Mafic Volcanic and Subvolcanic Rocks from the Yüksekova Complex in the İçme-Kesikköprü Province (East of Elazığ, Eastern Turkey): Whole-Rock Geochemistry and Confocal Raman Spectroscopy Characterization

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Abstract. The Late Cretaceous Yüksekova Complex within the southeastern Anatolia orogenic belt consists of mafic volcanic and subvolcanic rocks representing oceanic crustal products, which are the main focus of this study. The studied mafic lithologies from the İçme-Kesikköprü province east of Elazığ are characterized by a primary mineral assemblage of olivine, pyroxene, and plagioclase, and mainly display porphyric, intergranular, intersertal, vesicular, and amygdaloidal textures. Based on Raman peak positions, the pyroxenes of these mafic lithologies from Aşağı İçme, Pirimezartepe and Yolüstü were determined as augite. The studied mafic rocks are chemically classified as basalt and display tholeiitic-calc-alkaline transitional characteristics. In spider diagrams, they show prominent negative Nb anomalies, while their chondrite-normalized rare earth element patterns are LREE-depleted to almost horizontal [(La/Sm)N: 0.54-1.42, (La/Lu)N: 0.54-1.85]. The immobile trace element systematics suggests that these mafic volcanic and subvolcanic rocks have originated from a metasomatized mantle source fluxed by slab-derived fluids/melts. Overall geochemical features are consistent with their generation in an oceanic arc environment.

1. Introduction
This study was carried out in the İçme-Kesikköprü province, nearly 35 km east of Elazığ (Figure 1). The mafic volcanic and subvolcanic rocks characterizing the oceanic crustal products of the Late Cretaceous Yüksekova Complex, which are found as ophiolite units within the orogenic belt in southeastern Anatolia, are the main topic of this study (Figure 2).

The Upper Cretaceous Yüksekova Complex represents a part of oceanic crust in the Amanos-Elazığ-Van ophiolite belt [1, 2] in southeastern Turkey. This unit was examined in detail in the study region by [3, 4, 5, 6]. The Yüksekova Complex is regarded as an oceanic arc-back arc pair that developed during the Cenomanian-Campanian interval based on paleontological and geochemical findings [5, 6]. The age of the Yüksekova Complex was dated as 81.9 ± 0.6 Ma to 78.7 ± 1 Ma by 40Ar/39Ar on hornblende [7, 8], which is also confirmed by radiolarian dating by [6]. The age of the unit extends to the end of the Maastrichtian based on palaeontological age findings [9, 10]. Besides, the Yüksekova oceanic units with back-arc basin affinity [5, 7, 11] may have formed in response to the
roll-back of the Southern-Tethyan slab and marginal basin opening to the south of the Anatolian Block, as also proposed for SW Iran [8, 12].

Figure 1. a) Distribution of the ophiolitic mélange complexes in Turkey (modified after [23]), b) the location map of the study area, c) The geological map of the study area (after [24]).

In the study area, the Yüksekova Complex comprises massive diabase, massive lava, pillow lava, and granitic intrusions cutting these. Similar mafic lithologies also exist near the Caferi village and are locally defined as the Caferi Volcanics [13, 14]. This mafic volcanic and subvolcanic rock assemblage is tectonically isolated from the units of the Guleman Ophiolite [13, 14]. A similar tectonic relationship is also observed near the İçme village, where the mafic lithologies tectonically overlie the ultramafics of the Guleman Ophiolite. The general idea, however, is that they are accepted as the volcanic cover of the Guleman Ophiolite [13, 14, 15, 16]. The Guleman group is thrust over the autochthonous Arabian platform and Lice Formation and tectonically overlain by Bitlis metamorphic massif [15, 16, 17, 18, 19].

In the study area, the Yüksekova Complex is overlain by the Upper Palaeocene Hazar Group limestones and partly post Eocene units (Figure 1). Some researchers [20, 21] proposed that on the northern flanks of Mastar Tepe and around İçme area, the Karadere Formation of the Maden Complex conformably covers the limestones from the upper levels of the Gehroz Formation. They stated that the Maden Complex in the study area is represented by agglomerate, tuff, volcanic sandstone, lava flows (including pillow lavas), and occasional intercalated reddish-brown mudstone. The study of [22] suggested that the Maden magmatism developed by lithospheric removal and asthenospheric upwelling associated with the extensional collapse of southeastern Anatolian in this region, during the Middle Eocene.
2. Analytical methods

A total of 15 samples were collected from the mafic volcanic and subvolcanic rocks of Upper Cretaceous Yüksekova Complex in the İçme-Kesikköprü province (east of Elazığ city, eastern Turkey) (Figure 1).

3. Results

3.1. Petrography

The mafic volcanic and subvolcanic rocks from the Upper Cretaceous Yüksekova Complex investigated in the İçme-Kesikköprü province (east of Elazığ) comprise plagioclase ± pyroxene ± olivine ± opaque minerals in the order of decreasing abundance with a secondary assemblage of epidote ± chlorite ± zeolite (Figure 3). Based on macroscopic and microscopic observations, the...
studied lithologies are fine- and occasionally medium-grained basalts and diabases. The samples include swallow-tail or spherulitic-shaped plagioclases, remnant pyroxene microliths with weathered edges, and pyroxene phenocrysts (occasional clear augites) in addition to microphenocrysts, and remnant and carbonatized olivine (Figure 3). Intergranular, intersertal, poikilitic, subophitic, seriate, microlithic porphyric, vesicular, amygdaloidal and variolitic textures are common.

