Almacık Complex—an exhumed lower to middle crust in northwest Anatolia

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Abstract: The Almacık Complex is a tectonic unit of high-grade metamorphic rocks in the Intra-Pontide Suture Zone in northwest Turkey. It consists mainly of amphibolite, metauamphibolite, and gneiss, which are intruded by numerous pre-, syn-, and post-tectonic felsic veins. The Almacık Complex is variously interpreted as a Cretaceous or Neoproterozoic ophiolite, or a Permian ultramafic-mafic complex representing the middle to lower crust of the Sakarya Zone. Herein, new petrological and geochronological data were presented from the Almacık Complex. Two-pyroxene geothermometry in the metawebsterites indicated that the Almacık Complex has undergone upper amphibolite-facies metamorphism at 750 ± 30 °C and 8 ± 4 kbar. U-Pb zircon and Ar-Ar ages from 11 samples indicate the presence of late Neoproterozoic, Permian, and Jurassic thermal events. Most of the Almacık Complex consists of late Neoproterozoic amphibolites and gneisses, representing the basement of the İstanbul Zone. This basement was intruded by voluminous mafic magma during the Late Permian. The basement and the Permian ultramafic-mafic rocks subsequently underwent upper amphibolite-facies metamorphism during the Jurassic, possibly at the base of a magmatic arc.

Key words: Almacık Complex, lower crust, metawebsterite, U-Pb zircon, Ar-Ar, geothermometry

1. Introduction
The Pontides, the orogenic belt north of the İzmir-Ankara Suture, consist of three tectonic terranes: the Strandja Massif, the Sakarya, and the İstanbul zones (Figure 1a). The tectonic boundary between the Istanbul and Sakarya zones is constituted by the İntra-Pontide Suture. The geological evolution and significance of the İntra-Pontide Suture are controversial. Şengör and Yılmaz (1981), who first introduced the term, regarded the suture as the trace of an İntra-Pontide ocean, which opened during the Early Jurassic and closed between the Paleocene and Middle Eocene. Yılmaz et al. (1995), based on their fieldwork in the Armutlu Peninsula and Almacık Mountains, followed this model. Especially, a metamorphic ultramafic-mafic series, which crops out in the İntra-Pontide Suture zone in the Armutlu Peninsula and Almacık region, was regarded by Yılmaz et al. (1995) as a Cretaceous ophiolite representing part of the İntra-Pontide oceanic crust and mantle. However, subsequent studies considered the metamorphic ultramafic-mafic series as Neoproterozoic in age based on tenuous correlation with the basement of the İstanbul Zone in the Bolu Massif (Yiğitbaş et al., 2004; Akbayram et al., 2013). Bozkurt et al. (2013a), on the basis of isotopic data, suggested that the metamorphic ultramafic-mafic series, named the Almacık Complex, was formed during the Permian. Recently Sunal et al. (2022) reported late Neoproterozoic U-Pb zircon ages from gneisses of the Almacık Complex. The age and significance of the Almacık Complex are important in understanding the evolution of the İntra-Pontide Suture. Herein, new geological, petrological, and geochronological data were provided on the Almacık Complex in northwest Turkey. The new data indicated that most of the Almacık Complex consists of late Neoproterozoic amphibolites and gneisses, which were intruded by mafic magma during the Permian. The whole complex underwent high amphibolite facies metamorphism during the Middle to Late Jurassic.

2. Geological setting
The Almacık Block is a lozenge-shaped mountainous region south of Düzce bounded by strands of the North Anatolian Fault in the north and south (Figure 1b). Geologically, it consists of several NNE-trending and steeply dipping (>70°) tectonic units, as shown in Figure 2 (Abdülselamoğlu 1959; Yılmaz et al., 1981, 1982, 1995; Yiğitbaş et al., 2004; Robertson and Ustaömer, 2004;
Figure 1. a) Tectonic map of Türkiye and the surrounding region showing the location of the Intra-Pontide Suture (modified from Okay and Tüysüz, 1999); and b) geological map of northwest Anatolia with the location of the Almacık Block (modified from Aksay et al., 2002; Türkecan and Yurtsever 2002).
Figure 2. Geological map and cross-section of the Almacık Block (based on Gedik and Aksay 2002; Pehlivan et al., 2002, and the mapping of the current study). For locations, see Figure 1b.
Bozkurt et al., 2013a). These are from west to east: a) A low-grade, greenschist-facies metamorphic sequence composed mainly of phyllite, metasandstone, and recrystallized limestone with minor metavolcanic rocks. The eastern boundary of this low-grade metamorphic sequence is marked by a tectonic slice of cataclastic, sheared, and variably serpentinized peridotite (Figure 2). East of the serpentinite slice, there is an one-km-thick tectonic sliver composed of metabasite, red and green siliceous slate, and phyllite, possibly representing a metamorphosed ophiolitic mélangé (Yılmaz et al., 1995). Akbayram et al. (2013) correlated this unit with the Sapanca Complex of the Armutlu Peninsula, which is a slightly metamorphic Cretaceous accretionary complex. It is in contact in the east with the Almacık Complex, consisting mainly of amphibolite, metultramafic rock, and gneiss. The Almacık Complex is in turn bounded in the east by another low-grade metamorphic sequence of slate, metasandstone, and metaconglomerate, which is correlated with the Paleozoic sequence of the İstanbul Zone (Abdüsselamoğlu, 1959; Yılmaz et al., 1982; Yiğitbaş et al., 2004). Abdüsselamoğlu (1959) described Devonian trilobites and brachiopods from this metasedimentary sequence. The Almacık Block is bounded in the south along the Mudurnu valley by the North Anatolian Fault. The Jurassic-Cretaceous sedimentary sequence south of the North Anatolian Fault is typical of the Sakarya Zone (Figure 2). Structurally, the Almacık Block is generally interpreted as a steeply east-dipping thrust stack (Yılmaz et al., 1981, 1982; Bozkurt et al., 2013a).

