 0.05 (2). *G 24 qtz* average represents four different spots across a 7-cm-wide slice of the hand sample (13.13, 13.29, 13.13, 13.23‰) and three unspecified analyses from another slice with 13.06‰ ± 0.01 (3). *G22 qtz* average represents three different spots across a 4-cm-wide hand specimen with 13.09, 12.95 and 13.23‰. *Mu* muscovite, *bi* biotite, *gt* garnet, *ky* kyanite, *sill* sillimanite, *qtz* quartz

[a]Temperatures calculated using the equation $1000 \ln \alpha (A–B) = A*10^6/T^2$. Qtz–Ky/Sill: A = 2.25 (Sharp 1995). Qtz–Gt: A = 3.1 (Matthews 1994; Rosenbaum and Mattey 1995). Qtz–Mu: A = 1.7 (Kohn and Valley 1998). Qtz–Bi: A = 2.6 (Kohn and Valley 1998)

[b]$\sigma(T)$ = error on temperature estimates assigned to analytical errors of $\delta^{18}O$ measurements

foliation in the host-rock schists developed during syn- to post-peak M2 metamorphism (Buick 1991).

The veins studied in most detail were a set of veins at Stavros (Fig. 1, Fig. 2) aligned subparallel to each other within 1–2 m spacing. These veins are oblique to the foliation with the tips bending into the foliation. Kyanite + quartz ± sillimanite ± white mica form the vein assemblage. The vein samples usually contain coarse-grained blue kyanite and locally the crystals are sometimes several cm in length. Sparsely distributed sprays or needles of texturally later fibrolitic sillimanite are also present in some veins. Sillimanite, like white mica, is only an accessory phase (ca. < 5 vol%). The host rock contains biotite + quartz + kyanite + plagioclase ± garnet ± opaque. Kyanite porphyroblasts are coarse grained in the host rock. Quartz occurs either as fine-grained crystals in the matrix of the host rock or in mm-scale

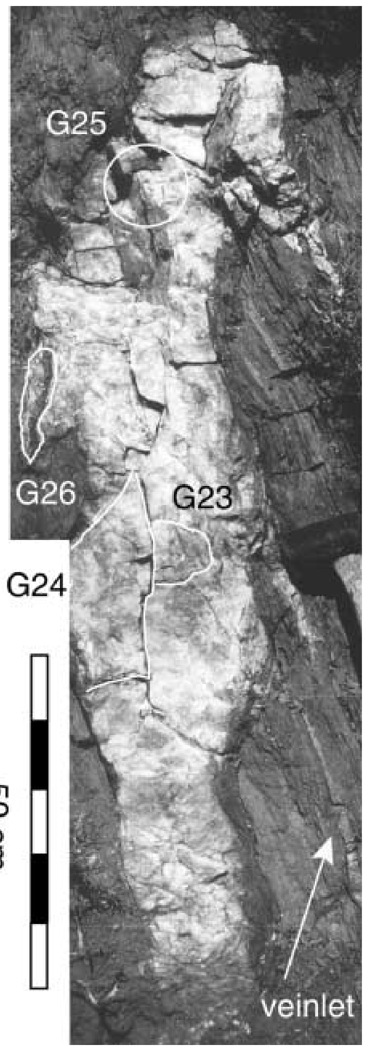


Fig. 2. Photograph of vein B at the Stavros locality. The positions of the sampled hand specimen (G23–G26) in the vein are indicated. The type of s-parallel veinlets sampled together with the host rock is visible at the *lower right*, but the position of the host-rock samples (G27, G28) and its veinlets is outside the photograph (to the *right*), about 30 cm away from the vein. The head of a hammer is visible next to sample G23

veinlets which are parallel to the foliation. The locations of the hand specimens sampled in one of the Stavros veins are shown in Fig. 2. The vein sampled at Appolon is shown in Fig. 3; visible are coarse-grained kyanite crystals intergrown with quartz. In contrast to the Stavros locality, the veins are orientated parallel to the foliation plane of the host rock.

