

Prograde versus retrograde chlorite-amphibole intergrowths in a calc-silicate rock

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ABSTRACT

Transmission electron microscopy was used to determine structural relationships between chlorite and amphibole and to distinguish prograde from retrograde intergrowths. The prograde reaction chlorite + calcite + quartz = calcic amphibole + anorthite + CO₂ + H₂O results in chlorite grains overgrown by amphibole. Prograde chlorite inclusions occur with *hk0* zone axes subparallel to the amphibole *c* axis but have incoherent and fractured boundaries. These relations are consistent with mimetic growth of amphibole in the chlorite foliation but not with topotaxial replacement.

Some retrograde chlorite in amphibole occurs with chlorite (001) and amphibole (100) planes parallel and the amphibole *c* axis parallel to chlorite [100], [$\bar{1}$ 10], or [$\bar{1}$ $\bar{1}$ 0]. Coherent boundaries occur parallel to chlorite (001) layers, with no apparent misfit strain. Growth ledges of talc-like layers occur along coherent boundaries, showing that chlorite growth can occur by a single-layer mechanism. Boundaries that are not parallel to chlorite layers are strained such that chlorite layers bend to promote coherence.

Most retrograde intergrowths are associated with fractures and consist of chlorite with minor amounts of talc and unidentified phyllosilicates. These intergrowths vary from coherent crystallites to incoherent and poorly crystallized material, reflecting varied conditions of alteration. Wide-chain defects are another retrograde alteration product.

INTRODUCTION

The metamorphosed argillaceous-carbonate rocks of the Waterville Formation of south-central Maine have been extensively studied (Ferry, 1976a, 1976b, 1983), and many possess reaction textures. Sample 18, the subject of the present study, contains prograde intergrowths where reactant chlorite is overgrown by product amphibole, as shown in Plate 1B of Ferry (1976a). The purpose of the present study was to investigate orientation and boundary relationships between prograde chlorite inclusions and host amphibole in order to determine possible reaction relations. The discovery of fine-scale retrograde alteration of amphibole to chlorite, other phyllosilicates, and wide-chain material has allowed a comparison of prograde and retrograde textures within amphibole crystals.

The term "prograde" is used here for reactions that result from the addition of heat and that produce assemblages reflecting equilibrium at the peak temperature of metamorphism. Depending on the composition of the intergranular fluid, prograde reactions in metacarbonate rocks result in decarbonation and dehydration reactions. Prograde chlorites described here are remnants of material that was not consumed by the amphibole-forming reaction but that remains as inclusions within amphibole porphyroblasts.

The term "retrograde" is used here for reactions that

occur with decreasing temperature after the peak of metamorphism. Many of these reactions involve hydration of minerals. Because of the low permeability of metamorphic rocks under low fluid pressure, fracturing is usually required for fluids to become available for retrograde hydration reactions. Minerals that are more hydrous than the host amphibole and that occur in fractures or along grain boundaries are interpreted as resulting from retrograde metamorphism. Chlorite in amphibole that is not associated with fractures is interpreted as remnants of incomplete prograde reaction.

Because of the small sizes of intergrowths, transmission electron microscopy (TEM) is an important technique for distinguishing prograde from retrograde minerals and for interpreting reaction mechanisms. TEM studies of altered orthoamphiboles have revealed a variety of alteration products including chlorite, talc, serpentine, and wide-chain biopyriboles (Veblen and Buseck, 1979, 1980, 1981; Cressey et al., 1982; Whittaker et al., 1981). All of these reaction products can be coherently intergrown with the orthoamphibole. Retrograde hydration reactions are common in rocks that have experienced complex metamorphic and tectonic histories, and so it is possible to find minerals that could be of either prograde or retrograde origin. Distinguishing between the two origins is important for understanding metamorphic processes and histories.

GEOLOGIC SETTING

The sample studied is from the Waterville Formation, which belongs to a 5000-m-thick Silurian turbidite sequence that fills the Merrimack synclinorium in eastern New England. Protolith rocks consisted of graywackes interbedded with thin layers of quartzite and argillaceous limestone, with local horizons of pure carbonate rocks (Ferry, 1976a; Osberg, 1979). These sedimentary units were deformed, metamorphosed, and intruded by granites during the Acadian orogeny of Devonian age.

The Acadian orogeny compressed and thickened the Merrimack sedimentary unit in three folding events, resulting in a polymetamorphic history. The metamorphism in the Waterville area appears to fit a two-stage model similar to the thermal model of Chamberlain and England (1985). Initial crustal thickening resulted in large alpine-scale (F1) folding (Bradley, 1983; Osberg, 1979) and possibly an early metamorphic event correlative with the initial Acadian metamorphism (M1) of central Maine (Novak and Holdaway, 1981; Holdaway et al. 1988). A second crustal thickening event resulted in the F2 folding (Osberg, 1979) and the peak of regional metamorphism. Intrusion of the Hollowell group of granitic plutons occurred at about the same time as the peak of regional metamorphism. The combined regional and contact effects appear to correlate with M3 of Holdaway et al. (1988). A third folding event occurred synchronously with or slightly after the peak of metamorphism, with no observed metamorphic effect. Additional granitic plutons were intruded in southwestern Maine as late as the Carboniferous, resulting in M5 prograde and retrograde metamorphism to the southwest of the Waterville area (Holdaway et al. 1988; Lux and Guidotti, 1985).

PETROLOGY

Metamorphic conditions for the chlorite-amphibole reaction in sample 18 were determined by Ferry (1976a, 1976b, 1983), and the following summary is based on his work. The pressure at the peak of metamorphism was 3500 ± 200 bars. On the basis of the regional temperature trend, the peak temperature reached by sample 18 was 460 °C. The metamorphic intergranular fluid was nearly a binary H₂O-CO₂ mixture, with $X_{\text{CO}_2} \leq 0.3$ during peak metamorphism of amphibole-zone rocks.