Most of the Almacık Block is covered by dense forests; outcrops are largely restricted to the road cuts; especially, the road between Dokurcun and Taşkesti cuts through the fabric of the Almacık Complex and provides good exposure. Dirt roads leading north from Taşkesti to the highlands (Yaylas) also provide good outcrops. Most studies on the Almacık Block, including the current research, have concentrated on these road sections.

3. Previous data and interpretations on the Almacık Complex

Abdüsselamoğlu (1959), who published the first detailed geological map of the Almacık Block, described the Almacık Complex as consisting of gneiss, diorite, amphibolite, and serpentinite. The NE-trending steep fabric of the Almacık Complex and two ultramafic belts are clearly shown in his geological map. Yılmaz et al. (1982, 1995) interpreted the Almacık Complex as an intact east-dipping Late Cretaceous ophiolite consisting of peridotite, gabbro, and metabasite; however, no data for the Late Cretaceous age were provided. Yiğitbaş et al. (2004) accepted the ordered ophiolite interpretation of Yılmaz et al. (1982, 1995) but suggested that the “ophiolite” was not Late Cretaceous but Neoproterozoic in age, and named it “Çele ophiolite”. Bozkurt et al. (2013) correctly stressed the high-grade metamorphic nature of the Almacık Complex and pointed out that it did not resemble an ordered ophiolite. They also provided the first isotopic data (zircon U-Pb and Rb-Sr biotite) from the Almacık Complex and on the basis of these data, interpreted the age of formation of the ultramafic-mafic complex as Permian and that of its high-grade metamorphism as Middle Jurassic. Bozkurt et al. (2013) suggested that the Almacık Complex represents the exhumed middle-lower crust of the Sakarya Zone. Recently Sunal et al. (2022) published late Neoproterozoic U-Pb zircon ages (555–560 Ma) from two gneiss samples from the eastern part of the Almacık Complex.

Previous U-Pb zircon work in the Almacık Complex, discussed above, indicated the presence of three sets of isotopic ages: late Neoproterozoic, Permian, and Jurassic (Bozkurt et al., 2013a; Sunal et al., 2022). The significance of these ages and their relation to the different rock types are not clear. The principal aim of the present study was to constrain the P-T conditions, the age of the formation, and metamorphism of the Almacık Complex. To this aim, geological and petrological data and U-Pb zircon and Ar-Ar ages from 10 samples from the Almacık Complex are provided herein.

4. Methods

The analytical methods used in this study comprised electron microprobe analysis, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), and Ar-Ar dating. Minerals were analyzed using the Camebax SX-50 electron microprobe ( Cameca, Gennevilliers Cedex, FR) at the Ruhr University Bochum, from polished sections prepared in İstanbul. The analytical conditions for the spot analyses were a 1–2-µm spot size; 15-kV accelerating voltage, 10-nA beam current, and wavelength-dispersive spectroscopy.

Zircon, hornblende, and biotite fractions from the rock samples were separated at Istanbul Technical University using standard mineral separation procedures. This included crushing whole rock samples into sand-sized grains, sieving, repeated rinsing, and cleaning of the samples in water and acetone, and passing the samples through a Frantz magnetic separator. For zircon separation, sodium polytungstate was used as a heavy liquid. The zircons were picked from the heavy residua under a stereographic microscope and mounted in epoxy, and then polished. They were analyzed using LA-ICP-MS at the University of California, Santa Barbara. For details about the method employed, see Kylander-Clark et al. (2013) and Okay et al. (2014). The long-term reproducibility in the secondary reference materials was <2% and, as such, this should be used when comparing ages obtained within this analytical session to ages elsewhere.
Hornblende and biotites were dated using the Ar-Ar single-grain fusion method at the Open University in the United Kingdom. For details about the method used, see Okay et al. (2014). The U-Pb and Ar-Ar analytical data, and the Universal Transverse Mercator (UTM) locations of the samples are given in Tables S1 and S2, respectively (https://data.mendeley.com/datasets/97y7fkjkxv/71).

5. The Almacık Complex
The Almacık Complex is a high-grade metamorphic unit composed principally of amphibolite, metaultramafic rock, and gneiss. Amphibolite is the dominant lithology, making up more than 80% of the Almacık Complex, followed by metaultramafic rock (15%) and gneiss (5%). Amphibolites and gneisses show a color banding defined by different concentrations of mafic and felsic minerals. All of these lithologies are cut by a large number of felsic veins showing various stages of deformation and metamorphism.

