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Article

The mineralogical composition of the zeolitic rocks of Santorini Island and their potential use as feed additives and nutrition supplements

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Abstract

The zeolitic rocks of Akrotiri, on Santorini Island (Aegean Sea, Greece), can be grouped according to the zeolite minerals present. The first group includes zeolitic rocks that contain only clinoptilolite, the second group contains clinoptilolite and mordenite and the third group contains only mordenite. Clinoptilolite accounts for up to 56 wt.% and mordenite for up to 69 wt.% of the rocks. All samples contain feldspars (8–36 wt.%), clay minerals (6–8 wt.%), quartz (3–6 wt.%), opal-CT (2 wt.%), amphibole (2–4 wt.%) and amorphous materials (4–7 wt.%). The studied samples were classified chemically as andesites or dacites. The ammonium-exchange capacity of the studied samples was 104–158 meq 100 g^{-1}. According to Commission Implementing Regulation (EU) No. 651/2013, zeolitic rocks that contain ≥80 wt.% clinoptilolite, ≤20 wt.% clay minerals and are free of fibrous minerals and quartz can be used as feed additives in animal husbandry. Zeolites with fibrous habit (mordenite, erionite, secondarily roggianite and mazzite) and SiO_2 minerals such as quartz, cristobalite and tridymite can be dangerous to both humans and animals. The mineralogical study showed that, due to their low clinoptilolite content and the presence of both quartz and fibrous mordenite, the studied zeolitic rocks do not conform with European Regulation No. 651/2013. As a result, their use as feed additives and nutrition supplements is prohibited.

Keywords: clinoptilolite, feed additives, fibrous zeolites, mordenite, nutrition supplements, Santorini

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A typical zeolitic volcaniclastic formation refers to a rock with high contents of one or more zeolite minerals. In Greece, there are many widespread zeolite occurrences across the country, the most promising of which are located in north-east Greece, especially in the regional units of Evros and Rhodope. In addition, significant occurrences are located in the Aegean Islands, specifically those of Samos, Kimolos, Polyegos, Milos and Santorini (Stamatakis *et al.*, 1996; Kantiranis *et al.*, 2006; Tsirambides & Filippidis, 2012).

Natural zeolites are a group of crystalline hydrated aluminosilicate microporous minerals that have as their main property the reversible dehydration and removal of water without destroying their crystal structure (Holmes, 1994). Zeolites are a class of microporous materials with outstanding properties because of their large pore volume, high specific surface area and thermal stability (Meier, 1986). Regarding their structure, they consist of tetrahedra units of silica (SiO_4) and alumina (AlO_4) that form three-dimensional networks. These tetrahedral units are linked by sharing all apical oxygen atoms, forming channels that contain exchangeable cations (potassium, sodium, calcium, etc.), and water molecules (Rehakova *et al.*, 2004; Jha and Singh, 2011; Król, 2020). Their crystal structure consists of distinct extra-framework positions in which cations are exchanged. The positions of these extra-framework cations and water molecules bound within the crystal framework of the mineral depend on the nature of the cations involved in the ion exchange (Armbruster & Gunter, 1991; Gunter *et al.*, 1994).

In nature, 67 types of zeolites are known, while more than 200 types of zeolites have been obtained synthetically (Baerlocher *et al.*, 2007). Zeolite-rich rocks contain significant amounts of one or more types of zeolite and have specific mineralogical, chemical, morphological and radiological characteristics (natural radionuclides in zeolite-rich rocks). Through the process of diagenesis and under specific conditions (e.g. of temperature, pressure, pH, salinity), mainly volcanic materials can be completely or partially converted into zeolites in various environments. Under these conditions, occurrences in mafic volcanic rocks that lack economic value can be found, while deposits of sedimentary origin can be formed during diagenesis (Colella, 2005).

Of the various zeolite species, HEU-type zeolites (heulandite–clinoptilolite) are widely used in various industrial and environmental applications. HEU-type zeolites form tabular crystals, and the presence of nano/micropores in their framework is characteristic and results in channels with 10- and 8-member rings and dimensions of 7.5×3.1 Å, 4.6×3.6 Å and 4.7×2.8 Å. Greek zeolite-bearing volcaniclastic rocks also contain HEU-type zeolites with similar characteristics (Misaelides *et al.*, 1995; Baerlocher *et al.*, 2007; Filippidis & Kantiranis, 2007; Filippidis *et al.*, 2008, 2015a, 2015b, 2016a, 2016b, 2019; Filippidis, 2010; Mitchell *et al.*, 2012; Vogiatzis *et al.*, 2012; Papastergios *et al.*, 2017; Floros *et al.*, 2018).

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The use of inorganic materials as feed additives is restricted by several regulations due to their potential toxicity to humans and animals. According to Commission Implementing Regulation (EU) No. 651/2013, only zeolitic tuffs containing ≥80 wt.% clinoptilolite and ≤20 wt.% clay minerals and that are free of fibres and quartz can be used as feed additives in animal husbandry and therefore as nutrition supplements. The existence of fibrous zeolites (mordenite, erionite, roggianite and mazzite) and SiO_2 polymorphs (cristobalite, tridymite, quartz) in HEU-type zeolitic tuffs prevents their use as feed additives and nutrition supplements (Filippidis *et al.*, 2016a, 2019), as they can be dangerous to both humans and animals (Davis, 1993; Driscoll, 1993; Ross *et al.*, 1993).

