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Geological and Geochemical Characteristics of Late Ordovician Volcanic Levels of the Gözdağ Formation in the İstanbul-Zonguldak Tectonic Unit (NW Turkey): Implications for Global Events During the Ordovician

İstanbul-Zonguldak Tektonik Birliği'ndeki Gözdağ Formasyonu'nun Üst Ordovisiyen Yaşlı Volkanik Seviyelerinin Jeolojik ve Jeokimyasal Özellikleri (KB Türkiye): Ordovisiyen Sırasındaki Küresel Olaylar İçin Çıkarımlar

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This paper is respectfully dedicated to a geologist the late Sinan Biberoğlu, who graduated with a master's degree from *ITÜ* in 1984 and hired young geologists in the engineering projects of İstanbul, and who was instrumental in collecting geological data from underground-construction excavations.

Abstract: The İstanbul-Zonguldak Tectonic Unit is regarded as the easternmost fragment of Avalonia-Carolina and designated as Far East Avalonia. Its stratigraphy is characterized by discontinuous sedimentation from Late Ediacaran to Late Carboniferous. In the western part of the block, known as İstanbul Terrane, the Gözdağ Formation is represented by lagoonal sedimentary rocks consisting of shale-sandstone with limestone of Middle Ordovician-Lower Silurian age. Here, I report on stratigraphic positions and petrographical and geochemical data of fine- and coarse-grained tuffs and lavas in the Late Ordovician strata of the Gözdağ Formation. The fine- and coarse-grained tuffs have pyroclastic and the lavas have porphyritic, vitrophyric and aphanitic textures. The fine-and coarse-grained tuffs are of Sandbian and Katian ages, and the lavas have Hirnantian ages, according to the stratigraphic positions of the Late Ordovician volcanic rocks. The fine-grained tuffs have high potassium calc-alkaline, and the coarsegrained tuffs and lavas have a calc-alkaline character. They are devoid of noticeable with-in plate components, as deduced by the presence of obvious negative Nb anomalies, and they have subduction signatures. In conjunction with data from the literature, the Sandbian fine-grained tuffs were deposited in a lagoonal depocenter in the İstanbul-Zonguldak Tectonic Unit in the earliest Late Ordovician due to multiple Plinian-type eruptions during the last phase of the Taconic orogeny, which formed between the Piedmont Terrane and Laurentia. The Katian coarse-grained tuffs were products of volcanic activities formed in the arc settings during the last stage of depletion of the Teisseyre-Tornquist Ocean, lying between Avalonia and Baltica. The Hirnantian lavas were formed by flowing in a lagoonal depocenter of the İstanbul-Zonguldak Tectonic Unit during the soft-docking of Avalonia and Baltica, known as the pre-Caledonian orogeny.

Keywords: Far East Avalonia, Gözdağ Formation, İstanbul-Zonguldak Tectonic Unit, Ordovician, Volcanic Rocks.

Öz: İstanbul-Zonguldak Tektonik Birliği, Avalonya-Karolina'nın en doğudaki parçası olarak kabul edilir ve Uzak Doğu Avalonya'yı temsil eder. Stratigrafisi ayrıca Üst Ediyakaran'dan Üst Karbonifer'e kadar kesintili sedimantasyon

ile karakterize edilir. Bloğun İstanbul Birliği olarak bilinen batı kesiminde Gözdağ Formasyonu, Orta Ordovisiyen-Alt Silüriyen yaşlı şeyl-kumtaşı kireçtaşından oluşan lagünel tortul kayaçlarla temsil edilmektedir. Burada, Gözdağ Formasyonu'nun Üst Ordovisiyen tabakalarındaki ince- ve kaba-taneli tüflerin ve lavların stratigrafik konumları ile petrografik ve jeokimyasal verilerini rapor ediyorum. İnce- ve kaba- taneli tüfler piroklastik, lavlar ise porfirik, vitrofirik ve afanitik dokuludur. Üst Ordovisiyen yaşlı volkanik kayaçların stratigrafik konumlarına göre, ince- ve kaba-taneli tüfler Sandbiyen ve Katiyen, lavlar ise Hirnansiyen yaşlıdır. İnce-taneli tüfler yüksek potasyumlu kalkalkali, kaba-taneli tüfler ve lavlar kalk-alkali karaktere sahiptir. Fark edilebilir negatif Nb anomalilerinin varlığından anlaşıldığı gibi, bariz plaka içi bileşenlerden yoksundurlar ve yitim imzalarına sahiptirler. Literatürden elde edilen verilerle bağlantılı olarak, Sandbiyen ince-taneli tüfler Piedmont Birliği ile Lavrensiya arasında en erken geç Ordovisiyen' de oluşan Takonik orojenezinin son evresi sırasında çoklu pliniyen-tipi patlamaların bir sonucu olarak İstanbul-Zonguldak Tektonik Birliği 'ndeki bir lagün alanında çökelmiştir. Katiyen kaba-taneli tüfler Avalonya ile Baltika arasında uzanan Teisseyre-Tornquist Okyanusu'nun tüketilmesinin son aşamasında yay ortamında meydana gelen volkanların ürünleridir. Hirnansiyen lavları ise Kaledoniyen öncesi orojenezi olarak bilinen Avalonya ve Baltika'nın yumuşak yanaşması sırasında İstanbul-Zonguldak Tektonik Birliği'nin bir lagün ortamında akarak oluşmuştur.

Anahtar Kelimeler: Gözdağ Formasyonu, İstanbul-Zonguldak Tektonik Birliği, Ordovisiyen, Uzak Doğu Avalonya, Volkanik Kayaçlar.

The

INTRODUCTION

The Ordovician time represents chaotic processes in the ancient blue planet (Figure 1). After the rifting of Avalonia-Carolina during the Late Ediacaran (Pollock and Hibbard, 2010; Landing et al. 2019; Şen, 2021a), Carolina-Ganderia collided with Laurentia during the latest Late Ordovician (Acadian orogeny; Hibbard et al., 2007) before the Piedmont Terrane docked with Laurentia during the earliest Early Ordovician (Taconic orogeny; van Staal et al., 2007). Avalonia also softly docked with Baltica during the latest Late Ordovician, known as the pre-Caledonian orogeny after the consumption of the Teisseyre-Tornquist Ocean, which was the eastern branch of Iapetus (Cocks and Fortey, 2009). In addition, after Cadomia rifted off from West Gondwana-land, known as the opening of the Tethys Ocean (Linnemann et al., 2007 after Landing et al., 2019), Hirnantian glaciation and Late Ordovician mass extinction have taken place in Cadomia, together with Minoa and Gondwanaland during the latest Late Ordovician (e.g., Huff et al., 1992; Fortey and Cocks, 2005; Huff, 2008).

is an Amazonian craton-derived continental block accreted to Baltica during the latest Late Ordovician (Sen, 2023a) and is regarded as the eastward extension of the Avalonia-Carolina micro-continent (Ustaömer et al., 2011; Şen, 2021a). The continental fragment was located on the margin of NE Amazonia in the west of the Morocco-Anti Atlas (Bozkurt et al., 2008) during the Late Ediacaran (Sen, 2021a) and represents Far East Avalonia (Oczlon et al., 2007; Şen, 2021a). In this study, the Gözdağ Formation in the İstanbul Terrane, which forms the western sector of the Istanbul-Zonguldak Tectonic Unit, is emphasized in order to contribute to the interpretation of these chaotic processes in the Ordovician planet. The Gözdağ Formation consists of alternations of sandstone, shale and greywacke of the Middle Ordovician-Lower Silurian age deposited in a lagoonal depocenter (Sayar and Cocks, 2013). This paper reports their stratigraphic positions together with petrographical and geochemical data for Late Ordovician volcanic levels of the Gözdağ Formation, with the aim of shedding light on the global and local Ordovician geodynamic evolution.

İstanbul-Zonguldak

Tectonic

Unit



OMZ: Ossa-Morena Zone; P: Pyrenees; SXZ: Saxo-Thuringian Zone; TBU: Tepla-Barrandian Massif; WALZ: West Australian Loneliness Massif for Cadomia. Triangle on McKerrow (1995) in Laurentia and Dennis et al. (2012), Zagorevski et al. (2008) in Carolina-Ganderia – 456-453 Ma; 2Compston and Williams (1992), Tucker (1992), Tucker Figure 1. Simplified tectonic map of the peri-Gondwanan terranes within the Appalachian belt of North America, the Variscan belt of southern-central Europe, the Simplified and in the Mediterranean belt (after Sen, 2021a). The location of MINOA is taken from Sen (2021a, b). See abbreviations for East Avalonia, Far East Avalonia, Cadomia and MINOA. 'T-TO S' represents suture of Teisseyre-Tornquist Ocean in Far East Avalonia. AW: Anglo Welsh; BRM: Brabant Massif; CGCZ: Central German Crystalline Zone; J: Lizard Ophiolite; M: Mororabo-Silesian Zone; MC: Midland Craton; RM: Rhenish Massif; S: Sudetes; SI: Sleza Ophiolite; SPZ: South Portugal Zone; T: Tatra for East Avalonia; D: Dobrogea; EC: East Carpathia; [ZTU: [stanbul-Zonguldak Tectonic Unit; KR: Kraishte; M: Moesia; OC: Ograzhdenian Complex; RM: Rhodope Massif; SMM: Cantabrian Zone; FMC: French Massif Central; GTOM: Galica-Tras os Montes Zone; IC: Iberia Chains; IM: Iberia Massif; MM: Maurers Massif; MZ: Moldanubian Massif; collision of Laurentia and Piedmont Terrane). Red dots stand for the localities of arc-related Late Ordovician volcanism during the consumption of the Teisseyre-Tornquist Ocean and orange dots also represent localities syn-collision-related latest Late Ordovician volcanism during soft-docking between Avalonia and Baltica in Avalonia. Radiometric ages are taken from 1Bergström et al. (1995); Adams et al. (1960), Kunk et al. (1985), Samson et al. (1989), Tucker et al. (1990), Tucker (1992), Tucker and and McKerrow (1995), Kolata et al. (1996), Bauert et al. (2014) in Baltica – 456-453 Ma; 3this study; 4Stillman and Francis (1979) and 5Linnemann et al. (2012) – 453-448 Ma and 457 Ma; 6Balintoni et al. (2010) – 458 Ma; 7Zagorchev et al. (2015) – 456-451 Ma; 8Antić et al. (2016) – 456 Ma; 9Okay et al. (2008) – 457-446 Ma; 100czlon et he sutures indicates subduction polarity. Green twin triangles represent the localities of syn-collision-related Late Ordovician tuffs formed during the Taconic orogeny ectonic map of the peri-Gondwanan terranes within the Appalachian belt of North America, the Variscan belt of southern-central Europe, the south and west of the Black Sea. Serbo-Macedonian Massif; SC South Carpathia; SM: Strandja Massif for Far East Avalonia; AM: Armorican Massif; BM: Bohemian Massif; CIZ: Central Iberia Zone; CZ: al. (2007) – Late Ordovician; 11Noble et al. (1993) – 445 Ma; 12Linnemann et al. (2012) – 445 Ma; 13Sen (2023a) – 445-443 Ma.