The decarbonation reaction that produced amphibole from chlorite in the Waterville Formation was driven by fluid infiltration. A generalized form of the reaction is given by Ferry (1976a) as chlorite + calcite + quartz + intermediate plagioclase = calcic amphibole + calcic plagioclase + water + carbon dioxide; written for end-member compositions, this reaction becomes $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8 + 3\text{CaCO}_3 + 7\text{SiO}_2 = \text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2 + \text{CaAl}_2\text{Si}_2\text{O}_8 + 3\text{CO}_2 + 3\text{H}_2\text{O}$. Mixing of the H₂O-rich infiltrating fluid with that produced by the reaction resulted in an increase in X_{CO_2} with increasing temperature, producing a reaction zone and preservation of reaction textures.

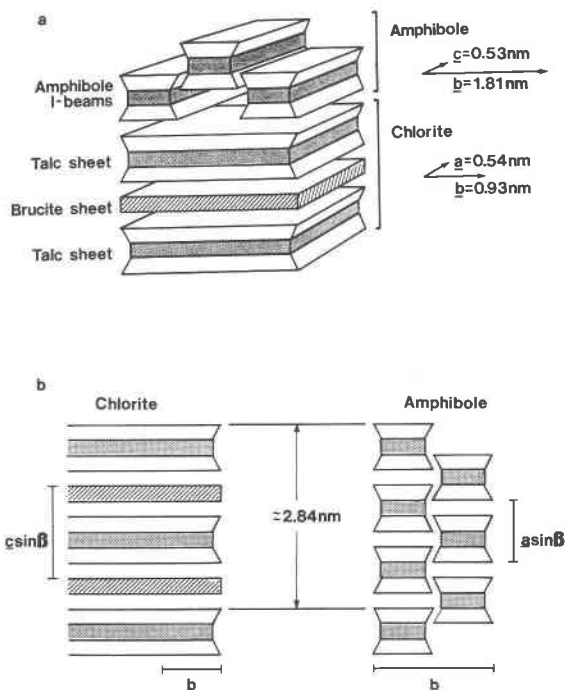


Fig. 1. Schematic illustration of the coherent orientation relationship between chlorite and amphibole. (a) The c unit vector of amphibole is parallel to and nearly equal in length to the a unit vector of chlorite, and the b unit vector of amphibole is parallel and approximately twice the length of the b unit vector of chlorite. (b) Two chlorite layers are nearly equal in thickness to three amphibole I-beams.

MINERAL STRUCTURES AND STRUCTURAL RELATIONSHIPS

Chlorite and amphibole have structural elements that allow coherent or semicoherent intergrowths. Knowledge of their structures helps in understanding the geometrical control in reactions and defects associated with intergrowths.

Chlorite consists of alternating talc-like $[\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2]$ and brucite-like $[\text{Mg}_3(\text{OH})_6]$ sheets (Pauling, 1930). The most common chlorite structure, making up 80% of all chlorites, is the I1b one-layer polytype. It has space group $C2/m$ with cell parameters $a = 0.54$, $b = 0.93$, $c = 1.42$ nm, and $\beta = 97^\circ$ (Bailey and Brown, 1962). This one-layer polytype commonly has a semirandom stacking sequence, which can be detected with electron diffraction by streaking parallel to c^* along $k \neq 3n$ rows in $[100]$, $[\bar{1}10]$, or $[\bar{1}10]$ zone-axis diffraction patterns (Spinnler et al., 1984; Iijima and Buseck, 1977).

Amphibole consists of I-beam-like structural units that are analogous to portions of the talc-like sheets of chlorite. Cell parameters for the calcic amphibole from the Waterville Formation were not determined, but they can be approximated by those of hornblende, which has space group $C2/m$ with cell parameters $a = 0.99$, $b = 1.81$, $c = 0.53$ nm, and $\beta = 105^\circ$ (Papike et al., 1969). Amphibole

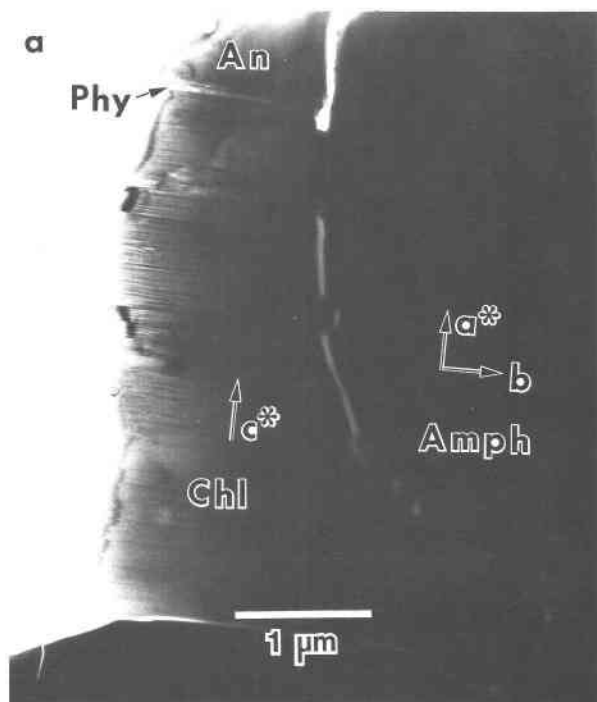


Fig. 2. TEM micrograph of a large chlorite (Chl) inclusion in amphibole (Amph), with the chlorite layers nearly parallel to the amphibole (100) planes. A small inclusion of anorthite (An) is present as well as phyllosilicates (Phy) along the chlorite-anorthite boundary.

is a member of a group of minerals that comprise the biopyribole polysomatic series and consists of a sequence of alternating mica (M) and pyroxene (P) slabs parallel to the (010) planes (Thompson, 1978). Because the different biopyribole minerals consist of the same basic structural units, it is possible to combine these units to form new mineral structures.

Although chlorite is not part of the biopyribole polysomatic series, the talc-like layer of chlorite is a mica unit and can fit coherently with amphibole I-beams. This fit occurs parallel to the talc-like layers, with an orientation relationship such that the chlorite (001) planes are parallel to the amphibole (100) planes (Fig. 1a). Because the tetrahedral sheet of the talc-like layer has pseudotrigonal symmetry, the amphibole I-beams can be coherently aligned such that amphibole [001] is parallel to [100], $[\bar{1}10]$, or $[\bar{1}\bar{1}0]$ of chlorite. If the chlorite has random stacking of one-layer polytypes, these directions appear equivalent in selected-area electron-diffraction (SAED) patterns.

