Transformation of kyanite to andalusite in the Benamocarra Unit (Betic Cordillera, S. Spain). Kinetics and petrological significance

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Abstract: Kyanite is directly replaced by andalusite in quartz–plagioclase veins included within graphite-bearing micaschists of the Alpine Benamocarra Unit (Betic Cordillera, Spain). Electron back-scattered diffraction indicates that: i) precursory kyanite contains planar defects; ii) andalusite growth was crystallographically controlled by the kyanite; and iii) the structure of both Al2SiO5 phases shares nearly the closest-packed oxygen array and chains of edge-sharing octahedra. The small entropy difference of the kyanite–andalusite polymorphic inversion makes it difficult to overcome the energy barrier of this transformation. The driving force needed for the kyanite-to-andalusite reaction was a temperature (T) increase during a pre-Alpine tectonometamorphic evolution. The low-P/medium-T metamorphic conditions that affected the rocks studied took place in relation to a late Variscan extensional collapse. The reaction pathway proposed here corresponds to the first part of a poly-orogenic tectonometamorphic evolution, consisting of a pre-Alpine metamorphism of high thermal gradient with mainly static growth of porphyroblasts, followed by an essentially dynamic metamorphism during the Alpine orogeny.

Key-words: polymorphic transformation; kinetics; kyanite; andalusite; aluminium silicate; metamorphism.

1. Introduction

Orogenic cores frequently record complex polymetamorphic histories. An example of a complex polymetamorphic history can be found in pre-Mesozoic metamorphic successions of the Alpine Internal Domains of the Betic Cordillera (Spain) and the Rif (Morocco). Recent studies have demonstrated that the Alpine evolution overprinted Variscan and older orogenic events in the Nevada-Filabride, the Alpujarride-Sebtide and the Malaguide-Ghomaride complexes (e.g. Puga et al., 1975; Bouybaouène et al., 1998; Martín-Algarra et al., 2009a and b; Rosetti et al., 2010, 2013; Gómez-Pugnaire et al., 2012; Sánchez-Navas et al., 2012, 2014). Variscan U-Pb ages obtained from zircon and monazite single crystals in pre-Mesozoic rocks have been interpreted as related to high-grade metamorphic or magmatic events (e.g., Priem et al., 1966; Boulin et al., 1969; Bernard-Griffiths et al., 1977; Andriessen et al., 1991; Montel et al., 1995) were considered inconclusive or else lacking in regional significance. In fact, before the publication of a few recent papers (Sánchez-Navas et al., 2012, 2014), no direct field or petrographic evidence related to the Variscan orogenesis had been found by most workers in the Alpujarride Complex of the Betic zone (e.g., Torres-Roldán, 1974, 1981; Tubia et al., 1997; García-Casco et al., 1993; García-Casco & Torres-Roldán, 1996, 1999; Azañón et al., 1998; Argles et al., 1999; Soto & Platt, 1999). Moreover, Alpujarride-Sebtide rocks of variable metamorphic grades dated with different radiometric systems (Rb-Sr, K-Ar, Sm-Nd and U-Pb) gave systematically Alpine ages (e.g., Loomis, 1975; Priem et al., 1979; Michard et al., 1983; Zeck et al., 1989a and b, 1996; Monié et al., 1991, Monié et al., 1994; Sánchez-Rodríguez et al., 1996; Platt & Whitehouse, 1999; Rossetti et al., 2010, 2013). Integrated field and detailed micro-structural studies of mineral transformations in relation to
the tectono-metamorphic evolution are essential to distinguish the part of the metamorphic mineral associations and tectonic fabrics currently visible in the Alpujarride rocks that belong to Alpine or to pre-Alpine (Variscan, and perhaps older) events.

The three polymorphs of Al₂SiO₅ are important index minerals to unravel pressure (P) and temperature (T) conditions during regional and contact metamorphism. The P-T phase equilibria involving kyanite, andalusite and sillimanite are affected by considerable uncertainty in calibration experiments, and erroneous petrological interpretations of the presence of coexisting polymorphs in rocks derive from the sluggish kinetics of reactions involving the aluminium silicates (Kerrick, 1990). The reaction mechanisms in the transformation of pre-Alpine andalusite porphyroblasts to Alpine small-sized kyanite and fibrolite (both related to Alpine foliations) in metapelitic rocks of the Upper Alpujarride Torrox Unit were studied by Sánchez Navas et al. (2012). In the present study, we examine the transformation of pre-Alpine kyanite porphyroblasts to pre-Alpine andalusite porphyroblasts in medium-T metapelites of the Benamocarra Unit, which tectonically overlies the Torrox Unit. This transformation was observed in the field first, and further confirmed by microstructural studies. This allows a detailed discussion of the crystallographic and kinetic controls of the Ky → And transformation, and on the geological consequences of this transformation. We also describe textural relations and mineral chemistry of the enclosing polytetramorphic, medium-T, graphite-bearing, Ms + Bt + Pl ± Cld ± Grt ± St ± Ky ± And ± Crd micaschists (abbreviations after Whitney & Evans, 2010). Finally, we discuss the geological significance of the Ky → And transformation as well as of the textures and mineral chemistry of the rocks studied, in order to decipher the pre-Alpine vs. Alpine polymetamorphic history of the Benamocarra Unit.