dalma polaritesini gösterir. Yeşil ikiz üçgenler, Takonik orojenezi (Lavrensiya ile Piedmont Terrane çarpışması) sırasında çarpışma ile ilişkili Üst Ordovisiyen tüflerinin Sekil I. Kuzey Amerika'nın Appalaş kuşağı, güney-orta Avrupa' nın Variskan kuşağı, Karadeniz'in güneyi ve batısı ve Akdeniz kuşağı içindeki Gondvana öncesi bölgelerin basitleştirilmiş tektonik haritası (Şen, 2021a). MINOA'nın lokasyonu Şen (2021a, b)'den alınmıştır. Doğu Avalonya, Uzak Doğu Avalonya, Kadomiya ve MINOA kısaltmalarına Orta Alman Kristalin Zonu; Li: Lizard Ofiyoliti; M: Mororabo-Silesian Zonu; MC: Midland Kratonu; RM: Rhenish Masifi; S: Sudetes; SI: Sleza Ofiyoliti; SPZ: Güney Portekiz Zonu; T. Tatra; Uzak Doğu Avalonya için; D: Dobruca; EC: Doğu Karpatlar; IZTU: İstanbul-Zonguldak Tektonik Birliği; KR: Kraishte; M: Moesya; OC: Ograzhdenian Moldovalı Masifi; OMZ: Ossa-Morena Zonu; P: Pyrenees; SXZ: Sakso-Thüringen Zonu; TBU: Tepla-Brandiya Masifi; WALZ: Batı Avusturya Masifi. Süturlardaki üçgen verlerini temsil eder. Kırmızı noktalar, Teisseyre-Tornquist Okyanusu'nun tüketilmesi sırasında yay ile ilişkili Üst Ordovisiyen volkanizmasının yerlerini ve turuncu noktalar bakınz. 'T-TO S' Uzak Doğu Avalonya' daki Teisseyre-Tornquist Okyanusu' nun süturunu temsil eder. Doğu Avalonya için AW: Anglo Welsh; BRM: Brabant Masifi; CGCZ: Kompleks; RM: Rodop Masifi; SMM: Strp-Makedon Masifi; SC Günev Karpatlar; SM: Istranca Masifi; Kadomiya için AM: Armorikan Masifi; BM: Bohemya Masifi; CIZ: Orta İberya Zonu; CZ: Kantabriya Zonu; FMC: Orta Fransa Masifi; GTOM: Galica-Tras os Montes Zonu; IC: İberya Silisesi; IM: İberya Masifi; MM: Maurers Masifi; MZ:

da Avalonya'daki Avalonya ile Baltika arasındaki yumuşak yanaşma sırasında meydana gelen çarpışma ile ilişkili Üst Ordovisiyen volkanizmasını temsil eder. Radyometrik yaşlar Lavrensiya'da 1Bergström vd. (1995); Adams vd. (1960), Kunk vd. (1985), Samson vd. (1989), Tucker vd. (1990), Tucker (1992), Tucker ve McKerrow (1995) ve Karolina-Ganderya' da Dennis vd. (2012), Zagorevski vd. (2008) - 456-453 My; Baltika' da 2Compston ve Williams (1992), Tucker (1992), Tucker ve McKerrow (1995), Kolata vd. (1996), Bauert vd. (2014) – 456-453 My; 3bu çalışma; 4Stillman ve Francis (1979) ve 5Linnemann vd. (2012) - 453-448 My and 457 My; 6Balintoni vd. (2010) - 458 My; 7Zagorchev vd. (2015) - 456-451 My; 8Antić vd. (2016) - 456 My; 9Okay vd. (2008) - 457-446 My; 10Oczlon vd. (2007) - Üst Ordovisiyen; 11Noble vd., (1993) – 445 My; 12Linnemann vd. (2012) – 445 My; 13Şen (2023a)' dan – 445-443 My alınmıştır.

GEOLOGICAL SETTING

The Pontides contain three continental fragments amalgamated during the earliest Early Permian time (Sen, 2022b). These are the Rhodope-Strandja Massif, İstanbul-Zonguldak Tectonic Unit and Sakarya Zone (e.g., Yiğitbaş et al., 1999, 2004) (Figure 2). The Rhodope-Strandja Massif and İstanbul-Zonguldak Tectonic Unit are parts of the metamorphosed and unmetamorphosed fragments of Far East Avalonia (Sen, 2021a, b) whereas the Sakarya Zone is derived from the Minoan terrane (Ustaömer et al., 2012; P.A. Ustaömer, 2012), which rifted from Laurentia during the Middle Neoproterozoic (Sen, 2023b), including continental blocks extending from the Alps to the Kopegh Dagh in the Mediterranean province (Sen, 2021a). The İstanbul-Zonguldak Tectonic Unit (IZTU), located along the southwestern Black Sea coast, contains Late Neoproterozoic metamorphic basement rocks overlain by a discontinuous and well-developed sedimentary sequence extending from Ediacaran to Carboniferous (Sen, 2021a) (Figure 3). Stratigraphic differences are observed in the western and eastern section of the IZTU (e.g., Göncüoğlu, 1997). It is accepted as two different terranes, consisting of the İstanbul Terrane (İT) and Zonguldak Terrane (ZT) according to lithological differences that are seen after the Silurian-Devonian transition (Göncüoğlu, 1997; Kozur and Göncüoğlu, 1998) (Figure 2 & 3). On the other hand, it can be explained by lateral facies changes following the Silurian-Devonian transition (Okay and Topuz, 2017). The southern part represents the Iapetus Ocean and the Teisseyre-Tornquist Ocean and the northern part contains the continentalmargin sedimentary rocks of the Rheic Ocean during the Ediacaran-Ordovician time (Şen, 2021a, 2023a) (Figure 3).

Stratigraphy of the İstanbul-Zonguldak Tectonic Unit (İZTU)

The Late Neoproterozoic rock assemblages consist of high-grade metamorphic rocks in the southern sector of the IZTU, observed in the Armutlu peninsula, Sünnice mountain and Karadere (Yiğitbaş et al., 1999, 2004; Sen, 2021a) (Figure 2 & 3). In the Armutlu peninsula, the basement rocks are composed of a high-grade amphibolite gneiss sequence, known as the Armutlu metamorphics (AM) and the Avalonian magmatic bodies intruding them (c. 591-569 Ma; Okay et al., 2008; Akbayram et al., 2013), and the Late Ediacaran metaophiolite that amphibolites are interbanded with layers of metaperidotite and metagabbro called the Pamukova metamorphics (PM) (c. 564 Ma; Özbey et al., 2021) (Figure 3). The AM juxtaposed with the PM during the latest Late Ediacaran to earliest Early Cambrian (Sen, 2021a) (Figure 3). The basement rocks are cut by Middle-Late Ordovician intrusive granitic rocks (c. 464-446 Ma; Okay et al., 2008).

In the Sünnice mountain, the basement is made up of a low-grade sequence, known as the Yellice metavolcanics, consisting of metaandesites with minor metarhyolites and meta-sedimentary rocks of the Middle-Late Ediacaran age (Yiğitbaş et al., 1999, 2004; Dr. T. Ustaömer, 2017; personal communication). They represent an Avalonian arc (Ustaömer and Rogers, 1999) intruded by the Avalonian intrusive granitic rocks (c. 576 Ma; Ustaömer et al., 2005) and completely cut by riftrelated Late Ediacaran intrusive magmatic bodies (c. 565-556 Ma; Şen, 2021a) (Figure 3). Geological and Geochemical Characteristics of Late Ordovician Volcanic Levels of the Gözdağ Formation in the İstanbul-Zonguldak Tectonic Unit (NW Turkey): Implications for Global Events During the Ordovician



Figure 2. Simplified geology map of the İZTU (modified from Yiğitbaş et al. 1999; Bozkurt et al. 2013) showing the distribution of Neoproterozoic basement rocks and Ediacaran-Carboniferous sedimentary rocks known as continentalmargin deposits of the Rheic Ocean (Şen, 2021a, b, 2023a), and subdivision of the İZTU into the İstanbul and Zonguldak terranes on the basis of Göncüoğlu (1997). Black box shows study area.

Şekil 2. Rheic Okyanusu'nun kıta kenarı kayaçları olarak bilinen Ediyakaran-Karbonifer sedimanter kayaçlarının (Şen, 2021a, b, 2023a) ve Neoproterozoyik temel kayaçlarının yayılımını ve İZTU'nun Göncüoğlu (1997)'ye göre İstanbul ve Zonguldak birliklerini gösteren İZTU'nun basitleştirilmiş jeoloji haritası (Yiğitbaş vd., 1999; Bozkurt vd., 2013' den değiştirilmiştir). Siyah kutu çalışma alanını gösterir.



