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Mineralogical and geochemical characterisation of granite columns from the ancient city of Tyana (Niğde, Türkiye) and implications for their origin

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1. Introduction

Natural stone is one of the main materials used in ancient buildings due to its durability and aesthetic properties. Natural stones such as marble, limestone, and granite were favored in public spaces such as temples and colonnades, especially in monumental buildings [1]. The natural stones used in historic buildings provided aesthetics and functionality, while simultaneously allowing them to resist environmental conditions. Identifying the sources of natural stone also plays an important role in the conservation and restoration of built heritage and monuments [2-8]. Among these natural stones, granite is an important building material with excellent physical and chemical durability and is widely used for various purposes, especially obelisks. Granite columns used in ancient architecture were not only a decorative element but also formed an important structural component that ensured the strength of built structures. Granite has played a critical role in the

Abstract

In this article, the mineralogical, petrographic and geochemical properties of the granite columns, which are significant architectural elements in the ancient city of Tyana in the Cappadocia region, are documented and their origins are inferred. Tyana granite columns have porphyro-aphanitic texture and are characterized by mega crystals. The main mineral assemblage in the the granite columns consists of K-feldspar, quartz, plagioclase, biotite, amphibole and accessoy titanite, zircon and opaque minerals. XRD analysis supports the primary mineral assemblage. CRS (Confocal Raman Spectroskopy) studies also revealed that the plagioclase is andesine and amphibolite is actinolite in composition. In addition, geochemical analyses revealed that the granite columns are calc-alkali and granodiorite in composition. In the tectonic evaluation, the granite samples are located in the area of volcanic arc granitoids. According to all analysis results, the Tyana granite columns are compatible with the Horoz granitoids. All the above features will be an important step for the conservation and restoration of future ancient structures.

preservation of many archaeological structures due to its long-term resistance to abrasion, climatic factors, and biological degradation [3, 9, 10].

Granitic rocks are some of the most important raw materials widely used throughout the Egyptian, Greek, Roman, Byzantine, and Ottoman eras for various purposes, including for obelisks, statues, temples, baths, sarcophagi, columns, and decorative building materials. Today, as in the past, many people (except geologists) use the term "granite" to refer to fully crystalline rocks of different colors. For this reason, many granitic rocks, especially those used in historic buildings, have been classified as granite without adequate petrographic research; however, geoscientists use the term "granite" without microscopic examination. Granite is composed primarily of K-feldspar (orthoclase and microcline), plagioclase (albite, oligoclase, and andesine), quartz, biotite, and amphibole. In recent years, multiple analytical approaches have been applied to identify the scientific characteristics and origins of granitic rocks of

uncertain provenance [11–19]. Studying the mineralogical, petrographic, and chemical properties of granite columns provides important insights into the sources, processing techniques, and transportation methods of the stone used in the periods when these structures were built.

The granite columns selected as the subject of this study are situated in the ancient city of Tyana. The ancient city of Tyana is located in the Cappadocia region in Turkey and was considered an essential trade center during the Roman Empire. The granite columns in this region stand are an important architectural feature in ancient buildings. Despite various studies on granite columns in many ancient city to date [20-22] the provenance of the Tyana granites remains poorly understood. To address this issue, in this article Tyana granite columns were analyzed in detail using optical microscopy, X-ray diffraction (XRD), X-ray fluorescence (XRF), and confocal Raman spectroscopy (CRS) techniques to reveal their mineralogical and petrographic properties, crystallographic structures, and chemical compositions. Mineralogical and petrographic investigations of the Tyana granite columns have indicated their potential relationship with the region's Horoz Granitoid and Üçkapılı Granite rocks. These comparisons can provide important clues regarding the origin of the columns. Here, the igneous processes affecting the formation of the granite columns were interpreted and compared with potential granite sources in the region. Understanding this relationship will help elucidate the commercial and architectural context of Tvana.