2. Geological setting

The Alboran-Kabylia-Peloritani-Calabria (AlKaNéCa) Alpine metamorphic belt (Bouillín et al., 1986) includes the internal domains of the Western Mediterranean Alpine Belts before its post-collisional Mid- to Late Miocene disintegration (Fig. 1a). This belt resulted from the Early Miocene collision of Iberia and Africa against the Meso-Mediterranean Microplate (Durand-Delga & Fontboté, 1980), which was a continental crustal block detached from Pangaea and bounded by narrow oceanic basins since mid-Jurassic times (Guerrera et al., 1993). The Alpujarride and Malaguide complexes of the Betic Cordillera (Fig. 1b) and the equivalent tectonic units of the Rif (Sebtide-Ghamraine units), of the Algerian Kabylas and of the Calabria-Peloritani Terrane of southern Italy were essential constituents of the AlKaNéCa belt (Perrone et al., 2006).

The Malaguide Complex constitutes the highest tectonic thrust unit of the Betic internal domain, and overlies the Alpujarride Complex, of which the highest tectonic units in the Malaga area are totally made up of medium- to high-grade metamorphic rocks (Fig. 1b). In this work, we study rocks belonging to the Benamocarra Unit (Aldaya et al., 1979; Elorza, 1982), which is located just below the Malaguide Complex to the east of Malaga (Fig. 1c).

The Benamocarra Unit is composed of Alpujarride-like graphite-rich metapelites and metapsammites crosscut by dikes of mafic subvolcanic rocks (Fig. 1d) with a gradual upward decrease in metamorphic grade (e.g. Elorza & García-Dueñas, 1981; Ruiz-Cruz, 1997; Ruiz-Cruz & Rodríguez-Jiménez, 2002). The Benamocarra Unit overlies the Torrox Unit, the widest and most typical Upper Alpujarride Unit in the area, from which it is detached by an extensional contact (Alonso-Chávez & Orozco, 2012). The Torrox Unit is made of a gneissic complex at its base (Sánchez-Nava, 1999; Sánchez-Nava et al., 2014), surrounded by a monotone succession of dark-coloured and graphite-bearing St-Grt-Ky-And-Fi micaschists (Sánchez-Nava et al., 2012) with metamorphic grade decreasing upwards. The upper part of the pre-Mesozoic succession of the Torrox Unit is made of andalusite-bearing graphite-rich metapelites and metapsammites that are similar to the rocks that constitute the lower part of the Benamocarra Unit.

The rock succession of the Benamocarra Unit is described in more detail below. It underlies a thick succession of fine-grained low-grade to very low-grade schists, slates, psammites, and stretched conglomerates of early Palaeozoic or older age, which constitute the stratigraphic base of the Malaguide Complex (Morales Formation: Martín-Algarra, 1987) and which are also crosscut by dikes identical to those of the Benamocarra Unit (Fig. 1d). The contact between the two rock successions corresponds to a low-angle extensional fault, which often is difficult to recognize in the field (Fig. 1c). Consequently, according to regional geological studies, it is debated whether the Benamocarra Unit constitutes the base of the Malaguide Complex or is a part, detached by low-angle faults, of the top of the highest Alpujarride (Torrox) Unit in the area (Aldaya et al., 1979; Elorza & García-Dueñas, 1981; Elorza, 1982).

The stratigraphically lower beds of the Malaguide Complex (Morales Fm.) are strongly foliated metapelites and metapsammites affected by low-grade metamorphism (Ruiz-Cruz, 1997; Ruiz-Cruz & Rodríguez-Jiménez, 2002). The lowest part of the Morales Fm. contains abundant sericitized relics of metamorphic minerals, randomly oriented in the foliation. Among them millimetric porphyroblasts of andalusite, biotite, and garnet are locally preserved. All these minerals gradually disappear upwards whereas their amount and size increase downwards, so that the lowest part of the Malaguide succession becomes very similar to the rocks of the upper part of the Benamocarra Unit. Upwards, the Morales Fm. is stratigraphically followed by a thick succession of Upper Ordovician to Upper Carboniferous siliciclastic and carbonate turbidites with pelagic horizons that have been dated mainly with conodonts (O’Dogherty et al., 2000;
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Fig. 1. (a) Western Mediterranean Alpine belts with indication of the AlKaPeCa fragments (black). (b) Tectonic map of the Betic Cordillera. (c) Geologic map of the Benamocarra area (modified from Elorza & García Duenas, 1981). The samples mentioned in the text, figures, and tables are indicated with their numbers. (d) Lithological succession of the Benamocarra Unit and overlying rocks. (online version in colour)
unit-cell parameters