Figure 3. Generalized stratigraphic section (not to scale) of the İZTU (after Şen, 2021a, b). Data from Chen et al. (2002)¹, Ustaömer et al. (2005)², Okay et al. (2008)³, Akbayram et al. (2013)⁴, Yiğitbaş et al. (1999)⁵, Biberoğlu (1984)⁶, Dean et al. (2000)⁷, Gedik and Önalan (2001)⁸, Boncheva et al. (2009)⁹, Sayar and Cocks (2013)¹⁰, Göncüoğlu

et al. (2014)¹¹, Aydın et al. (1987)¹², Abdüsselamoğlu (1977)¹³, Özgül (2012)¹⁴, Ustaömer et al. (2011)¹⁵, Tunç et al. (2012¹⁶, Yiğitbaş and Tunç (2020)¹⁷, Yalçın and Yılmaz (2010)¹⁸, Hamdi (1975)¹⁹, Okay and Topuz (2017)²⁰. Late Ediacaran dykes, Ordovician-Silurian dykes and Late Devonian to Late Carboniferous dykes were taken from Şen (2021a, b), Şen (2022a, b), Şen (2023a).

Şekil 3. İZTU'nun genelleştirilmiş stratigrafik kesiti (ölçeksiz) (Şen, 2021a, b). Veriler Chen vd. (2002)¹, Ustaömer vd. (2005)², Okay vd. (2008)³, Akbayram vd. (2013)⁴, Yiğitbaş vd. (1999)⁵, Biberoğlu (1984)⁶, Dean vd. (2000)⁷, Gedik ve Önalan (2001)⁸, Boncheva vd. (2009)⁹, Sayar ve Cocks (2013)¹⁰, Göncüoğlu vd. (2014)¹¹, Aydın vd. (1987)¹², Abdüsselamoğlu (1977)¹³, Özgül (2012)¹⁴, Ustaömer vd. (2011)¹⁵, Tunç vd. (2012)¹⁶, Yiğitbaş ve Tunç (2020)¹⁷, Yalçın ve Yılmaz (2010)¹⁸, Hamdi (1975)¹⁹, Okay ve Topuz (2017)²⁰ alınmıştır. Üst Ediyakaran daykları, Ordovisiyen- Silüryen daykları, Üst Devoniyen-Üst Karbonifer daykları Şen (2021a, b), Şen (2022a, b) ve Şen (2023a)'dan alınmıştır.

The Sünnice Group contains two lithotectonic rock assemblages. These are the Demirci metamorphic sequence that is structurally a lower assemblage of high-grade amphibolite-facies quartz–plagioclase–biotite–hornblende gneiss and the Çele metaophiolite that is structurally a higher assemblage of amphibolite-facies metaperidotite and amphibolites (Yiğitbaş et al., 2008). The Sünnice Group, corresponding to the Pamukova metamorphics (Yiğitbaş et al., 1999, 2004), is juxtaposed with the Yellice metavolcanics at 540 Ma (Şen, 2021a).

They are cut by Early Cambrian to Late Ordovician intrusive rocks (c. 517-511 Ma; Bozkurt et al., 2013; c. 484-443 Ma; Şen 2023a). In the Karadere area, the basement rocks are represented by the Doruk-Yayla metamorphics, consisting of meta-quartzites and gneisses of Tonian-Cryogenian age and the Avalonian intrusive granitic rocks cutting them (c. 590-568 Ma; Chen et al., 2002) (Figure 3).

The Yellice metavolcanics standing for the Avalonian arc are emplaced by Late Ediacaran rift-

related intrusive rocks (c. 565-556 Ma; Ustaömer et al., 2005; Sen, 2021a). This also corresponds to the beginning of the sedimentation time of the rift fills (Kurtköv Formation) that were are cut by Late Ediacaran rift-related small intrusions (c. 552-549 Ma; Sen, 2021a). They consist of red sandstone and conglomerate alternating with mudstone and shale. The fore-arc fills (Kocatöngel-Bakacak Formations) include very low-grade metamorphic rocks consisting of green and red shale-siltstone intercalations representing the turbiditic- and -deltaic fills of Middle-Late Ediacaran age. The fore-arc fills were thrust over the rift fills at 540 Ma (Sen, 2021a) (Figure 3). The rift fills are conformably and unconformably overlain by the siliciclastic platform (Kınalıada-Aydos Formations) consisting of white and red crossbedded quartz sandstones, locally with ripple marks (Abdüsselamoğlu, 1977; Özgül, 2012), and their depositional age is Early Cambrian-Middle Ordovician (Sen, 2021a) (Figure 3). The siliciclastic platform passes laterally and vertically into a sequence of shale-sandstone alternating with limestone and greywacke deposited in a lagoonal depocenter (Figure 3). The sedimentation of the lagoonal-fills, known as the Gözdağ-Dolayoba Formations, is Middle Ordovician-Late Silurian (Dean et al., 2000; Özgül, 2012; Sayar and Cocks, 2013). The rift- and -siliciclastic platform fills are cut by Late Ordovician intrusive rocks (c. 444-443 Ma; Sen, 2023), corresponding to felsic lavas in the Ordovician-Silurian transition in the IT (Figure 3). The Upper Silurian-Lower Devonian fills begin with laminated limestone-shale and pass upward into nodular limestones, known as the Istinye Formation (Önalan, 1981). However, the Pridoli Stage of the Upper Silurian and Lochkovian Stage of the Lower Devonian are absent in the İT (Yalçın and Yılmaz, 2010), corresponding to Late Silurian-Early Devonian unconformity in the ZT, as stated by Hamdi (1975). The Lower Devonian-Lower Carboniferous fills begin with turbiditic sandstone-limestone (Kartal Formation) and pass

upward into pelagic limestones and radiolarite shale (Büyükada-Baltalimanı Formations) and end up with turbiditic sandstone and shale alternating with limestone (Trakya Formation) (Figure 3). These sedimentary rocks represent the deep marine depocenter in the İT (Özgül, 2012; Okay and Topuz, 2017). The Late Paleozoic sequence ends with a thick sequence of Lower Carboniferous siliciclastic turbidites in the İT. Lower Devonian-Upper Carboniferous fills start with a shallow carbonate platform and pass upward into terrestrial clastic rocks consisting of a thick sequence of coal-bearing sandstone and shale in the ZT (Okay and Topuz, 2017). The pre-Silurian rocks are also cut by the Late Devonian-Late Carboniferous intrusive rocks in the İstanbul-Zonguldak Tectonic Unit (c. 381 Ma to 321-301 Ma; Şen, 2021b; 2022b) (Figure 3).

Gözdağ Formation in the İstanbul Terrane

The Gözdağ Formation that mainly contains micaceous feldspathic sandstone strata has been designated with different names by previous researchers. Paeckelmann (1938) defined these strata as Halysites-Grauwacken Horizont. Haas (1968) described them as Yayalar-Schichten and subdivided them into three members: Umur Deresi, Şeyhli and Kayalıdere, corresponding to the Gözdağ, Umurdere and Şeyhli members of the Yayalar Formation, as stated by Özgül (2012). Kaya (1978) designated them as Büyükdere shale, Gözdağ litharenite and Şeyhli subarkose. Later, Önalan (1981) defined them as two units, including the Gözdağ and Aydınlı Formations. Tüysüz et al. (2004) collected these strata under the Gözdağ Formation. In this study, the name Gözdağ Formation is preferred because the Gözdağ Formation defined by Tüysüz et al. (2004) also encompasses the Aydınlı Formation of Önalan (1981).

The lower levels of the lagoonal deposits in the IT are represented by the Gözdağ Formation and their upper levels correspond to the Dolayoba Formation (e.g., Özgül, 2012; Savar and Cocks, 2013). The Gözdağ Formation consists predominantly of an alternation of shale, sandstone and greywacke. It is an intermediate stratigraphic unit of the IT (e.g., Paeckelmann, 1938) and underlies a small part of metropolis of İstanbul, especially east of the Bosphorus (Figure 4). The Gözdağ Formation is more than 400 m thick (Savar and Cocks, 2013). The micaceous sandstones are greenish-blue and grey medium and the thin strata in the lower parts of the sequence and the feldspathic quartz-arenites are pinkish cream, greyish white, medium to thick strata in the upper part of the sequence (Tüysüz et al., 2004; Özgül, 2012; Sayar and Cocks, 2013). The oldest fossiliferous strata in the Gözdağ Formation, representing the lower level of the unit, are a shalechamosite intercalation of Darriwilian-Sandbian age (Aric, 1955; Sayar, 1964, 1970, 1984; Sayar and Cocks, 2013). Furthermore, Bozkaya et al. (2012) defined felsic lavas in strata representing the Ordovician-Silurian transition of the Gözdağ Formation, corresponding to the transition between the lower and upper levels of the unit.

Field characteristics

The Gözdağ Formation occurs in small locations in İstanbul although it is mostly observed on the Anatolian side city of İstanbul (Figure 4). However, these small areas where the unit could previously be observed can no longer be observed due to the dense constructions in İstanbul metropolitan area. Therefore, it is essential to observe and map the strata of the Gözdağ Formation during super-construction excavations. In this context, the Gözdağ Formation was mapped on a 1/1000 scale during the construction excavations at three different locations in city of İstanbul, including the Cekmeköy, Dudullu and Gözdağ areas, corresponding to the lower levels of the unit (Figure 5). According to the mappings, different volcanic rocks were identified at three different levels of the Gözdağ Formation (Table 1; Figure 6).



Figure 4. Geological maps of the study areas, modified from Özgül (2012) on the basis of Şen (2012). Isotopic ages are from Şen (2021a) for Late Ediacaran dykes, Şen (2023a) for Late Ordovician dykes, Şen (2022a) for Early Silurian intrusions, Şen (2021b, 2022b) for Late Devonian-Late Carboniferous dykes, Aysal et al. (2018) for Late Permian granite, Şen (2012), Yılmaz-Şahin et al. (2012) and Aysal et al. (2017) for Late Cretaceous intrusions, Şen (2020) for Middle Eocene sub-volcanic rocks. Black boxes show study areas.

Şekil 4. Çalışma alanlarının Şen (2012) temel alınarak Özgül (2012)' den değiştirilmiş jeoloji haritası. İzotopik yaşlar Üst Ediyakaran daykları için Şen (2021a)'dan, Üst Ordovisiyen daykları için Şen (2023a)'dan, Alt Silüryen intrüzyonları için Şen (2022a)' den, Üst Devoniyen-Üst Karbonifer daykları için Şen (2021b, 2022b)'dan, Üst Permiyen graniti için Aysal vd. (2018)'den, Üst Kretase sokulumları için Yılmaz-Şahin vd. (2012), Şen (2012) ve Aysal vd. (2017), Orta Eosen volkanik kayaçları için Şen (2020)'den gelir. Siyah kutular çalışma alanlarını gösterir.

