

Variscan relicts in Alpine high-*P* pelitic rocks from Samos (Greece): evidence from multi-stage garnet and its included minerals

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ABSTRACT Porphyroblastic garnet schists from northern Samos contain in their matrix the assemblage Ca-rich garnet + phengite + paragonite ± chloritoid equilibrated at ~530 °C and ~19 kbar during early Tertiary metamorphism. These high-pressure/low-temperature (HP-LT) metapelitic rocks also exhibit mineralogical and microstructural evidence of an older, higher temperature metamorphism. Large, centimetre-sized Fe-rich garnet showing growth zoning developed discontinuous, <0.5 mm thick, Ca-rich and Mn-poor overgrowths, compositionally matching small (<1 mm) high-*P* matrix garnet. Because the discontinuous garnet rims are in textural and chemical equilibrium with Alpine high-*P* minerals, the central parts of the garnet porphyroblasts were found to have formed prior to the Tertiary metamorphism. This is supported by electron microprobe U-Th-Pb dating of monazite inclusions yielding partly reset Variscan ages between 360 and 160 Ma. Monazite-xenotime and garnet-muscovite thermometry applied to inclusions in the pre-Alpine garnet yielded temperatures of 600–625 °C (at 3–8 kbar). Prismatic Al-rich pseudomorphs, possibly after kyanite/sillimanite, and inclusions in garnet composed of white K-Na mica + quartz ± albite ± K feldspar, interpreted as possible replacements of an intermediate K-Na feldspar, further support Variscan amphibolite facies conditions. The Samos metapelites thus experienced higher temperatures during the Variscan than during Alpine metamorphism. Diffusional relaxation was very limited between pre-Alpine garnet and Alpine garnet; both were filled with Alpine garnet along overgrowths and fractures. Fluid-mediated intergranular element transport, enhanced by deformation, appears crucial in transforming the Variscan garnet into a grossular richer composition during Alpine subduction-zone metamorphism. At such conditions, dissolution–reprecipitation appears to be a much more effective mechanism for modifying garnet compositions than diffusion. Amphibolite facies conditions are typical for Variscan basement relics exposed in central Cycladic and Dodecanese islands as well as in eastern Crete. The Samos metapelites studied comprise a north-eastern extension of these basement occurrences.

Key words: Alpine HP-LT metamorphism; monazite EMP dating; multi-stage garnet; Samos; Variscan amphibolite facies metamorphism.

INTRODUCTION

The Cycladic islands in the central Aegean Sea are composed mainly of the Cycladic blueschist unit, which experienced high-pressure/low-temperature (HP-LT) metamorphism (M1) during the Early Tertiary (e.g. Okrusch & Bröcker, 1990; Ring & Layer, 2003; Bröcker & Pidgeon, 2007). On several central Cycladic islands, the metamorphic volcano-sedimentary sequence of the Cycladic blueschist unit is underlain by pre-Alpine basement of continental affinity, i.e. paragneisses and orthogneisses, various schists, amphibolites, and acidic and basic intrusive rocks (Fig. 1). Petrological evidence generally indicates that the basement rocks shared the Tertiary metamorphic history with their mainly Mesozoic volcano-

sedimentary cover, so that they have been juxtaposed during the Late Cretaceous/Palaeocene subduction. The basement rocks, which record an amphibolite facies Variscan event, are best preserved on the islands of Ios and Sikinos (Van der Maar *et al.*, 1981; Henjes-Kunst & Kreuzer, 1982; Van der Maar & Jansen, 1983; Andriessen *et al.*, 1987; Franz *et al.*, 1993; Gupta & Bickle, 2004). On Naxos and Paros, the pre-Alpine mineralogies were obliterated during a Late Tertiary amphibolite facies event (M2) associated with partial melting (e.g. Jansen & Schuiling, 1976) but inherited Variscan ages from zircon have been obtained on both islands (Engel & Reischmann, 1998; Reischmann, 1998; Keay *et al.*, 2001).

The island of Samos occupies a transitional position between the Attic-Cycladic Complex (ACC) and the Menderes Complex (Fig. 1). The Tertiary metamorphic evolution of Samos closely resembles that of the

*Deceased on 9 April 2007.



Fig. 1. Map of the southern Aegean region showing occurrences of pre-Alpine basement relics in the Cyclades (stars), the Dodecanese islands (black) and eastern Crete (black). The island of Samos is located in the north-eastern part of the map. After Franz *et al.* (2005).

ACC: an Early Tertiary HP-LT metamorphism (M1 event) was followed by a Late Tertiary, medium-*P*, greenschist-grade overprint (M2 event) (e.g. Okrusch *et al.*, 1984; Chen, 1995; Will *et al.*, 1998). The M2 event occurred during the extension-related uplift of the blueschist facies rocks to higher crustal levels (Ring *et al.*, 1999, 2007; Ring & Layer, 2003).

Mica-rich schists and gneisses containing noticeably large garnet porphyroblasts (up to 1.5 cm in diameter) are exposed along the central north coast of Samos (Figs 2 & 3). Although the matrix of these metapelitic rocks contains a typical Tertiary HP-LT assemblage involving phengite + Ca-rich garnet + paragonite ± chloritoid, the zoning and multi-stage nature of the large garnet, together with relict inclusions, support

the view that these rocks have also experienced an earlier amphibolite facies metamorphic event. Mineralogical evidence of a pre-Alpine event is scarce in the strongly deformed matrix, which recrystallized pervasively during the Alpine orogeny. In the present contribution, the first comprehensive petrological and geochemical evidence to support a Variscan origin for the garnet-bearing metapelitic unit of northern Samos is presented. In particular, special emphasis is placed on the basis of the multi-stage growth of the garnet, its inclusions and U-Th-Pb electron microprobe dating of monazite in an effort to elucidate the polyphase metamorphic evolution of the Samos rocks.

GEOLOGICAL SETTING

The island of Samos is located in the eastern Aegean Sea, only a few kilometres from the Turkish coast (Fig. 1). Samos is built up of metamorphic nappe piles composed of alternating marbles, phyllitic to psammitic schists and gneisses with intercalations of meta-volcanics (greenschists and blueschists), metagabbros and ultrabasics (Papanikolaou, 1979; Theodoropoulos, 1979; Okrusch *et al.*, 1984; Chen, 1995; Ring *et al.*, 1999, 2007). The volcano-sedimentary metamorphic succession is dissected into three crystalline blocks by grabens filled with Neogene sediments and volcanics (Fig. 2). Four major structural units are distinguished from the bottom to top on the island.

The *Kerketefts unit*, occupying the mountainous region of western Samos, is the lowest (basal) tectonic unit. It consists of > 1000 m thick, partly dolomitic marbles with minor phyllites in its upper part. In contrast to the other three Samos units, the *Kerketefts unit* has not been affected by the Early Tertiary HP-LT metamorphism.

The *Agios Nikolaos unit* comprises the porphyroblastic garnet-mica schists, orthogneisses and minor carbonate rocks. The unit is found only along the central north coast of the island.

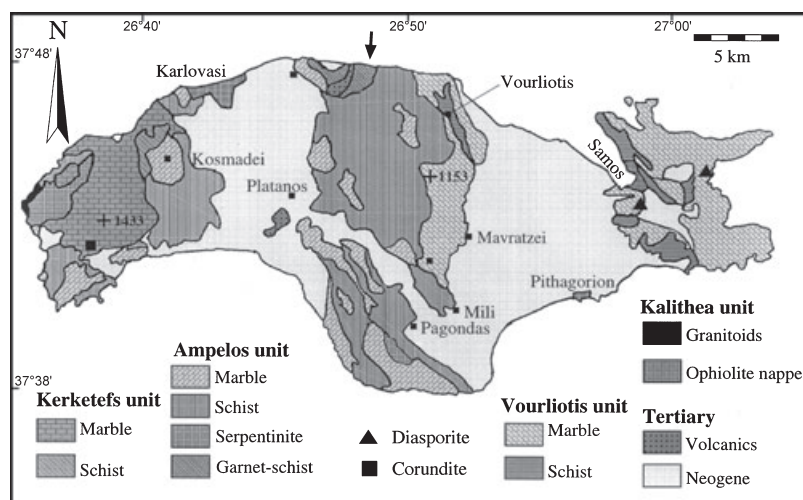


Fig. 2. Geological map of Samos with the locality of studied garnet-mica schists of the *Agios Nikolaos* nappe marked by arrow. Slightly modified after Theodoropoulos (1979) and Papanikolaou (1979).

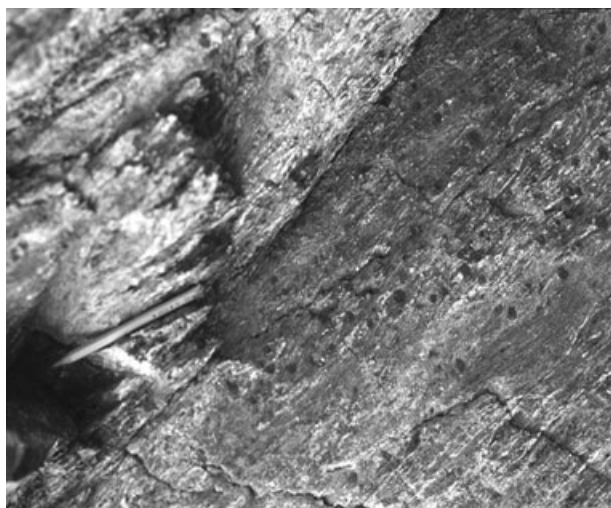


Fig. 3. Outcrop of porphyroblastic garnet schists along the north coast of Samos.

The *Ampelos unit* overlies the Agios Nikolaos and Kerketefs units; it is a highly variable sequence of alternating schists and marbles, locally containing intercalations of metabasic rocks (blueschists and greenschists), ultramafics (mainly serpentinites) and metagabbros. The unit dominates the central crystalline area of Samos and is composed of prominent upper and lower marble horizons with intercalated pelitic to psammitic schists.

Similar to the Ampelos unit, the *Vourliotis unit* is characterized by local occurrences of blueschists and greenschists. Serpentinites and metagabbros are confined to the part of the unit occurring in the central crystalline area. In east Samos several diasporite lenses with peculiar mineralogies are exposed in the upper marble horizon of the unit (Feenstra, 1997; Ockenga *et al.*, 1998; Ockenga, 2000; Feenstra *et al.*, 2003). A recent study suggests that the Ampelos and Vourliotis units should not be divided, but combined with the Turkish Dilek nappe to form the Dilek/Ampelos nappe (Ring *et al.*, 2007).

The Samos rocks record an Alpine metamorphic evolution similar to that of the ACC (Okrusch *et al.*, 1984; Chen, 1995; Chen *et al.*, 1995; Feenstra & Petrakakis, 1997; Will *et al.*, 1998; Ring *et al.*, 1999, 2007; Feenstra *et al.*, 2003; Ring & Layer, 2003). An early Alpine HP-LT metamorphism can be correlated with the Early Tertiary M1 event and a greenschist-grade overprint with the Late Tertiary Barrovian-type M2 event on the Cycladic islands. Geochronological data are rather limited for Samos. Chen *et al.* (1995) referred to unpublished K-Ar white mica dates by H. Kreuzer, that confirmed a two-stage Alpine evolution similar to that of the Cycladic islands. Ring & Layer (2003) obtained $^{40}\text{Ar}/^{39}\text{Ar}$ ages of *c.* 44–36 Ma (M1) for phengitic mica from the Ampelos and Agios Nikolaos nappes. These researchers also dated several mica-bearing samples from the upper part of the

Kerketefs unit, which yielded $^{40}\text{Ar}/^{39}\text{Ar}$ phengitic mica ages in the range 26 to 22 Ma (M2). The ages are interpreted to relate to the time of tectonic emplacement of the blueschist nappes (Agios Nikolaos, Ampelos and Vourliotis units) on top of the basal Kerketefs unit (Fig. 2) causing a mild glaucophane-schist facies metamorphism (8–10 kbar, 350–400 °C). It is likely that the M2-greenschist grade metamorphism, overprinting the blueschist units in other parts of Samos in variable degrees, may compare in age to this Late Tertiary tectonometamorphic event.

Petrological and geochronological data pertaining to the pre-Alpine history of Samos are scarce. In their detailed study of the structural evolution of Samos, Ring *et al.* (1999) reported Pb/Pb zircon evaporation ages of 240–230 Ma for an augengneiss (metagranitoid) from the Ampelos nappe and another age of *c.* 302 Ma for an orthogneiss sample collected from the Agios Nikolaos nappe. To our knowledge, geochronological data are not available for the studied porphyroblastic garnet schists from the Agios Nikolaos unit.

On the basis of petrogenetic considerations and geothermobarometry applied to (semi)pelitic and basic rocks, Chen (1995) derived for the Eocene HP metamorphism (M1) temperatures ranging from ~500 °C in central Samos (Ampelos unit) to ~470 °C in eastern Samos (Vourliotis unit) at pressures of ~12 kbar. Higher M1 conditions (~530 °C, 12–14 kbar) were obtained for metabasic glaucophane-garnet-phengite-paragonite-epidote rocks (Agios Nikolaos unit) located along the north coast (cf. also Chen *et al.*, 1995). On the basis of model calculations in the NCFMASH system applied to some of Chen's samples, Will *et al.* (1998) concluded that pressures were higher during the M1 event. For a garnet glaucophanite from the Agios Nikolaos unit, located close to the presently studied pelitic garnet micaschists, Will *et al.* (1998) obtained peak M1 conditions of ~520–530 °C and ~19 kbar. Their study also demonstrated that the metabasic rock followed a *P–T* path involving cooling during subsequent exhumation.

Conditions during the medium-*P* M2 metamorphism, a locally varying greenschist facies overprint related to tectonic emplacement of the blueschist facies units into higher crustal levels, are difficult to constrain. Chen (1995) estimated *P–T* conditions of 460–490 °C at ~7 kbar, without discernible regional variations in central and eastern Samos. Feenstra (1997) estimated that late formation of zincohögbomite and white mica in a diasporite from eastern Samos (Vourliotis unit) had occurred at temperatures as low as ~300 °C (at 5 kbar). Such conditions may represent, however, a late stage of the M2 event.

PETROLOGY OF GARNET MICASCHISTS OF THE AGIOS NIKOLAOS UNIT

The garnet micaschists studied are exposed in a kilometre-long section along the central north coast of

Samos (Figs 2 & 3). The conspicuous, strongly foliated rocks containing centimetre-sized garnet were already recognized by Theodoropoulos (1979) and mapped as the Agios Nikolaos unit, the lowest part of the Ampelos nappe pile (Fig. 2). In a few places these metapelitic rocks are in contact with massive metabasic rocks which locally display relic pillow textures. In his study of the metamorphic evolution of Samos island, Chen (1995) presented field evidence for an intrusive relationship between the metabasic rocks and garnet-mica schists. We were unable to find such evidence because of the intense Alpine deformation of the contacts between the two rock types. On the basis of microstructural and petrographic observations (e.g. parallel foliations) however, we concur with the view of Chen (1995) that basic and pelitic rocks have shared their metamorphic evolution at least since the M1 event. Chen (1995) interpreted the fabric and mineralogy of the porphyroblastic garnet rocks to indicate two successive stages of Alpine garnet growth. The main central parts of the garnet porphyroblasts were considered to have formed during the early Alpine HP-LT event (M1), whereas the thin discontinuous rims grew during the Late Tertiary greenschist facies overprint (M2).