Andalusite is orthorhombic, space group Pnnm, with unit-cell parameters $a = 7.7980$, $b = 7.9031$, and $c = 5.5566$ Å; kyanite is triclinic, space group $P^{-1}$, with $a = 7.1262$, $b = 7.8520$, $c = 5.5724$ Å, $\alpha = 89.99$, $\beta = 101.11$ and $\gamma = 106.03^\circ$ (from Winter & Ghose, 1979).

4. Results

4.1. Field relations

Metapelitic rocks of the Benamocarra Unit consist of alternating bands of quartz-rich and mica-rich domains inherited from the psammitic and pelitic layers of the sedimentary protolith (Figs 1d and 2a). The succession is lithologically very monotonous and, in the field, a gradual decrease in grain size is observed from bottom to top of the succession. Porphyroblasts of And and Cld are sometimes visible to the naked eye as dark crystals (Fig. 2b), and those of Grt as orange-redish spots, the latter being most abundant towards the top of the succession. The upward decrease in grain size is accompanied by the disappearance of And preserved only as relic pseudomorphs in many cases towards the top of the succession.

In addition to the lithological layering ($S_0$) defined by the alternation of minor amounts of pelites intercalated with psammitic layers, two foliations are visible in the field within the Benamocarra schists (Fig. 2a). The most evident foliation in the field, hereafter called $S_1$, transposes previous foliations $S_1$ and $S_2$. However, $S_1$ is observed only in thin section within Cld and Grt crystals and in graphite-rich microlithons (see below). The foliation $S_2$, visible in the field, is found within the graphite-rich pelitic bands, transposed by $S_3$ (arrows in Fig. 2a). In these graphite-rich metapelitic layers, andalusite prisms occur randomly oriented in foliation $S_2$ (Fig. 2b). Quartz segregations frequently containing millimetric to centimetric Ab and pink And crystals are very abundant and most of them certainly crosscut the $S_2$ foliation. Nonetheless, the late foliation $S_3$ frequently shears these And-bearing quartz-rich veins, which are commonly found parallelized to the latter. The less deformed veins contain random aggregates of pink And prisms (Fig. 2c). However, within the veins the pink And crystals more frequently appear fractured and tectonically re-oriented, boudinaged, and strongly elongated, along $S_3$. Exceptionally, blue kyanite prisms are intergrown with andalusite prisms in deformed veins parallel to the $S_3$ (Fig. 2d).

4.2. Petrography

Two main mineral associations have been recognized in the Benamocarra metapelitic/metapsammitic succession:

3. Sampling and analytical procedures

The studied samples were collected from four sections in the Benamocarra Unit and in the lowest beds of the Malaguide Palaeozoic succession: the Benamocarra schists: samples Ben10 and Ben11 (Fig. 1c) and coarse-grained micaschists (sample Ben54: Fig. 1c) by using a Cameca SX-50 electron microprobe. Operating conditions were 20 kV accelerating voltage, 20 nA beam current and a spot size between 5 and 7 μm. Standards were both synthetic oxides and minerals. Structural formulae of synthetic oxides and minerals. Structural formulae of minerals were calculated using the software of Ulmer (1986), with the exception of chloritoid (12-oxygen anhydrous basis, Chopin et al., 1992; and Fe3+ as 4–(Al + Ti), Azañon et al., 1997).