For the orientation relationship given above, a semi-coherent boundary along the (010) planes of the two structures is possible because of the coincidence of close-packed oxygen planes. The height of two chlorite layers ($2c \sin \beta = 2.84$ nm) approximates that of three amphibole I-beams ($3a \sin \beta = 2.86$ nm) (Fig. 1b). The close-packed planes of oxygen and hydroxyl ions parallel to chlorite (001) and amphibole (100) are nearly coincident, making local coherence possible along other boundary orientations.

SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUES

Thin sections were cut perpendicular to the foliation defined by the chlorite grains in order to maximize the possibility of viewing along chlorite layers. These sections were studied optically to investigate textural relationships and to choose suitable regions for TEM study. Areas were chosen that had amphibole grains with c axes nearly perpendicular to the plane of the thin section and with overgrowth textures on chlorite. Samples were ion-thinned with 5-kV Ar ions, and removal of amorphous material was done at 1 kV. Samples were carbon-coated to prevent charging in the electron beam.

Transmission electron microscopy was performed using a Philips EM 400T at an accelerating potential of 120 kV. Quali-

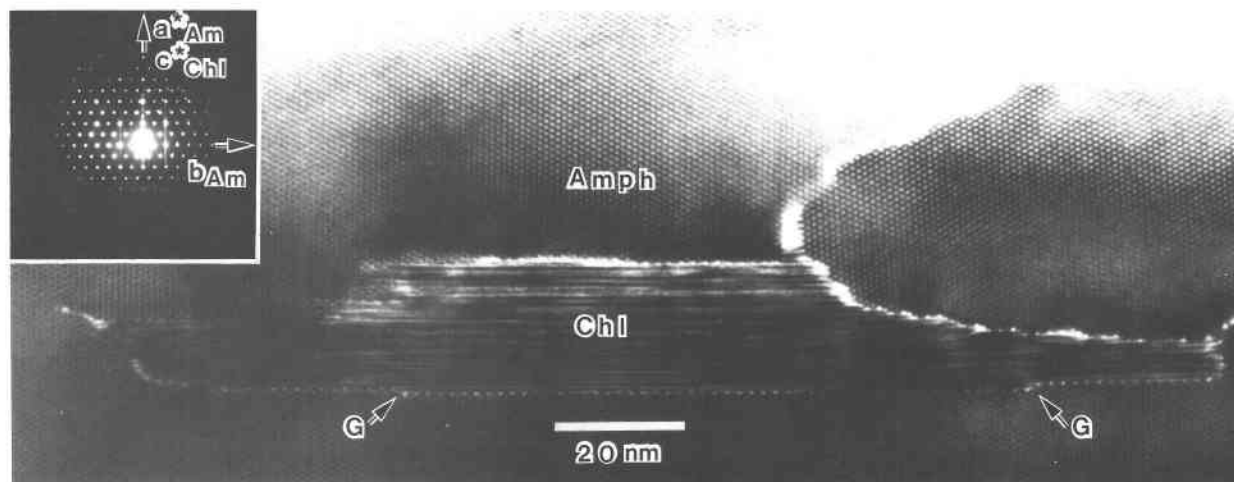


Fig. 3. TEM micrograph of a coherent chlorite inclusion in amphibole. The selected-area electron diffraction (SAED) pattern shows that chlorite c^* parallels amphibole a^* . The array of white spots along the coherent basal boundary represents tunnel structures. Growth ledges (G) occur along the basal boundary.