2. History of Tyana Ancient City

The ancient city of Tyana, an important settlement during the Hittite, Roman, and Byzantine eras, was built in the town of Kemerhisar in Niğde (Figure 1). Tyana, which is approximately 23 km from Niğde city center, is located approximately 5 km to the southeast of Bor district. In ancient times, its strategic location in the Cappadocia Region, connecting Cilicia and Cappadocia, led to the conquest of the city multiple times by different civilizations. Throughout history, Tyana was variously referred to as "Tuwanuwa" during the Hittite period, "Tuwana" during the Late Hittite period, "Dana" during the Persian and Hellenistic periods, "Tyana" during the Roman Empire, "Kilisehisar" during the Ottoman Empire, and "Kemerhisar" during the Republic of Turkey. During the Christian era, it was also known as "pilgrims' road (Hacıyolu)" because it was used by pilgrims going to Jerusalem due to its location on the pilgrimage route [8, 23–25].

According to Strabo, Tyana was a prominent settlement due to its fertile and flat lands, strong fortifications, and strategic location. Strabo also noted that Tyana was named Eusebeia, near the Taurus Mountains, distinguish it from Kaisareia to (Mazaka/Kayseri). After their liberation from Seleucid rule, two important cities in Cappadocia—Kaisareia and Tyana—were rebuilt by Ariarathes V Eusebes Philopator. Tyana was named "Eusebeia" in honor of its founder and is thought to be connected to the rites held for Zeus in the temple of Asbamaios near the sacred lake [23, 26, 27]. Septimius Severus' admiration for Apollonius of Tyana is recognized as one of the primary factors that bolstered the city's importance. In later periods, his son Caracalla also admired Apollonius greatly. During the Severus dynasty, various construction works were conducted in the city; structures such as aqueducts, the Roman Pool, a temple dedicated to Zeus Asbamaios, the Roman Baths, and the Heroon were built. Tyana, which gained importance during the empire of Caracalla (211-217 AD), was elevated to the status of "Colonia" and named Antoniana Colonia Tyana [28-30]. It is thought that Caracalla's declaration of Tyana as a Colonia was due to his desire to use this region as a base for his campaigns to the east by taking advantage of the city's strategic location extending to Syria [28]. In addition, Caracalla and his mother Julia Domna attached great importance to Tyana and carried out extensive reconstruction in the city. The aqueducts to the south of the city were also built during the reign of Caracalla and were constructed with a complex hydraulic system to bring water to the city from the hills. These aqueducts were designed to supply water to all residences in the city [24].



Figure 1. Location of study area

3. Geological Settings

Tyana is located in the Central Anatolia Region, 5 km from Bor district of Niğde province. The Niğde region is adjoined by the Aladağlar Mountains to the southeast and the Bolkar Mountains to the south. This region represents the area in which the Taurides and Anatolides meet [31]. The Niğde Massif is located to the southeast of Niğde and forms the southernmost part of the Central Anatolian Massif [31, 32]. The metamorphic rocks of the Niğde Massif form part of the Niğde Group and are divided into the Gümüşler, Kaleboynu, and Aşıgediği formations based on their lithology and are cut by the Üçkapılı granodiorite [32, 33]. The Niğde Group rocks, which underlie the study area, are medium-high-grade Paleozoic metamorphic rocks and form the southern part of the Central Anatolian Crystalline Complex. These metamorphic rocks are overlain by Upper Cretaceous ophiolites [32, 34].

In addition to the Gökbez formation and Kızılkaya ignimbrites in the Kemerhisar region, the Horoz Granitoid is an igneous unit that has contributed significantly to the geological evolution of the region [35–37].

The Horoz Granitoid is an intrusive rock belonging to the Central Anatolian Igneous Complex with similar petrographic and geochemical characteristics to the Üçkapılı Granodiorite in the southeast of the Niğde Massif. Similar to the Üçkapılı Granodiorite, which cuts Paleozoic Niğde Group metamorphic rocks, the Horoz Granitoid has intruded the area's variably metamorphosed metamorphic rocks. In the Kemerhisar region where the study area is located, the Kızılkaya ignimbrites and Gökbez formation unconformably overlie Niğde Group metamorphic rocks [38]. The Miocene-Pliocene Gökbez Formation occurs in large areas around the ancient city of Tyana and comprises marl-limestone-mudstone deposits with bituminous levels and travertine interlayers in the upper parts of the formation. The thickness of the Gökbez formation varies in the range of 50–150 m [33]. The travertine deposits in the upper part of the Gökbez formation, which is located close to the study area and thus a suitable source of blocks, were used in the construction of the Tyana aqueducts. The Gökbez formation consists of sediments deposited in a lake environment with transport from north to south, and during its deposition, it received clastic input from the Niğde Group metamorphic rocks and Havuzlu ignimbrites [8, 39, 40].