Methods

Vein samples were sliced and crushed, and minerals were hand-picked. Some samples were microsampled with a drilling device in order to investigate the isotopic variability at the millimeter scale. Portions or slabs of each host-rock sample, usually a few hundred grams, were crushed after removing small veinlets, and sieved. Concentrates of quartz from the host-rock schists were produced by magnetic separation and hand-picking. The quartz separate was etched with hydrofluoric acid to identify any remaining feldspar grains, which were removed. This treatment has no effect on the $\delta^{18}O$ value of the quartz. Between 1 and 2 mg of material was hand-picked from the concentrates for oxygen isotope analyses. The oxygen isotope analyses were made with the laser heating/mass spectrometer system at the University of Wisconsin-Madison using a CO_2 laser, BrF_5 reagent, and a Finnigan MAT 251 mass spectrometer (Valley et al. 1995; Spicuzza et al. 1998). The UWG-2 garnet standard was analyzed on each day of laser analysis. Daily averages were within the uncertainty of the recommended value $\delta^{18}O = 5.8 \pm 0.1‰$ (1 sd). All analyses were corrected to the UWG-2 standard and most of the samples were duplicated or triplicated. The deviation from the mean for replicates is routinely better than 0.1‰.

The analytical results are presented as average $\delta^{18}O$ values and uncertainties in Table 1 . Fractionations discussed in the text are expressed using the relation 1000 ln α (Qtz-Ky)$\cong\delta^{18}O$ (Qtz)–$\delta^{18}O$ (Ky). The fractionation factor used in temperature calculations is given by the expression α (Qtz–Ky) = $(1+\delta^{18}O\ (Qtz)/1000)/(1+\delta^{18}O\ (Ky)/1000) = (\delta^{18}O\ (Qtz)+1000)/(\delta^{18}O\ (Ky)+1000)$.

Results

The most detailed isotopic studies were made at Stavros and the results for this locality are summarized in Fig. 4.

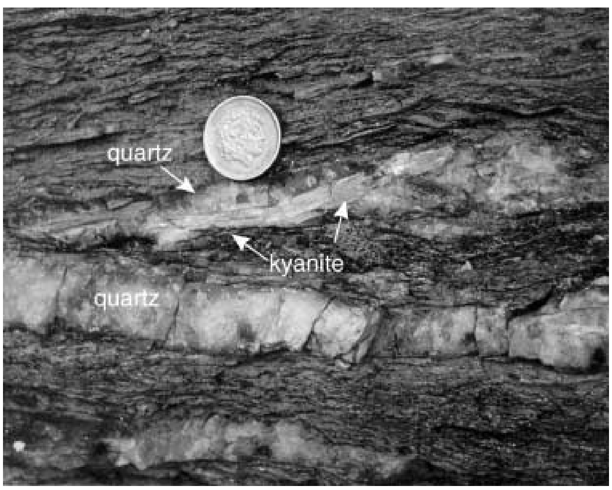


Fig. 3. Photograph of the s-parallel quartz–kyanite vein at Appolon. Coin is approximately 1.5 cm in diameter