Our petrographic and EMP studies of garnet schists indicate that the matrix is dominated by phengite, paragonite, chlorite and quartz, of which white mica defines the foliation of the rock (Figs 4a & 5a). Parallel intergrowths of phengite and paragonite, suggesting textural equilibrium between the K-Na mica, as well as crosscutting paragonite flakes are observed. Small garnet, <1 mm in diameter, is dispersed in the matrix of most samples (Fig. 6a). Chlorite is partly aligned with the foliation but mainly occurs as randomly orientated grains, particularly in pressure shadows of garnet. Fine-grained chlorite is common in thin cracks transecting the large garnet porphyroblasts. Chloritoid occurs in three samples (Table 1); it is typically intergrown with phengite and is found in direct contact with the small matrix garnet (Fig. 6). Minor glaucophane, which forms up to 0.5-mm-long crystals, is present in sample SA29, mainly in quartz-rich bands. Aggregates of intergrown hematite and goethite with an angular perimeter are common in most samples. Fe-sulphide often occurs in the central parts of these aggregates. These relics and FeS inclusions in the porphyroblastic garnet suggest that initial FeS in the matrix was oxidized to Fe-(hydr)oxide during a late stage of the rock history. Ilmenite, aligned in the foliation, is locally present in sample SA109A. Minor or accessory phases in the samples studied include rutile, graphite, calcite, tourmaline, zircon, apatite, monazite and xenotime (cf. Table 1).

Many large garnet porphyroblasts exhibit clear (inclusion-poor) cores surrounded by outer zones with abundant inclusions of white mica, quartz, rutile and graphite (Figs 4a,b & 7a,b; Appendices A2 & A3). Composite inclusions consisting of irregular inter-

growths of fine-grained mica, quartz and, more rarely, albite or K feldspar, are occasionally present in the outer garnet cores as well (Fig. 7c). Most large garnet shows clear microstructural evidence of at least a two-stage growth. The main central parts of the garnet display a foliation, defined by flaky graphite and fine-grained Fe-sulphide, which is discordant with the foliation in the matrix (e.g. Fig. 5a). The latter wraps around the rigid garnet porphyroblasts, which have developed pressure shadows filled with chlorite, white mica, quartz and rutile (Figs 4a & 5a). Virtually all large garnet show thin overgrowths ranging in thickness from <0.1 up to 0.8 mm (Figs 4 & 5; Appendices A1–A3). The overgrowths, which contain few inclusions, are in textural equilibrium with M1 matrix minerals such as phengite and chloritoid. The overgrowths are invariably rich in grossular and poor in spessartine components; compositionally they match the small garnet dispersed in the matrix (see the following section, Mineral chemistry). In some samples the garnet porphyroblasts are marginally transformed into small idiomorphic matrix garnet (Fig. 4d). The contact between first-generation garnet (M0 garnet) and Ca-rich overgrowths is mostly sharp and follows the embayed outline of the large porphyroblasts (Figs 4c & 5). In some cases, particularly in sample SA29, Ca-rich M1 garnet also formed in up to 1- to 20- μ m-wide cracks transecting the outer parts of the M0 garnet porphyroblasts (Fig. 4c). Thin, Ca-rich, Mn-poor overgrowths (<0.2 mm thick) also developed where quartz-filled veinlets cut the entire garnet porphyroblast (Fig. 5b & Appendix A1). These veinlets may have originated as pull-apart fractures during early Alpine deformation. Textures and results from EMP element mapping imply that the overgrowths post-date the main deformation affecting the M0 garnet porphyroblasts.

Small M1 garnet and the marginal parts of large garnet porphyroblasts (including M1 overgrowths) are replaced, in varying degrees, by texturally late, randomly orientated chlorite, together with minor amounts of hematite and goethite, coarse rutile and white mica. Many M0 garnet porphyroblasts are transected by thin (<20 μ m wide) cracks filled with fine-grained chlorite (Fig. 7). Textural evidence suggests that the chlorite-filled networks and chlorite pseudomorphs after garnet formed late in the cooling and uplift history of the rocks.

MINERAL CHEMISTRY

Electron microprobe analysis

Chemical compositions of minerals were determined by wavelength-dispersive X-ray analysis (WDS) techniques using CAMECA SX-100 electron microprobes. Preliminary EMP work was carried out at the Petrological Institute of the University of Vienna; additional EMP analyses and element X-ray distribution mapping

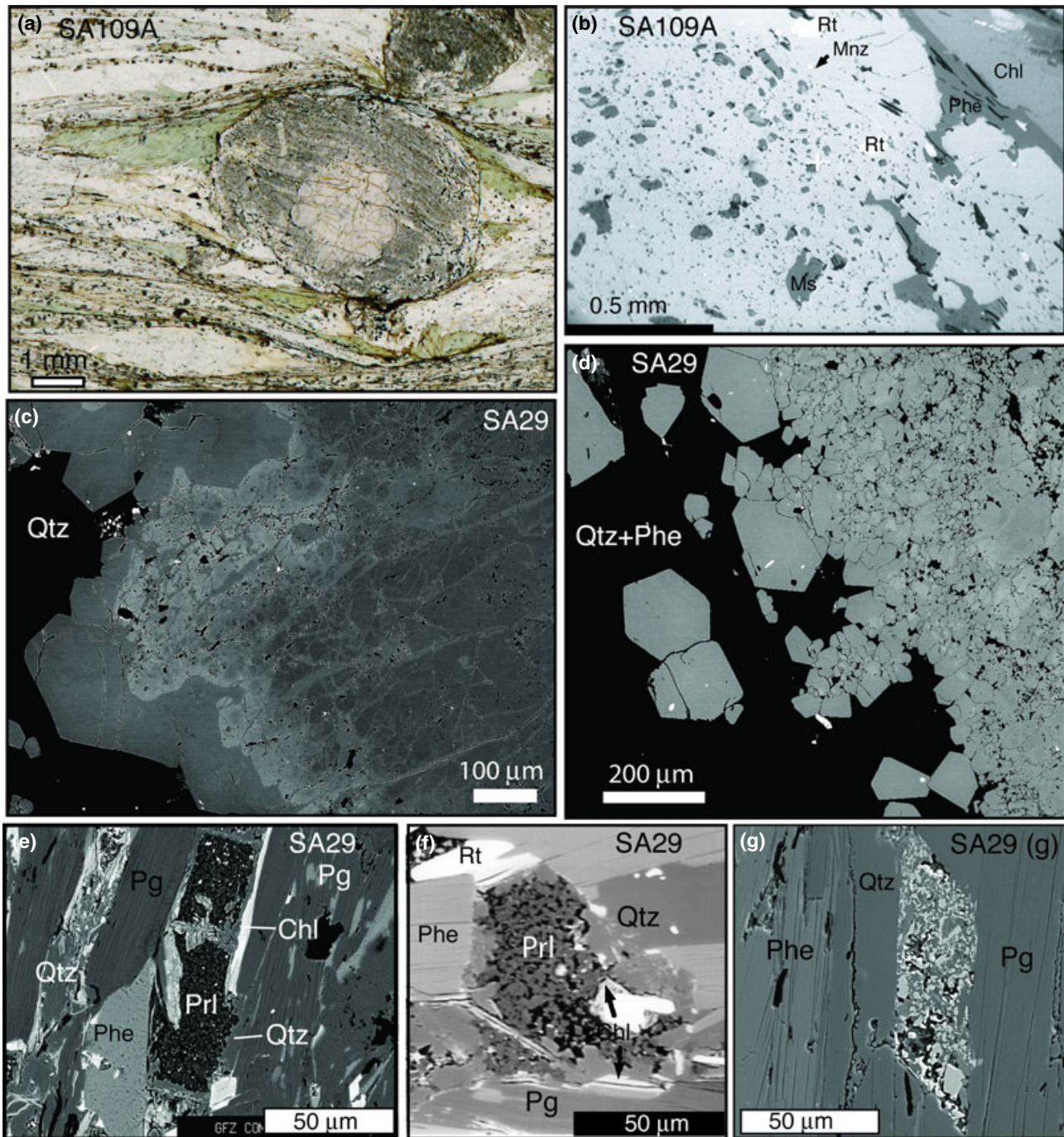


Fig. 4. Optical (a) and electron-microscope BSE images (b–g) of characteristic microtextures in polymetamorphic garnet-mica schists of the Agios Nikolaos unit. (a) Photomicrograph of zoned garnet porphyroblast in sample SA109A. Matrix consists of chlorite, phengite, paragonite, quartz, graphite (dark) and Fe-(hydr)oxide (dark). X-ray maps of Mn, Ca, Mg, Y, Fe and K distribution in large garnet blast are presented in Appendix A3. (b) BSE image depicting NE rim of garnet porphyroblast shown in (a). Inclusions of muscovite (Ms) are ubiquitous; other inclusions are rutile (Rt), monazite (Mnz), and graphite (black). Phengite and chlorite border garnet. (c) Pre-Alpine garnet blast showing up to ~0.2-mm-thick Alpine overgrowth (SA29). Brightest grey tone (high in Fe) marks irregular outline of zoned pre-Alpine garnet blast, which is transected by numerous healed fractures filled with Alpine garnet. (d) Pre-Alpine garnet porphyroblast marginally transformed into small Ca-rich, Mn-poor Alpine M1 garnet (sample SA29). Small bright grains are zircon and monazite. Contact between (pre-Alpine) core and Alpine overgrowth coincides with the disappearance of silicate inclusions and fracturing (black). (e) Prismatic pseudomorph dominated by pyrophyllite in quartz-mica matrix. Pyrophyllite is surrounded by thin quartz seam (SA29). (f) Pseudomorph replacement of a prismatic crystal by pyrophyllite, quartz, rutile and porosity (black). Matrix is composed of phengite, paragonite, quartz, rutile and minor chlorite. (g) Possible pseudomorph after ilmenite composed of fine-grained rutile (brightest phase) and quartz in mica-quartz matrix (SA29).

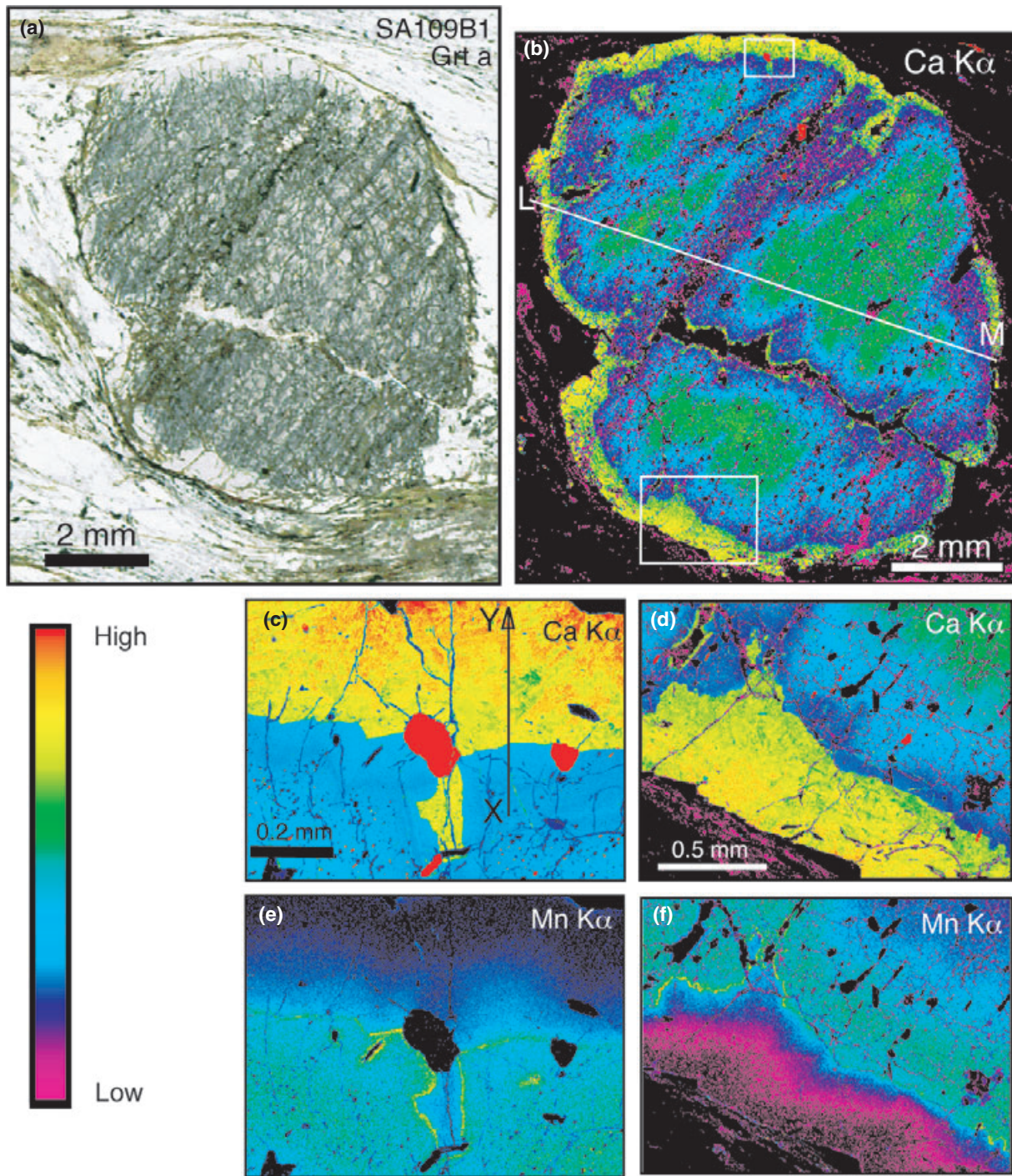


Fig. 5. Optical (a), EMP element X-ray distribution images (b–h), and compositional traverses (i & j) of centimetre-sized garnet porphyroblast displaying discontinuous Ca-rich-, Mn-poor rims (sample SA109B1). Note that NE–SW internal foliation in the garnet core terminates at beginning of Ca-rich overgrowth and is discontinuous with foliation in phengite-chlorite-quartz matrix. Fracture (black) parallel to L–M (b) with adjacent thin Ca-rich, Mn-poor garnet rim is filled with quartz. The two rectangles on the Ca-image (b) mark portions of garnet rims mapped in detail (2–4 μm steps) shown in (c–f). Note that Alpine Ca-rich overgrowths in (c–f) begin with tiny Mn-rich zones. Ca-rich inclusions in garnet are apatite. (i) Compositional traverses L–M across garnet porphyroblast as shown in (b). (j) EMP traverse X–Y depicting chemical discontinuity between garnet outer core and Ca-rich, Mn-poor overgrowth; see (c) for position. Atomic fractions shown in EMP traverses of (i) and (j) and Fig. 6b are defined as: $X_{\text{Ca}} = \text{Ca}/\sum R^{2+}$, $X_{\text{Fe}} = \text{Fe}/\sum R^{2+}$; $X_{\text{Mg}} = \text{Mg}/\sum R^{2+}$; $X_{\text{Mn}} = \text{Mn}/\sum R^{2+}$ with $\sum R^{2+} = \text{Ca} + \text{Fe} + \text{Mg} + \text{Mn}$; $\text{Mg} = \text{Mg}/(\text{Mg} + \text{Fe})$.