The primary aim of this study is to investigate the mineralogical, petrographic, and geochemical characteristics of granite columns located in the ancient city of Tyana in order to determine their provenance and evaluate their potential connections with nearby granitoid formations, particularly the Horoz Granitoid and Üçkapılı Granite. By employing a combination of analytical techniques—including optical microscopy, X-ray diffraction (XRD), X-ray fluorescence (XRF), and

confocal Raman spectroscopy (CRS)—this research seeks to clarify the geological origin, material properties, and historical usage of the granite columns.

4. Materials and methods

Based on the study's objectives, the granite column samples were first visually examined on-site, and their macroscopic characteristics were determined. It is believed that the studied granite columns were building materials used in courtyards, columns, and the porticoes of buildings. The Tyana granite columns were then characterized using the steps detailed below. Thin sections were prepared as a basic analysis method to examine the mineralogical and petrographic properties of the samples in detail, i.e., their mineral associations, grain sizes, and textures.

XRD spectroscopy is a powerful analytical technique that can be used to study the crystal structural properties of a substance. This technique allows the arrangement of atoms in the internal structure of materials to be determined and reveals the composition of minerals qualitatively. These analyses were performed with an Inel Equinox 1000 instrument using a Co tube with a wavelength of 1.788970 Å. The XRD analyses were performed using a Panalytical X'Pert Powder device at the Department of Mineral Analysis and Technology of the General Directorate of Mineral Research and Exploration. This device was used to examine the crystal structure of the granite columns, with the results providing important insights into the detailed mineralogical characteristics of the rocks.

For further mineralogical characterization, selected granite column samples were analyzed using the CRS technique. The CRS analyses were performed on polished thin sections using a Jobin Yvon (Horiba) LabRAM-800HR confocal Raman spectrometer at the Department of Geological Engineering, Ankara University. This instrument is equipped with a notch filter-based Raman microscope system, an Olympus BX41 optical microscope, a grating with 1800 grooves per mm, and a Peltier-cooled CCD detector. The Raman spectroscopy measurements were performed in the spectral range 100–4000 cm⁻¹ with a resolution of 2 cm⁻¹ using a He–Ne laser with a wavelength of 633 nm. Repeat measurements were obtained using the highest magnification to improve the signal-to-noise ratio, thus resulting in clearer spectra.

The main oxide and trace element compositions of the samples were analyzed via XRF spectroscopy. The XRF analyses were performed with a Panalytical Axios Max brand wavelength-dispersive XRF (WD-XRF) device in the Geochemical Analysis Laboratory of Aksaray University Application and Research Center Laboratory. The samples to be analyzed were first crushed with crusher devices and then pulverized to a size of approximately 20 microns in ball mills. The obtained powder samples were mixed with a binder material and pressed into pellets under a pressure of 12 bars. Major and trace element analyses were then performed on the prepared pellets using the WD-XRF technique.

5. Results

5.1 Mineralogy and Petrography

The fresh surfaces of the Tyana granite columns are grayish in color and show a porphyrophaneritic texture upon macroscopic examination (Figure 2a). Plagioclase, quartz, and mafic minerals can be visually identified in hand specimens of the granitic column (Figure 2b, c). Mafic minerals (biotite and amphibole) with black color and glassy luster were observed. In addition, mafic enclaves ranging in size from 5 to 10 cm, darker than the bedrock, are observed in the granite columns (Figure 2d). The granite columns are petrographically granodioritic in composition and exhibit а holocrystalline hypidiomorphic granular texture. The primary mineral assemblage comprises K-feldspar, quartz, plagioclase, mafic minerals (biotite and amphibole), and to a lesser extent titanite, zircon, and opaque minerals.