Three lithological units can be differentiated within the Almacık Complex: these are from west to east: 1) a 0.8-km-thick sequence of banded amphibolite, 2) a 2-km-thick section of metamorphosed ultramafic rock, and 3) an 8-km-thick series of banded amphibolite and gneiss (Figure 2). The dip of foliation is invariably steep throughout the Almacık Complex and generally trends N to NE. Although there are several cataclastic zones, possibly related to the North Anatolian Fault, there are no obvious post-metamorphic tectonic repetitions. Units two and three expose a 10-km-thick section ranging from metaultramafic rock in the west through amphibolite to an intercalation of amphibolite and gneiss in the east (Figures 2 and 3). Based on the presence of the metaultramafic rocks in the west, most studies consider that the Almacık Complex youngs eastward (e.g., Bozkurt et al., 2013a). The units of the Almacık Complex are briefly described below.

5.1. Western Banded Amphibolite Unit
This unit consists of homogenous, medium-grained, finely banded amphibolites. The banding is on a millimeter scale and is defined by different concentrations of hornblende and plagioclase (Figure 4a). Mineral assemblage in the amphibolites is hornblende + plagioclase + clinopyroxene + titanian (Figures 5a and 5b). The amphibolites are cut by undeformed andesite dykes and stocks, presumably of Eocene age.

5.2. Central Metalultramafite Unit
Two subunits can be differentiated within the metaultramafic rocks; in the west there are metadunites and metaharzburgites consisting mainly of olivine and orthopyroxene. The rocks show high degrees of serpentinization, ranging from 60% to 100%. There is also a thin band of amphibolite within the metaharzburgites (Figure 2). In the east, there are metawebsterites consisting of ortho and clinopyroxene with minor olivine and opaque.

In contrast to the metaperidotites, the metawebsterites are fresh with bright green diopside and brown orthopyroxene. They show a prominent subvertical banding defined by different concentrations of ortho and clinopyroxene (Figure 4b). All of the metaultramafic rock samples show a clear metamorphic fabric (Figures 5c and 5d).

5.3. Eastern Amphibolite-Gneiss Unit
Amphibolites constitute more than 80% of the Eastern Amphibolite-Gneiss Unit. They are commonly banded on a mm to cm scale with banding defined by the variable portions of hornblende and plagioclase. In rare cases, isoclinal fold hinges are preserved, indicating transposition of the banding (Figure 4c). In some places, coarse nebulous gabbroic stocks and veins are observed cutting through the fabric of the amphibolites (Figure 4d); these are interpreted as partial melts; in other localities these coarse gabbroic portions are deformed (Figure 4e). Such structures indicate late to post-tectonic partial melting. The mineral assemblage in the amphibolites is hornblende + plagioclase ± clinopyroxene ± biotite ± clinopyrozoisite/ epidote ± scapolite ± opaque. Geochemistry indicates a heterogeneous but broadly calc-alkaline composition for the amphibolites (Bozkurt et al., 2013a).

The eastern part of the Eastern Amphibolite-Gneiss Unit forms the structurally highest part of the Almacık Complex. Here, the amphibolites are interbanded with quartzo-feldspathic gneisses (Figures 3 and 4f), and locally, gneisses are more common than amphibolites; as an example, in the region west of the Derebalık Yaşla. Such gneisses have yielded late Neoproterozoic ages in the study of Sunal et al. (2022) and the present study (see later). The amphibolites are cut by a large number of felsic veins, which vary greatly in size and in the degree of deformation and metamorphism. A significant part of the new geochronological data in the current study come from such felsic veins.

6. Pressure-temperature conditions of metamorphism
The Almacık Complex has undergone an amphibolite-facies metamorphism (Bozkurt, 2013a). There is no obvious change in the metamorphic grade across the Almacık Complex. In order to constrain the temperatures of the metamorphism, the minerals in a metawebsterite were analyzed by electron microprobe. Sample 6948A consists of equal proportions of ortho- and clinopyroxene with minor phlogopite and opaque (Table 1). Orthopyroxene is enstatite-rich and has a uniform composition of \( \text{Mg}_{0.87} \text{Fe}_{0.13} \text{Ca}_{0.02} \text{Si}_{0.95} \text{Al}_{0.03} \text{O}_6 \) (Figure 6, Table 2). Clinopyroxene is diopside and has also a uniform composition of \( \text{Ca}_{0.95} \text{Na}_{0.03} \text{Mg}_{0.03} \text{Fe}_{0.06} \text{Si}_{1.95} \text{Al}_{0.04} \text{O}_6 \) (Figure 6, Table 2). The Fe-Mg partitioning between the coexisting ortho and clinopyroxene can be used as a geothermometer. For a pressure range of 5 to 10 kbars, the calibration of Brey
Figure 3. Schematic synthetic section of the Almacik Complex with the approximate locations of the new U-Pb zircon ages.
Figure 4. Field photographs from the Almacık Complex: a) banded amphibolites from the Western Amphibolite Unit. Hornblendes from this outcrop gave a Late Jurassic Ar-Ar age of ca. 158 Ma (see also Figure 5a); b. banded metawebsterites from the Central Metaperidotite Unit; c) banded and isoclinally folded amphibolites from the Eastern Amphibolite Unit; d) Pegmatitic gabbro cutting the foliation in the amphibolites in the Eastern Amphibolite Unit; e) deformed pegmatitic gabbro patches in the banded amphibolites in the Eastern Amphibolite Unit; and f) intercalation of the amphibolite and granitic gneisses from the eastern part of the Almacık Complex. For the locations of the photographs, see Figure 2.
Figure 5. Microphotographs from the Almacık Complex. The left panel shows the plane polarized and the right panel shows cross-polarized views. a-b) Amphibolite from the Western Amphibolite Unit. Hornblendes from this sample gave a Late Jurassic Ar-Ar age of ca. 158 Ma; c-d) metawebsterite consisting of ortho and clinopyroxene. Note the metamorphic texture; e-f) Quartzo-feldspathic vein composed of quartz, plagioclase, K-feldspar, and biotite. Zircons from this sample produced an Early Permian age of ca. 294 Ma (Figure 9b); g-h) metadioritic vein consisting of plagioclase, hornblende, clinozoisite, and garnet. Zircons from this sample yielded a U-Pb age ca. 163 Ma (Figure 10d). chl, chlorite; cpx, diopside; cz, clinozoisite; gt, garnet; hbl, hornblende; ks, K-feldspar; opx, orthopyroxene; pl, plagioclase; and qz, quartz.
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Table 1. Estimated modal amounts of the analyzed samples from the Almacık Complex