Electron back-scattered diffraction (EBSD) images and pole figures of the Ky→And transformation from a quartz-rich vein (sample Ben43: Fig. 1c) were made with a Leo GEMINI-1530 scanning electron microscope (SEM) equipped with an Inca Crystal detector. The diffraction pattern, once indexed, provides information on the orientation of the crystal lattice. Data from different positions were integrated to perform orientation maps, and represented as pole figures. In the sample, Z and Y axes coincide with normal direction to the polished section and the trace of the main or more pervasive foliation, respectively. Andalusite is orthorhombic, space group $Pnnm$, with unit-cell parameters $a = 7.7980$, $b = 7.9031$, $c = 5.5566$ Å; kyanite is triclinic, space group $P^{-1}$, with $a = 7.1262$, $b = 7.8520$, $c = 5.5724$ Å, $\alpha = 89.99$, $\beta = 101.11$ and $\gamma = 106.03^\circ$ (from Winter & Ghose, 1979).
i) Ms + Bt + Pl + Cld + Grt ± And (upper part); ii) Ms + Bt + Pl + Cld + Grt + And ± Ky ± St + Crd (lower part). The petrographic study is focused mainly on the textural relation between Cld, And, Grt, Crd, and foliations S1, S2, and S3. Chloritoid crystals have grown randomly oriented on a Gr-rich foliation (S1) in the Ms + Bt + Pl + Cld + Grt + And schists of the upper part of the Benamocarra Unit (Fig. 3a). Chloritoid frequently occurs as post-S1 prismatic crystals within Gr-rich micaceous domains moderately affected by S3 (Fig. 3a). In some cases, Cld prisms appear moderately deformed and partially or totally pseudomorphed by Qz + Ms + Bt and opaque phases (Fig. 3b). In addition, some Cld crystals are clearly reoriented and sheared by S3, and embedded in a Bt-rich matrix (Fig. 3c).

Andalusite appears strongly affected by the deformation D3, with tectonic reorientation, boudinage and microfolding associated with the development of the S3 foliation (Fig. 3d–f). The And porphyroblasts are post-kinematic to S2 and formed after Cld, Grt, and St (Fig. 3e). In some cases And overgrows Grt crystals including Cld or contains relics of St. The foliation S3 is well defined by micro-shear bands filled by Qz deforming the Gr-rich domains and And crystals (Fig. 3f).

Within the mica-rich and finer-grained domains that are less deformed by D3 in the Ms + Bt + Pl + Cld + Grt + And ± Ky ± St + Crd micaschists of the lower part of the Benamocarra Unit, the porphyroblasts of Cld and Grt grew first, and those of And and xenoblastic Crd formed later, enclosing both Grt and Cld (Fig. 4a–b). The Bt and And formed after destabilization of Grt (Fig. 4c). Indents on {110} of Grt indicate the dissolution of Grt perpendicular to these faces favoured by the presence of abundant inclusions of Qz distributed perpendicularly to these crystal faces (Fig. 4c). In some cases, such small Qz inclusions form a cross-like pattern that evokes the typical crystal-growth features of the And chiastolites (Fig. 4c). The plagioclase is prevalently albitic, commonly encloses graphite layers defining S1, and is frequently fractured when crossed by S3. Some relic St grains are preserved within poikilitic And crystals (Fig. 3e) but form preferentially small, isolated and dismembered porphyroclasts, sheared and wrapped by S2. Kyanite is very rarely present in the schists. The And + Crd association, postdating the Cld + Grt association, is strongly affected by the S3-related deformation (Fig. 4b–d).

The S3 foliation transposes the earlier foliations S1 and S2, which are preserved in graphite-rich micaceous micro-lithons or within porphyroblasts (S1 in early Cld, Fig. 3a–b, and S2 in later Crd/And, Figs 3d–f, 4b and d) in the micaschists of the whole Benamocarra succession. The S3 foliation forms a metamorphic banding made of alternating Qz-rich and micaceous layers (recrystallized Bt and Ms) anastomosed around the Qz grains and pelitic microlithons (Fig. 3a). Syn-S3 micas also grew as pseudomorphs of previous minerals such as Cld and Crd. A common
secondary mineral phase is Chl, which crystallizes as a product of destabilization of Bt, Grt, and Crd.

Kyanite crystals partially replaced by andalusite (Fig. 5) have been studied in detail from one Qz–Ab vein from the intermediate part of the Benamocarra succession (sample Ben43). This post-S2 vein is strongly deformed and parallel to the S3 foliation (Fig. 2d), which is defined by Ms within the vein itself. Both the Ky and the And crystals are folded and fractured (Fig. 5a). In some cases, a single Ky crystal is directly replaced by more than one And prism; this is apparent in optical images by the different crystallographic orientations observed for replacing And (Fig. 5b), and confirmed also in EBSD images (see below).

4.3. Mineral chemistry

Muscovite mineral chemistry shows two compositional groups (Table S1, freely available online as Supplementary material linked to this article on the GSW website of the journal, http://eurjmin.geoscienceworld.org/; Fig. 6a–b). Most analyses belong to the first group, which is constituted of Ms flakes, formed after D1 (primary Ms), with lower Si content (Si = 3.03–3.15 atoms per formula unit, a.p.f.u.), low celadonitic substitution (Fe + Mg = 0.03–0.12 a.p.f.u.) and low K/(K + Na + Ca). The second group includes the Ms formed in relation to the D3 deformation (recrystallized Ms) and exhibits a higher Si content.
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Biotite composition is intermediate between phlogopite and annite \((X_{Mg} = 0.44–0.54; \text{Table S2 in Supplementary Material})\). Some chemical analyses indicate that Bt is partially transformed to Chl. Sometimes, Bt that formed along S_3 is completely transformed to Chl, even if it preserves the usual optical features of Bt.