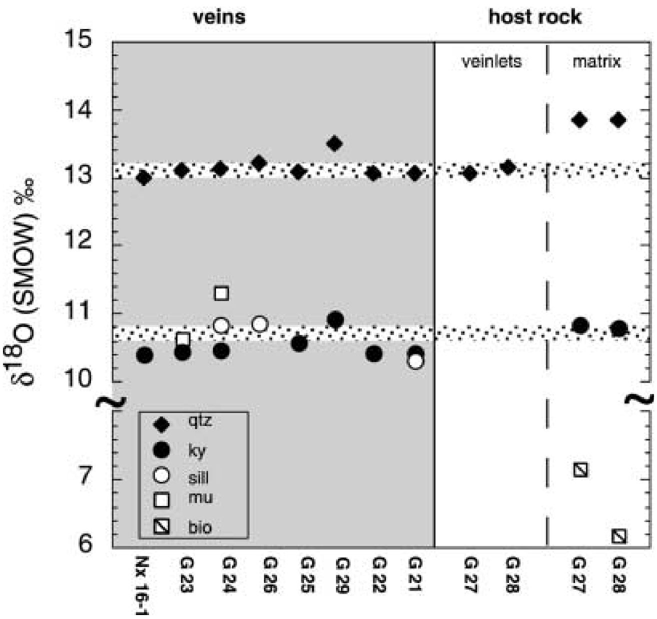


Fig. 4. Oxygen isotope composition of minerals at the Stavros locality. Background indicates whether sample is from vein or host rock (*shaded* vein, *nonshaded* host rock). *Qtz* quartz, *ky* kyanite, *sill* sillimanite, *mu* white mica, *bio* biotite

Analyses of eight samples from four veins show that oxygen isotopic ratios of quartz, kyanite and sillimanite are remarkably homogenous throughout individual veins, as well as throughout the outcrop. The $\delta^{18}O$ (Qtz) values vary from 13.1 to 13.5‰. Kyanite values show a similarly small $\delta^{18}O$ variation from 10.4 to 10.9‰. A core–rim pair microsampled from a single 10-mm blade of blue kyanite (sample G24 from vein B) gave $\delta^{18}O$ (Ky) values of 10.5‰ for the rim and 10.5‰ for the core, and two further analyses of the same crystal gave $\delta^{18}O$ (Ky) = $10.5 \pm 0.1‰$. Thus, there is no evidence for isotopic zoning during kyanite growth. Replicate analyses of quartz separates from different parts of two hand specimens (samples G22 and G24) indicate that the cm-scale variability of $\delta^{18}O$ is $< 0.3‰$ (footnote to Table 1). The quartz–kyanite fractionation of the Stavros samples is remarkably consistent at $2.6 \pm 0.1‰$ and independent of small variations in the mineral $\delta^{18}O$ values. Sillimanite $\delta^{18}O$ values range between 10.3 to 10.8‰ and the quartz–sillimanite fractionation averages at $2.5 \pm 0.3‰$.

The host rocks at Stavros show slight but significant differences compared to the veins. The fine-grained quartz of two samples from the host-rock matrix has a $\delta^{18}O$ value of 13.9‰, whereas quartz from s-parallel veinlets in these host-rock samples has values of 13.1 and 13.2‰. Thus, the veinlet quartz values are similar to those of the main quartz vein (average $\delta^{18}O = 13.2‰$), whereas the host rock quartz is slightly higher (Fig. 4). The kyanites from the two host-rock samples give $\delta^{18}O$ values of 10.8 and 10.9‰ (compared to the average value of 10.5‰ in the veins). The corresponding quartz–kyanite fractionations in these samples are 3.0 and 3.1. Muscovite in veins gives $\delta^{18}O$ values of 10.7 and 11.3‰, whereas host-rock biotite values are distinctly lower with $\delta^{18}O$ (Bio) = 7.2 and 6.2‰.

The results for the six other sites sampled in eastern Naxos are shown together with the Stavros results in Fig. 5. The sample series in Fig. 5 are presented in order of relative distance from the core and decreasing metamorphic grade according to their position relative to the sillimanite-in isograd and melt-in line. Generally, $\delta^{18}O$ (Qtz) values of veins range between 12.5 and 14.5‰, but notably lower values for quartz (and kyanite) are found at Kinidaros and Moni. The quartz–kyanite and quartz–sillimanite fractionations are similar, yet show small but consistent differences from those given by the vein samples at Stavros. Quartz–kyanite fractionations in veins from the two sites closer to the core (Kinidaros and Komiaki) are 2.5, whereas the sites further away from the core than Stavros generally give slightly larger fractionations (Appolon = 2.8; Mesi = 2.8; Moni = 2.7). At all localities, the quartz from small (s-parallel) veinlets is identical in $\delta^{18}O$ to that of the main vein. Host-rock matrix quartz again shows slight differences from the veins they enclose.