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Gneiss</th>
<th>Amphibolite</th>
<th>Quartzofeldspathic veins</th>
<th>Metawebsterite</th>
</tr>
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<tr>
<td>11622</td>
<td>11636</td>
<td>15913</td>
<td>11523 11538 11546 15912 15915</td>
<td>11544 11552 11609 11625 6948A</td>
</tr>
<tr>
<td>Garnet</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Biotite</td>
<td>2</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Muscovite</td>
<td>3</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>Plagioclase</td>
<td>32</td>
<td>38</td>
<td>38 33 56 38 64</td>
<td>78 56 37 38</td>
</tr>
<tr>
<td>K-feldspar</td>
<td>6</td>
<td>12</td>
<td>14</td>
<td>6</td>
</tr>
<tr>
<td>Quartz</td>
<td>71</td>
<td>44</td>
<td>36</td>
<td>13</td>
</tr>
<tr>
<td>Diopside</td>
<td>-</td>
<td>-</td>
<td>12</td>
<td>54</td>
</tr>
<tr>
<td>Enstatite</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>44</td>
</tr>
<tr>
<td>Hornblende</td>
<td>-</td>
<td>-</td>
<td>50 46 33 46 23</td>
<td>11 20</td>
</tr>
<tr>
<td>Opaque</td>
<td>-</td>
<td>-</td>
<td>3 2</td>
<td>2</td>
</tr>
<tr>
<td>Epidote</td>
<td>-</td>
<td>3</td>
<td>12</td>
<td>3</td>
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<tr>
<td>Chlorite</td>
<td>9</td>
<td>2</td>
<td>-</td>
<td>3</td>
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<tr>
<td>Apatite</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Scapolite</td>
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<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Phlogopite</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>tr, less than 0.5%</td>
<td></td>
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Table 3. Summary of the isotopic ages and the UTM coordinates of the dated samples.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Rock type</th>
<th>Location (UTM - European 1978 datum)</th>
<th>Method</th>
<th>Age (Ma)</th>
<th>Stratigraphic age</th>
<th>Figures and Tables</th>
</tr>
</thead>
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<tr>
<td>11552</td>
<td>Granitic vein</td>
<td>36 T 03 29 990 E - 44 95 810 N</td>
<td>Zircon U-Pb</td>
<td>46 ± 1</td>
<td>Middle Eocene</td>
<td>Figure 10f</td>
</tr>
<tr>
<td>15912</td>
<td>Amphibolite</td>
<td>36 T 03 27 278 E - 44 95 528 N</td>
<td>Zircon U-Pb</td>
<td>156 ± 2</td>
<td>Late Jurassic</td>
<td>Figure 11e</td>
</tr>
<tr>
<td>11546</td>
<td>Amphibolite</td>
<td>36 T 03 29 011 E - 44 96 560 N</td>
<td>Zircon U-Pb</td>
<td>158 ± 6</td>
<td>Late Jurassic</td>
<td>Table S1</td>
</tr>
<tr>
<td>11544</td>
<td>Metadioritic vein</td>
<td>36 T 03 29 137 E - 44 97 032 N</td>
<td>Zircon U-Pb</td>
<td>163 ± 2</td>
<td>Late Jurassic</td>
<td>Figure 10d</td>
</tr>
<tr>
<td>15915</td>
<td>Amphibolite</td>
<td>36 T 03 29 117 E - 44 96 256 N</td>
<td>Zircon U-Pb</td>
<td>254 ± 8</td>
<td>Late Permian</td>
<td>Figure 11b</td>
</tr>
<tr>
<td>11609</td>
<td>Granitic vein</td>
<td>36 T 03 29 109 E - 44 96 269 N</td>
<td>Zircon U-Pb</td>
<td>257 ± 4</td>
<td>Late Permian</td>
<td>Figure 9e</td>
</tr>
<tr>
<td>11625</td>
<td>Granitic vein</td>
<td>36 T 03 34 880 E - 44 99 700 N</td>
<td>Zircon U-Pb</td>
<td>294 ± 2</td>
<td>Early Permian</td>
<td>Figure 9b</td>
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<tr>
<td>15913</td>
<td>Granitic gneiss</td>
<td>36 T 03 28 579 E - 44 96 706 N</td>
<td>Zircon U-Pb</td>
<td>552 ± 11</td>
<td>Late Neoproterozoic</td>
<td>Figure 7b</td>
</tr>
<tr>
<td>11622</td>
<td>Granitic gneiss</td>
<td>36 T 03 35 225 E - 44 98 966 N</td>
<td>Zircon U-Pb</td>
<td>562 ± 4</td>
<td>Late Neoproterozoic</td>
<td>Figure 7d</td>
</tr>
<tr>
<td>11523</td>
<td>Amphibolite</td>
<td>37 T 03 23 409 E - 44 94 869 N</td>
<td>Hornblende Ar-Ar</td>
<td>158 ± 4</td>
<td>Late Jurassic</td>
<td>Table S2</td>
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<td>11625</td>
<td>Granitic vein</td>
<td>36 T 03 34 880 E - 44 99 700 N</td>
<td>Biotite Ar-Ar</td>
<td>210 ± 10</td>
<td>Late Triassic</td>
<td>Table S2</td>
</tr>
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</table>