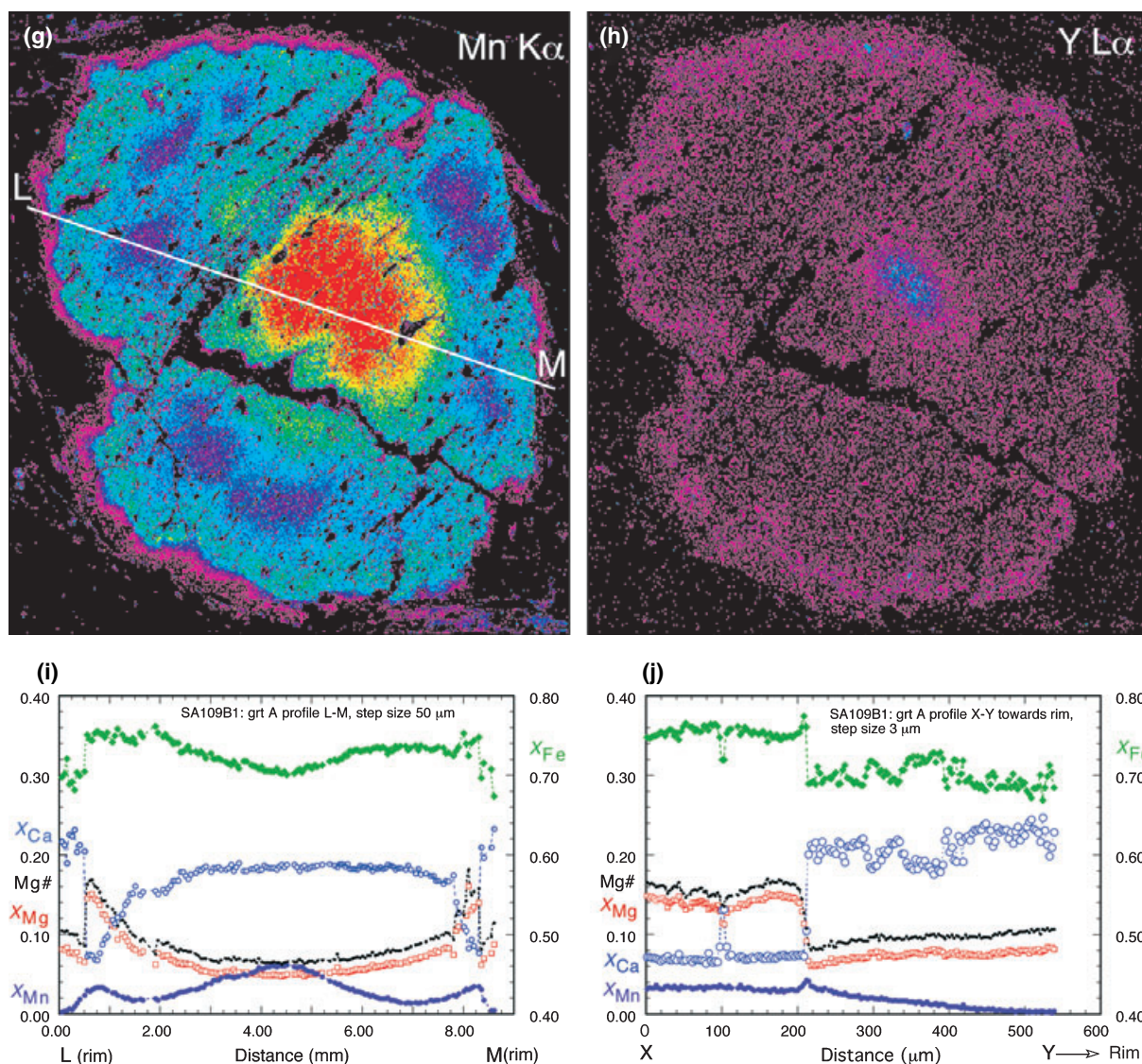


Fig. 5. *Cont'd.*

were performed at the GeoForschungsZentrum Potsdam. Operating conditions were 15 kV accelerating potential, 10–20 nA beam current and beam diameters of 1–10 μm . Peak counting times were 10–20 s for major and 20–40 s for minor elements; backgrounds were counted for 5–20 s. Standards used included the following synthetic and natural minerals and metals: garnet (Fe, Mn, Si, Al); ilmenite (Fe, Mn, Ti); rutile (Ti); wollastonite (Ca, Si); feldspar (Si, Al, Ca, Na, K); corundum (Al); hematite (Fe); periclase (Mg); eskolaite (Cr); barite (Ba); SrCO_3 (Sr); NiO (Ni); fluorite (F); metallic Ni and Co. The raw intensity data were corrected with the 'PAP' program (Pouchou & Pichoir, 1985). The quality and reproducibility of the analyses were monitored by including well-characterized standards (garnet, feldspar, mica) in the analysis sessions.

The chemical zoning of large porphyroblastic garnet and some small garnet was investigated by X-ray element mapping. The mapping was largely carried out in WDS mode moving the stage in steps of 2–50 μm , using a beam current of 40–100 nA, and counting times of 200–600 ms per step. Particularly, variations in X-ray intensities of Mn, Ca, Fe, Mg and Y were mapped. In some cases Cr, Ti and P were also mapped but these elements showed no obvious distribution patterns. A representative zonation pattern of porphyroblastic Samos garnet is presented in Fig. 5. (Other X-ray element maps and additional EMPA traverses of garnet in samples listed in Table 1 are available as online Appendices A1–A3. A hard copy of the appendices can be obtained from the third author.)

Monazite analyses were performed with an accelerating voltage of 20 kV, 40 nA beam current and peak

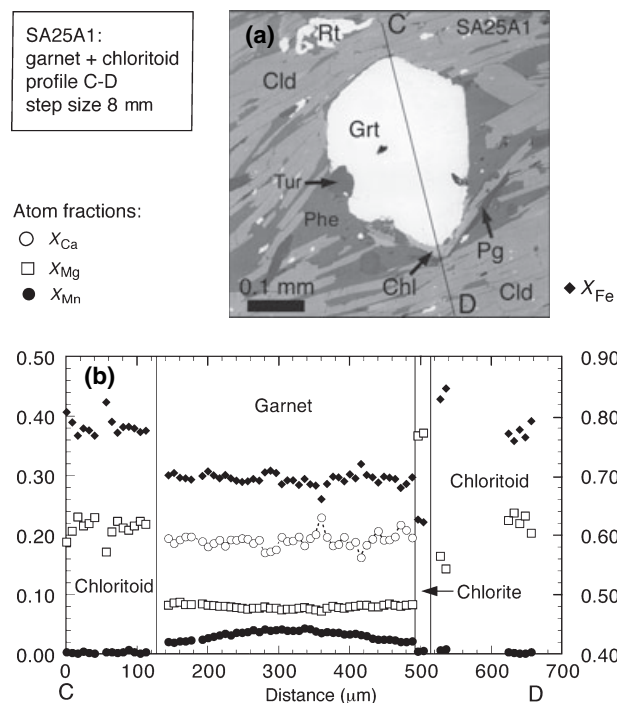


Fig. 6. (a) BSE-image of small Alpine (M1) garnet in contact with chloritoid and phengite (sample SA25A1). Minor amounts of paragonite, rutile and tourmaline are also present in the matrix. C–D indicates position of compositional traverse across garnet grain and adjacent chloritoid and chlorite shown in (b). Note that Ca is below detection limit of the EMP in both chloritoid and chlorite.

counting times of 20–300 s (Rhede *et al.*, 1996). Detection limits (in wt%) for the analysed rare earth elements were approximately 0.06 for La, Ce, and Nd; 0.07 for Pr and Sm; 0.08 for Tb and Dy; 0.09 for Gd and Er; 0.11 for Ho; 0.04 for Yb, Lu and Y.

Garnet

Both garnet generations, the first of large porphyroblasts (M0 garnet) and the second of thin overgrowths and small matrix grains (M1 garnet), are dominated by almandine, which varies between 62 and 80 mol.%. Estimates of ferric Fe on the basis of ideal garnet stoichiometry give minor or negligible amounts of Fe³⁺ (Table 2). The M0 porphyroblasts display pro-

grade growth-zoning with Mn, Ca and Y being highest in the core, while Mg and Fe increase towards the marginal parts (Fig. 5; Appendices A1–A3). Mg and Fe show clear antithetic relationships to Ca and Mn. Mn displays a flattened bell-shaped distribution with the spessartine component reaching up to 14 mol.% in the cores and decreasing to <4 mol.% at the marginal parts. In some cases X_{Mn} slightly increases towards the extreme rims (Fig. 5i). Most M0 garnet has Ca-rich cores with X_{Ca} between 0.17 and 0.20 (Fig. 5; Appendices A1–A3). In their outer parts X_{Ca} steeply decreases interrelated to increasing X_{Mg} and X_{Fe} . In general, Ca shows a more irregular distribution than Mn. The maximum pyrope content of ~17 mol.% is reached at the margins of the M0 porphyroblasts. The $Mg\#$ [=atomic fraction Mg/(Mg + Fe)] (total Fe as Fe²⁺) generally follows the variation of the pyrope content. Y maxima mimic those mapped for Mn (Fig. 5; Appendix A2). Such Y maxima are thought to mark the initial nucleation sites of the garnet crystals (Pyle & Spear, 1999; Otamendi *et al.*, 2002; Zeh, 2006). Y mapping revealed that the outer core parts of some garnet have elevated Y values as well (Appendix A2). Because Y is a highly compatible element with garnet, this enrichment may result from partial garnet resorption increasing the Y content of the residual rim. An alternative explanation is that the elevated Y concentrations at the garnet margins result from the breakdown of a Y-rich mineral (e.g. xenotime, allanite, epidote/zoisite) in the matrix during the final stages of garnet growth. EMP analyses of garnet adjacent to thin (late) cracks filled with fine-grained chlorite indicate that garnet did not change its chemical composition, in contrast to the Ca-rich overgrowths developed along thicker quartz-filled fractures cutting garnet porphyroblasts (Fig. 5b).

The garnet overgrowths show only minor variation in chemical composition. They are invariably richer in grossular ($X_{Ca} = 0.20$ –0.26) and poor in spessartine ($X_{Mn} \leq 0.04$) components; the pyrope component ranges from 7 to 10 mol.% and the $Mg\#$ covers a narrow range between 0.10 and 0.13 (cf. Table 2). From the internal to the external side of the thin overgrowths, EMP traverses measured with 2–5 μm steps indicate an overall slight increase in X_{Ca} and X_{Mg} , coupled with slightly decreasing X_{Mn} (Fig. 5j). X-ray mapping with a 2–6 μm pixel resolution illus-

Table 1. Mineralogy of porphyroblastic garnet-mica schists from Agios Nikolaos unit (north Samos).

Sample	Qtz	Grt	Cld	Chl	Phe	Pg	Ms	Ab	Cal	Rt	FeS	Fe-Ox	Gr	Tur	Ap	Mnz	Zrn	Other
SA1-3	X	X	X	(X) ^a	X	X	IcG	O	(O) ^b	O	O	(O) ^b	X	O	O	O,Xnt	O	(Prl,Kln) ^b
SA25A1	X	X	X	(O) ^a	X	X				O		(O) ^b	X	O				
SA26B1	X	X	X	(X) ^a	X	O	IcG		(O) ^b	O	O	(O) ^b	X	O		O,Xnt	O	
SA29	X	X		(O) ^a	X	X		O	(O) ^b	O	O	(O) ^b	O	O	O			Gln,Czo,(Prl) ^b
SA109A	X	X		(X) ^a	X		IcG			O	O	(O) ^b	X		O	O,Xnt	O	Ilm
SA109B1	X	X		(X) ^a	X	O		IcG	(O) ^b	O	O	(O) ^b	X		O		O	(Prl,Kln) ^b

Mineral abbreviations used are according to Kretz (1983): Fe-Ox, mixture of hematite and Fe-hydroxide; X, major mineral; IcG, only present as inclusion in pre-Alpine garnet; O, minor or accessory mineral.

^aMainly retrograde; ^bretrograde.

Table 2. Chemical compositions (wt%) and calculated formulae of early Alpine (HP-LT) M1 garnet.

Sample	SA1-3 (14) ^a	SA25A1 (20)	SA26B1 (33)	SA29 (29)	SA109A (5)	SA109B1 (254)
SiO ₂	37.76 (44) ^a	37.61 (25)	37.57 (45)	37.53 (23)	38.02 (19)	37.12 (25)
TiO ₂	0.08 (5)	0.05 (2)	0.14 (26)	0.07 (3)	0.20 (15)	0.09 (7)
Al ₂ O ₃	21.19 (15)	21.28 (24)	21.19 (37)	21.11 (16)	21.26 (17)	21.26 (53)
Cr ₂ O ₃	0.03 (2)	0.07 (11)	—	0.03 (8)	0.03 (3)	0.02 (2)
Fe ₂ O ₃	0.65 (58)	0.06 (11)	0.23 (36)	0.51 (41)	0.27 (31)	0.49 (65)
FeO	31.05 (48)	30.51 (94)	30.75 (46)	31.49 (48)	29.66 (87)	30.96 (69)
MgO	2.51 (26)	2.07 (10)	2.51 (44)	1.89 (9)	2.15 (63)	1.91 (14)
MnO	0.54 (12)	0.95 (15)	0.43 (26)	0.55 (25)	0.28 (29)	0.54 (40)
CaO	7.05 (31)	7.53 (92)	7.14 (43)	7.41 (39)	9.21 (97)	7.49 (67)
Total	100.85 (73)	100.12 (78)	99.99 (65)	100.59 (56)	101.06 (74)	99.87 (32)

Formulae on the basis of 12 oxygen

Site C						
Si	2.990 (27) ^a	3.000 (12)	2.997 (22)	2.989 (17)	2.995 (12)	2.975 (16)
Al ^(IV)	0.010	—	0.003	0.011	0.005	0.025
Total	3.000	3.000	3.000	3.000	3.000	3.000

Site B						
Ti	0.005 (3)	0.003 (1)	0.009 (16)	0.004 (2)	0.012 (9)	0.005 (4)
Al ^(VI)	1.967 (15)	2.000 (11)	1.989 (23)	1.971 (12)	1.969 (8)	1.984 (42)
Cr	0.002 (1)	0.004 (7)	—	0.002 (5)	0.002 (2)	0.002 (2)
Fe ³⁺	0.039 (34)	0.004 (6)	0.014 (22)	0.030 (24)	0.016 (18)	0.029 (39)
Total	2.013 (24)	2.006 (10)	2.013 (18)	2.006 (18)	1.998 (14)	2.020 (15)

Site A						
Fe ²⁺	2.056 (29)	2.035 (63)	2.051 (32)	2.098 (35)	1.954 (52)	2.075 (50)
Mg	0.296 (32)	0.246 (13)	0.298 (51)	0.224 (11)	0.252 (74)	0.228 (17)
Mn	0.036 (8)	0.064 (10)	0.029 (18)	0.037 (17)	0.019 (19)	0.037 (27)
Ca	0.598 (24)	0.643 (77)	0.611 (37)	0.632 (32)	0.778 (83)	0.643 (57)
Total	2.987 (18)	2.989(8)	2.989 (22)	2.992 (15)	3.002 (11)	2.983 (18)

X _{Mg}	0.099 (11)	0.082 (4)	0.098 (16)	0.075 (4)	0.084 (25)	0.076 (6)
X _{FeII}	0.689 (7)	0.681 (21)	0.686 (11)	0.701 (10)	0.651 (17)	0.696 (16)
X _{Ca}	0.200 (8)	0.215 (26)	0.204 (12)	0.211 (11)	0.259 (28)	0.216 (19)
X _{Mn}	0.012 (3)	0.021 (3)	0.010 (6)	0.012 (6)	0.006 (7)	0.012 (9)
Mg#	0.126 (12)	0.108 (4)	0.127 (19)	0.096 (4)	0.114 (31)	0.101 (8)

^aIn this table and Tables 3–6 numbers in parentheses after sample number indicate number of spot analyses, on which average is based; those after compositions give 1σ standard deviation in terms of the last digit(s).