Figure 2. a) Tyana granite column b) close-up view of granite column c) granite column sample showing porphyrophaneritic texture d) enclavs in granite columns

The observed K-feldspars typically have an orthoclase composition and occur as euhedral crystals with prismatic forms. Within the large orthoclase crystals, there are inclusions of plagioclase, quartz, and biotite interpreted as a poikilitic texture. Plagioclase occurs as subhedral to euhedral crystals, with Carlsbad twinning commonly observed in albite (Figure 3a). The plagioclases weathered to sericite and clay minerals have a slightly turbid appearance. The quartz minerals in the

thin sections generally show xenomorphic crystal forms. The biotite minerals exhibit strong pleochroism ranging from light yellow to dark brown. Some biotite minerals have undergone oxidation to iron oxides. Amphibole minerals are short prismatic and subhedral crystals, with strong pleochroism ranging from light yellow-green to dark green (Figure 3b,c,d). The sphene (titanite) is characterized by development of rhombohedral crystals distinguished by sharp edges.



Figure 3. Optical microscope images of Tyana granite column samples a) Plagioclase showing albite polysynthetic twinning b) Amphibole and biotite minerals c) Euhedral and subhedral amphibole minerals d) Altered plagioclase and amphibole minerals (Qtz: quartz, Pl: plagioclase, Amp: amphibole, Bt: biotite)

XRD analysis was performed to determine the main mineral phases in the Tyana granite column samples in addition to the above optical microscopy analyses. The XRD analysis confirmed the presence of major mineral phases including plagioclase, quartz, K-feldspar, biotite, amphibole and sphene, consistent with the observations from optical microscopy (Figure 4).



Figure 4. XRD graph of Tyana granite columns

5.2 Confocal Raman Spectroscopy (CRS)

The essence of Raman spectroscopy involves measuring a scattered beam produced by the irradiation of a powerful laser source in the visible or near-infrared wavelength region, which is used to illuminate a sample [2]. The difference in the wavelength of the scattered beam relative to the wavelength of the incident beam interacting with the molecule is referred to as a Raman shift. The Raman shift values of minerals act as "fingerprints" and can be used to effectively distinguish between minerals [41].

To determine the mineral characteristics of the Tyana granite column samples, CRS analyses were performed for plagioclase, amphibole, biotite, and quartz minerals. The characteristic peaks for biotite minerals are vibrations due to Mg-O and Fe-O bonds at 180–200 cm⁻¹, Si-O-Si vibrations at 270–300 cm⁻¹, Al-O and Fe-O vibrations at 680–700 cm⁻¹, and Si-O vibrations at 950–1100 cm⁻¹. The biotite mineral in the granite column samples shows a characteristic Raman spectrum, with the strongest peak at 189.46 cm⁻¹ corresponding to Fe-O bonds. This supports the formation of ferro-biotite. (Figure 5a).

The CRS measurements identified the amphibolite type as actinolite. The characteristic Raman peaks for actinolite are typically associated with Si-O-Si tensile vibrations, corresponding to a strong peak in the 670–680 cm⁻¹ range. These spectral features are distinctive features that allow the identification of actinolite-type amphiboles in Raman analysis (Figure 5b).

Strong peaks were detected in the CRS analysis of the plagioclase minerals, and the plagioclase species was identified as andesine (Figure 5c). The strongest peak corresponding to andesine was observed at 512.65 cm⁻¹. The prominent peaks in the Raman spectrum of the andesine-type plagioclase are Si-O-Si vibrations at 480– 510 cm⁻¹, Al-O-Si vibrations at 500–520 cm⁻¹, and Si-O vibrations at 950–1050 cm⁻¹. These peaks may differ between andesine and other plagioclase species, and the spectrum may exhibit slight variations. The 480–510 cm⁻¹ band is considered the most characteristic Raman peak for plagioclase minerals.

Quartz (SiO_2) exhibits highly distinct and strong peaks in CRS analysis. The most characteristic peak in the Raman spectrum of quartz is usually located at a wave number of 464 cm⁻¹. This is consistent with the results presented here, where the quartz measured in the samples shows a peak at 464.00 cm⁻¹ (Figure 5d).





5.3 Geochemistry

In this study, the geochemical properties of granite columns from the ancient city of Tyana were compared with those of the Horoz Granitoid, and Üçkapılı Granitoid. The Horoz granitoid has two members, granodiorite and granite. The geochemical data for the Horoz Granite and Granodiorite were taken from [38] while the data for the Üçkapılı Granitoid were taken from [42]. These comparisons provide important constraints on the potential source region and origin of the columns and a better understanding of the connection between the granite columns at Tyana and the surrounding granitoids. The main oxide and trace element compositions of the samples belonging to the Tyana granite columns, the average main oxide and trace element compositions of the Üçkapılı Granitoid and Horoz granotid are listed in Table 1.