and Köhler (1990) indicated a temperature between 748 and 756 °C for the peak metamorphism in the Almacık Complex. A second geothermometer involved the partitioning of Na between ortho and clinopyroxene, for which the calibration of Brey and Köhler (1990) indicated temperatures between 782 and 791 °C for the same pressure range. The Na contents of the orthopyroxenes in the metawebsterite were quite low (<0.03 wt% Na₂O), so the results of the Fe-Mg geothermometer were regarded as more reliable.

Metamorphic pressures are more difficult to constrain in the Almacık Complex. Garnet does not occur in the metaultramafic rocks and is rare in the gneisses, which suggests that the pressures were less than about 12 kbar.
A reasonable estimate for the peak P-T conditions in the Almacık Complex is 750 ± 30 °C and 8 ± 4 kbar.

7. Geochronological data from the Almacık Complex
Herein, U-Pb zircon age data from nine samples from the Almacık Complex were reported. The ages are summarized in Table 3, and the analytical data are provided in Table S1 (https://data.mendeley.com/datasets/97y7f7kvk7/1). The zircon U-Pb ages from the Almacık Complex are presented below in three categories: 1) Late Neoproterozoic ages from the gneisses, 2) ages from the felsic veins, and 3) Permian and Jurassic ages from the amphibolites.

7.1. Late Neoproterozoic U-Pb zircon ages from the gneisses
Sunal et al. (2022) reported two late Neoproterozoic zircon ages (560 ± 1 Ma and 557 ± 2 Ma) from the eastern part of the Almacık Complex. As discussed below, two of the samples in the current study also gave similar late Neoproterozoic ages. These ages came exclusively from quartz-feldspathic gneisses interbanded with the amphibolites.

7.1.1. Sample 15913: Quartz-feldspathic gneiss – late Neoproterozoic 552 Ma
The outcrop from which this sample was taken consists of amphibolite and gneiss; it is located in the western part of the Eastern Amphibolite-Gneiss Unit. As discussed below, two of the samples in the current study also gave similar late Neoproterozoic ages. These ages came exclusively from quartz-feldspathic gneisses interbanded with the amphibolites.

7.1.2. Sample 11622: Quartz-feldspathic gneiss – late Neoproterozoic 562 Ma
This sample came from the eastern part of the Eastern Amphibolite-Gneiss Unit, south of the Pürenli Yaya, where the samples of Sunal et al. (2022) were also located. The outcrop consists mostly of quartz-feldspathic gneisses with amphibolite bands; the gneisses and the amphibolites share the same foliation/banding and show no crosscutting relation. The mineral assemblage in the sample is quartz + plagioclase + biotite + opaque (Table 1). In the cathodoluminescence (CL) images, the zircons are subhedral and show magmatic zoning; they had thin homogeneous rims of metamorphic origin (Figure 7b). Th/U ratios in zircon have been widely used to differentiate metamorphic and magmatic zircons. Recent work has indicated that the distinction is not clear cut, and zircons with Th/U ratios of more than 0.1 can be igneous or metamorphic, whereas zircons with Th/U ratios of less than 0.1 are more likely to be metamorphic (Yakymchuk et al. 2018). Th/U ratios of the zircon cores from sample 15913 are between 0.56 and 1.28 (Figure 8). Seventeen zircons gave a U-Pb concordia age of 552 ± 11 Ma (Figure 7c).

7.2. U-Pb zircon ages from felsic veins
The amphibolites of the Almacık Complex are cut by a large number of quartz-feldspathic veins, which vary greatly
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Table 2. Representative mineral compositions from the metawebsterite sample 6948A.

<table>
<thead>
<tr>
<th></th>
<th>diop</th>
<th>diop</th>
<th>diop</th>
<th>ens</th>
<th>ens</th>
<th>ens</th>
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diop, diopside; ens, enstatite; phlog, phlogopite.

in size and in the degree of deformation. The thickness of the veins ranges from a few centimeters to several tens of meters, and they range from foliated metamorphosed veins to undeformed granitic veins.

7.2.1. Quartzo-feldspathic vein – Early Permian 294 Ma
Sample 11625 was collected on the road between Taşkesti and Pürenli Yalya (Figure 2). It came from a 6-cm-wide banded quartzo-feldspathic vein in the amphibolites (Figure 9a). The foliation in the vein is subparallel to that in the amphibolites, which suggests a late tectonic vein. The mineral assemblage in the sample is plagioclase + quartz + K-feldspar + biotite (Table 1). In the CL images, the zircons are elongated and show a distinct magmatic zoning with no metamorphic rims (Figure 9b). Twenty-three zircons gave a robust Early Permian concordia age of 293.8 ± 2.0 Ma (Figure 9c).