Discussion

Oxygen isotope thermometry of quartz–Al_2SiO_5 pairs

The oxygen isotope thermometry of quartz–Al_2SiO_5 pairs is critically influenced by the choice of calibration for the aluminosilicate fractionation factor. Several calibrations are available: empirical (Sharp 1995), semi-empirical (increment method) calculations (Richter and Hoernes 1988; Zheng 1993; Hoffbauer et al. 1994), and experimental (Tennie et al. 1998). Ghent and Valley (1998) showed that petrologically reasonable temperatures were obtained from quartz–kyanite pairs in high-grade metamorphic nodules using the empirical calibration of Sharp (1995), which was based on the analyses of $\delta^{18}O$ in natural coexisting quartz + kyanite + garnet assemblages and quartz–garnet isotopic thermometry. Vannay et al. (1999) determined petrologically significant temperatures for high-grade rocks of the Himalayan orogen using this calibration, and were able to demonstrate inverted metamorphic gradients. Similarly, Moecher and Sharp (1999) demonstrated excellent agreement between isotope thermometry utilizing the Sharp (1995) calibration and conventional phase equilibrium thermometry in mid to upper amphibolite facies rocks which had experienced one period of crystallization and mineral growth.

The calibration of Tennie et al. (1998) yields temperatures of 720–830 °C for the Naxos veins. These temperatures are not geologically reasonable because they would indicate that the host rocks should undergo melting, which is clearly not the case. Even higher temperature estimates are given by the increment calculations of Hoffbauer et al. (1994), whereas the Zheng (1993) calibration yields temperatures which are lower than those given by petrological estimates. Tennie et al. (1998) suggested that early growth of kyanite relative to quartz in a metamorphic assemblage might lead to disequilibrium quartz–kyanite fractionations. This possibility does not hold for the veins on Naxos, because quartz is the modally abundant mineral (> 95%) and thus cannot continue to exchange at any (theoretically) higher temperature. Moreover, the homogeneity of the quartz analyses at Stavros argues against any change in the $\delta^{18}O$ (Qtz) value. Correspondingly, if quartz–kyanite exchange occurred at lower temperatures, the quartz–kyanite fractionation will be relatively large and the $\delta^{18}O$ value of the kyanite core would be lower than that

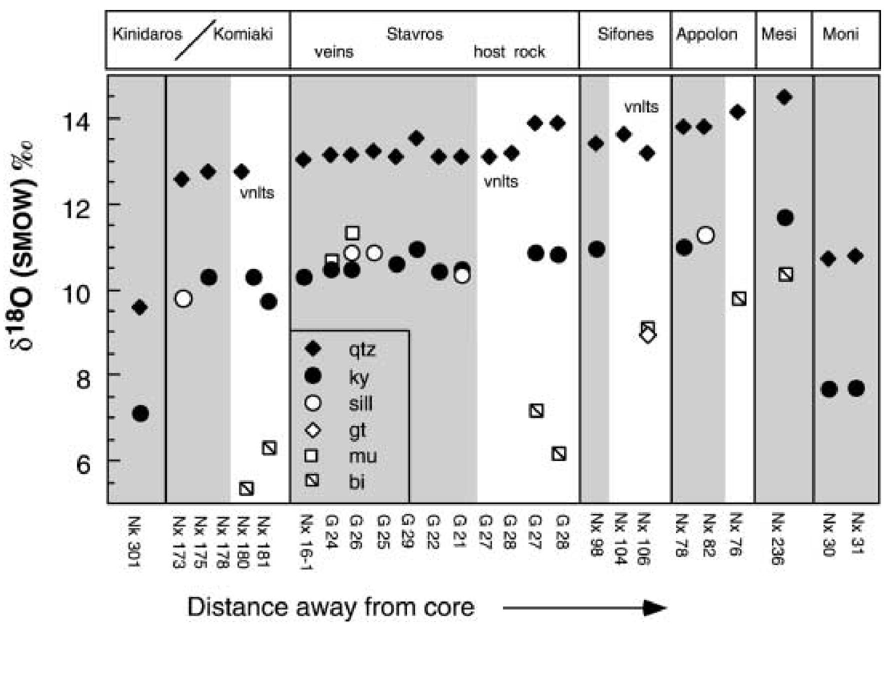


Fig. 5. Oxygen isotope composition of minerals from all the localities studied in this work. The sample localities are arranged from right to left in order of relative distance from the core and decreasing metamorphic grade according to their position relative to the sillimanite-in isograd and melt-in line. Background indicates whether sample is from vein or host rock (*shaded* vein, *nonshaded* host rock)