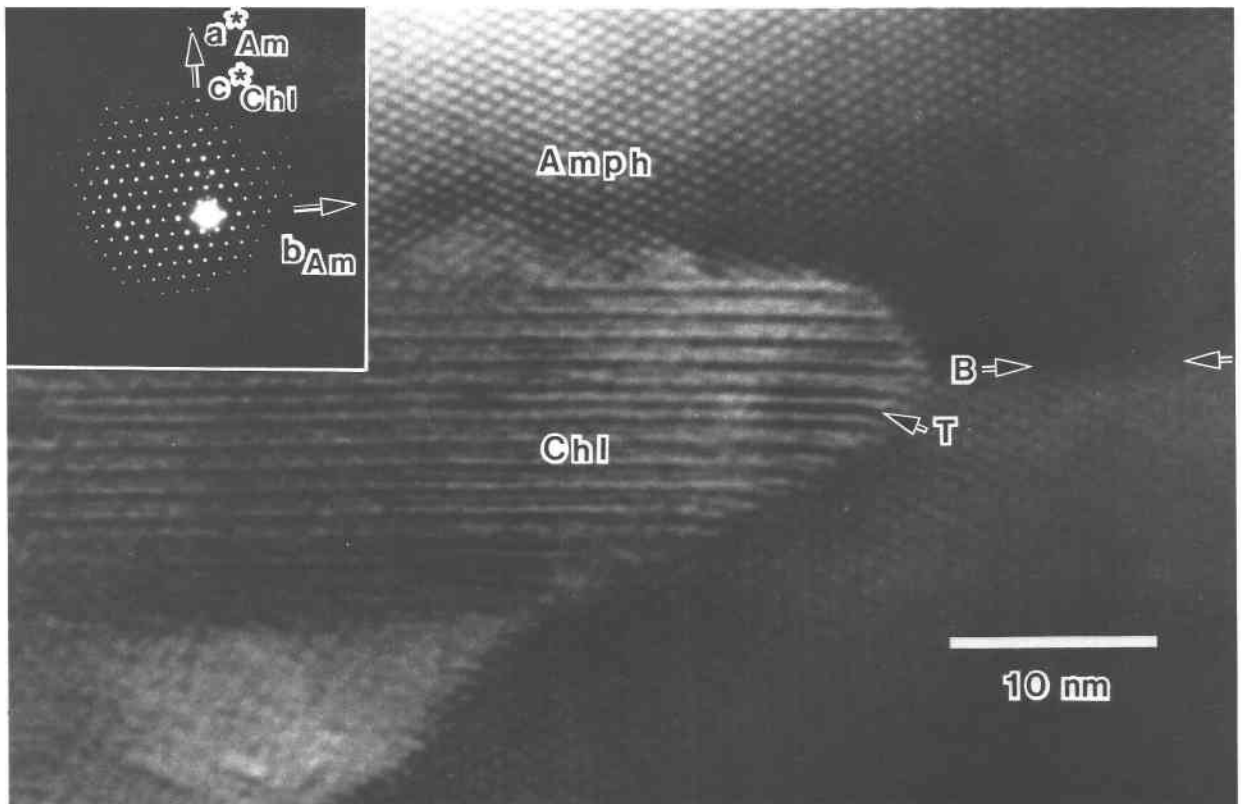


Fig. 4. TEM micrograph of a coherently intergrown chlorite (Chl) inclusion at a subgrain boundary (B) within amphibole (Amph). The SAED pattern shows that chlorite c^* is nearly parallel to amphibole a^* . Chlorite layers are slightly bent at the right-hand boundary to produce coherence. Two extra talc-like layers (T) are also present.

tative energy-dispersive X-ray spectroscopy (EDS) analyses were used for rapid identification of phases. Semiquantitative EDS analyses were produced using predetermined k factors on a PDP 11/24 computer with the FORTRAN program ANEDS, a modification of a program DANAX written at Arizona State University by P. G. Self. Images of amphibole and wide-chain defects within amphibole were interpreted in the same manner as those presented by Veblen and Buseck (1981), Whittaker et al. (1981), and Cressey et al. (1982). Images of chlorite were interpreted in terms of layer type and boundary relationships, following the work of Yau et al. (1984) and Veblen and Ferry (1983).

TEM OBSERVATIONS

Transmission electron microscopy was used to determine the structural and morphological relationships between chlorite and host amphibole. Three types of chlorite were found in the amphibole: (1) relatively large chlorite grains, several micrometers in length, that do not have strict orientation relationships or coherent boundaries with the host amphibole; (2) submicrometer chlorites that have coherent boundary relationships; (3) chlorites that are associated with fractures and that have various structural relationships to the amphibole. Additional alteration reactions produced wide-chain defects and other phyllosilicates.

Large incoherent chlorites

Chlorite that is observable with the petrographic microscope occurs in many amphibole grains, with (001) cleavage planes nearly parallel either to {110} or to (100) planes of amphibole. The angles between the chlorite [100] or [010] zone axes and the amphibole [001] zone axis were determined from TEM sample-stage tilts. The angles vary from 1.1 to 18.8° and average 5.0°, demonstrating that the chlorite (001) layers are subparallel to the amphibole c axis. However, the orientation of these layers relative to the amphibole (100) varies considerably. The incoherent relationship between amphibole and the large chlorites is inconsistent with topotaxy, but there is a subparallel mimetic relationship.

Boundaries between large chlorite grains and the host amphibole are commonly fractured (Fig. 2), but there is no indication that this chlorite results from alteration along fractures. Some of these fractured boundaries are filled with minerals such as quartz or very fine grained phyllosilicate (Fig. 2).

Because only the large chlorites are of sufficient size for EDS analysis, their compositions are compared to that of the chlorite that is not included in amphibole. The average composition of the large chlorite inclusions is $(\text{Mg}_{2.64}\text{Fe}_{2.01})$

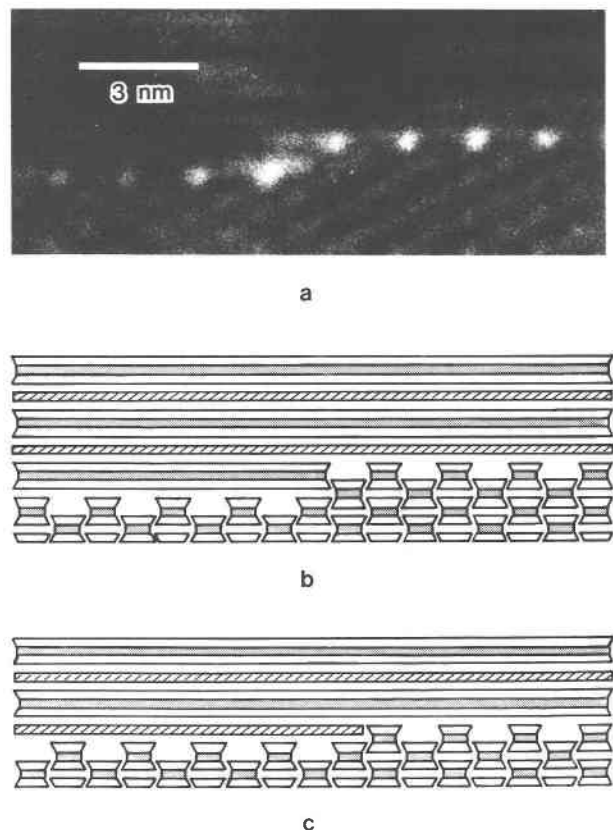


Fig. 5. High-magnification micrograph (a) of a growth ledge from Fig. 3 and schematic illustrations of (b) a talc-layer ledge and (c) a brucite-layer ledge. The spatial distribution of tunnels in (a) is consistent with that of the talc-layer ledge model of (b).

$\text{Al}_{1.10}\text{Ti}_{0.14}\text{Mn}_{0.03}\text{Al}_{1.35}\text{Si}_{2.65}\text{O}_{10}(\text{OH})_8$, as determined by semiquantitative EDS. The average composition of non-included chlorite in sample 18 is $(\text{Mg}_{2.73}\text{Fe}_{1.82}\text{Al}_{1.35}\text{Ti}_{0.01}\text{Mn}_{0.04})_{5.95}\text{Al}_{1.31}\text{Si}_{2.69}\text{O}_{10}(\text{OH})_8$, as determined by electron microprobe (Ferry, pers. comm. 1985).

Chlorite coherently intergrown with amphibole

Small chlorite grains that are unrelated to fractures in amphibole but are coherently intergrown with amphibole were observed only with TEM. These chlorites range in size from approximately 50 to 250 nm parallel to the basal layers and approximately 15 to 30 nm normal to the basal layers. They are much less common than either the large chlorite grains or fracture-filling material.