Important properties of natural zeolites include cation exchange, adsorption, dehydration–hydration, catalytic ability and diffusion capacity. Due to these properties, natural zeolites have been used successfully in animal nutrition and biotechnology to improve the health, safety and productivity of livestock animals and their products (Mumpton & Fishman, 1977; Pond & Mumpton, 1984; Elliot & Edwards, 1991; Papaioannou *et al.*, 2005; Nadziakiewicza *et al.*, 2019; Simona & Camelia, 2019; Mondal *et al.*, 2021; Souza *et al.*, 2023). Specifically, they prevent or reduce mycotoxin contamination in farm animals, decrease concentrations of ammonia and toxic heavy metals and improve immunity, general health and growth performance in animals of veterinary and biomedical importance (Karaca *et al.*, 2004; Wu *et al.*, 2013; Valpotic & Gracner, 2017). They have also been used as alternatives to antibiotics (Papatsiros *et al.*, 2013 and references therein). Many researchers have demonstrated the beneficial effects of zeolites on the average daily gain and/or feed conversion in sheep, cattle, rats (Pond & Yen, 1983; Saribeyoglu *et al.*, 2011), pigs (Papaioannou *et al.*, 2004; Ly *et al.*, 2007; Prvulovic *et al.*, 2007) and broilers (Miazzo *et al.*, 2000; Fendri *et al.*, 2012; Mallek *et al.*, 2012; Wu *et al.*, 2013). Zeolites also increase the milk yield of dairy cows (Olver, 1997; Miazzo *et al.*, 2000; Papaioannou *et al.*, 2002, 2005; Katsoulos *et al.*, 2006; Ly *et al.*, 2007; Dschaak *et al.*, 2010; Colella, 2011). However, such performance enhancement is related to the type of the zeolite used, its purity and physicochemical properties, as well as to the supplementation level used in these diets (Olver, 1997; Papaioannou *et al.*, 2002, 2005; Colella, 2011).

Clay minerals besides zeolites are also used as feed additives, and they have many beneficial effects due to their specific properties. For example, sepiolite is widely used as a feed additive supplied to broiler chickens and pigs (Rodríguez-Beltrán *et al.*, 2013). Smectites and kaolin minerals (kaolinite, dickite, nacrite, halloysite) have been tested as dietary supplements for pigs (Trckova *et al.*, 2009; Slamova & Trckova, 2011; Subramaniam & Kim, 2015), and attapulgite has been used as a food additive to promote the growth and health of pigs and broilers (Pappas *et al.*, 2010; Zhou & Tan, 2014).

The Pliocene zeolite-rich volcaniclastic rocks of Santorini Island (Aegean Sea, Greece) cover an area of ~1 km^2 west of the village of Akrotiri, and they have a thickness of at least 220 m. These zeolites were formed by the activity of meteoric water within the pile of volcaniclastic material. Variations in the heat flow, ionic activity and permeability of the meteoric water caused the development of the various mineralogical assemblages (Tsolis-Katagas & Katagas, 1989; Hall *et al.*, 1994; Francalanci *et al.*, 1995; Stamatakis *et al.*, 1996; Vougioukalakis, 2006; Pank *et al.*, 2022). The zeolitic rocks of Akrotiri have already been studied for their physicochemical characteristics as an industrial commodity that is a potential source of pozzolanic materials (Fytikas *et al.*, 1990; Kitsopoulos & Dunham, 1996; Kitsopoulos, 1997, 1999, 2001; Pank *et al.*, 2022).

In this study, the physicochemical characteristics (i.e. mineralogical and chemical composition and sorption ability) of representative samples of the zeolitic rocks of Akrotiri, Santorini Island (Greece), were studied to evaluate their potential as feed additives and nutrition supplements according to Commission Implementing Regulation (EU) No 651/2013. To the best of our knowledge, this is the first time that representative total samples from the rhyodacitic zeolitic rocks of Akrotiri have been evaluated for specific livestock uses.

Materials and methods

Four representative zeolitic rock samples (S1, S2, S3, S4) were collected from an area of ~1 km^2 located west of the village of Akrotiri on Santorini Island (Aegean Sea, Greece; Fig. 1). The locations of the surface rock samples were scattered throughout the zeolitic rocks of Akrotiri, so the samples were representative of the various types of zeolite occurring in the study area. In the broader area of Akrotiri, there are successive occurrences of volcanic rocks and volcaniclastic materials from the various volcanic eruptions of the Santorini volcano. This research focuses on the study of hornblende-bearing rhyodacitic volcaniclastic tuffs known as 'Akrotiri tuffs'. The exact locations (coordinates and distance) of each sample in relation to the village of Akrotiri are given in Table 1. Each sample was ground with an agate mortar and sieved to pass through a 0.125 mm sieve. The powdered sample was then divided into halves. One half was further powdered in an agate mortar and passed through 0.063 mm a sieve. The second half (with a grain size of <0.125 mm) was used for ammonium acetate saturation (AMAS) analysis, while that of grain size <0.063 mm was used for the mineralogical (powder X-ray diffraction; XRD) and chemical (X-ray fluorescence; XRF) analysers. Furthermore, polished thin sections of the rock samples were prepared to study their morphological and chemical characteristics using scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM-EDS).