The volcanic rocks in the Gözdağ Formation are divided into three types, including fine- and coarse-grained tuffs and lavas (Figure 6). The fine-grained tuffs (T_1) are above the chamosite strata. They consist of light brown and 50-60 cm thick-layered sandstone alternating with dark brown siltstone of 5–20 cm thick bedding. They are observed at a level of \sim 3 meters (Figure 6a, b). The coarse-grained tuffs (T₂) are \sim 70 meters above the fine-grained tuffs. They contain light brown and 3-4 cm thick-layered sandstone alternating with dark blue millimeter-scale parallel-laminated limestone of 1-2 cm thick bedding. They are exposed at a level of ~5 meters (Figure 6a, c). The lavas (L) are above 45 meters above the coarse-grained tuffs and they are about 2 meters below the limestones extending in the form of thin bands. They comprise greenish brown and off-white colored and 7-8 meters thick-layers alternating with green sandstone and greywacke of 30-40 cm thick bedding. They are exposed at a level of ~8 meters (Figure 6a, d, e, f). In addition, these volcanic rocks observed at different levels in the lower parts of the Gözdağ Formation have been severely affected by hydrothermal alteration, as stated by Bozkaya et al. (2012).



Figure 5. Geology maps of the Gözdağ Formation in (a) Çekmeköy, (b) Dudullu and (c) Gözdağ in the İstanbul Terrane.

Şekil 5.	İstanbul	Birliği'nde	(a)	Çekmeköy,	(b)	Dudullu	ve	(c)	Gözdağ	daki	Gözdağ	Formasyonu	'nun	jeoloji
haritalar	ч.													

Table 1. Petrographical features of volcanic rocks in the Gözdağ Formation. The naming of pyroclastic rocks, depending on their grain size, was made according to Fisher and Schmincke (1984).

Çizelge 1. Gözdağ Formasyonundaki volkanik kayaçların petrografik özellikleri. Piroklastik kayaçların tane büyüklüklerine bağlı olarak adlandırılması Fisher ve Schmincke (1984)'e göre yapılmıştır.

Tomos of Valessia Dealer	Mineral comp	_ Matrix /	Tenteres	Tomas of Altomation		
Types of volcanic Rocks	Main	Accessory	Groundmass	Texture	Types of Alteration	
Fine-grained tuff (T_1)	Bt + Pl + Afs + Q	Ap + Zr + Mz	Mf + Vc	Durra alastia	anusquiritization	
Coarse-grained tuff (T_2)	Amp + Pl + Afs + Q	Bt + Ap + Zr	Mf	Pyroclastic	+ chloritization	
Lava (L)	Px + Amp + Pl + Afs + Q	Ap + Zr	Mc	Porphyritic + vitrophyric +	+ kaolinization + sericitization	

Abbreviations: Px, pyroxene; Bt, biotite; Amp, amphibole; Pl, plagioclase; Afs, alkali feldspar; Qz, quartz; Ap, apatite; Zr, zircon; Mz, monazite; Mf, mineral fragments; Vc, vitroclastic clasts; Mc, Microcline.

Kısaltmalar: Px, piroksen; Bt, biyotit; Amp, amfibol; Pl, plajiyoklaz; Afs, alkali feldispat; Qz, kuvars; Ap, apatit; Zr, zirkon; Mz, monazit; Mf, mineral parçaları; Vc, vitroklastik kırıntılar; Mc, Mikroklin.



Figure 6. Field photographs (**b**- **f**) together with a measured stratigraphic log (**a**) of the Gözdağ Formation in the Istanbul Terrane. (**a**) The measured stratigraphic log of the Gözdağ Formation shows the locations of volcanic intercalations. (**b**) sandstone with altered fine-grained tuff intercalations. (**c**) laminated limestone with altered coarse-grained tuff intercalations. (**d**-**e**) Lava within the sandstone strata. (**f**) Altered lava. D-S: Darriwilian-Sandbian, LI: Llandovery, T_1 : fine-grained tuff, T_2 : coarse-grained tuff, L: lava.

Şekil 6. İstanbul Birliği'ndeki Gözdağ Formasyonu'nun ölçülü stratigrafik kesiti (a) ile birlikte arazi fotoğrafları (bf). (a) Gözdağ Formasyonu'nun ölçülü stratigrafik kesiti, volkanik ara katkıların yerlerini göstermektedir. (b) Altere ince-taneli tüf ara katkılı kumtaşı. (c) Altere kaba-taneli tüf ara katkılı lamınalı kireçtaşı. (d-e) Kumtaşı tabakaları içinde lav. (f) Altere lav. D-S: Darrivilyan-Sandbiyen, Ll: Landoveriyen, T_1 : ince-taneli tüf, T_2 : kaba-taneli tüf, L: lav.

SAMPLE MATERIALS AND ANALYTICAL METHODS

Sampling and thin-section petrography

Thirty samples of the volcanic rocks in the Gözdağ Formation were collected from Çekmeköy, Dudullu and Gözdağ. The fine-grained tuffs (T_1) (twelve samples), the coarse-grained tuffs (T_2) (eight samples) and the felsic lavas (L) (ten samples) were sampled on the Anatolian side of İstanbul metropolitan area. They were severely affected by hydrothermal alterations. Thus, I selected four samples per group which were used for bulk whole-rock geochemical analysis (Figure 5; Table 2). All samples were collected by the author during the years 2012 and 2016. Each sample weighed at least 1.5 kg (>5 L in volume) to provide representability for bulk whole-rock geochemistry (especially trace element concentrations).

Thin-section petrographical analysis was undertaken on twelve samples that represent different volcanic rocks in the Gözdağ Formation, using a Leica DM4 P at the Geology Department of İstanbul University and a Nikon Eclipse E200 at the Geology Department of Çanakkale Onsekiz Mart University.

Whole-rock major and trace element geochemistry

Thirty petrographic samples of the volcanic rocks in the Gözdağ Formation were selected for geochemical analyses at the Sample Preparation Laboratory of the Geology Department at İstanbul University. Each sample weighed at least 1.5 kg to provide representability for trace elements. Noticeably-altered parts were removed using a diamond saw. Samples were comminuted in a jaw crusher to pass through a 0.5 mm sieve, homogenized and split using cone-and-quartering to yield a 50 g subsample for pulverization in an agate-lined ball mill, to pass through a 200 mesh sieve (<75 µm). Blanks, blind duplicates, in-house and accredited standards (i.e., CANMET standards SY-4, STD SO-17, USGS standards W-2, AGV-1, G-2, GSP-2, BCR-2) were randomly interspersed throughout the sample series for quality control.

Analyses for major, trace and rare earth elements were conducted at the ACME Analytical Laboratories in Canada during the years 2012 and 2016. Major oxides were analysed by using an inductively coupled plasma atomic emission spectrometry (ICP-AES), and trace-rare earth elements were analysed by using inductively coupled plasma mass spectrometry (ICP-MS). For the assay of major elements, 0.2±0.001 g of sample powder was fused with 1.0±0.001 g of LiBO₂ in a 95Pt05Au crucible at ~1050 °C. The hot melt was poured directly in 100 mL of 1N HNO₃ acid, which ensures immediate and complete dissolution, for analysis of major element contents, as well as trace elements Ba, Cu, Ni, Sc, and Zn. Major element contents were converted to oxides assuming stoichiometry, Fe₂O₃^T represents total iron (oxide) content. Major elements (oxides) have lower limits of detection (LLD) on the order of 0.01 wt%; exact values are specified per oxide species in a separate column, together with the data. Additional trace elements and rare earth elements (REEs) in the same sample solution were analyzed by ICP-MS with a lower detection limit between 0.01 and 1 ppm ($\mu g \cdot g^1$).

Loss on ignition (LOI) was measured gravimetrically on a separate 1.0 ± 0.001 g sample aliquot upon ignition at 1000 °C for 2h. Analytical accuracy is within $\pm 3\%$ -relative. Results from the bulk whole-rock geochemistry are given in Table 2.

RESULTS

Petrography

Petrographic observations reveal that the volcanic rocks in the Gözdağ Formation are three different rock types. These include fine-grained tuffs (T_1), coarse-grained tuffs (T_2) and lavas (L), contained at different stratigraphic levels in the Late Ordovician strata of the Gözdağ Formation (Table 1; Figure 6, 7).

The fine-grained tuffs (T_1) have pyroclastic textures. The phenocrysts are biotite, plagioclase, fragmentary quartz and broken alkali feldspar. The mineral fragments and vitroclastic clasts consist mainly of highly altered feldspar grains. Apatite, zircon and monazite are conspicuous accessory minerals. Biotites are quite small prismatic crystals. Plagioclases form subhedral to anhedral crystal forms and are albite (An₈₋₆). Quartzes have anhedral forms (Figure 7a & b).

The coarse-grained tuffs (T_2) have pyroclastic textures. The primary rock-forming minerals are amphibole, plagioclase, alkali feldspar and quartz. The mineral fragments mainly contain highly altered feldspar micro-grains. Accessory minerals are also biotite, apatite and zircon. The amphibole crystals have euhedral to subhedral forms. Plagioclases are mostly gnawed and are oligoclase (An_{22-18}). Alkali feldspars are anhedral crystals. Quartzes are anhedral and fragmental crystal forms (Figure 7c & d).

Table 2. The results of whole-rock major (wt.%), trace (ppm), and rare earth elements (REE) (ppm) geochemical analysis of volcanic rocks in the Gözdağ Formation.