Atomic fractions: $X_{Mg} = Mg / (Mg + Fe^{2+} + Ca + Mn)$; $X_{FeII} = Fe^{2+} / (Mg + Fe^{2+} + Ca + Mn)$; $X_{Ca} = Ca / (Mg + Fe^{2+} + Ca + Mn)$; $X_{Mn} = Mn / (Mg + Fe^{2+} + Ca + Mn)$; $Mg\# = Mg / (Mg + Fe^{2+})$.

trates that, despite the overall small spessartine content of the overgrowing garnet, the overgrowth starts with a very narrow Mn-rich zone (cf. Fig. 5e, f). However, the composition of the thin overgrowing garnet fluctuates much more than that of the garnet porphyroblasts over short distances of some tens of micrometres. In particular, the grossular and almandine components display short-range opposite variations of several mol.%, whereas the pyrope and spessartine components change more regularly over longer distances (Fig. 5j). The Ca variations are visible on X-ray maps as patchy patterns (Fig. 5c, d) and also show the occurrence of intergranular apatite.

The small garnet in the rock matrix, typically < 1 mm in diameter, are essentially homogeneous and their composition matches that of the overgrowths. Cores of the M1 garnet may be weakly enriched in Mn (Fig. 6; $X_{Mn} \leq 0.04$). As was the case for the Alpine overgrowths, X_{Ca} and X_{Fe} slightly fluctuate in an antipathetic way, whereas X_{Mg} and X_{Mn} vary smoothly in the measured profiles (Fig. 6b). The relatively low Mn content of the small matrix garnet and the overgrowths implies that most Mn has been removed from

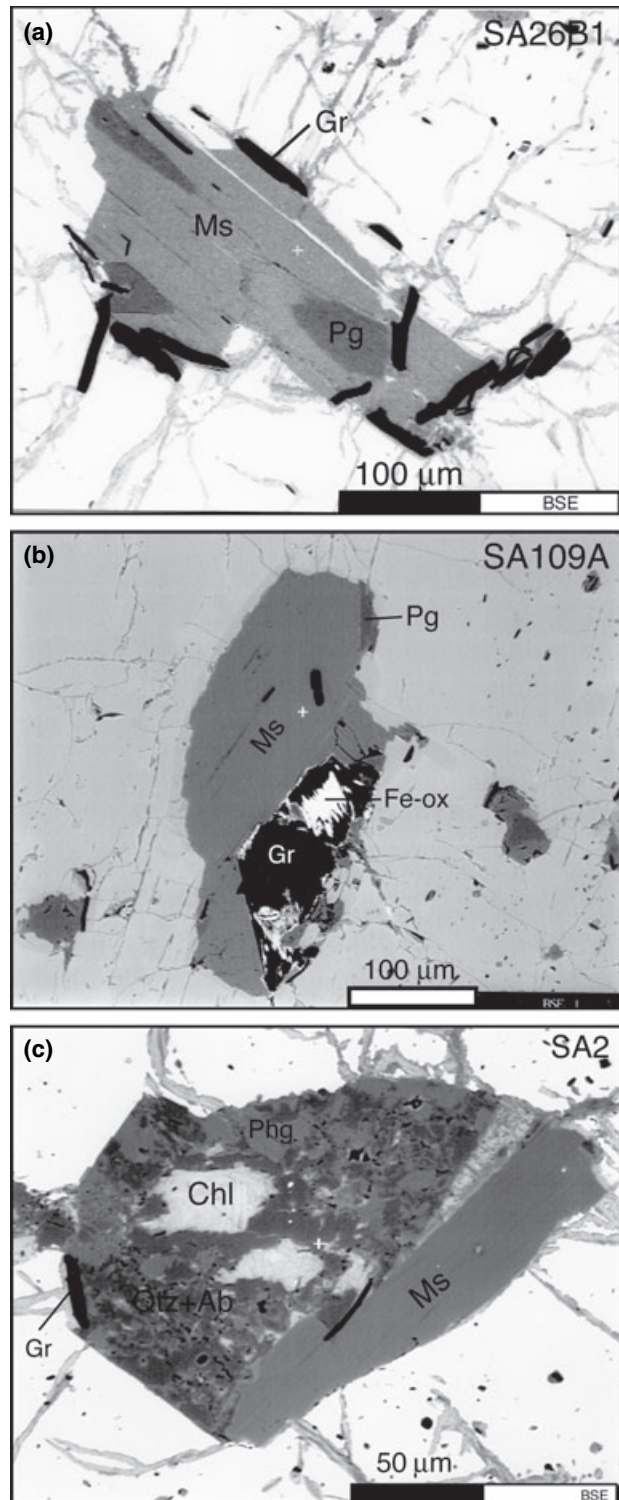


Fig. 7. BSE images of characteristic inclusions in pre-Alpine Samos garnet. (a) Ti-rich muscovite in garnet of sample SA26B1. The muscovite is associated with paragonite and graphite. (b) Inclusion containing Ti-rich muscovite (ms), paragonite (pg) and graphite (black) in SA109A. (c) Inclusion composed of a coarse muscovite grain and 'wormy' aggregate of quartz, albite, phengite and chlorite (replacement of K-Na feldspar?). In (a) and (c) thin cracks in garnet are filled with late chlorite.

the reacting rock system during the growth of the M0 garnet porphyroblasts.

White mica

Matrix phengite contains between 6.46 and 7.01 Si atoms per formula unit (apfu) while the Mg + Fe is between 0.59 and 1.15 apfu (Fig. 8a; Table 3). The analyses plot parallel to the Tschermak's substitution but at somewhat lower Si values than for the ideal exchange vector $\text{Si}(\text{Mg,Fe})\text{Al}_2$ and have some deficit in site-A cations along with excess in site-B cations. These deviations may partly be caused by the presence of some ferric Fe and a pyrophyllite component in phengite. The phengite ranges in Mg# from 0.57 to 0.81 (Fig. 8d) and contains up to 0.19 Na apfu ($X_{\text{Na}} \leq 0.10$; Fig. 8c, e). The Si content is inversely correlated with the Na content (Fig. 8c). Such a reverse relationship is common for white K-Na mica in HP metamorphic rocks and appears to result mainly from crystallochemical controls (e.g. Guidotti & Sassi, 2002). White K-mica included in the small matrix garnet and the Ca-rich overgrowths on large garnet porphyroblasts (e.g. in SA26B1) was also analysed; this textural type is similar in chemical composition to the most Si- and (Fe + Mg)-rich phengite in the matrix of the sample.

K-mica with compositions typical of muscovite formed at amphibolite-grade metamorphic conditions occurs as inclusions in the large garnet porphyroblasts (Figs 4b & 7). The Si content of such mica inclusions is ≤ 6.20 apfu, Fe + Mg ranges from 0.19 to 0.58 apfu and Mg# from 0.39 to 0.58 (Fig. 8). In addition, the muscovite can be distinguished from the matrix phengite by a markedly higher Ti content of 0.07–0.11 apfu (0.70–1.16 wt% TiO_2 ; Fig. 8f) and higher X_{Na} of 0.11–0.23 (Fig. 8e). K-mica with a muscovitic composition only occurs in the porphyroblastic garnet, particularly in their outer parts (Fig. 4b & Appendix A3f). Muscovite was never found within the Ca-rich garnet overgrowths, which in places contain minor phengite. However, not all K-mica included in the garnet porphyroblasts has a muscovitic composition. In particular, in those cases where the mica inclusions formed in fractures and/or coexist with additional quartz, the mica chemistry matches that of matrix phengite. Mica in composition intermediate between the measured muscovite and phengite seems to be scarce in the samples studied.

Paragonite not only occurs in the matrix but is also present as lamellae in the muscovite inclusions within garnet (Fig. 7a). The chemical composition of both paragonite types is close to that of the end-member (Table 3).

Chlorite

Variable amounts of chlorite are present in all samples. Chlorite, for which textures suggest possible

equilibrium with phengite and chloritoid, was particularly selected for EMP studies (Table 4). The average Mg# of the chlorite ranges from 0.46 to 0.53, and the Si content is between 5.40 and 5.56 apfu. The individual analyses display a significant compositional variation in samples SA1-3 and SA25A1 (Fig. 9) which could relate to retrograde reactions. EMP analyses of fine-grained chlorite occurring in thin cracks transecting the garnet porphyroblasts and randomly orientated chlorite occurring in partial pseudomorphs after garnet (data not shown in Fig. 8) indicate that such chlorite varies more widely in composition than chlorite aligned along the foliation.

Chloritoid

Chloritoid occurs as a matrix phase in three samples, with Mg# ranging from 0.21 to 0.26 (Table 5). Formulae calculated assuming ideal stoichiometry show no evidence for the presence of significant ferric Fe. Similar to many natural chloritoids (e.g. Chopin *et al.*, 1992), the Samos chloritoid contains slightly more Si than the ideal value of 2.00 cations (Table 5).

Phosphates

Several thin sections of samples SA1-3, 26B1 and 109A were examined by EMP for the presence of REE-Y phosphates, zircon and other heavy minerals. Monazite, xenotime and zircon were detected in all three samples. Monazite is present both as inclusions in the pre-Alpine garnet porphyroblasts and in the quartz-mica-chlorite matrix. The former monazite, which particularly occurs in the outer parts of the garnet, forms subhedral crystals up to 30–40 μm in diameter, some of which are intergrown with zircon and/or rutile. In the matrix, monazite generally occurs as small crystals (< 5 – $15 \mu\text{m}$ in diameter) forming irregular clusters, in which minor amounts of fine-grained xenotime and rutile are also present. Within pre-Alpine garnet only a few xenotime grains (< 5 – $10 \mu\text{m}$ in diameter) were detected. Similar to the REE-Y phosphates in the matrix aggregates, the small grain size hampers accurate EMP analysis. Monazite included in garnet was analysed more easily.

Monazite inclusions in garnet contain 3.5–6.3 wt% ThO_2 , 0.3–1.0 wt% UO_2 and up to 2.2 wt% Y_2O_3 (Fig. 10a,b). The PbO content of the inclusions amounts up to 0.12 wt% (Fig. 10c), whereas Pb in matrix monazite is generally below the detection limit for the analytical setup used (< 0.012 wt% PbO for 2σ uncertainty). Compositionally, the matrix monazite can be distinguished from that included in garnet by its lower UO_2 (< 0.18 wt% UO_2) and Y_2O_3 (< 1.2 wt%) (Fig. 10). The Th content of the matrix monazite strongly varies from below detection limit up to 11.7 wt% ThO_2 (Fig. 10a).

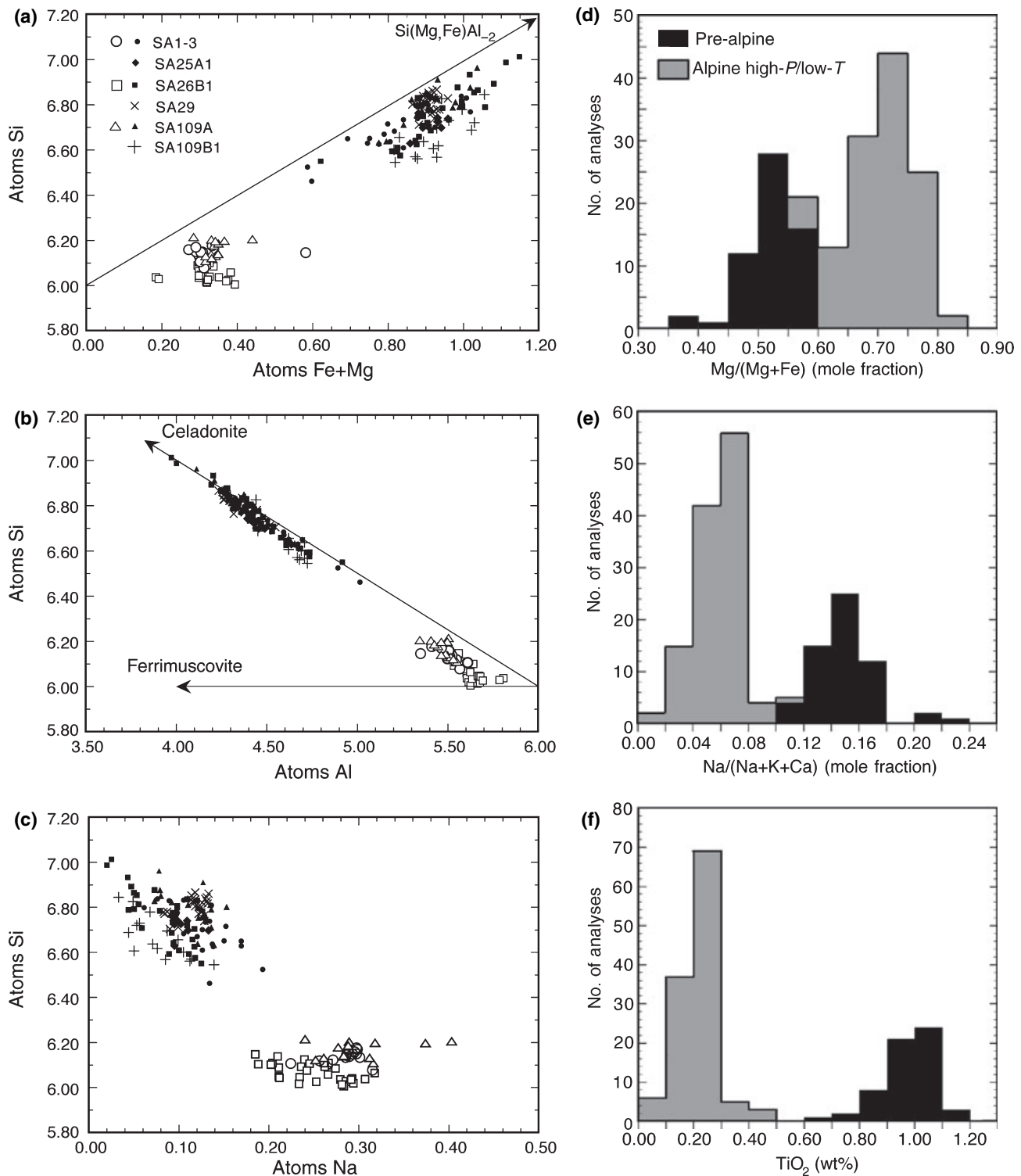


Fig. 8. Chemical variation of white K-mica in terms of (Fe + Mg)-Si (a), Al-Si (b) and Na-Si (c) variation diagrams. Histograms of Mg (d), X_{Na} (e) and TiO₂ (f) depict compositional differences between pre-Alpine muscovite (included in porphyroblastic M0 garnet) and Alpine phengitic muscovite present in the matrix. Cations were calculated on the basis per 22 oxygen assuming all Fe is ferrous. Large open symbols designate K-mica included in pre-Alpine garnet; other symbols indicate K-mica in the matrix and as inclusions in Ca-rich Alpine garnet.