Powder XRD was used to determine the mineralogical composition of randomly oriented samples using a Philips PW1710 diffractometer with Ni-filtered Cu-$K_{\_}$ radiation. The counting conditions were: start angle 3°2θ, end angle 63°2θ, step size 0.02°2θ, time per step 1 s and scan speed 0.02° s^{-1}. Mineral abundance was estimated using (1) intensity (counts) of certain reflections, (2) density of the examined mineral and (3) the mass absorption coefficient for Cu-$K\alpha$ radiation. Finally, for the refining of the results, a Rietveld-based refinement routine was used (TOPAS 6.0® (2016) software). The routine is based on the calculation of a single mineral-phase pattern according to the crystalline structure of the respective mineral. The refinement of the pattern uses a non-linear least squares routine. The quantification errors were determined without an internal standard and calculated for each phase according to Bish & Post (1993). The clay minerals present were identified from air-dried, saturated in glycol and heat-treated (550°C for 2.5 h) oriented samples scanned from 3° to 23°2θ at a scanning speed of 1.2° min^{-1}. The amorphous (volcanic glass) content of the studied samples was determined using the fitting method on the broad background hump between 10° and 20°2θ in the powder XRD trace (Kantiranis *et al.*, 2004b, 2005).

The cation-exchange capacity (CEC) of the studied materials was evaluated according to their efficiency at exchange their extra-

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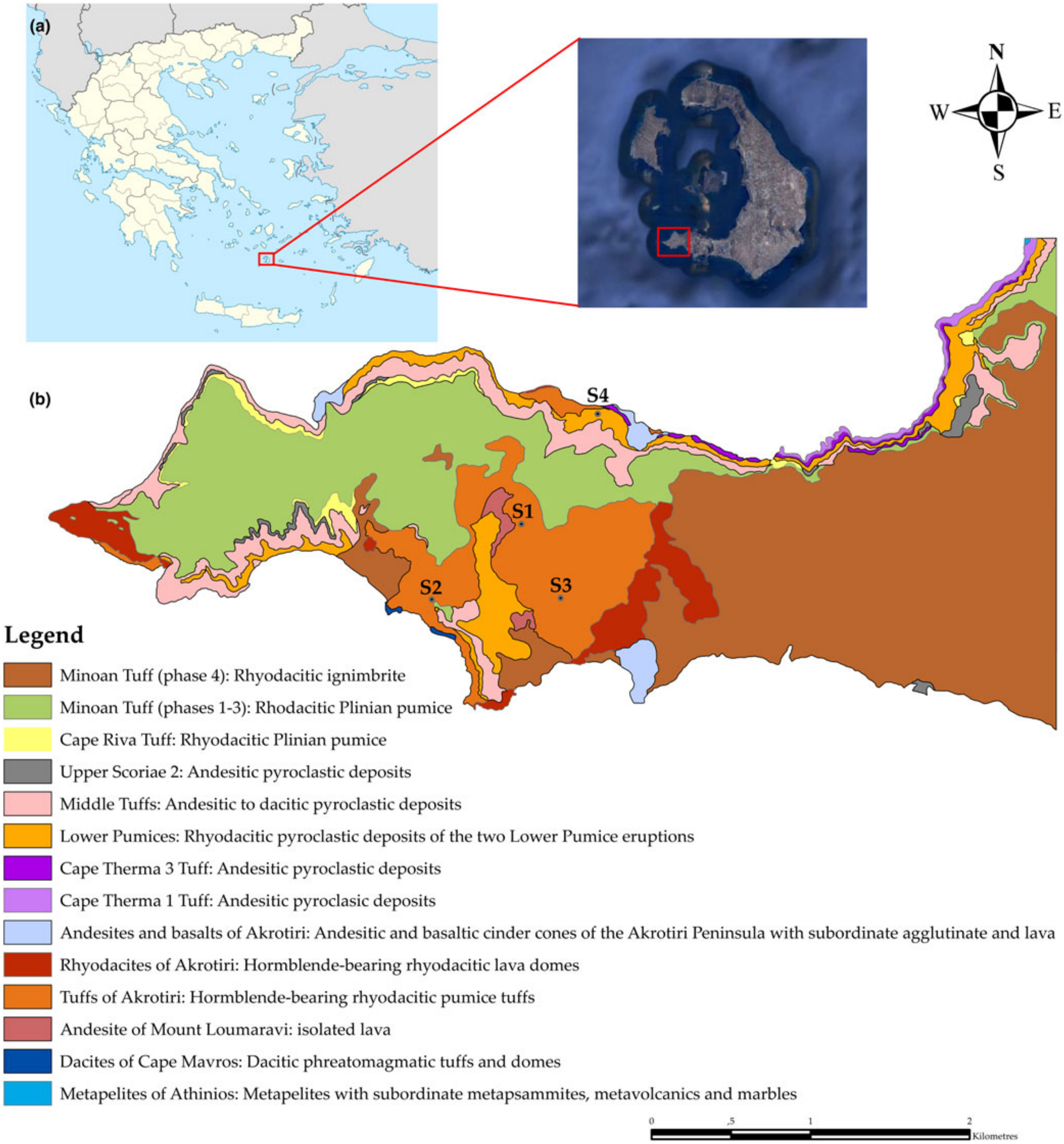

Figure 1. (a) Location of Santorini Island, Greece, and (b) geological map and location of zeolite sampling points in Akrotiri, Santorini Island (modified after Druitt *et al.*, 1999).

framework cations with the ammonium ion. Consequently, the ammonium-exchange capacity (sorption ability) was determined using the ammonium acetate (CH_3COONH_4) saturation (AMAS) method (Bain & Smith, 1987; Kitsopoulos, 1999; Kantiranis *et al.*, 2004a, 2005).