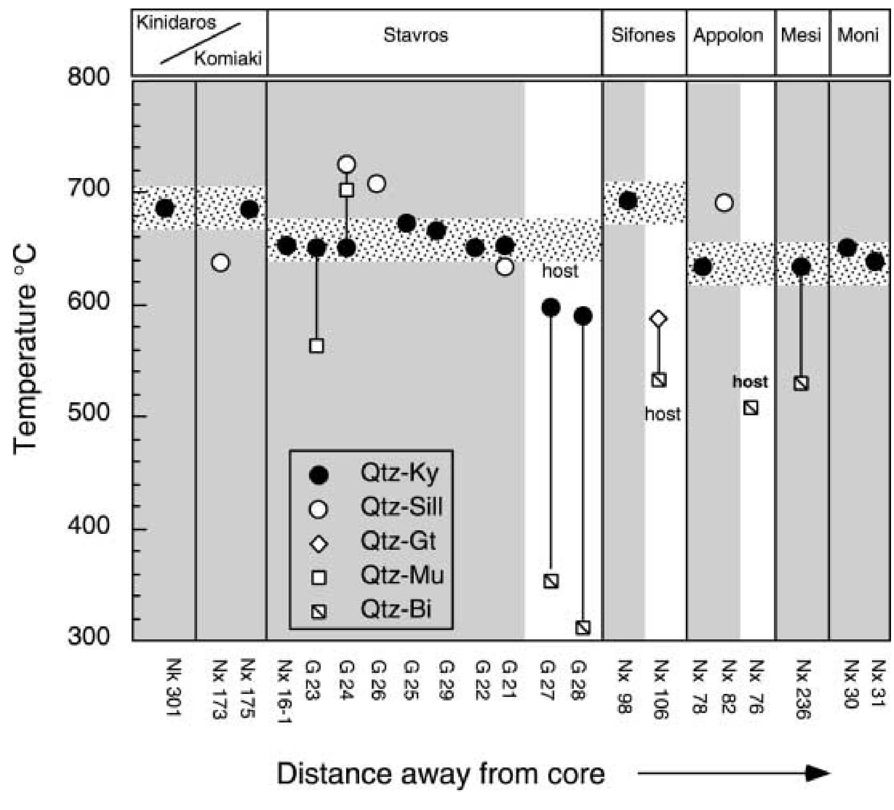
of the rim formed subsequently; isotopic zoning was not found in this study. Given that the Sharp (1995) calibration consistently results in the geologically most consistent temperatures, our work follows that of Ghent and Valley (1998), Moecher and Sharp (1999) and Vannay et al. (1999) in using this equation: 1000 lnα (Qtz–Al_2SiO_5) = $2.25\times10^6/T^2$ (T in °K).

The oxygen isotope temperatures are given in Table 1 and plotted in Fig. 6. Quartz–kyanite temperatures vary from 635 °C at the Appolon and Mesi sites to 690 °C at Kinidaros and Komiaki. Quartz–kyanite temperatures at the Stavros locality range from 650 to 680 °C and average 660 ± 10 °C. Lower temperatures of 590 and 600 °C are estimated from the quartz–kyanite pairs of the two host rocks at Stavros. The range of temperatures agrees well with the petrologically deduced peak temperatures of 620–700 °C for the kyanite–sillimanite zone. Moreover, the trend of temperatures is generally consistent with the increase in metamorphic grade from the sillimanite-in to the melt-in isograd. This can be seen in Fig. 6 by comparing the temperatures at Appolon and Mesi (located near the sillimanite-in isograd) to the higher temperatures at the Stavros, Komiaki and Kindaros localities. Possible exceptions to this direct correlation between petrological and isotopic temperatures are the vein samples at Sifones, where a slightly higher temperature of 690 ± 20 °C is deduced, and at Moni, where temperatures of 640 ± 30 and 650 ± 25 °C are obtained despite the fact that these veins were sampled outside the sillimanite-in isograd (Fig. 1). Bearing in mind the uncertainties in both the petrological and isotopic temperature estimates, these differences are not significant. Moreover, the sillimanite-in isograd in the Moni area is very steep compared to the north of the island (Jansen and Schuiling 1976), and thus the geographical distance from the sample site to the sillimanite-in isograd is small.