Garnet composition is close to that of almandine: \(\text{Alm} = 63–74\%\), \(\text{Grs} = 5–20\%\), \(\text{Prp} = 4–10\%\), and \(\text{Sps} = 0–9\%\) (Table S3, Fig. 6c–d). In addition, representative Grt composition data reveal differences between cores and rims (Table S3): cores show a higher content of spessartine \((X_{\text{Sps}} = 0.04–0.09)\) and a relative lower abundance in almandine \((X_{\text{Alm}} = 0.63–0.70)\) whereas rims are depleted in spessartine \((X_{\text{Sps}} = 0.00–0.04)\), with correlative increase in almandine \((X_{\text{Alm}} = 0.70–0.74)\). The Mg number does not change from cores to rims, however. Ca is slightly higher in garnet cores than in rims (Fig. 6c).

Chloritoid is a Fe-Cld (Table S4) with a very low Mn content \((0.01–0.03\ a.p.f.u.)\). The Mg content invariably increases from cores \((X_{\text{Mg}} = 0.11–0.13)\) to rims \((X_{\text{Mg}} = 0.13–0.16)\).

Chlorite forms at the expense of Bt and, compositionally, is a chamosite with an \(X_{\text{Mg}}\) from 0.37 to 0.39.

4.4. EBSD study of andalusite pseudomorphs after kyanite

As mentioned above, in the deformed Qz–Ab vein with abundant Ky and And of sample Ben43, elongated Ky crystals are topotactically transformed to And. First, we describe the partial replacement of a single Ky crystal by two And crystals with a different crystallographic orientation (Figs 5b, 7, 8) and, later, the textural relations between Ky relics and enclosing neo-formed And (Fig. 9).

Figure 7 shows the results of the EBSD study corresponding to Zone 1 of Fig. 5b. Poles corresponding to the direction normal to the \((100)\) Ky planes locate close to the Z axis in some pieces of the Ky crystal: e.g. central part and lower left-hand side of the Ky (Z) orientation map (Fig. 7e). Nevertheless, in other pieces of the Ky crystal the poles of the \((010)\) planes are located along the Z axis (upper and lower parts of the main Ky crystal in Fig. 7e). As shown by the Ky (X) orientation map and the corresponding 001 pole figure, different orientations are also observable for Ky (Fig. 7f). However, the poles corresponding to the normal to the \((001)\) planes of the Ky crystal mainly locate near the X direction in the sample. The c crystallographic axis of the And crystal is sub-parallel to...
the Z direction in the And (Z) orientation map and the corresponding 001 pole figure (Fig. 7d).

Figure 8 shows the orientation of the second And crystal replacing Ky in Zone 2 of Fig. 5b. In this case, the c crystallographic axis of the And crystal is sub-parallel to the poles corresponding to the normal to the (001) planes of the precursory kyanite single crystal (compare Fig. 8 with Fig. 7f).
Figure 9 corresponds to the EBSD study of an And pseudomorph after Ky. In this case, small non-transformed relics of the precursory Ky single crystal still remain within the And crystal (high-relief areas in background electronic-image). The crystallographic relations between the Ky single crystal and the And are similar to those visible in Zone 2 of Fig. 5b. Because EBSD orientation mapping covers a large area, it results in a large numbers of maxima in the pole figures (Fig. 9g) due to the presence of small pieces of Ky and And with different orientation. When the scanned region is restricted to a small area (so that only And close to the almost completely transformed Ky is taken into account), it can be appreciated that the c crystallographic axes of both phases are parallel, whereas the a and b axes are interchanged, with an angular deviation of 6° and 13° between the \( a_{\text{And}} \) and \( b_{\text{Ky}} \) and between the \( b_{\text{And}} \) and \( a_{\text{Ky}} \), respectively (Fig. 9h–i).

5. Discussion

5.1. Crystallography of the transformation of kyanite to andalusite

The Ky \( \rightarrow \) And transformation described here is a solution-mediated, solid-solid reaction in which \( \text{Al}_2\text{SiO}_5 \) undergoes structural changes without compositional change. According to the crystallographic relationships observed...
for Ky and And, this transformation is structurally controlled. It means that the crystallographic orientation of the And was controlled by the orientation of Ky. The structurally controlled Ky → And transformation began at a reaction site of high-energy density that, in the study case, corresponds to a particular crystallographic plane of the Ky crystal structure. At that site the atoms of the Ky reactant have enough energy to surmount the activation barrier and to reorganize themselves to form And. As previously shown, the Ky crystals partially transformed to And contain planar defects (Fig. 7e).