Initially, a solution of 1 N ammonium acetate with pH value 7.0 was prepared (using a Hanna Instruments HI2002-01 Edge® Dedicated pH/ORP Meter). Each sample passed through the 0.063 mm sieve (Retsch®) was divided into four aliquots of 100–150 mg each that were placed into 15 mL test tubes. Some 10 mL of 1 N CH_3COONH_4 solution (Chem-Lab NV) was then added and stirred vigorously by hand for a few seconds. The tubes were then placed in a rotary stirrer (Heidolph Reax20) for 24 h before being centrifuged at 1500 rpm for 4 min. The supernatant was decanted and 10 mL of fresh 1 N CH_3COONH_4 solution added following the same procedure. A 10 day saturation procedure was followed to achieve complete sorption of ammonium ions by the studied zeolite-rich materials (Bain & Smith,

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Table 1. Mineralogical composition (wt.%) of the zeolitic rocks from Akrotiri (Santorini Island, Greece).

Mineral composition	S1	S2	S3	S4	Error (%)
Location and distance from the village of Akrotiri	830 m W5S	1430 m W19S	780 m W40S	700 m W29S	
HEU-type (clinoptilolite)	46	54	56	–	±1
Mordenite	–	10	11	69	±1
Clay minerals	6	7	7	8	±2
Quartz	3	3	3	6	±1
Opal-CT	2	2	2	2	±1
Feldspars (K-feldspar and plagioclase)	36	17	13	4	±3
Amphibole	3	2	2	4	±1
Amorphous material	4	5	6	7	±1

1987; Kitsopoulos, 1999; Kantiranis *et al.*, 2004a). After the 10 day saturation procedure, the samples were rinsed with 99% isopropyl alcohol (Chem-Lab NV) to remove excess NH_4^+. Specifically, 10 mL of isopropyl alcohol was added to each test tube, which was stirred vigorously and centrifuged at 2500 rpm for 5 min (Rotanda 460, Hettich Zentrifugen). The washing process was repeated six times. After the sixth washing cycle, the supernatant was collected in a beaker and checked for precipitates by adding Nessler reagent (alkaline solution $K_2[HgI_4]$; Chem-Lab NV) and concentrated NaOH solution (Chem-Lab NV). The formation of a brown precipitate or brownish-yellow solution (Bain & Smith, 1987) indicates an excess of NH_4^+ ions, meaning that washing needs to be repeated. Finally, the samples were allowed to dry at room temperature. A JENWAY 3340 ion/pH meter combined with an ORION ammonia electrode was used to measure sorption ability. Four measurements were taken from each dry sample, and the mean average sorption ability was calculated. The method was evaluated using standard mixtures of amorphous material and crystalline phases and the standard deviation was found to be 5 meq 100 g^{-1} (Drakoulis *et al.*, 2005).

Chemical analysis of the Akrotiri samples was performed using a Bruker S4-Pioneer XRF wavelength-dispersive spectrometer equipped with a Rh tube and six analysing crystals, a gas-flow proportional counter (P10 gas, a mixture of 90% argon and 10% methane), a scintillation detector or a combination of the two detectors. A fused glass bead was used for the analysis of the major elements at tube-operating conditions of 60 kV and 45 mA. Theoretical alpha factors and measured line overlap factors for the measured raw intensities were applied to correct the matrix effects in the samples. The standards used to calibrate the major element analyses were AGV-1 (andesite), JG-1 (granodiorite), JB-1 (granodiorite), NIM-G (granite), GA (granite) and GH (granite).

A JEOL JSM-840A SEM device equipped with an X-ray EDS micro-analytical system (SEM-EDS; with a LINK 10000 AN energy dispersion analyser) was used for the morphological study and microanalysis of the Santorini samples. Corrections were made using *ZAF-4/FLS* software provided by LINK. To reduce the volatilization of alkali metals from the zeolite framework, the spot size of the electron beam was enlarged whilst the counting time was decreased (accelerating voltage 15–20 keV, beam current 0.4 mA, spot size 50–60 μm, EDS live time 60–80 s). Minerals such as micas, feldspars and carbonates, as well as pure metals, were used as probe standards. The average chemical formula for the studied zeolites (clinoptilolite and mordenite) was calculated from the chemical microanalysis based on the formulas $(Na,K)_6(Al_6Si_{30}O_{72})\cdot 20H_2O$ for clinoptilolite and $(Na_3KCa_2)(Al_8Si_{40}O_{96})\cdot 28H_2O$ for mordenite (Gottardi & Galli, 1985).

Results and discussion

The mineral and amorphous phase contents of the studied samples are listed in Table 1, whereas representative powder XRD traces of the clinoptilolitic sample (S1), mordenitic sample (S4) and a representative powder XRD trace of the mixed samples (S2 and S3) are shown in Fig. 2. Samples 2 and 3 have comparable mineralogical compositions. As a consequence, only sample S2 was selected for further analysis. Mineral phases were identified using the PDF-4$^+$ database with *SIeve*$^+$ search indexing software from the International Centre for Diffraction Data.

The zeolitic rocks contain up to 56 wt.% HEU-type zeolite (clinoptilolite), up to 69 wt.% mordenite, 4–36 wt.% feldspars (both K-feldspar and plagioclase), 6–8 wt.% clay minerals, 3–6 wt.% quartz, 2 wt.% opal-CT, 2–4 wt.% amphibole and 4–7 wt.% amorphous material (volcanic glass).

The main clay mineral phase in all samples is smectite, and kaolinite is also present in minor amounts.