Sample -		Fine-grained Tuffs (T ₁)				(Coarse-grained Tuffs (T ₂)				Andesite-Dacite Lavas (L)			
		1663	1911	1745	1732	1688	1671	1901	1931	1668	1681	1701	1915	
Coordinates		35T0680787 / 4544724	35T0683608 / 4542926	35T0689467 / 4530418	35T0689506 / 4530350	35T0680755 / 4544826	35T0680990 / 4544813	35T0683451 / 4543190	35T0689434 / 4530434	35T0681109 / 4545325	35T0680934 / 4544891	35T0683432 / 4543266	35T0689485 / 4530366	
	SiO ₂	63.58	65.57	65.85	68.07	70.51	69.63	71.34	70.19	67.82	66.54	62.42	61.78	
_	TiO ₂	0.21	0.26	0.19	0.24	0.84	0.76	0.57	0.78	0.69	0.92	1.12	1.37	
ıt%	Al ₂ O ₃	20.14	20.81	19.21	17.68	13.21	13.98	14.41	12.03	15.17	15.92	15.93	14.98	
s <u>v</u>	MnO	0.21	4.39	4.08	5.87 0.21	5.05 0.24	0.32	5.15 0.27	0.18	4.03	5.05	7.28	0.74	
ent	MgO	4 57	4 13	4 29	3.98	2.17	1.28	0.27	1.04	1.64	1.42	2.64	3.01	
ont	CaO	1.63	1.02	1.39	1.27	1.63	3.33	2.65	2.17	3.07	3.66	4.62	4.95	
le c	Na ₂ O	0.34	0.58	0.33	0.27	3.52	4.17	3.98	4.67	5.72	4.96	3.94	4.78	
oxic	K ₂ O	2.27	2.41	2.61	2.63	1.97	1.33	1.01	1.45	0.97	1.02	1.08	1.17	
ij.	P_2O_5	0.14	0.11	0.16	0.28	0.18	0.21	0.28	0.34	0.21	0.31	0.29	0.25	
M	Cr ₂ O ₃	0.02	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	
	LOI	8.8	8.2	9.6	10.6	7.1	8.6	7.6	10.9	8.1	8.8	9.4	10.3	
	Sum	98.39	99.44	98.91	98.51	99.92	100.03	99.91	99.22	100.05	99.96	99.54	99.23	
	SC V	21	32 9	28 14	35	15 21	10	12 25	0 19	10 55	21 49	29	43 114	
	Cr	0 014	0.007	0.007	0.007	0 014	0.007	0.007	0.007	0.007	0.007	0.007	0.007	
	Co	21.6	25.4	26.7	27.2	3.4	1.2	1.5	4.2	15.7	11.9	25.8	21.2	
	Ni	15	21	20	25	14	11	15	16	24	21	11	9	
<u>_</u>	Zn	55	58	61	73	71	55	68	70	57	50	58	55	
	Ga	15.7	16.2	16.4	17.9	18.2	13.4	19.3	17.7	18.3	15.7	14.2	11.3	
	Rb	142.5	171.2	168.7	182.8	36.4	31.7	34.2	35.5	15.4	14.6	15.6	12.7	
	Sr	98	137	135	149	190	152	199	185	285	267	301	277	
.5 H	Y Zr	38 201	35	35 217	255	44	41	4/	43 140	33 265	31	30	33 192	
as	Nb	9.1	10.2	11.6	12.1	7.6	60	7.0	73	203 5 1	203	4.8	4.2	
шd	Th	11.8	12.7	12.3	13.4	6.7	4.2	6.9	6.2	47	3.9	3.4	3.2	
d	Cs	0.4	0.6	0.6	0.9	0.8	0.3	0.9	0.7	0.2	0.1	0.3	0.3	
ents	Ba	125	134	139	158	121	112	135	126	155	147	138	131	
onto	Pb	6.1	6.6	7.3	8.1	6.9	5.1	7.6	6.2	8.3	7.6	4.8	3.1	
с Э	Та	0.3	0.4	0.4	0.5	0.9	0.6	1.1	0.8	0.5	0.4	0.3	0.4	
RE	Hf	5.1	5.4	5.6	6.3	6.1	5.1	6.3	5.7	4.8	4.3	4.3	3.9	
pu	U	1.1	1.8	2.1	2.4	1.8	1.1	2.1	1.5	1.8	1.6	1.5	0.9	
it ai	La	8.5	9.2	9.8	11.7	27.2	22.1	28.6	24.3	14.2	13.1	12.4	9.3	
ner	Ce	27.2	35.7	42.3	49.3	35.6	34.1 5.0	36.4	33.3	33.4	27.3	24.6	21.1	
eleı	PI Nd	23.1	25.3	3.9 26.7	27.3	0.2 26.7	5.9 24.6	0.5 27.2	0.2 26.1	4.2	5.9 15.6	5.2 16.7	2.7 13.6	
lce	Sm	3.81	23.3 4 47	4 92	7 21	20.7 4 71	3 44	4 93	4.62	4 52	4 26	4 11	3.96	
Tra	Eu	1.23	1.41	1.49	1.52	1.32	1.21	1.35	1.29	1.61	1.26	1.34	1.26	
	Gd	5.41	5.95	5.73	6.62	5.51	4.32	5.63	5.19	5.36	4.51	5.56	5.34	
	Tb	1.12	1.17	1.39	1.57	1.21	1.14	1.35	1.19	1.19	0.98	1.28	1.01	
	Dy	5.31	5.46	4.58	6.53	5.63	5.09	5.68	5.53	5.38	4.93	6.39	5.34	
	Но	1.1	1.3	1.5	1.6	1.4	1.1	1.5	1.4	1.2	1.1	1.1	1.0	
	Er	3.82	4.02	4.11	4.28	4.21	4.19	4.25	4.22	3.41	3.21	4.26	3.91	
	Tm	0.42	0.48	0.59	0.63	0.45	0.32	0.51	0.55	0.61	0.51	0.48	0.41	
	Yb	3.6	4.0	4.1	4.6	2.8	2.6	3.5	2.6	3.5	3.3	3.1	3.1	
	Eu/Eu*	0.41	0.52	0.39	0.65	0.33	0.42	0.03	0.31	0.00	0.91	0.49	0.41	
	CeN/YhN	2.01	2.54	2.13	1.96	3.26	3 01	2 73	2 53	1 42	1 36	1 21	116	
	LaN/YbN	1.58	1.57	1.60	1.72	6.67	5.71	5.56	6.23	2.72	2.68	2.69	2.04	
	GdN/YbN	1.28	1.23	1.12	1.17	1.62	1.34	1.31	1.59	1.23	1.11	1.44	1.22	
	Mg#	0.63	0.65	0.64	0.67	0.43	0.69	0.78	0.25	0.41	0.36	0.78	0.47	

Çizelge 2. Gözdağ Formasyonu'ndaki volkanik kayaçların majör (ağırlıkça %), iz (ppm) ve nadir toprak elementleri (REE) (ppm) tüm-kaya jeokimyasal analizlerinin sonuçları.

LOI (loss on ignition) was determined gravimetrically on separate aliquots

 $Fe_2O_3^T = total-Fe$. assumed as Fe^{3+}



Figure 7. Thin section micrographs of volcanic rocks in the Gözdağ Formation. (a) The fine-grained tuff with marked positions of vitroclastic clasts. (b) The fine-grained tuff contains many tiny fragments of volcanic glass exhibiting shard-shapes. (c) The coarse-grained tuff contains abundant plagioclase (gnawed), quartz, amphiboles and opaque minerals in groundmass forming from vitroclasts. (d) Plagioclase (gnawed) and amphibole phenocrysts are observed in the coarse-grained tuff. (e-f) Pyroxene, amphibole and plagioclase phenocrysts in the dacite lavas. Amp-amphibole, Opq-opaque minerals, Pl-plagioclase, Px-pyroxene.

Şekil 7. Gözdağ Formasyonundaki volkanik kayaçların ince kesit mikrofotoğrafları. (a) Vitroklastik kırıntıların belirgin konumlarına sahip ince-taneli tüf. (b) İnce-taneli tüf kırık şekiller sergileyen çok sayıda küçük volkanik cam kırıntıları içerir. (c) Kaba-taneli tüf, vitroklastlardan oluşan hamur içinde bol miktarda plajiyoklaz (kemirilmiş), kuvars, amfiboller ve opak mineraller içerir. (d) Kaba-taneli tüflerde plajiyoklaz (kemirilmiş) ve amfibol fenokristalleri gözlenir. (e-f) Dasit lavlarında piroksen, amfibol ve plajiyoklaz fenokristalleri. Amp-amfibol, Opq-opak mineraller, Pl-plajiyoklaz, Px-piroksen.



Figure 8. Classification diagrams of the volcanic rocks in the Gözdağ Formation. (a) Nb/Y–Zr/Ti diagram after Pearce (1996); (b) Co–T diagram after Hastie et al. (2007); (c) Zr - Nbn/Zrn diagram after Thieblemont and Tegyey (1994); (d) Primitive mantle-normalized multi-element diagrams after Sun and McDonough (1989); (e) chondrite-normalized REE diagrams after McDonough and Sun (1995). The compositions of the representative samples of E-MORB and WPB are Sun and McDonough (1989). The geochemical data of the Late Ordovician intrusive rocks were taken from Şen (2023a). E-MORB, enriched mid-ocean ridge basalt; WPE, within-plate basalt. B: Basalt; BA/A: basaltic andesite and andesite; D/R: dacite and rhyolite; IAT: island-arc tholeiite; CA: calc-alkaline; H-K: high-K series.

Şekil 8. Gözdağ Formasyonu içindeki volkanik kayaçların sınıflandırma diyagramları. **(a)** Pearce (1996)'den sonra Nb/Y–Zr/Ti diyagramı; **(b)** Hastie vd., (2007)' den Co–T diyagramı; **(c)** Thieblemont ve Tegyey (1994)'den sonra Zr - Nbn/Zrn diyagramı; **(d)** Sun ve McDonough (1989)'dan sonra primitif manto-normalize çoklu-element diyagramı; **(e)** McDonough and Sun (1995)'den sonra kondrit-normalize REE diyagramı. E-MORB ve WPB' nin temsili örneklerinin bileşimleri Sun ve McDonough (1989)'dan alınmıştır. Geç Ordovisiyen sokulum kayaçlarının jeokimyasal verileri Şen (2023a)'dan alınmıştır. E-MORB. zenginleştirilmiş okyanus ortası sırt bazalt; WPE, plaka içi bazalt. B: Bazalt; BA/A: bazaltik andezit ve andezit; D/R: dasit ve riyolit; IAT: ada yayı toleyiti; CA: kalk-alkalin; H-K: yüksek-K serisi.