7.2.2. Late tectonic granitic vein – Late Permian 257 Ma
Sample 11609 came from a 40-cm-wide, coarsely grained pegmatitic granitic vein, which crosscut the amphibolites (Figure 9d). The vein was late tectonic and showed a weak banding. The mineral assemblage in the sample is quartz + plagioclase + K-feldspar + muscovite (Table 1). In the CL images, the zircons are mostly euhedral and show igneous zoning (Figure 9e). Th/U ratios of the zircons are less than 0.12 (Figure 8), which is common among metamorphic zircons, although some igneous zircons also exhibit such low Th/U values (e.g., Yakymchuck et al., 2018). Sixteen zircons produced a Late Permian concordia age of 256.7 ± 3.7 Ma (Figure 9f).

7.2.3. Metadioritic vein – Late Jurassic 163 Ma
Sample 11544 was collected from a 15-m-wide metadioritic vein within banded amphibolites. The dioritic vein cuts
Figure 7. Neoproterozoic gneisses and their zircons from the Almacık Complex: a) banded gneiss and amphibolite with the location of sample 15913, b) CL images of the dated zircons, c) U-Pb zircon concordia diagram of gneiss sample 15913, d) CL images of the analyzed zircons from Neoproterozoic gneiss sample 11622, and e) its concordia age diagram.
the amphibolites but also showed fine-scale banding and isoclinal folding (Figure 10a, b). The mineral assemblage in the sample is plagioclase + hornblende + garnet + biotite + muscovite + scapolite with late epidote and chlorite (Figure 5g and 5h, Table 1). The rock has a metamorphic granular texture, and the garnet is of metamorphic origin. In the CL images, the zircons show magmatic-type zoning (Figure 10c) and the Th/U ratios of the zircons range from 0.22 to 0.34 (Figure 8). Eight concordant zircons gave a Late Jurassic concordia age of 162.6 ± 1.6 Ma (Figure 10d). Bozkurt et al. (2013a) also dated this prominent vein (sample 60-I), which they interpreted as a plagiogranite vein related to Permian magmatism, which subsequently underwent Jurassic metamorphism. This view was based on the LA-ICP-MS analysis of the zircons from the vein, which produced concordia ages of 255.0 ± 1.3 Ma and 167.1 ± 2.1 Ma, for the cores and rims of the zircons, respectively (Bozkurt et al., 2013a). We suggest that the metadioritic vein was produced by the partial melting of the amphibolites during the Late Jurassic, and hence, Permian zircon cores represent xenocrysts from the amphibolites.

7.2.4. Granitic vein – Middle Eocene 45 Ma
Sample 11552 was taken from a 7-m-thick granitic vein in the amphibolites (Figure 10e). In contrast to the other samples, the vein does not show any banding or deformation, and is clearly posttectonic. The mineral assemblage in the sample is plagioclase + hornblende + quartz + K-feldspar with late chlorite and epidote (Table 1). Th/U ratios of the zircons range from 0.5 to 1.0. Twenty-four zircons yielded a well-defined Middle Eocene (Lutetian) concordia age of 45.8 ± 0.4 Ma (Figure 10f).

7.3. U-Pb zircon ages from the amphibolites
7.3.1. Amphibolite – Late Permian 254 Ma
Sample 15915 was collected from an outcrop of finely banded amphibolite. The banding is on a scale of 1–5 mm and is defined by different concentrations of hornblende and plagioclase (Figure 11a). The sample was preferentially taken from the plagioclase-rich bands; the mineral assemblage in the sample is plagioclase + hornblende + biotite + quartz + opaque (Table 1). In the CL images, the zircons have magmatic cores and homogeneous metamorphic rims (Figure 11b). Th/U ratios of the zircons have a narrow range of 0.33 to 0.39 (Figure 8). Eight zircons gave a Late Permian lower intercept age of 253.8 ± 7.6 Ma (Figure 11c).

7.3.2. Amphibolite – Late Jurassic 158 Ma
Sample 11546 was collected from banded plagioclase-rich amphibolites. The mineral assemblage in the sample is
Figure 9. Felsic veins in the amphibolites of the Almacık Complex: a) banded, foliated quartzo-feldspathic vein (sample 11625) in the amphibolites, b) CL images of the analyzed zircons, c) U-Pb zircon concordia diagram, d) Late tectonic Late Permian granitic vein (sample 11609) cutting the amphibolites, e) CL images of the analyzed zircons, and f) its concordia U-Pb zircon age diagram.
Figure 10. Felsic veins in the amphibolites of the Almacık Complex: a) banded, foliated metadioritic vein (sample 11544) in the amphibolites, b) details of the foliation and folding in the metadiorite, c) CL images of the analyzed zircons, d) U-Pb zircon concordia diagram, and e-f) Eocene granitic vein cutting the amphibolites and the U-Pb zircon concordia diagram of the dated zircons (sample 11552).
plagioclase + hornblende + muscovite + quartz + opaque (Table 1). The sample yielded only one concordant zircon age, which was Late Jurassic (158 ± 6 Ma, Table S1).