Concerning zeolite types (Table 1), sample S1 contains only HEU-type zeolite (clinoptilolite; 46 wt.%), samples S2 and S3 contain HEU-type zeolite (clinoptilolite; 54 and 56 wt.%, respectively) and mordenite (10 and 11 wt.%, respectively) and sample S4 contains only mordenite (69 wt.%). The high alkali content of the Akrotiri rhyodacitic–dacitic (Tsolis-Katagas & Katagas, 1989; Kitsopoulos *et al.*, 2001) volcaniclastic tuffs favours environments with high pH that allow increased silica activity from the volcanic glass that, in turn, leads to the formation of clinoptilolite instead of heulandite (Gottardi & Galli, 1985). However, under active geothermal conditions, extensive alteration of the Akrotiri dacitic tuffs further favours not only the formation of clinoptilolite but also the formation of mordenite (Seki, 1970).

Tsolis-Katagas & Katagas (1989) and Kitsopoulos *et al.* (2001) studied the altered dacitic pre-caldera pyroclastic rocks of the Santorini volcano to the east of the village of Akrotiri and observed that K-rich and (K,Ca)-rich clinoptilolite, mordenite and opal-CT authigenic minerals and clay minerals are abundant. Inhomogeneities in the chemical composition of dacitic materials control HEU-type mineral formation, whereas mordenite presence follows the formation of HEU-type zeolites and opal-CT.

Filippidis *et al.* (2007) studied zeolitic samples taken near the village of Akrotiri and found that they contained clinoptilolite between 33 and 57 wt.% and mordenite between 15 and 56 wt.%, while the total microporous mineral content varied between 47 and 86 wt.%. Additionally, CEC of the samples measured using the AMAS method varied between 118 and 177 meq 100 g^{-1}.

The CEC of the zeolitic rock samples from Akrotiri varied between 104 (sample S1) and 158 meq 100 g^{-1} (sample S4; Table 2). The CEC of zeolitic rocks mainly depends on the total zeolite content (clinoptilolite and mordenite), as these are the most typical microporous minerals, as well as on the total content of clay minerals and amorphous materials (Tables 1 & 2).

The CEC (104–158 meq 100 g^{-1}) of the studied zeolitic rocks shows a strong correlation ($R^2 = 0.9982$) with the total zeolite (clinoptilolite + mordenite) content (46–69 wt.%). Similar behaviour is observed when the CEC is compared to the total content (52–77 wt.%) of microporous minerals (zeolites + clay minerals) and the total content (56–84 wt.%) of microporous minerals plus amorphous materials (Fig. 3).

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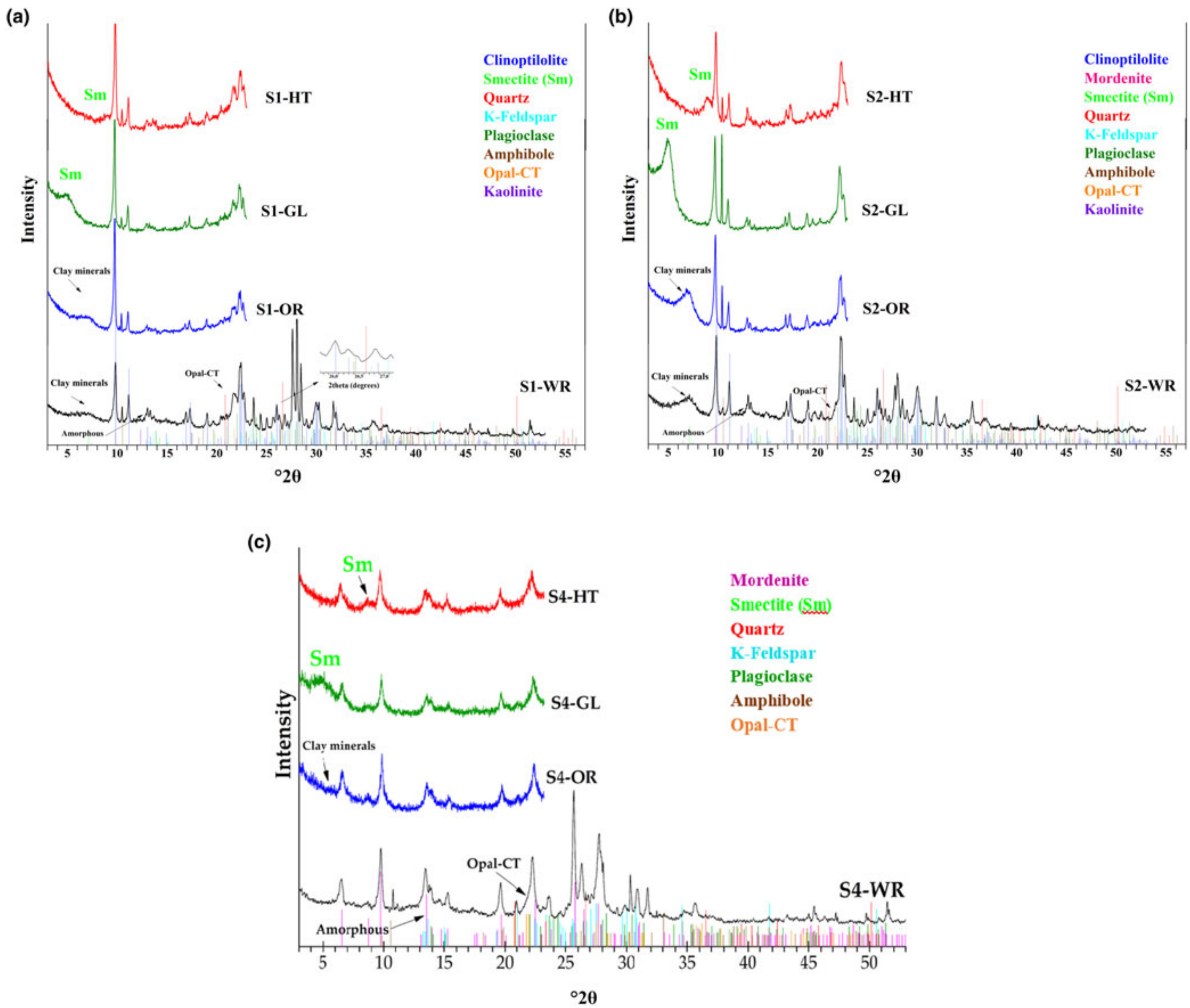