The lavas (L) have porphyritic, vitrophyric and aphanitic textures. Pyroxene, amphibole, plagioclase, alkali feldspar and quartz are the main phenocrysts. Accessory minerals are apatite and zircon. Pyroxenes and amphiboles have euhedral to subhedral crystal forms. Plagioclases have polysynthetic twinning. They are andesine (An₄₄₋ ₃₆) in Çekmeköy and Dudullu, and oligoclase (An₂₄₋₁₆), in Gözdağ, respectively. Alkali feldspars have perthitic texture defining an intergrowth of two feldspars. Quartzes have anhedral forms (Figure 7e & f).

The fine- and coarse-grained tuffs (T_1-T_2) and the lavas (L) are affected entirely by severe hydrothermal alteration, including saussuritization, chloritization, kaolinization and sericitization (Table 1).

Geochemistry

The geochemical database contains analyses of a total of 12 representative samples collected from various stratigraphic levels of the Gözdağ Formation (see Figs. 4-5 for sample locations). The majority of analyzed samples are tuffs (8 samples), and the others are represented by lavas (4 samples). I present the geochemical data in Table 2, dividing it into three volcanic series, together with the locations of each sample in terms of the UTM coordination system. I plotted the data in the diagrams in this chapter based on the petrographic division.

All samples have high LOI values, ranging from 7.1 to 10.9, due to high hydrothermal alteration (Table 2). Therefore, diagrams with trace elements were used to determine the classification and tectonic discrimination of volcanic rocks in the Gözdağ Formation.

The analyzed samples fall into the calcalkaline field in the Nb/Y - Zr/Ti diagram of Pearce (1996) and the fine-grained tuffs fall into the High-K calc-alkaline field in the Th/Co diagram of Hastie et al. (2007). In addition, the lava samples plotted display a narrow compositional range from dacite to andesite, falling predominantly in the calc-alkaline field (Figure 8b). The fine-grained tuffs and lavas plot into a collision setting and the coarse-grained tuffs fall into a volcanic arc setting in the Zr - Nbn/Zrn diagram of Thieblemont and Tegyey (1994) (Figure 8c).

On the primitive mantle-normalized element concentration diagram of Sun and McDonough (1989), the fine-grained tuffs (T_1) show negative anomalies in Ba, Nb, La, Sr and Ti and positive anomalies in Rb, Th, K, Pb and Zr. The coarsegrained tuffs (T_2) display negative anomalies in Ba, Nb, Ce, Sr and Ti and positive anomalies in U, K, Pb, Zr and Y. The lavas (L) show negative anomalies in Ba, Nb, Ce, Pr, Nd and Ti and positive anomalies in U, K, Pb, Sr, Zr and Y. They contain subduction components (Figure 8d).

The volcanic rocks in the Gözdağ Formation have dissimilar REE patterns in the chondritenormalized REE diagrams of McDonough and Sun (1995) (Figure 8e). The coarse-grained tuffs (T_{2}) and lavas (L) show a prominent enrichment in LREEs (those from La to Nd), MREEs (from Sm to Ho), and HREEs (from Er to Lu); on the other hand, the fine-grained tuffs (T_1) display a prominent depletion in LREEs. The fine-grained tuffs (T₁) show negative anomalies in Eu, Dy and Tm and positive anomalies in Pr, Tb, Er and Yb. The coarse-grained tuffs (T_2) demonstrate negative anomalies in Ce, Eu, Dy and Tm and positive anomalies in Pr, Tb and Er. The lavas (L) exhibit negative anomalies in Eu and Tm and positive anomalies in Tb. Negative Eu anomalies (Eu/Eu* = 0.67-0.96) in the T₁, T₂, and L are related to negative Ba and Nb anomalies, representing crystallization of plagioclase and apatite. Chondrite (C1)-normalized REE patterns of the T₂ display weak fractionation ($Ce_N/Yb_N =$ 2.53-3.26); however, the T_1 and L do not show Ce anomalies $(Ce_N/Yb_N = 1.96-2.54 \text{ for } T_1 \text{ and}$ 1.16-1.42 for L) (Table 2) (Figure 8e). La_N/Yb_N

and Gd_N/Yb_N ratios of the T_1 and L range from 1.57 to 2.72 and from 1.17 to 1.49; however, the same values of the T_1 range from 5.56 to 6.67 and from 1.31 to 1.62. Mg# values range from 0.25 to 0.78 (Table 2). Their formation is also related to fractionation by differential setting.

DISCUSSION

Petrography of volcanic rocks in the Gözdağ Formation

The volcanic rocks in the various stratigraphic levels of the Gözdağ Formation are divided into three petrographically different groups (Table 1) (Figure 7). They include biotite-bearing finegrained tuffs in mainly matrix-forming vitroclastic clasts (T₁), amphibole-bearing coarse-grained tuffs in generally matrix-composing mineral fragments (T₂), and pyroxene-bearing lavas in groundmassforming microclines (L). There are distinct mineral paragenesis differences in the pyroclastic rocks, including biotite- and amphibole-bearing tuffs. This shows that the tuffs are different from each other. Plagioclases in the pyroxene-bearing lavas are and esine $(\mathrm{An}_{_{44\text{--}36}})$ and oligoclase $(\mathrm{An}_{_{24\text{--}}})$ 16). Hence, the lavas are composed of andesite and dacite. This causes the lavas to be divided into two subgroups among themselves. Therefore, the volcanic rocks in the different stratigraphic strata differ petrographically from each other (Figure 7).

Age of volcanic rocks in the Gözdağ Formation

The sedimentation age of the Gözdağ Formation is Middle Ordovician-Late Silurian (Sayar and Cocks, 2013). The lower age of the unit comes from the chamosite strata, which is the first fossiliferous layer of the İT and the age of chamosite strata is Darriwilian-Sandbian (Arıç, 1955; Sayar, 1964, 1970, 1984). Its upper age comes from greywacke, which are part of the 'Halysites Graywackes' as firstly defined by Paeckelmann (1938), and the age of the greywackes is Aeronian-Telychian (Sayar, 1964, 1975). The fine-grained tuffs are ~120

meters above the chamosite level of Darriwilian-Sandbian age, and they are ~70 meters below the laminated limestones of Katian age (Sayar and Cocks, 2013) (Figure 6a). According to stratigraphic levels, the age of the fine-grained tuffs (T₁) is Sandbian. The coarse-grained tuffs are intercalated with Upper Katian laminated limestones (Sayar, 1984) Figure 6c). Thus, the age of the coarse-grained tuffs (T_2) is Katian, too. The lavas are ~45 meters above the coarse-grained tuffs (Figure 6a). The lavas are conformably covered by fine-grained sandstone alternating with laminated limestone (Figure 5). The laminated limestone is represented by the Ordovician-Silurian transition in the IT (Dr. M. Cemal Göncüoğlu, 2016; personal communication). Thus, the age of the lavas (L) is Hirnantian.

All in all, the fine- and coarse-grained tuffs (T_1 and T_2) and lavas (L) in the Late Ordovician strata of the Gözdağ Formation in the İT are Sandbian, Katian and Hirnantian, respectively.

Tectonic settings of the Late Ordovician volcanic rocks in the Gözdağ Formation

The fine-grained tuffs (T_1) have high potassium calc-alkaline, and the coarse-grained tuffs and lavas $(T_2 \text{ and } L)$ have a calc-alkaline character according to the diagrams of Pearce (1996) and Hastie et al. (2007) (Figure 8a, b). They are devoid of clear with-in plate components, as deduced by the presence of noticeable negative Nb anomalies, and they have subduction components based on the diagram of Sun and McDonough (1989) (Figure 8d-e). The fine-grained tuffs (T_1) and lavas (L) are associated with a syncollisional setting, whereas the coarse-grained tuffs (T_2) are related to a volcanic arc setting according to the diagram of Thieblemont and Tegyey (1994) (Figure 8c).

The volcanic rocks exhibit opposed patterns in the chondrite-normalized REE diagram of McDonough and Sun (1995) (Figure 8e). The finegrained tuffs (T_1) show a considerable depletion in LREEs; however, the enrichment is obvious in others. Another difference is that there is a weak LREE enrichment in the coarse-grained tuffs (T_2) (Ce_N/Yb_N = 2.53-3.26) while no such anomaly is detected in the lavas (L). This indicates that they may have formed in different geodynamic settings within the Gözdağ Formation during the Late Ordovician.

Geodynamic implications of the Late Ordovician volcanic rocks in the Gözdağ Formation and global events during the Ordovician

The fine- and coarse-grained tuffs $(T_1 \text{ and } T_2)$ and lavas (L) with Late Ordovician ages represent the first record of syncollisional-related Sandbian, arc-related Katian and syncollisional-related Hirnantian volcanism in the İZTU belonging to Far East Avalonia. These volcanic rocks in the Gözdağ Formation of the İT are not associated with a possible rifting event because volcanic rocks formed during a rifting setting show enrichment in Nb relative to Ce. Besides, the riftbound volcanic rocks display negative anomalies in the Th, K and positive anomalies Ba, Nb (Sun and McDonough, 1989) (Figure 8d). On the opposite, Late Ordovician volcanics in the Gözdağ Formation rocks exhibit depletion in Nb relative to Ce and commonly show negative anomalies in Nb and Ti and positive anomalies in K, Pb and Zr (Figure 8d). For this reason, they are considered as being derived from geodynamic settings whose geodynamic origin is volcanic arcs during the Late Ordovician.