Table 3. Chemical compositions (wt%) and calculated formulae of muscovite (Ms), phengite (Phe) and paragonite (Pg) in Agios Nikolaos rocks.

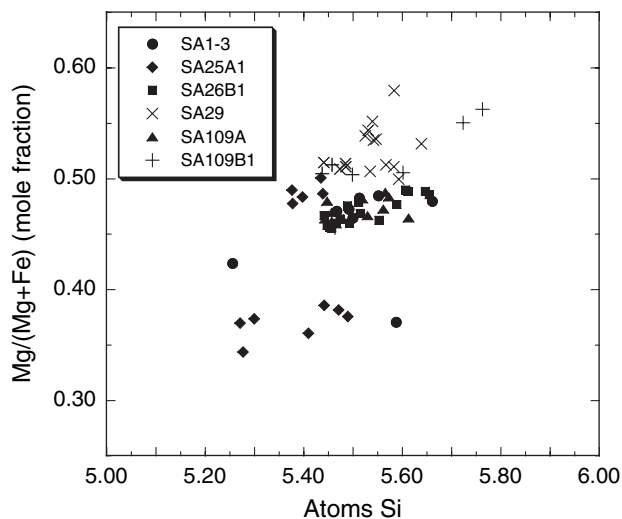
Sample Mica type	SA1-3 (14) Ms in M0 Grt	SA1-3 (22) Phe in matrix	SA25A1 (9) Phe in matrix	SA25A1 (5) Pg in matrix	SA26B1 (31) Ms in M0 Grt	SA26B1 (13) Phe in M1 Grt	SA26B1 (18) Phe in matrix	SA26B1 (15) Pg in matrix	SA29 (24) Phe in matrix	SA29 (7) Pg in matrix	SA109A (14) Ms in M0 Grt	SA109A (18) Phe in matrix	SA109A (2) Pg in matrix	SA109B1 (16) Phe in matrix
SiO ₂	46.04 (68)	50.50 (137)	50.71 (42)	46.96 (26)	46.44 (51)	52.11 (120)	51.53 (74)	47.20 (42)	51.09 (57)	47.49 (40)	47.14 (79)	51.42 (93)	47.85 (37)	50.86 (114)
TiO ₂	0.92 (8)	0.23 (7)	0.20 (2)	0.06 (1)	1.01 (10)	0.15 (10)	0.22 (4)	0.07 (2)	0.22 (6)	0.06 (2)	0.96 (8)	0.22 (8)	0.06 (1)	0.24 (7)
Cr ₂ O ₃	0.04 (2)	0.03 (4)	0.13 (18)	0.05 (7)	0.05 (3)	—	0.04 (4)	—	0.09 (15)	0.08 (9)	0.04 (3)	0.04 (3)	—	—
Al ₂ O ₃	35.00 (86)	28.95 (113)	28.52 (49)	40.01 (69)	36.50 (61)	28.16 (162)	29.33 (92)	40.50 (51)	27.65 (73)	39.48 (44)	35.52 (47)	28.02 (93)	39.57 (11)	29.60 (77)
FeO	1.43 (48)	2.34 (29)	2.27 (11)	0.57 (14)	1.36 (20)	2.31 (35)	2.17 (43)	0.40 (10)	2.54 (21)	0.38 (8)	1.51 (17)	2.32 (42)	0.97 (49)	2.65 (25)
MgO	0.83 (12)	2.90 (64)	3.37 (18)	0.18 (8)	0.85 (13)	3.72 (61)	3.38 (41)	0.17 (6)	3.17 (16)	0.12 (3)	0.90 (10)	3.31 (49)	0.17 (1)	3.26 (43)
Na ₂ O	1.10 (8)	0.49 (12)	0.40 (5)	6.58 (15)	0.99 (14)	0.23 (12)	0.41 (6)	6.23 (31)	0.45 (6)	7.44 (30)	1.18 (18)	0.45 (9)	6.82 (34)	0.30 (12)
K ₂ O	9.46 (22)	9.87 (18)	9.99 (18)	0.87 (24)	9.20 (46)	9.64 (44)	9.55 (42)	0.84 (22)	9.90 (45)	0.63 (13)	9.09 (69)	9.82 (42)	0.71 (7)	9.46 (67)
CaO	—	—	—	0.15 (2)	—	—	—	0.13 (2)	—	0.12 (2)	—	—	0.15 (4)	—
BaO	0.15 (4)	0.11 (5)	0.17 (5)	—	0.28 (6)	0.10 (6)	0.21 (4)	—	0.19 (5)	—	0.20 (4)	0.14 (6)	0.06 (4)	n.a.
Total	95.01 (126)	95.46 (138)	95.79 (61)	95.47 (88)	96.71 (55)	96.50 (85)	96.86 (83)	95.59 (34)	95.33 (83)	95.83 (73)	96.59 (99)	95.76 (116)	96.38 (36)	96.42 (69)
<i>Cations on the basis of 22 oxygen, all Fe is ferrous</i>														
Site C														
Si	6.138 (26)	6.704 (101)	6.718 (39)	5.984 (25)	6.069 (40)	6.816 (135)	6.719 (91)	5.987 (45)	6.804 (44)	6.031 (21)	6.165 (37)	6.799 (82)	6.047 (41)	6.665 (95)
Al(IV)	1.862 (26)	1.296 (101)	1.282 (39)	2.016 (25)	1.931 (40)	1.184 (135)	1.281 (91)	2.013 (45)	1.196 (44)	1.969 (21)	1.835 (37)	1.201 (82)	1.953 (41)	1.335 (95)
Total	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000
Site B														
Ti	0.092 (7)	0.023 (7)	0.020 (2)	0.006 (1)	0.099 (10)	0.015 (10)	0.021 (4)	0.006 (2)	0.022 (6)	0.005 (2)	0.095 (7)	0.022 (8)	0.006 (1)	0.023 (7)
Cr	0.004 (2)	0.004 (4)	0.014 (18)	0.005 (7)	0.005 (3)	—	0.04 (4)	—	0.010 (16)	0.008 (9)	0.004 (3)	0.004 (3)	—	0.002 (3)
Al(VI)	3.638 (50)	3.236 (95)	3.170 (39)	3.993 (45)	3.689 (48)	3.158 (127)	3.226 (50)	4.041 (29)	3.144 (49)	3.941 (22)	3.638 (41)	3.164 (60)	3.941 (51)	3.238 (57)
Fe	0.159 (56)	0.260 (33)	0.251 (12)	0.061 (15)	0.149 (22)	0.252 (39)	0.236 (47)	0.042 (10)	0.283 (24)	0.041 (8)	0.165 (19)	0.257 (47)	0.102 (53)	0.290 (28)
Mg	0.164 (26)	0.574 (121)	0.666 (34)	0.033 (15)	0.165 (26)	0.724 (117)	0.657 (80)	0.032 (12)	0.628 (28)	0.023 (5)	0.176 (20)	0.653 (94)	0.031 (2)	0.636 (80)
Total	4.060 (38)	4.099 (36)	4.124 (22)	4.098 (23)	4.111 (32)	4.156 (22)	4.147 (24)	4.126 (32)	4.090 (43)	4.020 (22)	4.082 (31)	4.102 (27)	4.084 (5)	4.192 (44)
Site A														
Na	0.285 (23)	0.126 (31)	0.103 (13)	1.627 (42)	0.252 (37)	0.059 (30)	0.103 (15)	1.532 (81)	0.116 (16)	1.833 (74)	0.299 (45)	0.116 (24)	1.671 (86)	0.078 (30)
K	1.610 (44)	1.673 (45)	1.689 (32)	0.141 (39)	1.535 (85)	1.609 (73)	1.588 (70)	0.136 (36)	1.683 (87)	0.101 (21)	1.518 (123)	1.656 (74)	0.114 (11)	1.583 (126)
Ca	—	—	—	0.021 (3)	—	—	—	0.018 (3)	—	0.016 (2)	—	—	0.021 (6)	—
Ba	0.008 (2)	0.006 (3)	0.009 (3)	—	0.014 (3)	0.005 (3)	0.011 (2)	—	0.010 (2)	—	0.010 (2)	0.007 (3)	0.003 (2)	n.a.
Total	1.905 (62)	1.806 (66)	1.802 (41)	1.789 (70)	1.802 (95)	1.675 (66)	1.703 (79)	1.687 (76)	1.809 (100)	1.952 (78)	1.828 (107)	1.779 (91)	1.809 (89)	1.662 (141)
Mg(Mg + Fe)	0.514 (55)	0.687 (62)	0.726 (17)	0.338 (83)	0.525 (45)	0.739 (34)	0.734 (63)	0.428 (102)	0.689 (26)	0.363 (55)	0.516 (27)	0.715 (65)	0.253 (89)	0.685 (41)

Ms in M0 Grt, muscovite inclusions in pre-Alpine (M0) garnet; Phe in M1 Grt, phengite inclusions in Alpine (M1) garnet; —, below detection limit; n.a., not analysed.
Mn and Ni were below detection limit for all mica analyses.

Table 4. Chemical compositions (wt%) and calculated formulae of chlorite.

Sample	SA1-3 (8)	SA25A1 (5)	SA26B1 (16)	SA29 (15)	SA109A (10)	SA109B1 (7)
SiO ₂	25.40 (102)	25.66 (21)	25.73 (41)	26.12 (25)	26.13 (43)	26.16 (80)
TiO ₂	0.06 (1)	0.04 (2)	0.05 (3)	0.04 (3)	0.06 (2)	0.07 (6)
Cr ₂ O ₃	—	0.06 (7)	0.03 (3)	0.06 (1)	—	0.03 (3)
Al ₂ O ₃	19.99 (72)	20.75 (22)	20.25 (64)	20.39 (33)	20.42 (40)	20.27 (86)
FeO	27.65 (146)	27.41 (86)	27.15 (54)	24.61 (75)	27.70 (32)	24.87 (150)
MgO	13.07 (142)	14.63 (20)	13.58 (46)	15.36 (38)	13.98 (41)	14.77 (122)
MnO	0.18 (21)	0.06 (3)	0.04 (3)	0.05 (3)	0.04 (2)	0.54 (31)
ZnO	0.12 (4)	—	—	0.03 (6)	0.16 (5)	—
NiO	0.05 (10)	—	—	—	—	—
CaO	0.04 (3)	—	—	0.03 (4)	—	0.03 (2)
Na ₂ O	0.03 (2)	—	—	—	—	—
K ₂ O	0.03 (4)	—	0.03 (3)	0.08 (10)	—	0.09 (11)
Total	86.62 (143)	88.68 (91)	86.89 (87)	86.84 (59)	88.56 (70)	86.84 (86)
<i>Cations on the basis of 28 oxygen, all Fe is ferrous</i>						
Si	5.50 (12)	5.40 (3)	5.53 (7)	5.54 (5)	5.52 (6)	5.56(13)
Al ^(IV)	2.49 (12)	2.60 (3)	2.47 (7)	2.46 (5)	2.48 (6)	2.44 (13)
Total	8.00	8.00	8.00	8.00	8.00	8.00
Ti	0.01 (0)	0.01 (0)	0.01 (0)	0.01 (1)	0.01 (0)	0.01 (1)
Cr	—	0.01 (1)	0.01 (1)	0.01 (0)	—	0.01 (1)
Al ^(VI)	2.61 (10)	2.55 (8)	2.65 (7)	2.63 (4)	2.59 (7)	2.65 (11)
Fe	5.02 (39)	4.83 (12)	4.88 (11)	4.36 (14)	4.89 (7)	4.42 (29)
Mg	4.22 (36)	4.59 (6)	4.35 (14)	4.85 (11)	4.40 (12)	4.68 (36)
Mn	0.03 (4)	0.01 (1)	0.01 (1)	0.01 (1)	0.01 (0)	0.10 (6)
Zn	0.02 (1)	—	—	0.01 (1)	0.03 (1)	—
Ni	0.01 (2)	—	—	—	—	—
Ca	0.01 (1)	—	—	0.01 (1)	—	0.01 (1)
Na	0.01 (1)	—	—	—	—	—
K	0.01 (1)	—	0.01 (1)	0.02 (3)	—	0.03 (3)
Total	11.94 (8)	12.01 (4)	11.91 (3)	11.92 (2)	11.94 (4)	11.90 (3)
Mg#	0.457 (39)	0.488 (9)	0.471 (12)	0.526 (13)	0.473 (9)	0.514 (35)

—, below detection limit.

**Fig. 9.** Si v. Mg in chlorite (atoms calculated per 28 oxygen).

The different compositions of monazite occurring in garnet and matrix indicate that monazite inclusions within garnet may have preserved their initial Y-U-rich pre-Alpine compositions, particularly when the garnet is rather undeformed and devoid of cracks. In contrast, matrix monazite (if present during pre-Alpine times) completely recrystallized or newly formed during the

Alpine tectono-metamorphic events. Pre-Alpine monazite in the matrix and included in deformed (cracked) garnet thus largely lost its U and Y during the Alpine tectono-metamorphic history, probably in connection with water infiltration into the initially 'drier' (high-grade) pre-Alpine metapelites. As Y is an immobile element, monazite destruction can locally provide the Y seen in some garnet rims. The remainder can be contained in the fine-grained xenotime locally found in the matrix monazite aggregates. A U-rich phase was not identified in the matrix of samples, suggesting that U was taken up by xenotime and apatite. The Alpine redistribution of Th appears irregular, as is implied by the large variation in the ThO₂ content of the matrix monazite compared with that of the pre-Alpine monazite relics in garnet (particularly in sample SA26B1; cf. Fig. 10a).

Subhedral grains of apatite (up to 250 µm in size) are present both as inclusions in garnet and in the matrix. Textural relationships between apatite and monazite/xenotime were not observed in the samples studied. Like monazite, apatite inclusions appear to be most abundant in the outer cores of the garnet porphyroblasts (cf. Fig. 5c–f). In samples SA1-3 and 109A, compositions of apatite included in garnet and in the matrix are both close to that of the fluorine end-member (Table 6). Both apatite types are poor in REE. Apatite inclusions in garnet tend to be somewhat higher in Fe and slightly lower in fluorine than matrix apatite. One matrix apatite grain with an abnormal composition was found in sample SA109A; it contains several wt% LREE and is significantly higher in SiO₂ than other apatite analysed (cf. Table 6). Perhaps the grain contains submicroscopic cheralite inclusions.