Figure 2. Representative XRD traces of (a) the clinoptilolite-rich sample (S1), (b) the mixed clinoptilolite–mordenite sample (S2) and (c) the mordenite-rich (S4) sample. GL = glycol saturated; HT = heat treated; OR = air dried; WR = whole rock.

The chemical compositions of the studied samples are shown in Table 3. Based on SiO_2 content, the samples can be classified as intermediate to acidic volcanic rocks. SEM images of the studied samples are presented in Fig. 4. Both zeolites grow in empty pores as a result of volcanic glass alteration of the andesitic fragments. More specifically, clinoptilolite grows as elongated, fine, tabular crystals (Fig. 4a) from the outer parts of volcanic glass shards towards the centre of those shards. The radial growth of the tabular clinoptilolitic crystals is clearly indicated in Fig. 4b. Mordenite grows in similar empty spaces and presents a characteristic fibrous structure (Fig. 4c).

Table 2. CEC values of the zeolitic rocks of Akrotiri and their correlation with zeolite content, microporous minerals and microporous minerals plus amorphous materials.

Property/sample	S1	S2	S3	S4
CEC (meq 100 g^{-1})	104	144	152	158
Minerals (wt.%)				
Zeolite content (clinoptilolite + mordenite)	46	64	67	69
Microporous minerals (zeolites + clay minerals)	52	71	74	77
Microporous minerals + amorphous material	56	76	80	84

The spot chemical analyses (average of five analyses for each phase) for clinoptilolite and mordenite are listed on Table 4. As the two zeolite phases in all four samples are mordenite and clinoptilolite, the highest and the lowest values of each oxide are shown in the chemical analyses. The clinoptilolite and mordenite have comparable SiO_2 contents. It is clear that clinoptilolite is richer in Ca than mordenite. Finally, mordenite contains greater amounts of Na_2O and K_2O than clinoptilolite.

The chemical analysis was used to calculate the chemical formulae of the two zeolites. The formulae obtained were: clinoptilolite = $(Fe_{t0.016–0.311}Mg_{0.525–0.797}Ca_{0.955–2.763}Na_{0.867–2.461}K_{0.461–1.291})(Al_{5.883–6.032}Si_{28.911–29.981})O_{72}(13.72–14.18)H_2O$ and mordenite = $(Fe_{t0.000–0.295}Mg_{0.338–0.660}Ca_{0.552–1.045}K_{2.001–2.229}Na_{2.544–6.092})(Al_{7.795–8.805}Si_{39.362–39.471})O_{96}(13.17–13.19)H_2O$.

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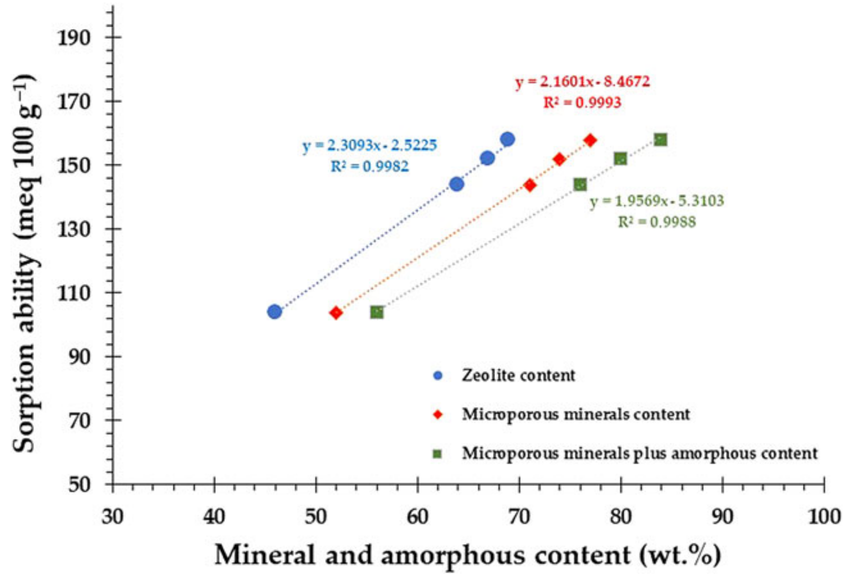

Figure 3. Variation in CEC (meq 100 g^{-1}) with mineral and amorphous matter content (wt.%).

Table 3. Chemical composition (wt.%) of the zeolitic rocks of Akrotiri (Santorini Island, Greece).

Chemical composition	Sample			
	S1	S2	S3	S4
Location and distance of sample from the village of Akrotiri	830 m W, 5°S	1430 m W, 19°S	780 m W, 40°S	700 m W, 29°S
SiO_2	64.29	60.75	60.26	65.04
TiO_2	0.23	0.29	0.23	0.24
Al_2O_3	13.58	16.26	17.26	14.48
Fe_2O_{3t}	2.66	3.42	2.61	1.42
MnO	0.06	0.05	0.11	0.04
MgO	1.13	2.29	2.49	0.84
CaO	2.81	3.04	2.51	1.52
SrO	0.02	0.03	0.02	0.02
BaO	0.02	0.03	0.05	0.02
K_2O	2.07	1.79	1.93	2.44
Na_2O	3.21	2.82	3.05	3.85
LOI (at 1050°C for 150 min)	9.32	8.82	9.12	9.97
Total	*99.39*	*99.58*	*99.63*	*99.89*

LOI = loss on ignition.