Figure 3. Microphotographs showing mineralogy and textures of the mafic volcanic and subvolcanic rocks of the Yüksekova Complex in the İçme-Kesikköprü province (E Elazığ, eastern Turkey); a) The hyalo-microlithic porphyritic texture of the basalts, Yolüstü area, b) Swallowtail plagioclases and relict pyroxene microlites in the basalts, Yukarı İçme area, c) Amygdaloidal textured basalt, İçme area, d) Intergranular-textured basalt, Pirimezartepe area, e) Glomeroporphyric-textured basalt, Pirimezartepe, f) Intergranular and microlitic-textured basalt, Aşağı İçme area, Abbreviations: pl: plagioclase, px: pyroxene, chl: chlorite.

The studied samples are variably altered, displaying carbonatization, chloritization, epidotization, and opacification. Veins and fractures exist, which are filled by calcite, silica, and epidote. While uralitization and epidotization are observed in pyroxene, albitization, chloritization, and sericitization are common in plagioclase.
3.2. Whole-rock geochemistry
The studied rocks show basaltic composition according to Nb/Y vs. Zr/TiO$_2$ diagram [25] (Figure 4a), while based on the plot of Zr vs. Y [26, 27], they display tholeiitic calc-alkaline transition features (Figure 4b). Trace element plots normalized to normal mid-ocean ridge basalt (N-MORB) of rock samples indicate the followings; 1) Variable Th enrichment, 2) MORB-like HFS element abundances (except for Nb, which is more depleted), and 3) prominent negative Nb anomaly (Figure 4c). The chondrite-normalized REE patterns [(La/Sm)$_N$: 0.54-1.42, (La/Lu)$_N$:0.54-1.85] of samples are nearly flat to LREE-depleted and indicate tholeiitic character (Figure 4d). On the plot of Nb/Yb vs. Th/Yb diagram [28], the samples appear to display low Nb/Yb ratios, similar to N-MORBs. The Th/Yb ratios, on the other hand, are high and displaced above the MORB array (Figure 4e).

Figure 4. Selected discrimination diagrams for the studied volcanic and subvolcanic rocks of the Yüksekova Complex; a) chemical classification using the Zr/TiO$_2$ vs. Nb/Y diagram [25], b) Zr vs. Y diagram of [26] adapted from plots revised by [27], c) N-MORB-normalized spider diagram, d) Chondrite-normalized REE diagram, e) Nb/Yb vs. Th/Yb diagram [28]. Normalization values for N-MORB and Chondrite are from [29].
3.3. Confocal Raman Spectrometer (CRS) Studies

The Confocal Raman spectra for pyroxene minerals in the mafic rocks from Aşağı İçme, Pirimezar Tepe and Yolüstü locations reveal that the type of pyroxenes is augite in composition. The augite-type pyroxenes have Raman shifts around 320-400, 500, 600, 800-1000 cm⁻¹ (Figure 5).

The Raman spectrums of pyroxene mineral from three different localities have similar Raman shifts with some differences. The augite from Aşağı İçme has Raman shifts at 325, 393, 470, 550, 626-665, and 819-917-1010 cm⁻¹ (Figure 5a). The augite from Pirimezar Tepe has Raman shifts at 326-256-392, 538-555, 664 and 865-1009 cm⁻¹ (Figure 5b).

The augite from Yolüstü has Raman shifts at 326-360-394, 666 and 863-1010 cm⁻¹ (Figure 5c). All augites have three significant Raman shifts around 300 cm⁻¹ at the first spectral region (Figure 5). This spectral region is characteristic for the SiO₄ rotation and metal-oxygen translation modes based on [30]. The shifts between 500 and 760 cm⁻¹ belong to the Si-O bending modes in the structure of augites. Si-O bending modes of augites from three localities have some differences (Figure 5).

The third spectral region is characteristic for the Si-O stretching modes. The shifts between 1200-1600 cm⁻¹ may be characterized by OH bonds and the alteration degree of augites decrease from Yolüstü location to Aşağı İçme. The Raman spectrums of all augites are similar to the spectrum of monoclinic pyroxenes by [30].

4. Discussions and conclusions

This study investigated mafic volcanic and subvolcanic rocks from the Yüksekov Complex east of Elazığ (İçme-Kesikköprü province), which are the products of an accretionary prism in the Southeast Anatolian orogenic belt. The mineralogical and geochemical characteristics of mafic rock samples from this region show that the Yüksekov Complex, previously accepted as an intra-oceanic arc-back arc pair [5, 6], has a broader extent than previously thought before. The studied mafic lithologies here are the less evolved products of this oceanic arc-basin system, reflecting tholeiitic-calc-alkaline transitional characteristics.

On the N-MORB- and chondrite-normalized diagrams, the samples display subduction-related trace element characteristics. The presence of prominent Nb anomaly (and relative enrichment in Th and La) indicates a mantle source metasomatized by slab-derived materials. This is also supported by the high Th/Yb for a given Nb/Yb (Figure 4e), suggesting the contribution of subduction component in the petrogenesis of the studies samples. On the other hand, the depleted Nb contents (lower than that of N-MORB) and low Nb/Yb, suggest a mantle source, even more depleted that of N-MORBs. Overall, the trace element systematics of the samples is somewhat akin to magmas generated in an oceanic arc environment.

All these data suggest that the melts generating the mafic volcanic and subvolcanic rocks around İçme-Kesikköprü (east of Elazığ) may have developed in an intra-oceanic subduction system, and probably represent oceanic arc products. Additionally, the compositions of the pyroxene from the Aşağı İçme, Pirimezar Tepe, and Yolüstü samples are all similar and appear to be augite (Figure 5). Although this may indicate that these arc-related mafic rocks may have originated from a somewhat similar parental magma, the distinct trace element systematics are suggestive of parental magmas with diverse origins.
Figure 5. The Raman spectrum of pyroxene minerals from (a) Aşağı İçme, (b) Pirimezar Tepe and (c) Yolüstü locations (The spectral regions from [31]).
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