The orientation relationship between the coherent chlorite and the host amphibole is as described in the Mineral Structure section. The chlorite c^* and amphibole a^* axes are parallel (Figs. 3 and 4), showing that the chlorite (001) layers are parallel to the (100) planes of amphibole. Streaking parallel to c^* precludes distinguishing among the [100], $[\bar{1}10]$, or $[\bar{1}\bar{1}0]$ chlorite zone axes.

Boundaries parallel to chlorite (100) have clearly visible tunnel structures (Fig. 3) that indicate coherence

through the 10- to 20-nm thickness of the sample. The length of the coherent boundaries along chlorite (001) relative to lengths of other boundary orientations suggests that growth was most rapid parallel to the chlorite layers. Strained boundaries are indicated by preferential beam damage (Fig. 3). Boundaries that are not parallel to the chlorite (001) layers show considerable bending of the chlorite layers (Fig. 4).

Growth ledges occur along some chlorite (001) boundaries (Figs. 3 and 5). The talc-like layer model (Fig. 5b) is consistent with the pattern of tunnels in the micrographs, whereas the brucite-like layer model (Fig. 5c) is not. Single brucite-like layer ledges have not been observed.

Chlorite and other phyllosilicates in fractures

Chlorite and other phyllosilicates are common in narrow fractures cutting amphibole. Three types of fracture-filling materials occur: (1) chlorite that is coherently or semicoherently intergrown with amphibole, (2) variously oriented chlorite, and (3) other poorly crystalline phyllosilicates that also occur along fractured grain boundaries.

Fracture-filling chlorite that is semicoherently intergrown with amphibole (Fig. 6) occurs with approximately the same orientation relationship as the coherently intergrown chlorite described in the previous section. Curvature of chlorite layers results in deviations of up to 9.5° from the amphibole (100) planes. Tunnel structures and bent chlorite layers along boundaries (Fig. 6) indicate regions of significant coherency. Much of the fracture-filling material has a packet-like texture consisting of 10- to 50-nm-wide crystallites of chlorite, together with minor talc and mixed-layer material.

Chlorite in cleavage fractures is also oriented so that its (001) layers parallel the amphibole cleavage planes (Fig. 7). As with coherent and semicoherent intergrowths, chlorite [100] (or $\langle 110 \rangle$) directions are parallel to amphibole [001]. Defects and subgrain textures are abundant in such intergrowths.

Chlorite and other phyllosilicates are common in fractures along inclusion boundaries, indicating that the fracturing post-dates the formation of the inclusions. Fracture-filling material consists of variously oriented phyllosilicate packets and chrysotile-like material (Fig. 8). Because of the small size and the lack of any control on the orientation of the crystallites, the material is not easily identified. These intergrowths are the most disordered and loosely intergrown of the observed fracture-filling material.

Wide-chain defects

Wide-chain defects occur in the calcic amphibole and consist primarily of isolated triple chains, but wider-chain defects and groups of defects are also present. Although isolated triple chains could be growth defects, groups associated with fractures (Fig. 6) demonstrate that alteration has also occurred by a chain-widening mechanism. These