7.3.3. Amphibolite – Late Jurassic 156 Ma
Sample 15912 was taken from banded amphibolites close to their contact with the metaperidotite body (Figures 2 and 11d). The mineral assemblage in the sample is plagioclase + hornblende + diopside + scapolite (Table 1). In the CL images, the zircons are homogeneous, suggesting a metamorphic origin (Figure 11e). Th/U ratios of the zircons have a narrow range of 0.11 to 0.16 (Figure 8). Eight zircons yielded a Late Jurassic (Kimmeridgian) U-Pb age of 155.5 ± 2.1 Ma (Figure 11f).
7.4. Ar-Ar and Rb-Sr ages

Considering the high temperatures of metamorphism in the Almacık Complex, the Ar-Ar and Rb-Sr ages from the Almacık Complex represent cooling ages. Previously Akyayram et al. (2013) reported an Early Cretaceous Rb-Sr biotite age of ca. 127 Ma from a garnet-micaschist from the Eastern Amphibolite-Gneiss Unit (Figure 2). A similar Early Cretaceous Rb-Sr biotite age of 139 ± 2 Ma was obtained by Bozkurt et al. (2013a) from the metadioritic vein (Figure 10a), which, in the current study, yielded a U-Pb zircon age of 162 ± 3 Ma (sample 11544, see above). In the present study, Ar-Ar ages were obtained from two samples from the Almacık Complex, as described below. The analytical data for the Ar-Ar ages are provided in Table S2 (https://data.mendeley.com/datasets/97y7f7kvk7/1).

7.4.1. Amphibolite – Late Jurassic 158 Ma

Sample 11523 is an amphibolite from the Western Amphibolite Unit (Figure 2). The mineral assemblage in the sample is hornblende + plagioclase + epidote (Table 1). The sample shows no alterations, and the hornblende grains are fresh (Figure 5a). Twelve hornblende grains yielded a coherent Late Jurassic Ar-Ar age of 157.7 ± 4.2 Ma (Figure 12a).

7.4.2. Quartzo-feldspathic vein – Late Triassic 210 Ma

Sample 11625 came from a felsic vein in the amphibolites. Zircons from the sample yielded a robust Early Permian U-Pb age of 294 ± 2 Ma (see above and Figure 9b). The mineral assemblage in the sample is plagioclase + quartz + K-feldspar + biotite (Table 1). The sample shows no alterations and the biotites are fresh (Figure 5e). Twelve biotite grains from the sample gave a Late Triassic (Norian) age of 210.0 ± 9.5 Ma (Figure 12b).

The Ar-Ar and Rb-Sr ages reinforce the complex thermal history of the Almacık Complex. The ages range from Late Triassic to Early Cretaceous. Especially the Late Triassic biotite Ar-Ar age is difficult to interpret.

Figure 12. Ar-Ar age data from the Almacık Complex. For the analytical data, see Table S2.
considering that zircons from several amphibolites have yielded Jurassic ages. We suggest that this is likely due to argon build-up in the biotites that would ordinarily escape to the grain boundary network by diffusion, but was unable to do so due to quartz shielding (e.g., Kelley, 2002). The parentless argon component possibly remained in the biotites to varying degrees, resulting in ages that were artificially elevated.

7.5. Exhumation of the Almacık Complex
In the eastern part of the Almacık Complex, south of Pürenli Yayla, the amphibolites and gneisses are unconformably overlain by Upper Cretaceous (late Campanian-
Maastrichtian) shallow marine limestones of the Akveren Formation (Figure 2, Pehlivan et al., 2002), which provide an upper age for the exhumation of the Almacık Complex. Sunal et al. (2022) reported a zircon (U-Th)/He age of 81.8 ± 1.4 Ma from a late Neoproterozoic gneiss from the Almacık Complex. This age is compatible with the Upper Cretaceous sedimentary cover of the Almacık Complex, considering that the ZrHe thermochronometer has a closure temperature of 140–190 °C. The apatite fission-track ages from the Almacık Complex are, on the other hand, Oligo-Miocene (Cavazza et al., 2012; Sunal et al., 2019), and indicate reburial of the Almacık Complex after its initial exhumation in the Late Cretaceous.

8. Discussion

Previous and new geochronological data illustrate the complex and multiphased thermal history of the Almacık Complex. Such complex thermal histories are common in lower to middle crustal rocks, which have resided at high temperatures for long periods (>10 my; e.g., Real et al., 2023). The presence of a late Neoproterozoic basement in the Almacık Complex is clearly indicated by U-Pb zircon ages between 562 and 552 Ma from the quartzofeldspathic gneisses reported herein and those by Sunal et al. (2022). The late Neoproterozoic zircons show igneous zoning and are interpreted as reflecting the ages of the igneous protolith. Similar ages were reported from the basement of the İstanbul Zone in the Bolu Massif, in the Karadere area and in the Armutlu Peninsula (Chen et al., 2002; Ustaömer et al., 2005; Okay et al., 2008; Akbayram et al., 2013). Especially important are the late Neoproterozoic (565–576 Ma) granites intruding into the low-grade metavolcanic rocks in the Bolu Massif (Figures 1 and 13a) (Ustaömer et al., 2005; Bozkurt et al., 2013b).