	Tyana		Horoz granitoid		Üçkapılı
Element	gra	anite	granodiorite	granite	granitoid
	Column samples		average	average	average
Na ₂ 0%	3.41	3.58	3.85	3.72	3.27
MgO%	2.84	2.81	1.97	1.04	0.47
Al ₂ O ₃ %	13.85	13.82	17.77	15,05	13.59
SiO ₂ %	63.8	64.8	64.36	71.06	73.52
P2O5%	0.37	0.36	0.13	0.13	0.04
K20%	4.73	4.7	3.68	3.53	2.78
CaO%	3.71	3.63	3.05	1.77	1.99
TiO ₂ %	0.49	0.46	0.29	0.22	0.21
Mn0%	0.11	0.1	0.07	0.03	0.04
Fe ₂ O ₃ %	4.04	4.01	3.88	2.47	2.45
LOI	0.64	0.92	0.72	0.82	0.8
Co (ppm)	17.48	17.3	27.51	27.28	9.46
Zn (ppm)	42.54	42.3	25.22	22.04	57.66
Ga (ppm)	18.35	18.35	15.2	14.78	18.46
Rb (ppm)	209.43	210.3	109	98.1	95.63
Sr (ppm)	858.66	859.1	353.59	385.22	385.23
Y (ppm)	46.14	45.2	18.42	13.19	47.23
Zr (ppm)	229.57	230.3	187.31	152.32	151.2
Nb (ppm)	0.91	0.91	17.72	17.63	15.43
Ba (ppm)	1062.63	1064.2	431.25	477.99	395.53
Hf (ppm)	8.98	8.98	3.71	3.28	4.7
Pb (ppm)	47.79	47.6	0.66	4.2	2.46
Th (ppm)	22.45	22.45	11.65	27	9.2
U (ppm)	13.9	13.9	3.49	6	2.1

Table 1. Major oxide (wt.%) and trace (ppm) element analyses of Tyana granite columns, Üçkapılı granitoid (data taken from [42]), and Horoz granitoid (data taken from [38])

According to the total alkali (Na₂0 + K₂0)-silica (SiO₂) classification diagram [43], the Tyana granite columns and the Horoz Granodiorite samples are located in the granodiorite field, while the Ückapılı Granitoid and the Horoz Granite samples are located in the granite field (Figure 6a). According to [44], all the rock groups show calc-alkaline features used to distinguish sub-alkaline rocks (Figure 6b). According to the $(Na_2O + K_2O) - SiO_2$ (wt.%) diagram, the granite columns lie within the alkali granite field [43] (Figure 6a). In the Ab-An-Or classification diagram, Tyana granite columns and Horoz and Üçkapılı granodiorite samples are located in the granodiorite area. The granite samples of Horoz granotoid were observed in the granite field. (Figure 6c). While the average K_2O/Na_2O ratio of the studied granite columns is 1.27, the value of this ratio is 0,85 for the Üçkapılı Granitoid and 0,95 for the Horoz Granitoid. These ratios indicate that all three granitic rocks are K-

series igneous rocks [45]. In the Q-P classification diagram based on the cationic ratio of quartz, K-feldspar, and plagioclase [46], the studied columns are classified as granite (Figure 6d). Overall, considering the classification diagrams as a whole, the Tyana granite columns exhibit more similarity to the Horoz Granitoid samples.

The Harker diagrams against SiO_2 for Tyana granite columns and other granitoid samples were drawn and the chemical changes of elements against SiO_2 were analyzed (Figure 7). The changes of the elements in the Harker diagrams of all the rock groups generally show non-regular chemical variations; however, the Tyana granite columns exhibit chemical behavior overall more consistent with the Horoz Granitoid in the studied samples. All the granitoid samples show general negative correlation trends for MgO, FeO_{tot}, TiO₂, and CaO and positive correlation trends for Na₂O and K₂O.