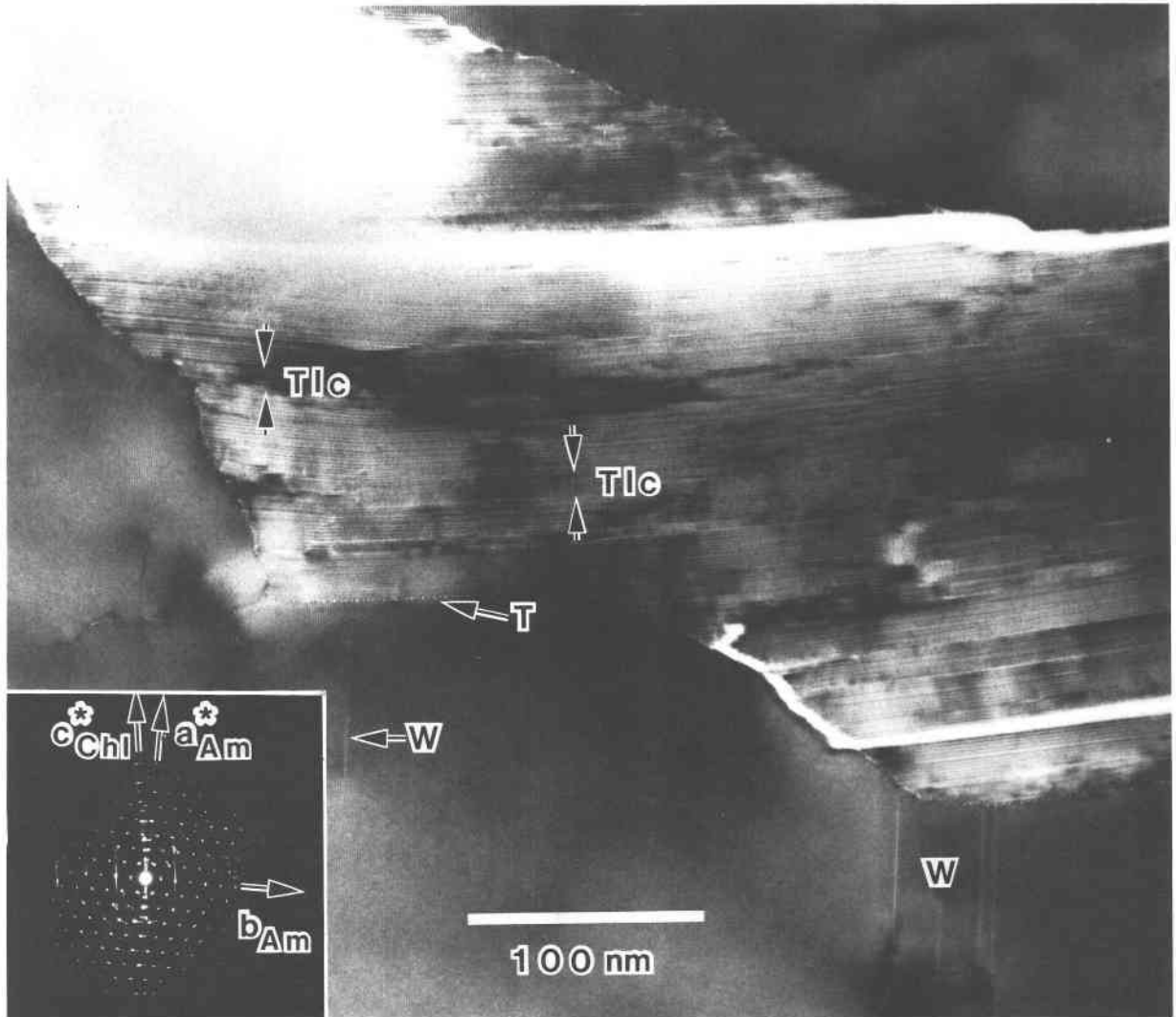


Fig. 6. TEM micrograph of chlorite and minor talc (Tlc) that is semicoherently intergrown with amphibole along a fracture. The SAED pattern shows that c^* of chlorite and talc are nearly parallel to amphibole a^* . Tunnels (T) are evident along some boundaries. Wide-chain defects (W) extend into the amphibole from the fracture walls.

defects do not have coherent terminations like those observed by Veblen and Buseck (1980), but groups commonly have cooperative terminations (Fig. 9) and appear to form a reaction front for chain-widening alteration.

DISCUSSION

Distinguishing prograde from retrograde intergrowths in thin sections is difficult if the features are very small. TEM can provide detailed information on intergrowth morphology, crystallinity, orientation, and boundary relationships that can be used to make the distinction. Most prograde and retrograde chlorite can be differentiated by morphology and by their structural relationships with amphibole. Because these relationships reflect reaction processes, they can also be used to interpret prograde and retrograde reaction mechanisms. The variety of retro-

grade products and textures reflects alteration under changing conditions through the cooling history.

Prograde microstructures

The large chlorites that do not fill fractures in amphibole are interpreted as remnants of prograde chlorite, consistent with Ferry's interpretation (1976a) of amphibole overgrowths on chlorite. The average chemical composition of the large incoherent chlorite is similar to that of nonincluded chlorite determined by Ferry (pers. comm.). This chemical similarity is consistent with, but not proof of, the prograde interpretation.

The orientations of the large incoherent chlorites are inconsistent with topotaxial amphibole growth. However, the near coincidence of the amphibole [001] zone axes and chlorite (001) layers indicates that the amphibole is oriented within the foliation defined by the chlo-

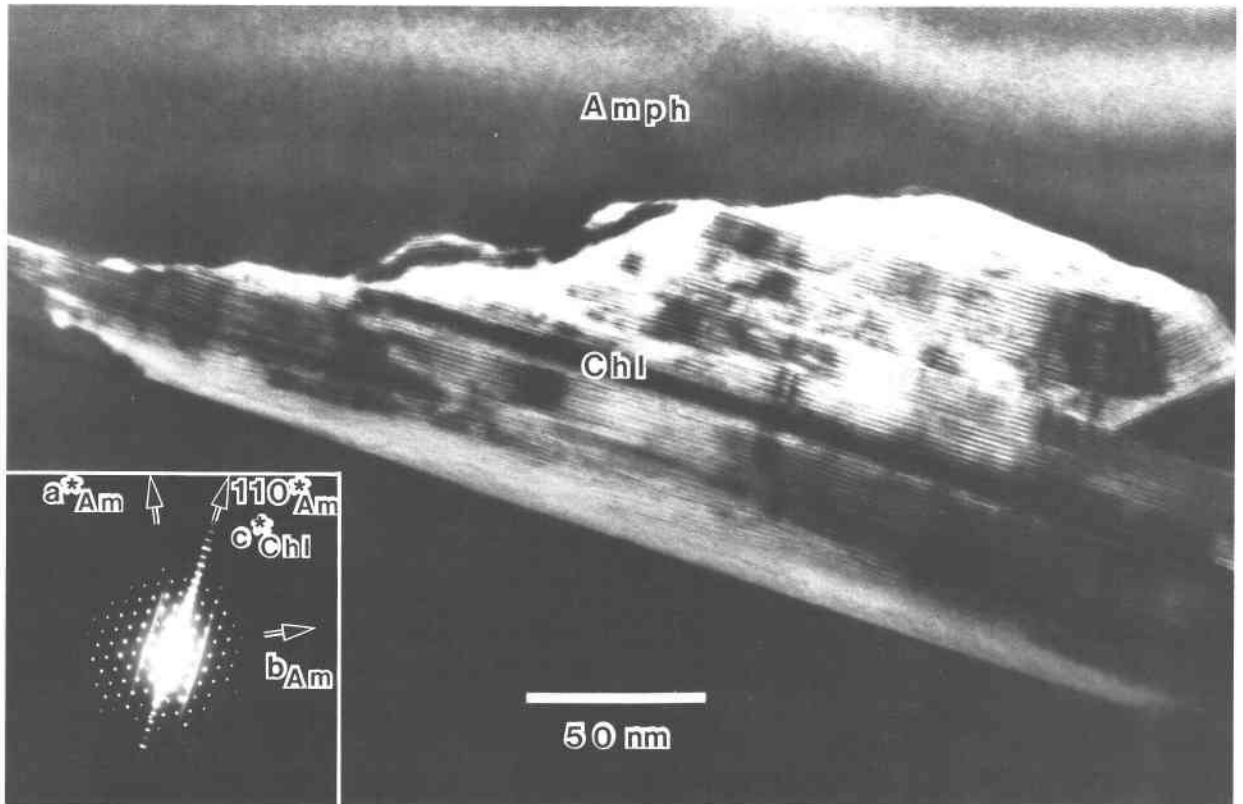


Fig. 7. TEM micrograph of chlorite along amphibole cleavage. The SAED pattern shows that most of the chlorite is oriented parallel to the amphibole (110) planes, but other orientations also occur.

rite grains. A possible origin of this orientation relationship is coherent nucleation of amphibole porphyroblasts on chlorite basal surfaces. The porphyroblastic texture of amphibole grains suggests that nucleation was rate-limiting. Coherent nucleation on only a fraction of the chlorite grains could have resulted in the apparent orientation relationship. Other subparallel chlorite grains that were not nucleation sites form the majority of included chlorite.