The rocks on Naxos differ both in type and geological environment from those used in the Sharp (1995) calibration. Still, this calibration yields self-consistent temperature estimates which are in excellent agreement with previously established petrologic thermometry. The overall picture is that quartz–kyanite vein temperatures provide accurate and self-consistent estimates of peak metamorphic temperature on Naxos. The quartz–sillimanite (fibrolite) temperatures are significantly more variable than the quartz–kyanite temperatures, varying from 635 to 730 °C, and they do not show the systematic increase with grade revealed by the quartz–kyanite temperatures. Nevertheless, their range and average (680 ± 35 °C) broadly correspond with the isograd and quartz–kyanite vein temperatures, and indicates that quartz, kyanite, and sillimanite formed at similar temperatures.

The wider variability of sillimanite, relative to kyanite temperatures, is consistent with textural observations. Kyanite forms in these veins as coarse-gemmy idiomorphic crystals or aggregates, whereas sillimanite forms later as fine fibrous needles, often on shear surfaces, and therefore may be more susceptible to post-formation exchange or sporadic growth at variable temperatures. Several workers (Jansen and Schuiling 1976; Buick 1988) have noted reactions between the two Al-silicate miner-

Fig. 6. Oxygen isotope thermometry of mineral pairs. Calibrations used in the compilation are given in Table 1 . Background indicates whether sample is from vein or host rock (*shaded* vein, *nonshaded* host rock). Temperatures for quartz–kyanite are highly precise in veins, but more variable and apparently reset in the matrix



als. Common observations are pseudomorphs of sillimanite after kyanite and incompletely reacted kyanite, indicating prograde growth of sillimanite. However, our data and observations of Jansen and Schuiling (1976) and Buick (1988) suggest that the aluminosilicates grew close to the sillimanite–kyanite phase-equilibrium boundary, and the position of the sillimanite-in isograd is also complicated by the development of retrograde sillimanite. Accordingly, Jansen and Schuiling (1976) mapped a wide kyanite–sillimanite transition zone (on average 600 m). The presence of kyanite or sillimanite inside the sillimanite-in isograd may depend on the degree of thermal overstep and other factors affecting nucleation and growth kinetics, such as deformation (Jansen and Schuiling 1976; Kerrick 1990; Todd and Engi 1997).

Vein versus host-rock temperatures

The oxygen isotope apparent temperatures of 590–600 °C given by the host-rock samples at Stavros are systematically lower than those given by the veins at this locality (Fig. 4). This observation also holds for quartz–biotite temperatures (Fig. 6). Quartz–biotite temperatures of 310–530 °C are obtained using the empirical calibration of Kohn and Valley (1998). The experimental calibration of Chacko et al. (1996) yields lower temperatures in the range 260–460 °C, whereas the empirical calibration of Bottinga and Javoy (1975) gives slightly higher temperatures of 400–620 °C. The lower quartz–biotite temperatures in the high-grade host rocks are consistent with previously published data by Rye et al. (1976). They observed a reasonable agreement between oxygen isotope and mineralogical temperatures in the lower grade rocks (450–550 °C), but found that isotopic temperatures in higher grade rocks were generally lower than the mineralogically deduced temperatures. High rates of volume diffusion for oxygen in biotite have been determined experimentally by Fortier and Giletti (1991). Thus, the lower host-rock temperatures most probably reflect the retrograde resetting of mineral isotopic compositions during cooling and the consequent modal chemistry controls on fractionations (Giletti 1986; Eiler et al. 1992, 1993).