Considering the geodynamic meaning of the Sandbian fine-grained tuffs (T_1) , it is understood that it is a rock group that contradicts the geological history of Avalonia, in as far as there were two different collisional events in its geological evolution. These include (a) softdocking between Avalonia and Baltica during the latest Late Ordovician (c. 445-443 Ma; Cocks and Fortey, 2009; Linnemann et al., 2012) and (b) the collision of Avalonia + Baltica and Laurentia during the Late Silurian-Early Devonian (c. 425-410 Ma; Cocks and Fortey, 2009). In addition, Carolina-Ganderia collided with Laurentia during the latest Late Ordovician (Hibbard et al., 2007). Thus, it is clear that there were no collisional events in Avalonia and Carolina-Ganderia during the Sandbian. Looking at the geological history of Cadomia derived from NW Africa Craton, it is known that Cadomia separated from West Gondwana-land during the Early to Middle Ordovician and changed to a passive continental margin during the Middle-Late Ordovician (Linnemann et al., 2007 after Landing et al. 2019).

Sandbian fine-grained The tuffs (or K-bentonites) are observed in Laurentia, Baltica and Carolina-Ganderia (Scotese and McKerrow, 1991) (Figure 1). They are defined as Millbrig and Deicke bentonites in Laurentia (c. 456-453 Ma; Bergström et al., 1995; Adams et al., 1960; Kunk et al., 1985; Samson et al., 1989; Tucker et al., 1990; Tucker, 1992; Tucker and McKerrow, 1995; Dennis et al., 2012; Zagorevski et al., 2008) and they are also known as Kinnekulle bentonites in Baltica (c. 456-453 Ma; Compston and Williams, 1992; Tucker, 1992; Tucker and McKerrow, 1995; Kolata et al., 1996; Bauert et al., 2014). The Millbrig-Deicke-Kinnekulle bentonites were deposited in a shallow marine depocenter in Laurentia, Carolina-Ganderia and Baltica as a result of multiple Plinian-type eruptions during the last phase of the Taconic orogeny formed during the earliest Late Ordovician between the Piedmont Terrane and Laurentia (c. 458-450 Ma; Huff et al., 1992; Haynes et al., 1995; Huff, 2008; Bauert et al., 2014) (Figure 9a). These multiple Plinian-type eruptions are the cause of global warming in the Katian time in Gondwana-land and Cadomia prior to the Hirnantian glaciation (Boda event; Fortey and Cocks, 2005). These Plinian-type eruptions in the last phase of the Taconic orogeny are the cause of the onset of the Hirnantian glacial period in Gondwana and Cadomia after global warming and the Late Ordovician mass extinction that occurred during the Hirnantian time (Huff et al., 1992; Fortey and Cocks, 2005; Bauert et al., 2014). All in all, the fine-grained tuffs (T1) are part of the Millbrig-Deicke-Kinnekulle bentonites extending to the southeast in the Iapetus and Rheic Ocean paleogeography (Figure 9a). The presence of these bentonites, which are accepted as the cause of the Hirnantian glacial period, is important in the IZTU as they are the first bentonites detected in Avalonia.

When the IZTU is divided into two sectors along the north and south axis, the north part represents the Rheic Ocean (back-arc section) and the south side stands for the Iapetus and Teissevre-Tornquist Ocean (magmatic arc section) during the Ediacaran-Ordovician (Şen, 2021a, Şen, 2023a). The continental margin successions of the Rheic Ocean were deposited on the north side and arc magmatism occurred on the south side from the Middle Ediacaran to the Late Cambrian (c. 590-500 Ma; Sen, 2021a). In the southern part of the IZTU, the Teisseyre-Tornquist Ocean, the east branch of Iapetus, continued to subduct under the Far East Avalonian terranes during the Early to Late Ordovician (c. 490-445 Ma; Şen, 2023a). The Middle-Late Ordovician arc magmatism in the Armutlu peninsula of the IT (c. 464-446 Ma; Okay et al., 2008 after Sen, 2023a) and the Early Ordovician arc magmatism in the Sünnice mountain of the ZT (c. 484 Ma; Sen, 2023a) represent Ordovician arc-related magmatism that took place during the consumption of the Teisseyre-Tornquist Ocean. Besides, the chondrite-normalized REE pattern of the Katian coarse-grained tuffs (T_2) is represented by LREE enrichment ($Ce_N/Yb_N = 2.53-3.26$) (Table 2). The pattern of the Late Ordovician magmatic body in the Armutlu peninsula (c. 446 Ma; Okay et al., 2008 after Sen, 2023a) is compatible with those of the Katian coarse-grained tuffs (Figure 8e). Therefore, it shows that their origin is arc magmatism in the Armutlu peninsula (Figure 9b).



Figure 9. Late Ordovician paleogeography showing the location of the İZTU (modified from Scotese and McKerrow, 1991; Torsvik and Rehnström, 2003; Cocks and Torsvik, 2005). C-G: Carolina-Ganderia, EA: East Avalonia, FEA: Far East Avalonia, İZTU: İstanbul-Zonguldak Tectonic Unit, L: Lavas. PT: Piedmont Terrane, T-TO: Teisseyre-Tornquist Ocean, T-TO S: Teisseyre-Tornquist Ocean Suture, T_1 : fine-grained tuffs, T_2 : coarse-grained tuffs, WA: West Avalonia.

Şekil 9. İZTU'nun yerini gösteren geç Ordovisiyen paleocoğrafyası (Scotese ve McKerrow. 1991; Torsvik ve Rehnström, 2003; Cocks ve Torsvik, 2005'ten değiştirilmiştir). C-G: Carolina-Ganderia, EA: Doğu Avalonya, FEA: Uzak Doğu Avalonya, İZTU: İstanbul-Zonguldak Tektonik Birliği, L: Lavlar, PT: Piedmont Birliği, T-TO: Teisseyre-Tornquist Okyanusu, T-TO S: Teisseyre -Tornquist Okyanus Süturu, T_1 : ince-taneli tüfler, T_2 : kaba-taneli tüfler, WA: Batı Avalonya.

The Hirnantian andesite-dacite lavas (L) show negative anomalies in Eu and Tm and positive anomalies in Tb, according to the diagram of McDonough and Sun (1995). Their pattern is compatible with those of the Hirnantian syncollisional andesite-dacite dykes intruding in the northern and southern sections of the İZTU (c. 444-443 Ma; Sen, 2023a) (Figure 8e). There is petrographic data to support it. The Hirnantian andesite-dacite lavas in the Gözdağ Formation of the IT and the Hirnantian andesite-dacite dykes intruding the pre-Upper Ordovician rocks in the İZTU (c. 444-443 Ma; Şen, 2023a) have pyroxenebearing volcanic rocks. Thus, the Hirnantian andesite-dacite dykes intruding on the İZTU (Sen, 2023a) were feeder dykes of the lavas (L) in the Gözdağ Formation. The latest Late Ordovician collisional event in the İZTU stands for the softdocking between Avalonia and Baltica, just as reported by Cocks and Fortey (2009). Some data sets support it. There are no unconformities in the Ordovician-Silurian transition in the İZTU, which is the presence of Baltican faunas in the post-Ordovician beds (Sayar and Cocks, 2013), just as in the other parts of Avalonia, as stated by Cocks and Fortey (2009). The Late Ordovician syncollisional intrusive rocks intrude into the arc-part and back-arc-part, just as in the other parts of Avalonia as stated by Linnemann et al (2012). In other words, the Hirnantian lavas (L) together with the Hirnantian dykes represent the soft-docking of Avalonia and Baltica, known as the pre-Caledonian orogeny, after the Teisseyre-Tornquist Ocean was consumed during the Early to Late Ordovician (Figure 1, 9b-c).

Spahić et al. (2023) reported that the Late Ordovician arc magmatism and volcanism in the Carpathian-Balkan sector of the Serbo-Macedonian Massif are related to the geodynamic events in the north Gondwana, known as the Cenerian (Sardic) event. However, the Getic Zone of the Serbo-Macedonian Massif was an intra-oceanic basin of the Ediacaran age, known as the Kraishte Terrane, and the Serbo-Macedonian Massif and Rhodope Massif were parts of an accretionary prism of the Ediacaran age, called the Ograzhdenian Complex (Zagorchev et al., 2015; Tunç et al., 2012; Yiğitbaş and Tunç, 2020; Şen, 2021a). The Ograzhdenian Complex attached to Far East Avalonia during the Ediacaran and the Kraishte Terrane collided with Far East Avalonia during the latest Late Ediacaran to the earliest Early Cambrian (Şen 2021a). Thus, the Cambrian-Ordovician arc-related magmatism and volcanism in the Carpathian-Balkan sector of the Serbo-Macedonian Massif are related to the consumption of the Teisseyre-Tornquist Ocean in Far East Avalonia (Şen, 2023a).

CONCLUSIONS

The volcanic rocks at various stratigraphic levels of the Gözdağ Formation are fine- and coarse-grained tuffs and lavas. According to the stratigraphic positions of the Late Ordovician volcanic rocks, the fine-and coarse-grained tuffs $(T_1 \text{ and } T_2)$ are Sandbian and Katian ages, and the lavas (L) are Hirnantian ages. Geochemically, thefine grained tuffs (T_1) have High-K calc-alkaline affinity and the coarse-grained tuffs and lavas $(T_2$ and L) have a calc-alkaline character. They are devoid of obvious with-in plate components, as deduced by the presence of noticeable negative Nb anomalies, and they have subduction signatures.

In conjunction with data from the literature, the Sandbian fine-grained tuffs (T1) were deposited in a lagoonal depocenter in the IZTU as a result of multiple Plinian-type eruptions during the last phase of the Taconic orogeny, which formed between Piedmont Terrane and Laurentia during the earliest Late Ordovician. The Katian coarsegrained tuffs (T2) were the products of volcanic activities that occurred in the arc settings during the last stage of the depletion of the Teisseyre-Tornquist Ocean lying between Avalonia and Baltica. The Hirnantian lavas (L) were formed by flowing in a lagoonal depocenter of the IZTU during the soft docking of Avalonia and Baltica, known as the pre-Caledonian orogeny.

GENİŞLETİLMİŞ ÖZET

İstanbul-Zonguldak Tektonik Birliği, Avalonya-Karolina'nın en doğudaki parçası olarak kabul edilir ve Uzak Doğu Avalonya'yı temsil eder. Stratigrafisi Üst Ediyakaran'dan Üst Karbonifer'e kadar kesikli sedimantasyon ile karakterize edilir (Şen, 2021a, b; Şen, 2023a). Bu kıtasal bloğun İstanbul Birliği olarak bilinen batı kesiminde Gözdağ Formasyonu, Orta Ordovisiyen-Alt Silüriyen yaşlı şeyl-kumtaşı kireçtaşından oluşan lagünel tortul kayaçlarla temsil edilir (Özgül, 2012).