Figure 10a shows the projection of diverse close-packed oxygen layers that form the anion sub-lattice in the Ky structure onto the (110) Ky crystallographic plane. The coordination environment of anions forming the close-packed layers appears in Fig. 10b. Anion (110) layers (here designated as A, B, and C) form a closely packed, roughly cubic array of oxygen atoms. The closest-packed array occurring in the Ky structure allows the development of complex stacking sequences (Fig. 10c) and can be responsible for the occurrence of planar defects in Ky (disoriented domains in the map of Fig. 7e).

One specific crystallographic relation between reaction product and reactant is found in topotactic replacements among Al-silicates, i.e. in the case of replacement of andalusite by mullite/sillimanite (\(c_{\text{And}}\)|\(c_{\text{Sil/ Mul}}\), \(a_{\text{And}}\)|\(b_{\text{Sil/ Mul}}\), \(b_{\text{And}}\)|\(a_{\text{Sil/ Mul}}\); Hülsmans et al., 2000; Cesare et al., 2002). The mutual crystallographic orientation of Ky and And obtained from EBSD data in small areas of both phases (Fig. 10h–i) deviates slightly from those topotactic relationship proposed in the literature. Nevertheless, the And follows at least two main orientations when replacing Ky (Figs 5b, 7 and 8). It has been illustrated in Fig. 11a–b, where two And crystals grow with their \(c\) crystallographic axes contained in Ky (110) planes, that one of them coincides with \(c_{\text{Ky}}\).
Worden et al. (1987) made a noteworthy observation in relation to structurally controlled replacements among oxygen-bearing minerals of different composition. According to these authors, the crystallographic plane parallel to the interface between reactant and product corresponds to a close-packed plane of the oxygen sub-lattice of their respective structures. The two coexisting phases share nearly the closest-packed anion layers in topotactic replacements where a definite crystallographic relation is observed between host and inclusions (e.g., Shau et al., 1991). Lattice strain is reduced at the interface defined by the shared closest-packed anion layers, because interatomic distances and type of arrangement (hexanet) in oxygen layers are approximately the same on both sides of the interface. Figures 11c and d show the oxygen packing in (110) and (320) planes of the structures of Ky and And, respectively. The oxygen arrangement along the c crystallographic axis of the And structure, indicated in Fig. 11d, fits any of the three directions within the (110) plane of the Ky (Fig. 11c).

Atoms at the interface of one phase are partially bonded to different neighbours in the adjacent phase. Consequently the change of oxygen coordination environment at the interface with respect to the atom within the crystal lattice affects the energy of the anion coordination polyhedron. Burdett & McLarnan (1984) established the idea that there is a tight positive correlation between the electron-band structure energy of polymorphs and energy computed by adding only local contribution from each anion coordination polyhedron. These authors emphasized the importance of the environment of anions where most of the valence electrons are located. Moreover, in their orbital interpretation of Pauling’s second rule, they concluded that the anions with higher coordination numbers lead to a
structural destabilization. In the case of silicates, these anions correspond to the so-called oversaturated oxygen anions of Zachariasen-Baur (Baur, 1970), which are responsible for unusually long Si-O bonds, thus favouring bond-breaking. Experimental evidence of minor structural stability around oxygen atoms with higher coordination number was provided by Bell & Wilson (1977) and Meike (1989), who demonstrated that muscovite required more strain energy to bring about dislocations than did biotite, and that faulting goes through the octahedral layer (closest-packed oxygen layers with chains of edge-sharing octahedra within these anion layers).

The presence of chains of edge-sharing octahedra in the structures of the three polymorphs of Al_2SiO_5 also weakens their stability according to rule 3 of Pauling. Burdett & McLarnan (1984) showed that structures with edge or face sharing have distorted anion environments, resulting in poor anion hybridization and weaker metal-anion bonds. The weathering series Ky → And → Sil has been explained from a crystal chemical standpoint. In Ky, all Al atoms locate in octahedral sites whereas, in And, half the Al atoms occupy five-coordinated sites and, in Sil, half occupy four-coordinated sites. According to Velbel (1999), relative weathering rates within the Al_2SiO_5 group vary with the coordination number of Al: the Al_2SiO_5 polymorph weathers more easily when the coordination number of Al is higher. Nevertheless, the tradition of considering only the cation coordination was condemned as early as Bragg (1930): if the environment of anions (and, therefore, half of the atoms of the structure where most of the valence electrons are located) is ignored, the structural transformations among minerals cannot be well explained.