Other minerals

Zircon is a common accessory in the rocks studied; it occurs as inclusions in garnet and is also a regular matrix phase in all three samples examined systematically by BSE-imaging for the presence of heavy minerals. In contrast to monazite, which preferentially concentrated in the marginal parts of the garnet cores (Fig. 4b), zircon is more evenly distributed within the garnet porphyroblasts. The zircon contains 1.1–1.7 wt% HfO₂, up to 0.6 wt% UO₂ and 0.07 wt% PbO.

Glaucophane (Mg# = 0.61; Table 5) was only found in the matrix of sample SA29. In the same sample, clinozoisite [molar Fe³⁺/(Fe³⁺ + Al) = 0.14] occurs as rare inclusions in the discontinuous Ca-rich M1 garnet rims. Albite and K-feldspar, mainly present in multiphase inclusions within the garnet porphyroblasts (e.g. Fig. 7c), have compositions close to their end-members; albite contains <2 mol.% Kfs and <4 mol.% An component, whereas K feldspar contains 6–8 mol.% Ab component.

Rutile is a ubiquitous matrix phase and a common inclusion in most minerals as well. Up to 1.1 wt%

Table 5. Chemical compositions (wt%) and calculated formulae of chloritoid (Cld) and glaucophane (Gln).

Sample	SA1-3 (8)	SA25A1(33)	SA26B1 (11)	SA29 (7)			
Mineral	Cld	Cld	Cld	Gln	Cations per formula unit ^a		
SiO ₂	24.87 (11)	24.57 (14)	24.93 (20)	SiO ₂	57.54 (65)	Si	7.907 (49)
TiO ₂	0.03 (5)	—	0.05 (7)	TiO ₂	0.02 (1)	Al(IV)	0.093 (49)
Al ₂ O ₃	40.69 (10)	40.54 (19)	40.66 (44)	Al ₂ O ₃	12.07 (15)	Total	8.000
Cr ₂ O ₃	0.06 (2)	0.06 (4)	0.05 (3)	Cr ₂ O ₃	—	Site C	
FeO	21.72 (67)	22.76 (58)	21.49 (43)	Fe ₂ O ₃	1.45 (59)	Ti	0.002 (1)
MgO	4.23 (42)	3.38 (33)	4.22 (30)	FeO	10.03 (56)	Al(VI)	1.862 (32)
MnO	0.05 (3)	0.10 (4)	0.06 (3)	MgO	8.94 (10)	Cr	—
ZnO	0.09 (3)	—	—	MnO	—	Fe ³⁺	0.150 (62)
Total	91.75 (26)	91.43 (41)	91.47 (70)	CaO	0.48 (19)	Fe ²⁺	1.152 (60)
<i>Formulae on the basis of 12 oxygen,</i>				Na ₂ O	7.25 (13)	Mn	—
<i>total Fe is ferrous</i>				K ₂ O	0.02 (1)	Mg	1.833 (25)
Si	2.039 (5)	2.033 (6)	2.046 (10)	BaO	—	Total	5.000
Ti	0.002 (3)	—	0.003 (5)	Total	97.83 (82)	Site B	
Al	3.931 (10)	3.952 (10)	3.933 (19)			Ca	0.071 (27)
Cr	0.004 (1)	0.004 (3)	0.003 (2)			Na	1.919 (21)
Fe	1.489 (49)	1.575 (42)	1.475 (32)			Ba	—
Mg	0.517 (50)	0.417 (40)	0.516 (36)			Total	1.990 (15)
Mn	0.003 (2)	0.007 (3)	0.005 (2)			Site A	
Zn	0.006 (2)	—	—			Na(A)	0.013 (18)
Total	7.991 (12)	7.988 (15)	7.981			K(A)	0.003 (1)
Mg/(Mg + Fe)	0.258 (25)	0.209 (20)	0.259 (17)			Total	0.016 (19)
						Mg#	0.614 (15)

^aGlaucophane formula calculated on the basis of 23 oxygen and (number of cations – Ca – Na – K) = 13.

—, Below detection limit; Ni was below detection limit for all chloritoid analyses.

Fe₂O₃ and 0.22 wt% Cr₂O₃ was measured in rutile. Fe-(hydr)oxides occurring in angular-shaped aggregates contain up to several wt% SiO₂, while low EMPA totals suggest that it is largely hydroxide. Relict FeS in the Fe-(hydr)oxide aggregates contains up to 2.2 wt% nickel. Ilmenite present in the matrix of sample SA109A seems to be free of ferric Fe and contains 4–6 mol.% MnTiO₃ component.

U-Th-Pb DATING OF MONAZITE

To obtain information on the chronological evolution of the metapelitic rocks studied, monazite was dated by the electron microprobe U-Th-Pb method (Rhede *et al.*, 1996) in samples SA1-3, 26B1 and 109A. As discussed previously, the PbO content of matrix monazite is generally below the detection limit of the EMP method (<0.012 wt% PbO for the analytical conditions used), suggesting an overall Alpine age. Monazite included in garnet can also be low in PbO, where it is spatially related to cracks in strongly deformed garnet. The highest PbO contents (up to 0.12 wt% PbO; Fig. 10c) were typically measured in monazite included in relatively unaltered and uncracked parts of pre-Alpine (M0) garnet.

Using the contents of UO₂, ThO₂ and PbO measured by EMPA, single-point ages of monazite were calculated by solving the equation for the radioactive decay of U and Th with an iteration procedure (Rhede *et al.*, 1996). In the calculation, it was assumed that all Pb is radiogenic and the decay constants of U and Th recommended by IUGS (Steiger & Jäger, 1977) were used. The single-point ages obtained are listed in Appendix A4 and shown in Fig. 11 as a histogram;

ages range from 360 to 160 Ma, with maxima around *c.* 320 and 220 Ma. The limits of error for the single-point age are about 30–35 Ma. Although the maximum at *c.* 320 Ma yields clear geochronological evidence that the rocks studied have been affected by a Variscan (Carboniferous) metamorphic event, the second broad peak centred around *c.* 220 Ma may be interpreted in essentially two ways.

It is possible that the maximum at 220 Ma originated from a younger (Triassic) tectono-thermal event. On the other hand, it should be noted that the EMP data suggest that the U-Th-Pb system of monazite included in garnet did not always remain closed during the post-Variscan history of the rocks, particularly in highly deformed and cracked garnet. Complete Alpine resetting is obvious for monazite inclusions occurring in close proximity to abundant (micro)-cracks; such monazite contains PbO below detection limit and its mineral chemistry matches that of the Alpine matrix monazite (i.e. low UO₂ and Y₂O₃; see previous section). We also observed that rims of some monazite inclusions yielded ages younger than those of the cores. Incomplete shielding of monazite grains by garnet may thus locally have led to loss of Pb and partial resetting of monazite ages leading to a broad distribution of EMP ages. Textural evidence supports this scenario. All monazite dated is located in the outer parts of the pre-Alpine garnet porphyroblasts and monazite was never found in the garnet cores. A relationship between spatial position of monazite in garnet and age is thus missing. On the basis of our data, a discrete Permian–Triassic orogenic event cannot entirely be ruled out, but we favour the interpretation that the age accumulation around 220 Ma is accidental. In any

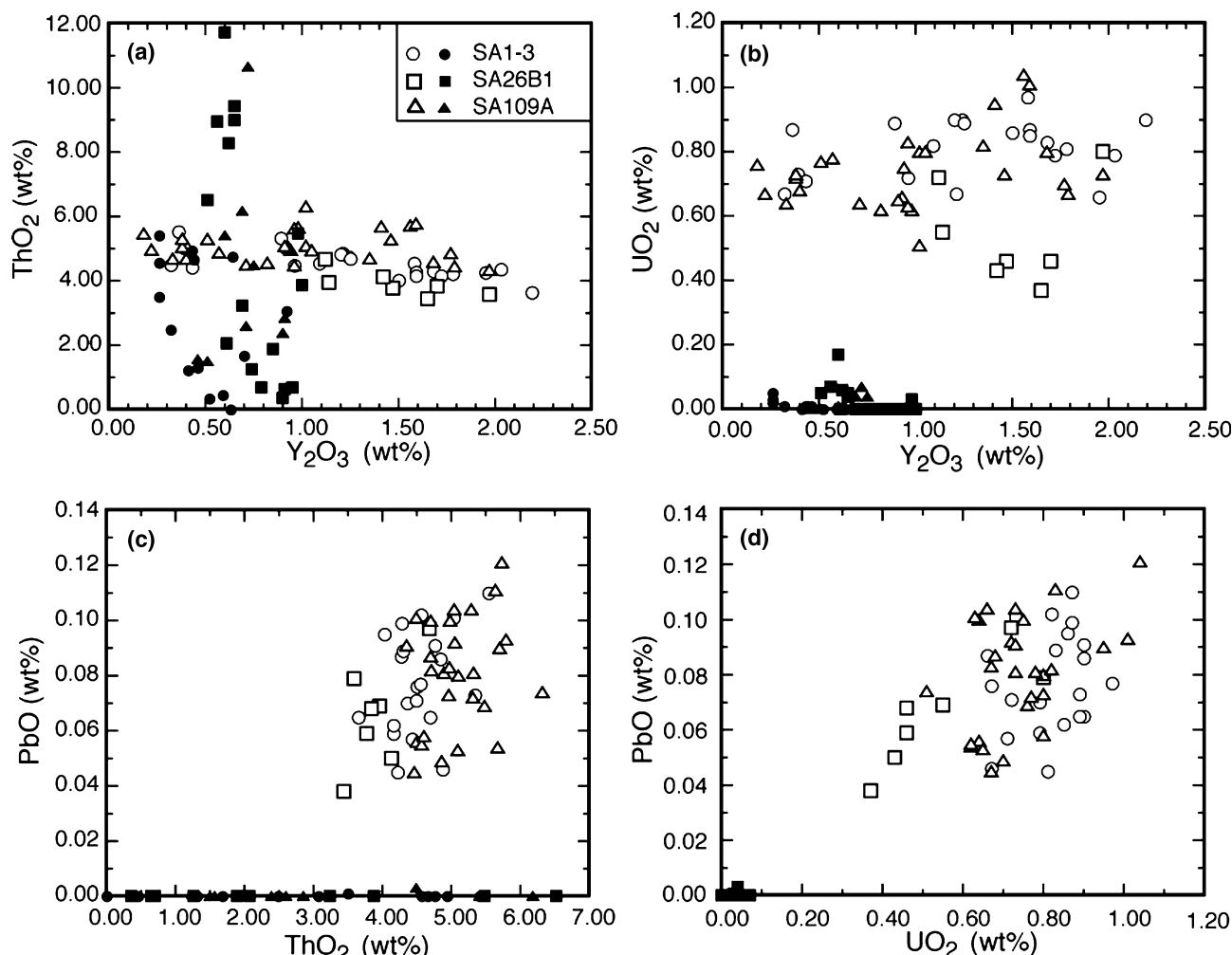


Fig. 10. Compositional variation of monazite: (a) Y_2O_3 v. ThO_2 ; (b) Y_2O_3 v. UO_2 ; (c) ThO_2 v. PbO ; (d) UO_2 v. PbO . Open symbols indicate monazite included in porphyroblastic M0 garnet, closed symbols monazite in the matrix. Note that monazite inclusions in garnet are higher in UO_2 , PbO and Y_2O_3 than matrix monazite.

case, it is clear that at least Variscan (Carboniferous) and Alpine orogenic events affected the Samos rocks.

PETROGENETIC EVOLUTION OF THE AGIOS NIKOLAOS GARNET SCHISTS

Pre-Alpine metamorphic evolution

The U-Th-Pb ages obtained for monazite relics within the garnet porphyroblasts provide conclusive evidence that the Samos rocks studied have been affected by a Variscan metamorphic event. Microstructural and petrological observations further support the pre-Alpine origin of the large garnet porphyroblasts:

(i) The M0 garnet porphyroblasts display an internal foliation (delineated by graphite and pyrrhotite) which is discordant with the foliation in the matrix and the

Ca-rich Alpine overgrowths, as far as a foliation is recognized in these rims.

(ii) The chemical zoning displayed by the M0 porphyroblasts is inconsistent with the Alpine P - T conditions. The smoothed nature of the zoning in most garnet cores (Fig. 5i; Appendices A1–A3) implies that an initial growth zoning was partly homogenized. Because of the slow rates of cation diffusion in aluminosilicate garnet (Chakraborty & Ganguly, 1991; Carlson, 2006; Chakraborty, 2006), the modification of the initial growth zoning by intracrystalline diffusion can only take place when the rocks have been subjected to at least amphibolite facies temperatures for periods of several million years (e.g. Spear, 1993; Faryad & Chakraborty, 2005; Vielzeuf *et al.*, 2007). Because our EMP studies indicate that diffusional relaxation across the chemical discontinuity between pre-Alpine garnet and Alpine overgrowths was very restricted (Fig. 5j), the overall diffusional flattening of the growth zoning

Table 6. Representative compositions of pre-Alpine monazite and average compositions of apatite occurring within pre-Alpine garnet and matrix.