Ordovisiyen zamanı, antik mavi gezegendeki kaotik sürecleri temsil eder. Cünkü Ordovisiven döneminde riftleşme süreçleri ile birlikte birçok orojenez meydana gelmiştir. Antik Ordovisyen dünyasında bu olaylar olurken, Ordovisiyen buzullaşması ve kitlesel yok oluşlar aynı anda gerçekleşmiştir. Ordovisiyen antik dünyasındaki bu olaylara katkı sağlamak amacıyla, İstanbul-Zonguldak Tektonik Birliği' nin batı kesimini oluşturan İstanbul Birliği' ndeki Gözdağ Formasyonu üzerinde durulmuştur. Birim ağırlıklı olarak bir lagün ortamında çökelmiş şeyl, kumtaşı ve grovak ardalanmasından oluşur (Sayar ve Cocks, 2013). Birimin birbirinden farklı Üst Ordovisiyen tabakalarında üç farklı volkanik kayaç tespit edilip haritalanmıştır. Bu volkanik kayaçlar stratigrafik konumları ve petrografik özelliklerine göre ince- ve kaba-taneli tüfler (T, ve T,) ve lavlar (L) olmak üzere üç gruba ayrılır.

İnce-taneli tüfler (T_1) şamozit tabakalarının yaklaşık 120 metre üstündedir. 50-60 cm kalınlığındaki açık kahverenkli kumtaşı ve 5-20 cm kalınlığındaki koyu kahverenkli silttaşı ardalanmasından oluşurlar. Yaklaşık 3 metrelik kalınlıkta gözlenirler. Kaba-taneli tüfler (T_2) incetaneli tüflerin yaklaşık 70 metre üstündedir. 3-4 cm kalınlığındaki açık kahverenkli kumtaşı ve mavi renkli milimetre ölçekli paralel laminalı 1-2 cm tabakalı ardalanmalı kireçtaşı içerirler. Yaklaşık 5 metrelik kalınlıkta gözlenirler. Lavlar (L) kabataneli tüflerin yaklaşık 45 metre üstünde ve ince bant şeklinde yayılımı olan limanlı kireçtaşlarının

yaklaşık 2 metre altındadır. Yeşilimsi kahverengi ve kirli beyaz renkli, 7-8 metre kalınlığında tabakalı, yeşil kumtaşı ve 30-40 cm kalınlığında grovak ardalanmasından oluşurlar. Yaklaşık 8 metre kalınlıkta gözlenirler. Petrografik olarak incelendiğinde, ince-taneli tüfler (T_1) piroklastik dokuya sahiptir. Biyotit, plajiyoklaz, parçalanmış kuvars ve alkali feldspat fenokristallerinden oluşur, ve mineral parçaları ile vitroklastik kırıntılılar matriksi oluşturur. Kaba-taneli tüfler (T_{\star}) piroklastik dokuya sahiptir. Başlıca kayaç oluşturan mineraller amfibol, plajiyoklaz, alkali feldispat ve kuvarstır ve mineral parçaları matriksi oluşturur. Lavlar (L) porfirik, vitrofirik ve afanitik dokuludur. Piroksen, amfibol, plajiyoklaz, alkali feldspat ve kuvars başlıca fenokristallerdir ve hamur mikrolinlerden oluşur. Üst Ordovisiyen yaşlı volkanik kayaçların stratigrafik konumlarına göre, ince- ve kaba- taneli tüfler $(T_1 ve T_2)$ Sandbiyen ve Katiyen, lavlar (L) ise Hirnansiyen vaşlıdır. Jeokimyasal olarak, ince-taneli tüfler (T₁) yüksek potasyumlu kalk-alkali, kaba-taneli tüfler ve lavlar (T, ve L) kalk-alkali karaktere sahiptir. Fark edilebilir negatif Nb anomalilerinin varlığından anlaşıldığı gibi, bariz plaka içi bileşenlerden yoksundurlar ve yitim imzalarına sahiptirler. İnce-taneli tüfler ile lavlar $(T_1 ve T_2)$ çarpışma ile eş-zamanlı bir tektonik ortamda oluşurken kaba-taneli-tüfler (T,) volkanik yay ortamında oluşmuştur. Gözdağ Formasyonu' nun Üst Ordovisiyen tabakalarında gözlenen bu volkanik kayaçlar kondrite göre normalize edilmiş REE diyagramında zıt desenler sergiler. İncetaneli tüfler (T_i) , LREE' lerde önemli bir azalma gösterir; ancak, diğer volkanik kayaçlarda zenginleşme açıktır. Diğer bir fark ise kaba-taneli tüflerde $(T_{,})$ zayıf bir LREE zenginleşmesi varken $(Ce_{N}Yb_{N} = 2.53-3.26)$ lavlarda (L) böyle bir anomali saptanmaz. Bu da bu volkanik kayaçların geç Ordovisiyen sırasında Gözdağ Formasyonu içinde farklı jeodinamik ortamlarda oluşmuş olabileceklerini göstermektedir.

Literatürden elde edilen verilerle bağlantılı olarak, Sandbiyen ince-taneli tüfler (T_1) en erken geç Ordovisiyen' de Piedmont Terrane ile

Lavrensiya arasında meydana gelen Takonik orojenezi sırasında bir lagün ortamında çökelmiştir. İstanbul-Zonguldak Tektonik Birliği' nde çökelen Sandbiyen yaşlı ince-taneli tüflerin global ölçekte eşleniği Lavrensiya' da Millbrig-Deicke bentonitleri ve Baltika' da ise Kinnekulle bentonitleridir (c. 456-453 My; Bergström vd., 1995; Adams vd., 1960; Kunk vd., 1985; Samson vd., 1989; Tucker vd., 1990; Compston ve Williams, 1992; Tucker, 1992; Tucker ve McKerrow, 1995; Kolata vd., 1996; Dennis vd., 2012; Zagorevski vd., 2008; Bauert vd., 2014). Takonik orojenezinin son evresi sırasında çoklu pliniyentipi patlamaların bir sonucu olarak, Hirnansiyen buzullaşması öncesi Gondwana ve Minoya ile birlikte Kadomiya'daki Katiyen zamanında küresel ısınmanın (Cocks ve Torsvik, 2005; Boda olayı) nedenidir. Küresel ısınmanın ardından Gondwana ve Minoya-Kadomiya' da Hirnansiyen buzul çağının başlamasına ve Hirnansiyen zamanında meydana gelen Geç Ordovisiyen kitlesel yok oluşuna neden olmuştur (Huff et al., 1992; Fortey and Cocks, 2005; Bauert et al., 2014). Hirnansiyen buzul çağının nedeni olarak kabul edilen bu kayaçların İstanbul-Zonguldak Tektonik Birliği' ndeki varlığı Avalonya' da tespit edilen ilk bentonitler olması nedeniyle önemlidir.

Avalonya ile Baltika arasında uzanan Teisseyre-Tornquist Okyanusu, Ordovisiyen' in başından itibaren Avalonya' nın altına dalarak *yitmeye* başlamıştır (Şen, 2023a). Katiyen kaba-taneli tüfler (T,), Teisseyre-Tornquist Okyanusu' nun tüketilmesinin son aşaması sırasında volkanik yayla ilgili ortamlarda meydana gelen volkanlardan gelerek İstanbul-Zonguldak Tektonik Birliği'nin lagünel ortamında çökelmiştir. Ediyakaran-Ordovisiyen dönemleri boyunca İstanbul-Zonguldak Tektonik Birliği kuzey-güney eksen boyunca avrılır, kuzey bölümü Rheic Okyanusu'nun kıta-kenarı istiflerini ve güney bölüm ise Iapetus ve Teisseyre-Tornquist Okyanusu ile ilişkili magmatik yay bölümünü temsil eder (Şen, 2021a, 2023a). Bu kıtasal bloğun güney tarafında Ordovisiyen yay magmatizması tanımlanır (Şen, 2023a). Katiyen kaba-taneli tüflerinin (T_2) kondrite göre normalize REE paterni, LREE zenginleşmesi ile temsil edilmektedir (Ce_N/ Yb_N = 2.53-3.26). Güney kuşaktaki Ordovisiyen yaşlı sokulumlarının paterni Katiyen kaba-taneli tüfleriyle (T₂) uyumludur. Dolayısıyla, Katiyen kaba-taneli tüflerin (T₂) kaynağının İstanbul-Zonguldak Tektonik Birliği'nin güney kuşağındaki Ordovisiyen yay magmatizması olduğunu gösterir.

Hirnansiyen lavları (L) Avalonya ve Baltika'nın yumuşak yanaşması sırasında İstanbul-Zonguldak Tektonik Birliği'nin bir lagün ortamında akmıstır. Hirnansiven lavları (L) andezit ve dasit bilesimindedir, ve Eu ve Tm'de negatif, Tb' de pozitif anomaliler gösterir. İstanbul-Zonguldak Tektonik Birliği'nin güney ve kuzey kuşağını kesen çarpışma ile eş-yaşlı Hirnansiyen andezit-dasit sokulumları ile uyumludur. Hirnansiyen lavları ile daykları aynı zamanda piroksen içerir (Şen, 2023a). Dolayısıyla, İstanbul-Zonguldak Tektonik Birliği'nin Üst Ordovisven öncesi tabakalarını kesen Hirnansiyen daykları, Gözdağ Formasyonu' nun Ordovisven-Silürven gecisindeki Hirnansiven lavlarının besleyici bacaları olduğunu gösterir. Hirnansiyen lavları (L), Hirnansiyen dayklarıyla birlikte Teisseyre-Tornquist Okyanusu' nun geç Ordovisiyen sırasında tüketildikten sonra Kaledoniven öncesi orojenezi olarak bilinen Avalonya ve Baltika' nın yumuşak yanaşmasını temsil eder.

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