Retrograde microstructures

Fracture-filling chlorite in amphibole is interpreted as the result of retrograde alteration. Because chlorite was being consumed to form amphibole (Ferry, 1976a, 1983), it is unlikely that chlorite-filled fractures in amphibole formed during prograde metamorphism.

The small, coherent chlorites are interpreted as retrograde because of their association with subgrain boundaries and coherent relationship to amphibole. They appear to be the result of heterogeneous nucleation along subgrain boundaries. Growth of these chlorites occurs at ledges involving (001) layers along coherent (001) boundaries.

Alteration of amphibole also occurs by growth of wide-chain defects. Isolated wide-chain defects could be either

amphibole growth defects or alteration products (Veblen and Buseck, 1980). Groups of wide-chain defects represent an alteration mechanism where nucleation occurs on fracture walls or grain boundaries, with growth in the [100] and [001] directions. Groups of wide-chain defects in the present study are associated with semicoherent chlorite (Fig. 6), suggesting that they are the result of alteration under similar physical and chemical conditions.

The semicoherent chlorite in fractures appears to be the result of alteration at lower grade than the coherent chlorite. Like the coherent chlorite, the orientation of the semicoherent chlorite is controlled by amphibole and can be explained by coherent nucleation of chlorite on fracture walls and toptaxial replacement of amphibole. Mismatch of the fracture walls suggests significant replacement of amphibole. The texture of the semicoherent chlorite, and the presence of talc packets and mixed layers, is similar to disordered chlorite that formed at 165 °C (Ahn and Peacor, 1985); thus the semicoherent chlorite may have formed under similar conditions.

The majority of fracture-filling phyllosilicates are not coherently intergrown and possess many high-energy defects indicative of low-temperature conditions. Most consist of disordered chlorite that is accompanied by 10- and 7-Å-layer phyllosilicates. These intergrowths appear to

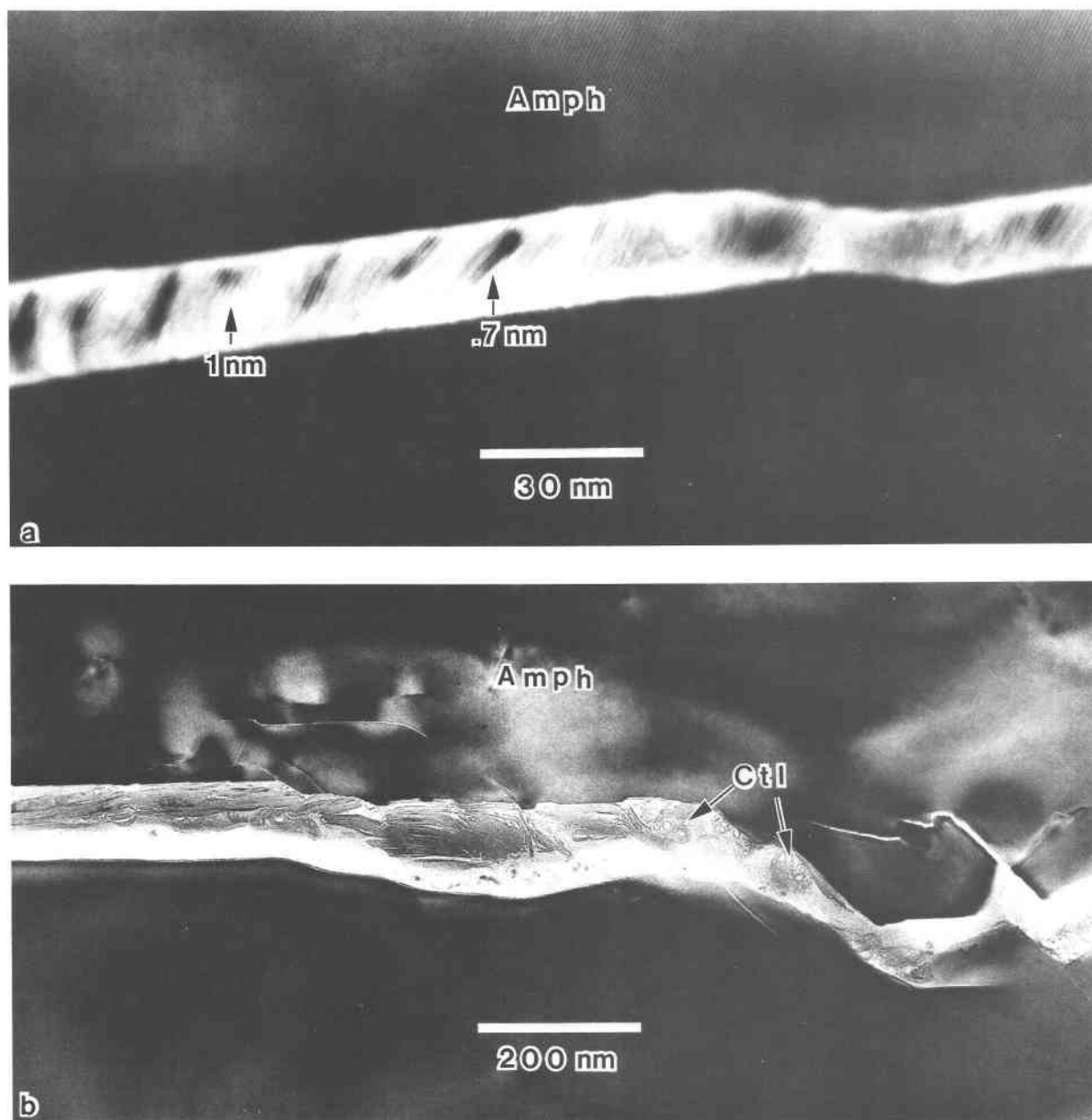


Fig. 8. TEM micrographs of poorly crystalline phyllosilicate in amphibole fractures. (a) Crystallites of 0.7- and 1.0-nm phyllosilicates fill an amphibole cleavage fracture, and (b) phyllosilicate packets and chrysotile-like (Ctl) material fill an amphibole fracture.

have grown from multiple nuclei by a variety of growth mechanisms. The most poorly crystalline phyllosilicate material represents the lowest-temperature alteration of these samples and is similar in texture to illite-smectite intergrowths in drill-core samples that formed at 70 °C (Ahn and Peacor, 1985).