Mercurio *et al.* (2012, 2016) studied the mineralogical (powder XRD) and chemical (XRF) composition of a zeolite-rich tuff derived from alteration of an ignimbrite. Although the presence of SiO_2 minerals (quartz, cristobalite, tridymite) was not discussed, these authors concluded that the studied phillipsite-rich tuff is suitable for use as a feed additive. By contrast, Filippidis *et al.* (2016a, 2019) studied a large number of zeolitic tuffs from Greece, mainly originating from areas of Thrace (north Greece) and Samos Island (east Aegean Sea), and found that all of the studied zeolitic formations contain quartz and/or clay minerals in prohibited amounts (according to Commission Implementing Regulation (EU) No 651/2013). Consequently, these zeolite-rich tuffs are not suitable for use as feed additives and nutrition supplements.

Numerous studies have been conducted on the application of high-quality natural zeolites as feed additives and nutrition supplements (Mumpton & Fishman, 1977; Pond & Yen, 1983; Pond & Mumpton, 1984; Elliot & Edwards, 1991; Olver, 1997; Miazzo *et al.*, 2000; Papaioannou *et al.*, 2002, 2004, 2005; Karaca *et al.*, 2004; Katsoulos *et al.*, 2006; Ly *et al.*, 2007; Prvulovic *et al.*, 2007; Trckova *et al.*, 2009; Dschaak *et al.*, 2010; Pappas *et al.*, 2010; Colella, 2011; Saribeyoglu *et al.*, 2011; Slaova & Trckova, 2011; Fendri *et al.*, 2012; Mallek *et al.*, 2012; Papatsiros *et al.*, 2013; Rodríguez-Beltrán *et al.*, 2013; Wu *et al.*, 2013; Zhou & Tan, 2014; Subramaniam & Kim, 2015; Valpotic & Gracner, 2017; Nadziakiewicza, 2019). Although particular attention has been given to the chemical composition of these materials, the presence and abundance of SiO_2 polymorphs (quartz, cristobalite, tridymite) and fibrous forms of zeolite have not been considered in sufficient detail to characterize and assess their suitability for these uses. For example, the effect of the zeolite (clinoptilolite) on meat quality has been reported for chickens (Mallek *et al.*, 2012), turkeys (Hcini *et al.*, 2018), geese (Larina *et al.*, 2020), pigs (Kim *et al.*, 2014) and fish (Paritova, 2014). The use of natural zeolite (with 87% clinoptilolite) improved the growth of female broilers by increasing the digestibility of nutrients and improving their intestinal health (Wawrzyniak *et al.*, 2017). Osman & Soliman (2021) also reported that supplementing zeolite in the feed of high-yielding lactating cows led to improved digestion coefficients, feed conversion, milk production and fat yields.

The zeolitic rocks from Akrotiri can be classified as follows: (1) sample S1 containing 46 wt.% clinoptilolite plus 3 wt.% quartz; (2) samples S2 and S3 containing 54–56 wt.% clinoptilolite plus 10–11 wt.% mordenite (fibrous zeolite) plus 3 wt.% quartz; and (3) sample S4 containing 69 wt.% mordenite (fibrous zeolite) plus 6 wt.% quartz (Table 1). All of the samples contain <20 wt.% clay minerals, but they do not contain significant amounts (≥80 wt.%) of clinoptilolite and are not quartz-free. Therefore, we conclude that the zeolitic rocks of the village of Akrotiri (Santorini Island, Greece) are not suitable as feed additives or nutrition supplements (according to Commission Implementing Regulation (EU) No 651/2013). However, Kitsopoulos & Dunham (1996), who studied heulandite- and mordenite-rich zeolitic tuffs from Santorini in the same area of Akrotiri, concluded that, following calcination, these materials may replace Portland cement at up to 4 wt.% in concrete mixtures and may increase the compressive strength of concrete.