As illustrated in Fig. 10b the oxygen coordination number in the close-packed (110) planes of Ky is higher than 3, whereas it is 3 or lower in the oxygen atoms of the And and Sil structure. Consequently, according to the above discussion, high-coordinated oxygen atoms in close-packed structures are responsible for high local structural instabilities that favour the breaking and/or reorganization of Si–O bonds in response to the change in P-T conditions during the Ky → And replacement.

5.2. Kinetics of the Ky → And reaction

In previous studies the Ky → And polymorphic inversion in Alpujarride rocks has been interpreted in relation to decompression during the Alpine orogeny (García-Casco & Torres-Roldán, 1996; Argles et al., 1999). Grambling (1981) and Grambling & Williams (1985) described the occurrence of Ky → And and And → Sil reactions during prograde conditions in rocks affected by a low-pressure regional metamorphism. Nevertheless, Pattison (2001) indicates that these Al_2SiO_5-bearing rocks were involved in decompressional P-T paths traversing, in order, the Ky, Sil and And fields. Kerrick (1988) studied the transformation of Ky → And in Al_2SiO_5-bearing segregations during retrograde decompression of rocks from the Lepontine Alps. He concluded that the Ky → And reaction was catalysed by fluids derived from metamorphic dehydration reactions in the host rock. Sánchez-Navas et al. (2012) have shown that the dissolution/precipitation of aluminosilicate minerals is easier if the reaction involves OH-bearing minerals. These authors studied the opposite transformation (And → Ky) in Grt ± St ± Ky ± And ± Fi ± Crd Gr-bearing micaschists of the Torrox Unit, which tectonically underlies the Benamocarra Unit, and concluded that dehydration reactions of Ms and Bt provided the chemical driving force needed to break Si–O bonds.

In the Benamocarra Unit, the energy necessary to overcome the activation barrier of the Ky → And reaction could have been provided by a temperature increase instead of a pressure increase. To envisage how a pressure increase helps the activation energy barrier to be overcome, we need to consider only the fact that energy density is (dimensionally) equivalent to pressure. Nevertheless, it is much easier to interpret the Ky → And reaction found within the Benamocarra schist sequence in relation to a
high-thermal-gradient metamorphism and maximum temperature close to 550 °C that reached a maximum pressure around 0.4 GPa, close to that defined by the Al$_2$SiO$_5$ triple point (see below).

5.3. Evidence of a high-thermal-gradient metamorphism

The reaction pathway proposed above for the Ky $\rightarrow$ And transformation found within Qz–Ab veins is compatible with the metamorphic evolution inferred from the enclosing schists. The petrographic data indicate an early prograde metamorphic stage related to burial and heating, evidenced in the schists by blastesis of post-S$_1$ Cld and Grt porphyroblasts (Figs 3a–c, 4a–c). The growth of Cld, Grt, St, and Ky in the schists was probably slightly older than (or coeval to) the opening of Q–Ab veins and related formation of cm-sized Ky crystals.

The blastesis of Cld, Grt, St, and Ky predated the polymorphic replacement of Ky crystals by And in the veins, which was probably associated with the generalized blastesis of post-S$_2$ And (and locally of Crd) in the schists. This reflects the evolution from an initial intermediate-$P$ Barrovian metamorphism to medium-$T$ and low-$P$ metamorphic conditions. Deformation during decompression led to the formation of the S$_2$ foliation, sealed by And, and in the widespread occurrence of post-S$_2$ veins filled by Qz, Ab, and And prisms, which is a common feature of medium-grade schists, equivalent to those of Benamocarra, frequently found in many Alpujarride units.

When well preserved, which is not always the case due to younger deformation events in the Benamocarra micaschists, the larger porphyroblasts postdating the foliations S$_1$ and S$_2$, in particular some of Grt and, especially, those of And, show textural evidence of crystal growth under static conditions (Fig. 4a and c). In chiastolitic andalusite the crystal-growth features consist of graphite accumulations at the edges of the prism faces resulting from crystal growth normal to the flat faces (Fig. 4a). In relation to Grt, the same conditions favoured the development of cross-like inclusion patterns of Qz grains perpendicular to rhombohedral faces (Fig. 4c). Both patterns result from a type of crystal-growth mechanism related to static blastesis and, for pre-Alpine And in the rocks of the Torrox Unit, this was called layeritic growth by Sánchez-Navas et al. (2012). According to this mechanism, the crystal-growth features of both And and Grt in the schists also occurred through a thermally activated fast growth normal to the flat faces of crystals. This growth was controlled by screw dislocations emergent at the centre of the F-faces under low-supersaturation conditions due to slow diffusion rates, where the low matter supply was related to low deformation rate (Sánchez-Navas et al., 2012). Therefore, the blastesis of And and Grt in the schists also occurred through a thermally activated process related to a prograde metamorphism, in the same way as previously proposed for the Ky $\rightarrow$ And transformation in the veins.