Sample Monazite (An. no.)	SA1-3 102n	SA26B1 211d	SA109A2 m2	Apatite (type)	SA1-3 (12) IcGrt	SA1-3 (18) In matrix	SA109A (12) IcGrt	SA109A (11) In matrix	SA109A (3) Matrix: REE-rich
P ₂ O ₅	29.54	29.68	29.63	F	3.21 (14)	3.57 (21)	3.38 (18)	3.48 (16)	3.06 (3)
SiO ₂	0.35	0.35	0.37	Cl	0.04 (2)	0.03 (1)	0.05 (1)	0.03 (2)	0.20 (1)
CaO	0.95	0.85	1.07	Na ₂ O	0.05 (3)	—	0.03 (3)	0.04 (2)	0.16 (3)
FeO	0.58	1.05	1.12	P ₂ O ₅	41.80 (44)	42.16 (71)	41.94 (46)	42.23 (43)	39.33 (50)
PbO	0.10	0.08	0.08	SiO ₂	0.03 (2)	0.02 (2)	0.06 (3)	0.04 (4)	1.57 (10)
ThO ₂	4.28	3.59	4.71	CaO	55.09 (20)	55.15 (95)	55.38 (16)	55.49 (21)	51.60 (29)
UO ₂	0.87	0.80	0.82	SO ₂	—	—	—	—	0.07 (2)
Y ₂ O ₃	1.59	1.97	1.35	MnO	0.03 (2)	—	0.03 (2)	0.02 (1)	0.17 (2)
La ₂ O ₃	13.74	13.29	13.74	FeO	0.41 (20)	0.06 (3)	0.39 (7)	0.08 (4)	0.14 (3)
Ce ₂ O ₃	28.44	28.53	28.80	SrO	0.12 (4)	0.21 (7)	0.12 (6)	0.12 (6)	—
Pr ₂ O ₃	2.84	2.85	3.07	Y ₂ O ₃	—	—	—	—	0.19 (3)
Nd ₂ O ₃	10.89	11.48	11.48	La ₂ O ₃	—	—	—	—	1.01 (16)
Sm ₂ O ₃	1.99	2.23	1.97	Ce ₂ O ₃	—	—	—	—	1.95 (14)
Gd ₂ O ₃	1.72	1.98	1.78	Nd ₂ O ₃	—	—	—	—	0.67 (5)
Tb ₂ O ₃	0.17	—	—	Sm ₂ O ₃	—	—	—	—	0.10 (3)
Dy ₂ O ₃	0.47	0.50	0.39	Gd ₂ O ₃	—	—	—	—	0.14 (11)
Ho ₂ O ₃	—	—	—	H ₂ O ^a	0.25 (7)	0.09 (8)	0.18 (7)	0.14 (7)	0.23 (2)
Er ₂ O ₃	0.16	0.19	0.16	O = F, Cl	−1.36 (6)	−1.51 (9)	−1.43 (8)	−1.48 (7)	−1.34 (1)
Total	98.68	99.42	100.54	Total	99.79 (72)	99.78 (164)	100.14 (59)	100.20 (54)	99.25 (90)
<i>Cations based on 16 oxygen</i>				<i>Apatite formulae calculated on the basis of 24 (O, OH, F, Cl)</i>					
P	3.953	3.938	3.912	Na	0.02 (1)	0.01(1)	0.01 (1)	0.01 (1)	0.05 (1)
Si	0.055	0.056	0.058	Si	0.01 (0)	0.00 (0)	0.01 (1)	0.01 (1)	0.27 (2)
Ca	0.162	0.142	0.179	P	6.00 (3)	6.01(3)	5.99 (3)	6.01 (3)	5.79 (3)
Fe	0.076	0.137	0.146	Ca	10.01 (7)	9.95(6)	10.00 (5)	9.99 (5)	9.62 (3)
Pb	0.004	0.003	0.003	S	—	—	—	—	0.01 (0)
Th	0.154	0.128	0.167	Mn	0.01 (0)	—	0.01 (0)	0.00 (0)	0.03 (0)
U	0.031	0.028	0.029	Fe	0.06 (3)	0.01 (1)	0.06 (1)	0.01 (1)	0.02 (1)
Y	0.133	0.164	0.112	Sr	0.01 (0)	0.02(1)	0.01 (1)	0.01 (1)	—
La	0.801	0.768	0.791	Y	—	—	—	—	0.02 (0)
Ce	1.646	1.637	1.644	La	—	—	—	—	0.07 (1)
Pr	0.163	0.163	0.175	Ce	—	—	—	—	0.13 (1)
Nd	0.615	0.643	0.639	Nd	—	—	—	—	0.04 (0)
Sm	0.109	0.120	0.106	Sm	—	—	—	—	0.01(0)
Gd	0.090	0.103	0.092	Gd	—	—	—	—	0.01 (1)
Tb	0.009	—	—	H ^a	0.15 (5)	0.05(5)	0.11 (5)	0.08 (4)	0.14 (1)
Dy	0.024	0.025	0.020	Mole fraction					
Ho	—	—	—	X _F	0.920 (23)	0.970 (24)	0.940 (20)	0.955 (23)	0.898 (7)
Er	0.008	0.010	0.008	X _{Cl}	0.005 (3)	0.004 (2)	0.008 (2)	0.005 (2)	0.031 (1)
Total cations	8.032	8.065	8.080	X _{OH}	0.075 (24)	0.026 (24)	0.053 (23)	0.040 (21)	0.071 (7)

IcGrt, inclusion within pre-Alpine garnet; —, below detection limit.

^aH₂O calculated from stoichiometry and charge balance.

in the garnet porphyroblasts must have occurred prior to the Tertiary.

(iii) The M0 garnet contain mineral inclusions that do not fit the Alpine HP-LT conditions. The occurrence of Ti-Na-rich muscovite in their outer parts (Figs 4b & 7a,b) implies that these outer zones grew during middle amphibolite facies conditions. Such conditions are supported by the presence of multiple inclusions composed of K-Na mica + quartz ± albite ± K feldspar (Fig. 7c), which may be Alpine replacements of an intermediate K-Na feldspar. Presuming that feldspar and muscovite once coexisted during pre-Alpine metamorphism, this would indicate amphibolite facies conditions near the continuous reaction: K-Na mica + quartz = Na-K feldspar + kyanite/sillimanite + water (e.g. Bucher & Frey, 2002; 'second sillimanite isograd').

(iv) During pre-Alpine metamorphism temperatures were estimated by garnet-muscovite Fe-Mg exchange thermometry. Compositions of muscovite inclusions were combined with average garnet compositions

measured in the vicinity of the inclusions; emphasis was given to sample SA26B1 (Table 7). The garnet-muscovite thermometer of Wu *et al.* (2002) was applied under the simplifying assumption that in muscovite all Fe is ferrous. As the precise pre-Alpine pressure is unknown for the Samos rocks, temperatures were calculated at both 3 and 8 kbar. The results confirm the rather weak pressure-dependence of the muscovite-garnet thermometer. Temperatures derived with the calibration of Wu *et al.* (2002) range from 600 to 625 °C (Table 7) and are in good agreement with the other estimates of the pre-Alpine metamorphic conditions discussed above.

(v) The monazite-xenotime solvus geothermometer, which is based on the compositions of the two coexisting phosphates (Gratz & Heinrich, 1997; Andrehs & Heinrich, 1998; Daniel & Pyle, 2006), may also provide information on pre-Alpine conditions. Because xenotime is a rare inclusion in pre-Alpine garnet, it is doubtful whether monazite and xenotime were always in equilibrium. Nonetheless the monazite-xenotime

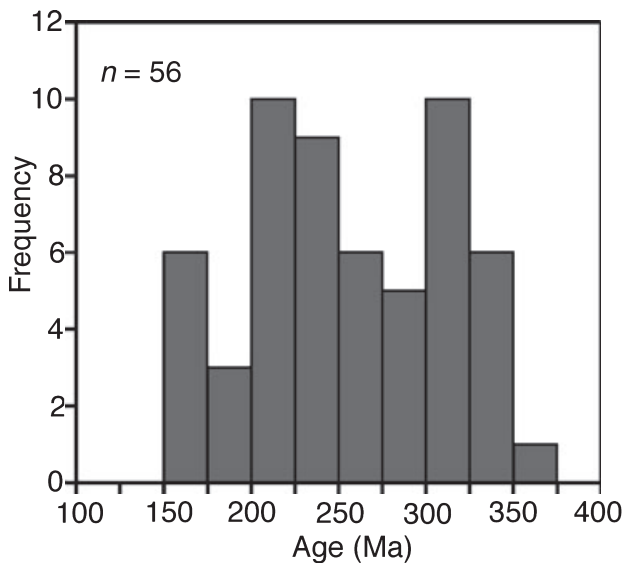


Fig. 11. Histogram of single point EMP ages obtained for monazite included in porphyroblastic garnet.

thermometer was applied using two different empirical calibrations derived from medium-*P* metapelitic rocks (Heinrich *et al.*, 1997; Pyle *et al.*, 2001). The same monazite was used as for the U-Th-Pb EMP dating (Appendix A4). Results depicted in histograms (Fig. 12) show, for both calibrations, skewed distributions with tails towards low temperatures. In particular, the thermometer of Heinrich *et al.* (1997) yields temperatures centred around 600 °C in agreement with the muscovite-garnet thermometer and other estimates of the pre-Alpine conditions, whereas the thermometer of Pyle *et al.* (2001) gives systematically lower tem-

peratures by about 100 °C. The reason for this difference is poorly understood. The low temperatures in the histograms may be explained by post-Variscan re-equilibration of monazite, or rather lack of equilibrium with xenotime during Variscan monazite growth.

(vi) Evidence for a pre-Alpine history is rarely found in the matrix of the rocks studied. In some samples prismatic ghost grains mainly composed of retrograde pyrophyllite, surrounded by a thin quartz seam (Fig. 4e, f), could possibly indicate pseudomorphs after a prismatic Al-rich mineral, such as kyanite or sillimanite. Such pseudomorphic textures typically occur in quartz-rich layers, where they occur together with platy pseudomorphs composed of rutile + quartz (Fig. 4g). The latter could represent pseudomorphs after pre-Alpine ilmenite.

Pseudomorphic textures comparable with those described above occur locally in the garnet-mica schists of the pre-Alpine basement of the Cycladic islands of Sikinos (Franz *et al.*, 1993) and Ios (A. Feenstra, unpublished data). In metapelites, intercalated in the pre-Alpine basement of the Dodecanese islands (Panormos unit) and eastern Crete (Myrsini unit), an amphibolite facies assemblage comprising staurolite + kyanite + garnet was documented by Franz *et al.* (2005). There, the aluminous minerals, which underwent Alpine brittle deformation and retrograde replacement by white mica and chlorite, are well preserved because the basement only experienced a low-*P* greenschist facies overprint during the Tertiary, unlike eastern Crete and the Cyclades, where the basement rocks underwent HP-LT Tertiary metamorphism. If the pseudomorphs observed in our Samos samples indeed formed after sillimanite/kyanite, the existence

Table 7. Results of garnet-muscovite and garnet-phengite thermometry.

Sample	Mica type	Garnet composition				Muscovite/phengite composition				T (°C)	
		X_{Mg}	X_{Fe}	X_{Ca}	X_{Mn}	X_{Mg}	X_{Fe}	$X_{Al(VI)}$	Mg#	Wu02 ^a	Wu02 ^b
SA1-3	Ms in M0 Grt	0.131	0.757	0.079	0.033	0.040	0.049	0.911	0.458	600	605
SA26B1	Ms in M0 Grt	0.148	0.756	0.068	0.029	0.044	0.039	0.917	0.527	611	616
SA26B1	Ms in M0 Grt	0.144	0.764	0.064	0.028	0.046	0.047	0.907	0.498	606	611
SA26B1	Ms in M0 Grt	0.147	0.759	0.067	0.027	0.043	0.037	0.920	0.539	609	614
SA26B1	Ms in M0 Grt	0.148	0.763	0.062	0.027	0.042	0.033	0.925	0.560	606	610
SA109A	Ms in M0 Grt	0.153	0.740	0.069	0.038	0.041	0.042	0.917	0.489	620	625
SA1-3	Matrix Phg	0.099	0.689	0.200	0.012	0.144	0.064	0.792	0.687	K&R79 ^c	G&H82 ^d
SA25A1	Matrix Phg	0.082	0.681	0.215	0.021	0.163	0.061	0.776	0.726	551	573
SA26B1	Matrix Phg	0.098	0.686	0.204	0.010	0.160	0.057	0.783	0.734	506	534
SA26B1	Phg in M1 Grt	0.098	0.686	0.204	0.010	0.175	0.061	0.764	0.739	521	547
SA29	Matrix Phg	0.075	0.701	0.211	0.012	0.155	0.070	0.775	0.689	518	545
SA109A	Matrix Phg	0.084	0.651	0.259	0.006	0.160	0.063	0.777	0.715	513	540
SA109B1	Matrix Phg	0.076	0.696	0.216	0.012	0.153	0.070	0.778	0.685	520	547
										518	544

Garnet composition: $X_{Mg} = Mg/(Mg + Fe + Ca + Mn)$; $X_{Fe} = Fe/(Mg + Fe + Ca + Mn)$; $X_{Ca} = Ca/(Mg + Fe + Ca + Mn)$; $X_{Mn} = Mn/(Mg + Fe + Ca + Mn)$.

Muscovite/phengite composition: $X_{Mg} = Mg/[Mg + Fe + Al(VI)]$; $X_{Fe} = Fe/[Mg + Fe + Al(VI)]$; $X_{Al(VI)} = Al(VI)/[Mg + Fe + Al(VI)]$; Mg# = $Mg/(Mg + Fe)$.

^aGarnet-muscovite thermometer of Wu *et al.* (2002) for 3 kbar.

^bGarnet-muscovite thermometer of Wu *et al.* (2002) for 8 kbar.

^cGarnet-phengite thermometer of Krogh & Råheim (1978) for 19 kbar.

^dGarnet-phengite thermometer of Green & Hellman (1982) for 19 kbar.

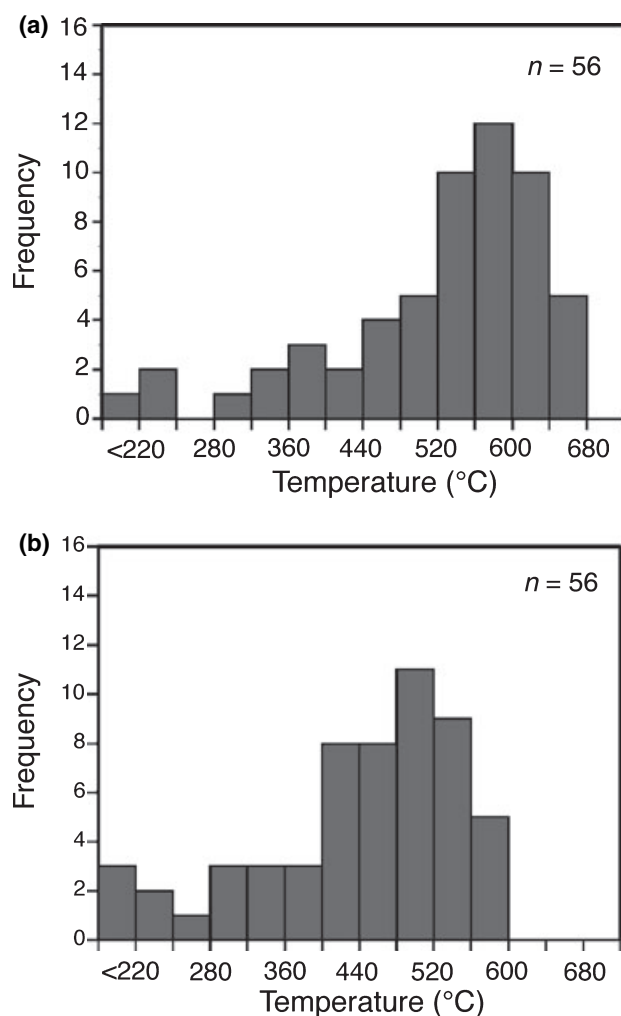


Fig. 12. Histograms showing pre-Alpine temperatures obtained from monazite-xenotime thermometry using empirical calibrations of (a) Heinrich *et al.* (1997) and (b) Pyle *et al.* (2001). Both calibrations are for medium-pressure rocks (3–7 kbar). Monazite analyses used are the same as plotted in Figs 10 & 11.

of the latter at pre-Alpine conditions would give a further hint to upper amphibolite facies conditions of the pre-Alpine basement.

Alpine metamorphic evolution

Because the present study is focused on the pre-Alpine history of the rocks, the Tertiary tectonometamorphic evolution will only briefly be discussed here. The P – T evolution of metabasic rocks containing glaucophane + garnet + clinozoisite + paragonite + phengite + chlorite which occur adjacent to the metapelites studied has been investigated in detail by Will *et al.* (1998), who derived peak M1 conditions of ~ 19 kbar and ~ 520 – 530 °C. For garnet glaucophanites of the same locality we obtained comparable P – T conditions (A. Feenstra & K. Petrakakis, unpublished data). Field and petrological evidence clearly suggest that

metabasic and metapelitic rocks shared the Tertiary metamorphic history in conjunction.