The so-called Fast Grain Boundary (FGB) diffusion model (Eiler et al. 1992) predicts that peak metamorphic temperatures will be best preserved by bimineralic rocks in which a mineral with slow oxygen diffusion rate is minor in amount compared to a mineral with faster diffusion of oxygen (e.g., RAM thermometry, Valley 2001). In this respect, the quartz–kyanite veins on Naxos fulfill the prediction and yield temperatures concordant with their position in the kyanite–sillimanite zone of the Naxos thermal dome. By contrast, the same mineral pair from the biotite-rich host rock at Stavros is reset to lower temperatures. This also fits the FGB prediction and is in accord with the results of Ghent and Valley (1998) on quartz–Al_2SiO_5 pairs from the Mica Creek (British Columbia). They modeled the effects of isotopic exchange during cooling in a rock of quartz + plagioclase + kyanite and predicted that the quartz–kyanite temperatures would be significantly reset and lower in their mineral system than for quartz–kyanite pairs of a two-phase assemblage. This is a consequence of quartz and plagioclase continuing to exchange oxygen isotopes at temperatures below the "closure temperature" for kyanite. This retrograde process would increase the $\delta^{18}O$ value for quartz (and decrease the $\delta^{18}O$ value for plagioclase), and consequently increase the value of Δ (Qtz–Ky) and lead to a lower temperature estimate. The slightly higher $\delta^{18}O$ values of the matrix quartz (vs. vein quartz) at the Stavros locality (Fig. 4) are consistent with retrograde exchange, bearing in mind the presence of significant modal amounts of plagioclase and biotite (both minerals with higher diffusion rates than kyanite) in the host-rock assemblage.

Conclusions

Oxygen isotope thermometric study of high-grade rocks on Naxos shows that quartz–kyanite pairs in synmetamorphic veins are precise and accurately record regional peak metamorphic temperatures, whereas minerals of host-rock samples have undergone isotopic exchange. Slight ^{18}O enrichment of the matrix quartz in the host rock relative to the vein quartz is interpreted in terms of closed-system diffusional exchange between quartz, plagioclase and biotite. Quartz–sillimanite fractionations in the veins, though more variable, give temperatures similar to quartz-kyanite pairs, and suggest that the veins grew near the kyanite–sillimanite boundary (6.5 to 7.5 kbar for temperatures of 635–685 °C). The similarity between the isotopic compositions of vein and host-rock quartz on Naxos suggests that the fluids involved in vein formation were in, or near isotopic equilibrium with the host rocks, thus favoring a mechanism of vein formation by local segregation at peak metamorphic temperatures. The vein thermometry thus provides valuable constraints on the regional metamorphic evolution of Naxos island.

Our study demonstrates that vein mineral assemblages such as quartz–kyanite are effective thermometers in high-temperature rocks. By contrast, retrograde exchange is a major problem for the thermometry of host-rock assemblages. Quartz-rich segregations are very common in high-temperature rocks (e.g., Kerrick 1990). Traditionally, isotopic studies of such segregations and veins have been used to infer fluid sources (e.g., Yardley and Bottrell 1992). Thermometric oxygen isotope studies of veins – and related host rocks – are particularly useful in petrology, because they integrate information about fluid sources, temperature of vein formation and metamorphism. The knowledge of an accurate temperature might also strengthen structural observations about timing of vein formation.

It would be interesting to re-examine the well-known Al_2SiO_5 segregations of the Lepontine Alps (Klein 1976;

Kerrick 1988; Todd and Engi 1997) and occurrences at other Alpine localities, such as the kyanite-bearing veins of Trescolmen (Heinrich 1986). New, precise temperature estimates for Al_2SiO_5-silicate-bearing veins, in combination with careful petrological and structural investigations, might resolve some of the inconsistencies in the P–T estimates.

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