The normal chemical zoning pattern observed from cores to rims in Grt also indicates a prograde growth, certainly due to a $T$ increase (Fig. 6c–d, Table S3).
increase in Mg content of Cld from core to rim (Table S4) further supports this T increase. The occurrence of Grt and Cld in these rocks is due to their Fe-rich composition and does not necessarily indicate higher pressure than that of the Al$_3$SiO$_5$ triple point. Almandine Grt and Fe-rich Cld ($X_{Fe} = 0.11–0.13$) can form at relatively low pressures because of the strong stabilizing effect of iron and other transition elements when they are incorporated into the structures of both minerals (Spear, 1993).

As stated above, Cld and Grt porphyroblasts were later partially consumed in the prograde reactions that formed And and Crd. In fact, Crd grew over Cld and And chiastolites that formed in the matrix instead of replacing Cld porphyroblasts directly (Fig. 4a–b). The persistence of Cld and Grt in And-Crd metapelites indicates that their breakdown extended across the growth interval of And and Crd (Fig. 4). It represents a chemical disequilibrium probably conditioned by a very rapid decompression or simply metastable persistence.

5.4. Tectono metamorphic history

In diverse zones of the Iberian Variscan Belt, the Variscan crustal thickening induced a prograde metamorphism of Barrovian type, which was followed by a H7-LP metamorphism after the collapse of the thickened continental crust (Ábalos et al., 2002; Valle-Aguado et al., 2005; Bea et al., 2006). This transition took place through isothermal decompression and resulted in high thermal gradients and widespread intrusions of granitoids (e.g. Ábalos et al., 2002). In the Upper-Alpujarride Torrox Unit, located structurally below the Benamocarra Unit, the coexistence of And and Crd in leuco-granitic dykes intruding high-grade paragneisses and schists (Sánchez-Navas et al., 2014) as well as the breakdown of large pegmatitic Ms forming And + Kfs intergrowths in orthogneisses (Sánchez-Navas, 1999) have been interpreted as result of a high-T low-P Variscan metamorphic event. Moreover, the strong metamorphic gradient observed through the crustal sequence in many Upper and Intermediate Alpujarride units, including those related to the Ronda peridotite emplacement, has been recently reinterpreted as developed under low-P and high-T conditions during the Variscan Orogeny (e.g. Acosta Vigil et al., 2014). According to our interpretation, Cld, St, Grt, and Ky are syn- to post-kinematic to D$_1$, and formed in relation to a Barrovian-type metamorphism of medium-P that affected the Benamocarra Unit probably during Variscan times. It reflects an initial episode of prograde metamorphism resulting from crustal thickening, represented by D$_1$ in the clockwise P-T path (I) of Fig. 12. This early Variscan tectono metamorphic evolution reached a maximum pressure around 0.4 GPa (Fig. 12). The second episode consisted of a late Variscan decompression (D$_2$) that ended with the blastesis of post-S$_2$ And and Crd at low P (around 0.2 GPa) and medium T (around 550 °C) conditions (Fig. 12).

A much more dynamic metamorphism was related essentially to the strong deformational Alpine history, which caused mylonitization and grain-size reduction of the previous larger minerals in the rocks studied. The Alpine overprint, which occurred along shear zones in relation to D$_3$, gradually decreased from bottom to top of the metapelitic-metapsammitic sequence. It gave rise to zones at different degrees of re-equilibration, from partly re-crystallized medium-fine grained mica-chatschists with abundant pre-Alpine minerals to pervasively restructred fine-grained mica phyllites. The T conditions of the Alpine metamorphic peak in the Benamocarra Unit were between 400°C and 450°C, in accordance to the formation of biotite and muscovite in the foliation (Figs. 3–4) and, in the case of biotite, also around garnet (Fig. 4c). According to phengite geobarometry (Massonne & Schreyer, 1987), the pressure of this Alpine event was around 0.5–0.6 GPa, as deduced from Si (3.23–3.21 a.p.f.u.) and Fe$^{2+} + 2Mg$ content (0.19–0.14) of phengitic muscovite (Table S1, Fig. 6a). The partial replacement of chiastolitic And by fine-grained Ky and fibrolitic sillimanite in the Torrox Unit (Sánchez-Navas et al., 2012) indicates that P and T were higher during the Alpine orogeny in tectonic units structurally below the Benamocarra Unit. The inferred metamorphic P-T path related to the major Alpine deformation phase D$_3$ is represented by the curve (II) of Fig. 12, which agrees well with intense
contractional tectonics associated with nappe emplacement during the Alpine orogeny.

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