There are conflicting data regarding the age of the amphibolites. A felsic vein cutting the amphibolites yielded a robust crystallization age of 294 ± 2 Ma (Figure 7a–7c), indicating that at least some of the amphibolites are Early Permian or older. Sunal et al. (2022) also stated that one of the late Neoproterozoic granitic gneisses from the Almacık Complex dated to 560 ± 1 Ma has intrusive contacts with the surrounding amphibolites. In the Armutlu Peninsula, amphibolites are cut by Neoproterozoic granitic veins with U-Pb ages of 569 ± 1 Ma (Okay et al., 2008). All of these data suggest a Neoproterozoic age for the amphibolites. However, zircons from one amphibolite sample yielded an apparently igneous age of 254 ± 8 Ma (Figure 11a–11c). Bozkurt et al. (2013a) also interpreted the age of crystallization of the amphibolites as Permian. In the southern part of the Bolu Massif, east of the Almacık Block, there is belt composed predominantly of amphibolites, called the Çele Mafic Complex (Figure 1) (Yiğitbaş et al., 2004; Bozkurt et al., 2013b). The zircon U-Pb ages from the amphibolites of the Çele Mafic Complex are predominantly Late Permian (ca. 258 Ma) and the Rb-Sr biotite ages are Late Jurassic (162–154 Ma), similar to those reported herein from the Almacık Complex (Bozkurt et al., 2013b). The conflicting amphibolite ages in the Almacık Complex can be explained by invoking two pulses of mafic magmatism, the first in the Late Neoproterozoic and the second in the Late Permian. There are data for Permian magmatism (262–255 Ma) in the İstanbul Zone in intrusive granites and volcanic rocks (Figures 1b and 13b) (Okay et al., 2013; Aysal et al., 2018; Babaoğlu et al., 2023). The two pulses of mafic magmatism, the presence of quartzofeldspathic gneisses, and the 8-km-thick monotonous amphibolite section indicate that the Almacık Complex does not represent an ordered ophiolite, as suggested by Yilmaz et al. (1982) and Yiğitbaş et al. (2004).

The high-temperature metamorphism in the Almacık Complex is probably Late Jurassic (ca. 160 Ma) in age. This was indicated by 1) the apparent Jurassic metamorphic zircon U-Pb ages (156 ± 2) from the amphibolites (Figure 11e), 2) the metamorphic nature of the Permian granitic veins (Figure 9a), and 3) the metamorphosed Jurassic (163 ± 2 Ma) dioritic veins with xenocrystic Permian zircons (Figure 10a–10d). A Late Jurassic metamorphic age is also supported by the Ar-Ar hornblende age of 158 ± 4 Ma from an amphibolite sample (11523, Figure 11a). The Late Triassic biotite Ar-Ar age (210 ± 10 Ma) from the metagranitic vein (sample 11625) could be explained as an artefact of an excess component of argon.

The late Neoproterozoic basement of the İstanbul Zone consists of granites, low-grade metavolcanic rocks, and amphibolites (Figure 13a). In the Almacık Complex, this basement was intruded by mafic magmas during the Permian (Figure 13b). Subsequently, the mafic intrusions along with the continental basement underwent high-grade metamorphism and deformation during the Late Jurassic (Figure 13c). This interpretation is similar to that proposed by Bozkurt et al. (2013a), except that they attributed the Almacık Complex to the Sakarya Zone. However, the presence of a late Neoproterozoic granitic basement, absence of Carboniferous metamorphism, and presence of Permian magmatism are features observed only in the İstanbul Zone.

The Middle to Late Jurassic was a period of intense magmatism in the Pontides related to the development of a magmatic arc (e.g., Okay and Nikishin, 2015). The metamorphism of the Almacık Complex probably took place at the base of the magmatic arc. A similar high-grade Jurassic metamorphic basement formed below a Jurassic arc was described from the Central Pontides (Okay et al., 2014; Gücer et al., 2019). The P-T conditions in this Gme Complex, 4 ± 1 kbar and 720 ± 40 °C, and the age of metamorphism, 172–162 Ma, are similar to those in
the Almacık Complex. It is important to note that the Jurassic metamorphism in the İstanbul Zone is apparently only observed in the Almacık Complex, which lies within the Intra-Pontide suture zone; the Neoproterozoic and Paleozoic units north of the Intra-Pontide suture zone are free of Jurassic deformation and metamorphism.

9. Conclusions
The Almacık Complex is a tectonic unit in the Intra-Pontide Suture zone composed of amphibolite, metaultramafic rock, and minor gneiss cut by a large number of felsic veins in various stages of deformation and metamorphism.

New petrological data indicate that the Almacık Complex underwent a high amphibolite facies metamorphism at 750 ± 30 °C and 8 ± 4 kbar.

New and published isotopic data indicate a complex and multiphase thermal history for the Almacık Complex. A significant part of the Almacık Complex consists of late Neoproterozoic amphibolites and gneisses. This old basement was intruded by mafic magma during the Late Permian. During the Late Jurassic, the Neoproterozoic basement and the Permian mafic intrusions underwent high temperature metamorphism.

The Almacık Complex is not a Cretaceous ophiolite related to the so-called Intra-Pontide ocean, as suggested by Yılmaz et al. (1982, 1995). It represents the modified basement of the İstanbul Zone.

Acknowledgments
We thank Sinan Yılmazer, Ezgi Sağlam, and Turgut Duzman for their help in the mineral separation, Ezgi Sağlam for her help with the data analysis, and the late Alvis Lisenbee and Gültekin Topuz for their discussions. This study was supported by The Scientific and Technological Research Institution of Turkey (TÜBİTAK) project 116Y127 and by the Turkish Academy of Sciences (TÜBA). We thank Alastair Robertson and Erding Yiğitbaş for their useful and constructive comments, which improved the manuscript.

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Supplementary Tables
Tables S1 and S2 cited in the manuscript can be accessed using the following link: https://data.mendeley.com/datasets/97y7f7kvk7/1