On the basis of the above interpretation of alteration grades, slight retrograde alteration of amphibole appears to have occurred at various times in the cooling history. The relatively high grade alteration could be the result of metamorphism associated with late granitic plutons. Pro-

grade effects of the Alleghenian Sebago batholith extend as far as 30 km north (Lux and Guidotti, 1985; Holdaway et al., 1988) but are not recognized in the Waterville area (60 km to the northeast). Retrograde metamorphism to the west of the Waterville area (Novak and Holdaway, 1981), as well as the relatively high grade alteration features observed in the present study, could be distal retrograde effects of the Sebago batholith. The low-grade alteration appears to represent interaction with fluids late in the cooling history and probably resulted from interaction with near-surface waters.

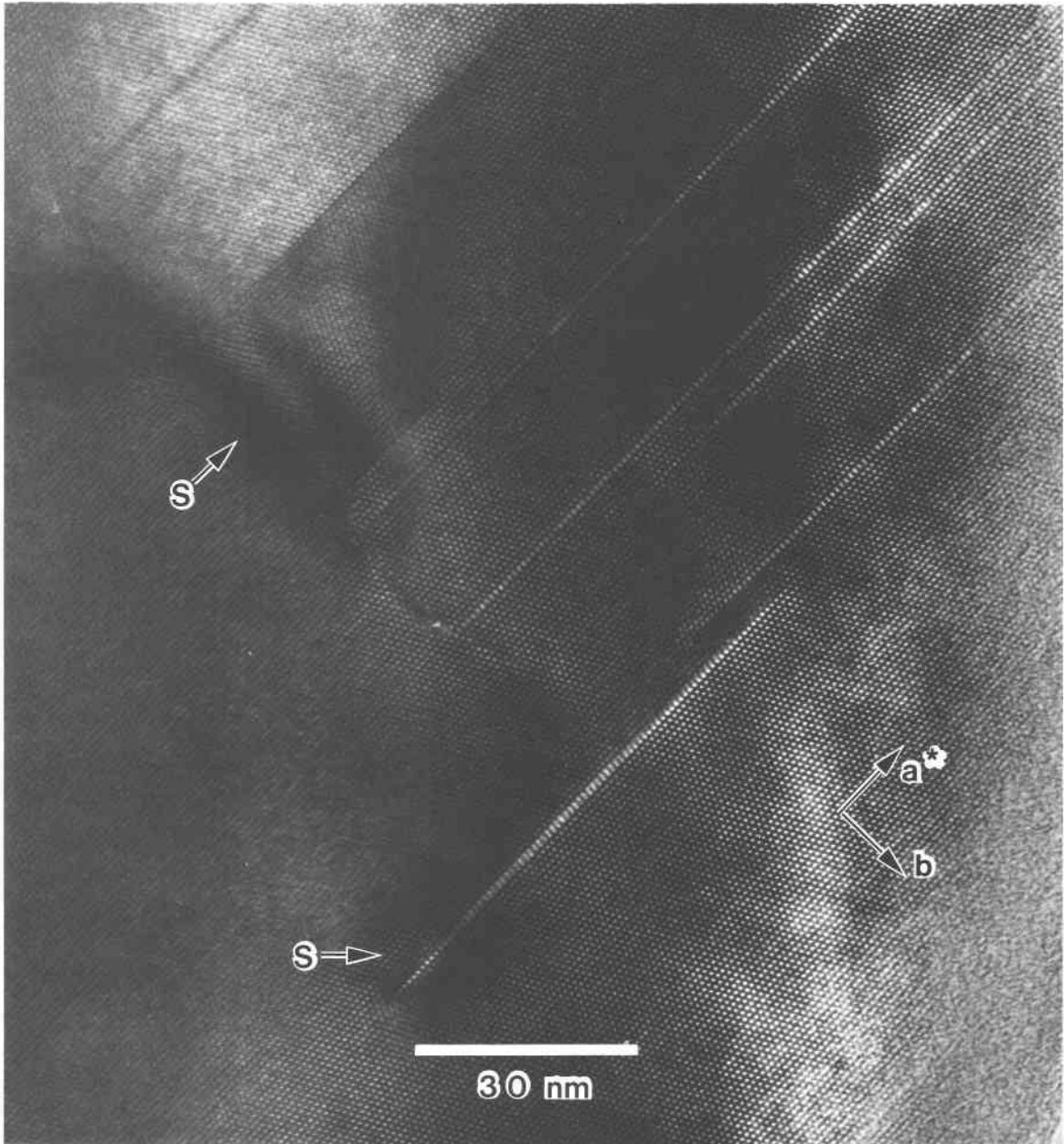


Fig. 9. TEM micrograph of chain-width defects terminating within amphibole. The terminations are cooperative but not coherent, resulting in strain fields (S) between terminations.

CONCLUSIONS

In metamorphic rocks, the mineral assemblages and textural relationships can be a result of prograde or retrograde processes. In favorable cases, fine-scale prograde and retrograde intergrowths, such as the chlorite-amphibole intergrowths in the present study, can be distinguished with TEM.

Relatively large chlorites included in amphibole are interpreted as remnants that were not consumed by the amphibole-forming reaction. Growth of amphibole over

chlorite grains was primarily reconstructive, involving incoherent or semicoherent boundaries. The [001] direction of amphibole is subparallel to (001) layers of chlorite, suggesting that amphibole grew in the foliation of the chlorite grains.

Retrograde chlorite and other phyllosilicates occur in submicrometer-sized intergrowths that are associated with fractures and subgrain boundaries. Coherent chlorites along subgrain boundaries are oriented such that chlorite (001) parallels amphibole (100) and chlorite [100], $[\bar{1}10]$, or $[\bar{1}\bar{1}0]$ parallels amphibole [001]. The fracture-filling

intergrowths range from well-crystallized and semicoherent intergrowths with amphibole to poorly crystallized and randomly oriented intergrowths. Wide-chain defects indicate another alteration mechanism. The variations in intergrowth textures suggest that alteration occurred at various times in the cooling history.

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