For the Agios Nikolaos metapelites, M1 conditions were estimated using the garnet-phengite geothermometers of Krogh & Råheim (1978) and Green & Hellman (1982) (see Table 7 for summary of results). Total Fe was assumed to be ferrous and applied both calibrations at 19 kbar, following Will *et al.* (1998). If significant amounts of ferric Fe are present in the phengite, temperatures would be lower (Schmid *et al.*, 2003). These estimates, therefore, give maximum temperatures. Compositions of matrix phengite were combined with M1 garnet compositions, i.e. of Ca-rich overgrowths and/or small matrix garnet. Using the Krogh & Råheim (1978) thermometer, temperatures ranging from 513 to 551 °C were obtained, which are, within uncertainty limits, in excellent agreement with the peak M1 temperature deduced by Will *et al.* (1998) from adjacent metabasites. The Green & Hellman (1982) calibration for low-Ca systems ($\text{CaO} < 2$ wt%) and phengite with an Mg# of ~ 0.67 was applied, as the metapelitic samples studied contain 1.3–2.2 wt% CaO (A. Feenstra & K. Petrakakis, unpublished XRF data) and phengite has a comparable composition (cf. Tables 3 & 7). Results fall in the range of 540–573 °C, about 20–30 °C higher than those obtained by the Krogh & Råheim (1978) calibration (Table 7). The somewhat different temperatures obtained may relate to compositional differences in the calibrations of the two geothermometers.

M1 garnet has overgrown and replaced the pre-Alpine garnet porphyroblasts to variable degrees. Detailed X-ray element mapping documents that in some samples (e.g. SA29) the earliest Alpine garnet grew in thin (1–20 μm wide) fractures transecting the outer parts of the M0 porphyroblasts (cf. Fig. 4c). The chemical composition of the garnet in the annealed microfractures is fairly constant matching that of the first, Mn-enriched, growth stage of the M1 rims (cf. Fig. 5e–f). The composition of M1 garnet in the microfractures also seems unrelated to that of adjacent M0 garnet, the latter varying as a result of pre-Alpine zoning (Fig. 4c). This and the sharp interphase between garnet in the fractures and host garnet supports the growth of M1 garnet by dissolution–reprecipitation processes in once-open cracks (Erambert & Austrheim, 1993; Putnis, 2002; Le Bayon *et al.*, 2006; Raimbourg *et al.*, 2007; see also Keller *et al.*, 2006).

The formation of microfractures filled with early Alpine M1 garnet was most likely connected to Alpine deformation. Brittle deformation and rupturing of the rigid pre-Alpine garnet porphyroblasts may have initiated the fractures which allowed penetration of high- P aqueous fluids or fluid films. The fluids must have brought in considerable amounts of Ca, and to a much lesser amount Mn, to the site of M1 garnet reprecipitation, whereas Mg and Fe were transported away to balance the compositional difference between the garnet

growing in the crack and the replaced M0 garnet. The Ca required for growth of M1 garnet may have been supplied by breakdown of pre-Alpine plagioclase in the matrix of the rocks. Plagioclase or another major Ca-rich phase has not been found in the matrix (Table 1), so that almost all Ca of the rocks is now contained in the thin garnet rim, if the small Ca-content in paragonite is neglected. Sodium that became available from decomposition of plagioclase may have been incorporated mainly into paragonite and/or glaucophane (only in sample SA29) during the M1 event.

M1 overgrowths are entirely or locally lacking for some of the M0 garnet porphyroblasts. For kinetic reasons Alpine garnet rims may never have developed, whereas in other cases textures suggest that overgrowths have been resorbed during very late Alpine stages, mainly through hydration to chlorite. The fact that the overgrowths do not exhibit distinct retrograde zoning as well as their replacement by late, post-tectonic, chlorite flakes suggest that garnet resorption occurred during waning Alpine stages.

Phengite is not only a ubiquitous phase in the matrix of the Samos rocks but is also occasionally found within multiple inclusions in the outer parts of the M0 garnet, where it is associated with paragonite, quartz and minor chlorite. In the EMP studies there was no significant chemical zoning in muscovite included in M0 garnet; either the pre-Alpine muscovite composition is preserved, or it is entirely converted into a phengitic composition matching that of phengite occurring in the matrix (cf. section on white mica mineral chemistry). The muscovite-phengite transformation appears to be complete when adjacent quartz is present and/or when abundant microveinlets surround the inclusion. Such veinlets may have allowed the transport of components between inclusion and rock matrix by means of a hydrous fluid, which also may have catalysed the high-*P* reactions. The availability of silica thus triggered the M1 transformation of initial pre-Alpine muscovite into phengite via Tschermak's exchange [$^{VI}Al^{IV}Al^{VI}(Mg, Fe^{2+})_{-1}Si_{-1}$] and pre-Alpine muscovite only survived in the absence of quartz (Fig. 7a, b). An exception to this is the composite inclusion shown in Fig. 7c, where a grain of pre-Alpine muscovite borders a fine-grained aggregate consisting of quartz, albite, phengite and chlorite. The left part of the inclusion is interpreted as a pseudomorphic replacement of pre-Alpine K-Na feldspar. Pre-Alpine muscovite is thus preserved in the right part, while M1 phengite formed in the left part during Alpine breakdown of K-Na feldspar.

DISCUSSION AND CONCLUDING REMARKS

The present study clearly demonstrates that monazite and muscovite of Variscan age trapped in garnet have survived the subsequent Alpine tectonometamorphic history. Several other examples of monazite grains shielded in garnet are described that provide infor-

mation on the early history of polyphase metamorphic rocks (e.g. Montel *et al.*, 2000; Catlos & Çemen, 2005; Baldwin *et al.*, 2006; Yang & Pattison, 2006). As in the Samos rocks, monazite occurring in the matrix of these rocks recrystallized entirely or were newly formed recording the latest metamorphic event.

Hydrous fluids in combination with deformation may have played a crucial role in transforming the amphibolite-grade Agios Nikolaos metapelites into more hydrous HP-LT rocks during the M1 event. The high-*P* fluids may originate from prograde devolatilisation of neighbouring volcano-sedimentary rocks, tectonically juxtaposed with the Agios Nikolaos basement during early Tertiary subduction. At the relatively low temperatures (< 550 °C) prevailing during M1 metamorphism on Samos, lattice diffusion is not an effective mechanism for modifying garnet compositions (Dohmen & Chakraborty, 2003; Chakraborty, 2006; Vielzeuf *et al.*, 2007). Mobilisation of elements by intergranular high-*P* fluids, assisted by microcracks, may have been the main mechanism increasing reaction rates during the M1 metamorphism.

Several studies have pointed out that during metamorphic garnet growth, Ca is the least mobile among the common divalent cations (Mg, Fe, Mn, Ca) constituting rock-forming garnet (e.g. Chernoff & Carlson, 1997; Spear & Daniel, 2001; Konrad-Schmolke *et al.*, 2005; Raimbourg *et al.*, 2007). Evidence comes from petrological observations recording local (irregular) variations in Ca contents within and between garnet grains, suggesting that transport of Ca to growing garnet is more limited than that of Mn, Fe and Mg. The transport-controlled supply of Ca may thus restrict Ca equilibration to small domains in rocks, e.g. to domains where Ca-rich minerals locally control Ca activity. On a somewhat larger scale (e.g. that of a thin section) equilibrium with regard to Ca may thus not have been attained. Our study of the Samos metapelites suggests that during the Variscan event the Ca flux to growing garnet was to some extent locally controlled, as is inferred from the irregularly shaped Ca-rich core domains of most garnet porphyroblasts (Fig. 5; Appendices A1–A3). Using a thermodynamic model for diffusion-controlled garnet growth, Konrad-Schmolke *et al.* (2005) argued that steep Ca-gradients in garnet zonation patterns, as displayed by most Samos M0 garnet, may result from local Ca equilibration.

During the Alpine HP-LT metamorphism the transport of Ca to the site of garnet growth appears not to have been restricted to an millimetre-to-centimetre scale. Not only within a single thin section, but also between several thin sections made from a single specimen, the M1 garnet is compositionally homogeneous within analytical accuracy (cf. Table 2). In addition, a significant chemical difference between M1 garnet rimming pre-Alpine garnet and that forming small grains in the matrix was not observed. As discussed before, M1 garnet may exhibit very weak

compositional zoning (Figs 5j & 6; Appendix A1g). Detailed EMP traverses and elemental maps also illustrate, that on a 10- to 100- μm scale, the composition of the overgrowth fluctuates antithetically in X_{Ca} and X_{Fe} by a few mol.% (cf. Fig. 5j). Probably, such short-scale chemical oscillations can be best explained by transient changes in fluid composition or pressure during garnet crystallization, which may be invoked to accompany deep hydrous subduction zone processes.

Multi-stage pelitic garnet, composed of pre-Alpine (Variscan) cores overgrown by Alpine rims, have been documented from several localities in the Alps (Ganne *et al.*, 2003; Faryad & Chakraborty, 2005; Gaidies *et al.*, 2006; Le Bayon *et al.*, 2006). As in the polymetamorphic rocks from Samos, the pre-Alpine garnet generation can be distinguished chemically and microtexturally from the Alpine generation, which not only rims pre-Alpine cores but also forms new smaller grains in the matrix. The geological evolution of the garnet-chloritoid-bearing micaschist of the Gran Paradiso nappe (western Alps) described by Le Bayon *et al.* (2006) compares to that of the studied Agios Nikolaos rocks in many aspects. Both occurrences have been subjected to a pre-Alpine amphibolite facies metamorphism followed by an early Alpine HP-LT event leading to complete Alpine re-equilibration of the matrix of the rocks. At both localities, the pre-Alpine evolution is recorded by a prograde growth-zoning of large garnet porphyroblasts, and the earliest Alpine garnet is characterized by a high grossular content (~ 20 mol.%). During late-stage exhumation, the Gran Paradiso rocks underwent moderate heating as deduced from decreasing X_{Ca} from core to rim in the Alpine garnet (Le Bayon *et al.*, 2006). Such decreasing X_{Ca} is not present in the irregularly zoned thin Alpine garnet rims from Samos, if anything the opposite. If our interpretation that the distribution of Ca across the thin rims is rather a disequilibrium feature (see above) is followed, the patterns of decreasing X_{Mn} and increasing Mg# are suggestive of moderate heating similar to the Gran Paradiso rocks. Heating during exhumation is increasingly being recognized in the Cyclades, possibly due to retreat of the subducting slab and thermal relaxation of the overriding plate (M. Okrusch, personal communication). This is at variance with older assumptions of cooling during exhumation (e.g. Will *et al.*, 1998).

Our study demonstrates that the Agios Nikolaos metapelites of Samos experienced an amphibolite facies metamorphism of Variscan age. Hence it is tempting to correlate the Samos example with other occurrences of Variscan amphibolite facies basement in the region (Fig. 1). In the Cycladic islands, basement rocks recording an amphibolite facies Variscan event are best preserved on the islands of Ios and Sikinos, whereas zircon geochronology also provides evidence for a Variscan event in the high-grade metamorphic core complexes of Naxos and Paros (Van der Maar *et al.*, 1981; Henjes-Kunst & Kreuzer,

1982; Van der Maar & Jansen, 1983; Andriessen *et al.*, 1987; Okrusch & Bröcker, 1990; Franz, 1992; Franz *et al.*, 1993; Engel & Reischmann, 1998; Reischmann, 1998; Keay *et al.*, 2001; Keay & Lister, 2002; Gupta & Bickle, 2004). Pre-Alpine crystalline basement has also been documented on the Dodecanese islands (Franz *et al.*, 2005), Central Crete (Kock *et al.*, 2007), eastern Crete (Franz, 1992; Finger *et al.*, 2002; Romano *et al.*, 2004; Franz *et al.*, 2005) and the island of Kithira (Xypolias *et al.*, 2006). On Crete and Kithira, the basement is intercalated within the Phyllite-Quartzite unit, which was affected by late Tertiary HP-LT metamorphism (Seidel *et al.*, 1982; Franz, 1992; Franz *et al.*, 2005). Unlike the basement of the Cyclades and Crete, which experienced Tertiary HP-LT metamorphism, the basement rocks exposed on the Dodecanese islands of Kalymnos, Leros and Lipsos were overprinted by low-pressure greenschist facies metamorphism during the Tertiary (Franz *et al.*, 2005). Apart from some Pan-African intrusion ages documented in the eastern Cretan basement (Keay & Lister, 2002; Romano *et al.*, 2004), and possibly on Ios island (Henjes-Kunst & Kreuzer, 1982), the studies of the basement units provide compelling evidence that Variscan magmatic and metamorphic activity was the earliest recognizable major orogenic event in the south-eastern Aegean. The radiometric ages cluster between *c.* 335 and *c.* 295 Ma. This interval corresponds to that found for basement occurrences in the Pelagonian zone (e.g. Vavassis *et al.*, 2000; Anders *et al.*, 2007) which is considered as the north-eastern continuation of the Attic-Cycladic Complex. On the other hand, the basement rocks of the neighbouring Menderes Crystalline Complex (western Turkey) lack evidence of a Variscan orogenic event and geochronological investigations typically record Pan-African metamorphism and magmatism (e.g. Loos & Reischmann, 1999; Candan *et al.*, 2001; Gessner *et al.*, 2004; Catlos & Çemen, 2005). The described polymetamorphic metapelites from northern Samos thus comprise the easternmost occurrence of Variscan basement relics found in the southern Aegean.

The available geochronological data, geological-lithological resemblance, and similar pre-Alpine metamorphic evolution of basement occurrences in the Cyclades, Dodecanese Islands and eastern Crete suggest that a coherent Variscan basement complex comprising amphibolite facies metamorphic rocks and associated magmatic rocks may once have existed in the southern Aegean region (e.g. Mposkos *et al.*, 2001; Reischmann *et al.*, 2001; Franz *et al.*, 2005; Krenn & Finger, 2006). Similar, pre-Alpine metamorphic *P-T* conditions have been documented from the NE Pelagonian Zone (e.g. Mposkos *et al.*, 2001). The precise extension and duration of the 'Variscan' orogenic event is, however, difficult to reconstruct because of the relatively large time span shown by the radiometric ages (zircon ages suggest that it lasted 60 Myr) as well

as the fragmentary nature of the basement occurrences. The latter is a result of the complex Tertiary geodynamic history of the area involving southern roll-back of the Aegean subduction zone accompanied by large-scale thrusting and extensional unroofing of the high-*P* rocks (e.g. Lister *et al.*, 1984; Gautier & Brun, 1994; Ring *et al.*, 1999, 2007; Jolivet *et al.*, 2003; Ring & Layer, 2003). Further investigations integrating detailed geochronological dating with petrological-structural studies are thus still needed to improve our understanding of the pre-Alpine history of the south-eastern Aegean region.

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SUPPLEMENTARY MATERIAL

The following material is available online at <http://www.blackwell-synergy.com>.

Appendix A1. (a–f) Optical and EMP element X-ray distribution images of two coalesced garnet grains, A1(g) compositional profile across garnet 1.

Appendix A2. (a–f) Optical and EMP compositional maps of pre-Alpine garnet porphyroblasts in sample SA26B1, A2(g, h) compositional profiles across garnet 7.

Appendix A3. (a–f) EMP element X-ray maps of garnet porphyroblast in sample SA109A. A3(g) compositional profile across garnet.

Appendix A4. Mineral chemistry of monazite inclusions in M0 garnet, and monazite electron microprobe U-Th-Pb dating and geothermometry.

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