Figure 6. Tyana granite columns and other granitoid samples, a)(Na₂O + K₂O) (wt.%) vs. SiO₂ (wt.%) diagram [43] b) AFM diagram [44] c) normative Ab-An-Or diagram (O'Connor (1965) d) Q-P diagram [46]

The slightly negative correlations of MgO_t , FeO_{ttot} , TiO_2 , and CaO_2 to SiO_2 can be interpreted as a result of the separation of these elements from the igneous system during fractional crystallization. In particular, the decrease of MgO and FeO_{tot} is associated with the crystallization of mafic minerals (e.g., biotite, amphibole, and pyroxene).

In contrast, the positive correlation of Na_2O and K_2O against SiO_2 indicates the crystallization of alkaline bearing phases such as plagioclase and K-feldspar. These chemical variations observed in the Harker diagrams support the interpretation that the Tyana granite

columns and the Horoz Granitoid underwent similar magmatic evolutionary processes and that both rocks belong to the calc-alkaline series. In this context, the Tyana granite columns exhibit a magmatic development process more consistent with the Horoz Granitoid than that of the Üçkapılı Granitoid. In general, in all the granitoid samples, a decrease in MgO, FeO_{tot}, TiO₂, and CaO content is observed with weathering of mafic minerals in the early crystallization periods, while the Na₂O and K₂O values increase with late-stage crystallization of alkaline minerals.



Figure 7. Major oxide Harker diagrams of all granitoid samples

[48] suggested a tectonic classification of granitic rocks based on discrimination diagrams using the elements Rb, Y, Nb, and Ta. In the Rb–(Y + Nb) diagram, which distinguishes between collisional granitoids (syn-COLG), volcanic arc granitoids (VAG), within-plate granitoids (WPG), and ocean ridge granitoids (ORG), the column samples plot within the VAG area (Figure 8a).

In the Nb–Y diagram, both the Tyana granite columns and the Horoz and Üçkapılı granitoid samples

plot within the volcanic arc granitoids (VAG/syn-COLG) domain (Figure 8b). The multi-cation R1 and R2 diagram proposed by Batchelor & Bowden (1985) is another widely used classification diagram used to describe the geotectonic environments in which acidic rocks were formed. In these diagrams, the Tyana granite columns and Üçkapılı Granitoid lie within the pre-plate collision area, while the Horoz Granitoid broadly plots within the post-collisional uplift and orogenic fields (Figure 8c).



Figure 8. a) Nb -Y tectonic separation diagram [48] b) Rb - (Y + Nb) tectonic separation diagram [48] c) Multi-cation R1-. R2 diagram [49]

6. Conclusion

In this study, the mineralogical, petrographic, and geochemical properties of Tyana granite columns were determined, and petrographic and geochemical analyses were applied to determine their possible origin. Some of the geochemical properties of the Tyana granite columns were compared with those of the nearby Horoz and Üçkapılı granitic rocks, which have been widely discussed in previous literature and are similar in appearance to the Tyana granite columns. The findings from these analyses reveal similarities between the Tyana granite columns and the Horoz granitoid. The results of this study can be summarized as follows. The granite columns of the ancient city of Tyana exhibit a heterogeneous structure consisting of Kfeldspar, plagioclase, quartz, and mafic minerals when evaluated mineralogically and petrographically. The presence of the main mineral phases determined by optical microscope analysis is also consistent with XRD analysis. The CRS studies revealed that the plagioclases have an andesine composition, the amphibole minerals have an actinolite composition, and the biotite minerals are ferro-biotite and biotite in composition.

The Roman granite columns have calc-alkaline affinity with granodiorite composition. In addition, the Roman granite column samples plot in the collisional granitoid (syn-COLG) and volcanic arc granitoid fields, with similar main oxide and trace element contents to those of the Horoz granitoid. The comparison of the geochemical data of the Horoz granitoid and the Tyana granite columns is also consistent with published data.

In conclusion, the mineralogical, petrographic, and chemical analyses of the granite columns in the ancient city of Tyana presented in this work provide valuable information about the origin of these structures. The analyzed features of the Tyana granite columns are an important input for the conservation and restoration of ancient structures in the future.

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Author contributions

Hacer BILGILIOĞLU: Conceptualization, Methodology, Field study, Data curation, Writing-Original draft preparation, Validation, Visualization, Investigation, Writing-Reviewing and Editing.

Conflicts of interest

There is no conflict of interest.

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