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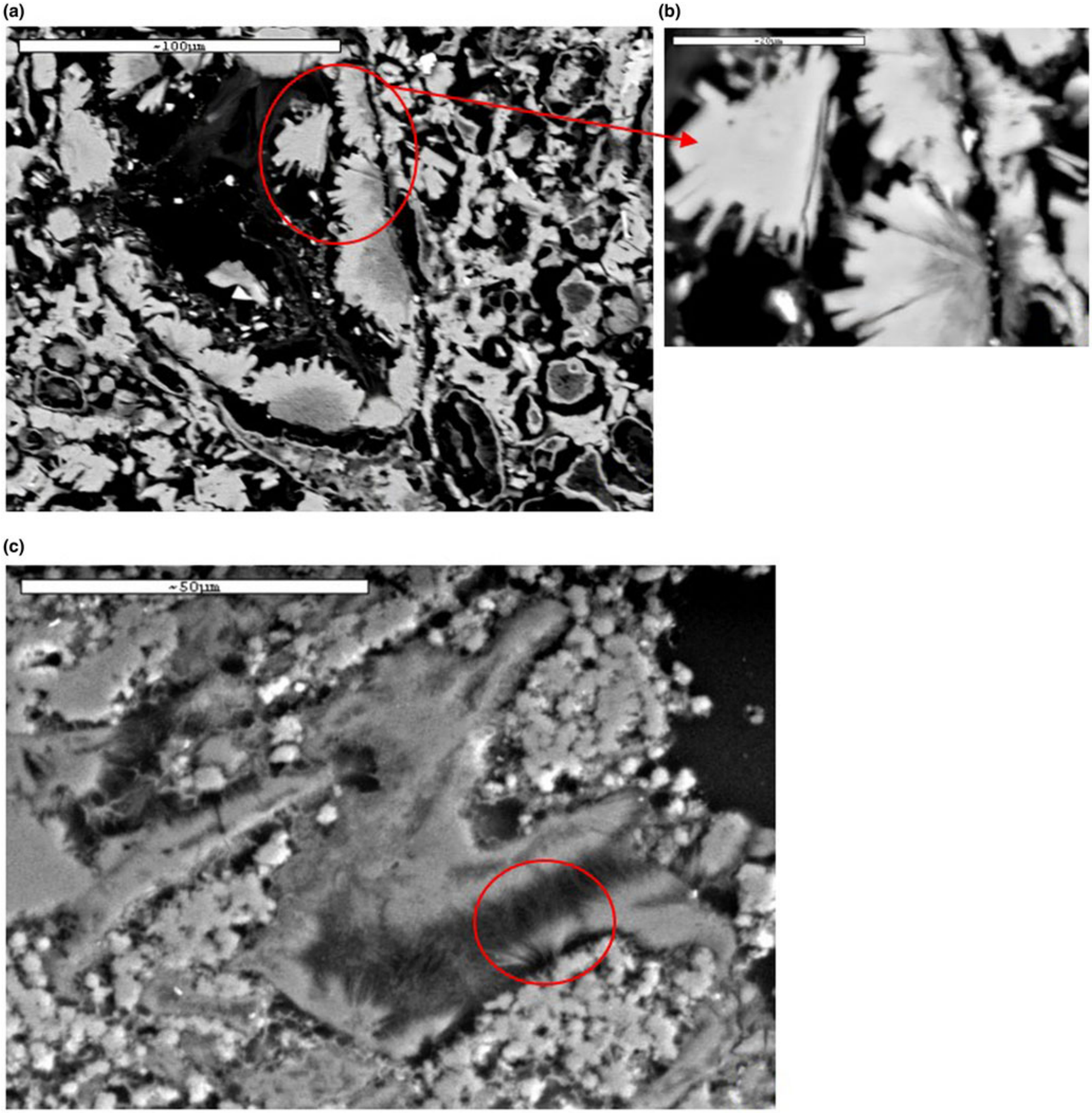

Figure 4. SEM images of the studied Akrotiri tuffs. (a & b) Tabular crystals of clinoptilolite in altered glass shards of sample S1 are highlighted in the red circle in (a), and a zoomed-in image is provided in (b). (c) Fibrous mordenite in altered glass shards of sample S2 highlighted in the red circle.

Summary and conclusions

The zeolitic rocks of Akrotiri on Santorini Island can be grouped as follows: (1) one sample contains only clinoptilolite (46 wt.%); (2) two samples contain clinoptilolite (54–56 wt.%) plus mordenite (10–11 wt.%); and (3) one sample contains only mordenite (69 wt.%). All samples contain 8–39 wt.% feldspars (K-feldspar + plagioclase), 6–8 wt.% clay minerals (mainly smectite and minor kaolinite), 3–6 wt.% quartz, 2 wt.% opal-CT and 4–7 wt.% amorphous materials. Based on their chemical composition according to SiO_2 content, the Akrotiri samples can be classified as intermediate to acidic volcanic rocks, whereas based on the total content of alkalis ($K_2O + Na_2O$) *vs* SiO_2 content they can be classified as andesites or dacites.

The CEC values of the zeolite rocks vary from 104 to 158 meq 100 g^{-1} and depend primarily on the total zeolite content (clinoptilolite + mordenite) and secondarily on the content of clay minerals and amorphous materials. The sorption ability of these rocks increases with increasing zeolite content, increasing content of microporous minerals and increasing content of microporous minerals plus amorphous materials.

Due to the measured mineralogical content of the studied clinoptilolite-bearing rocks, we conclude that none of them are

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Table 4. Chemical analysis from SEM-EDS of the clinoptilolite and mordenite.

	Clinoptilolite		Mordenite	
	Minimum	Maximum	Minimum	Maximum
SiO_2	62.84	67.41	65.76	66.53
TiO_2	0.08	–	–	–
Al_2O_3	10.85	11.51	11.02	12.63
FeO_{total}[a]	0.81	0.04	0.59	0.00
MgO	0.77	1.20	0.38	0.75
BaO	1.33	0.83	0.08	0.39
CaO	5.61	2.00	0.86	1.65
Na_2O	2.76	1.01	5.23	2.22
K_2O	0.79	2.28	2.91	2.65
Total	85.82	86.28	86.83	86.81
H_2O[b]	14.18	13.72	13.17	13.19

[a]Iron was measured as total FeO.
[b]Calculated by difference from 100 wt.%.

suitable as feed additives or nutrition supplements according to Commission Implementing Regulation (EU) No 651/2013. Specifically, three samples contain <80 wt.% clinoptilolite (46–56 wt.%) and 3 wt.% quartz, and two contain 10–11 wt.% of a fibrous zeolite (mordenite). The non-clinoptilolite-bearing sample contains 69 wt.% of the fibrous zeolite mordenite and 6 wt.% quartz, and therefore this sample cannot be used as a feed additive and nutrition supplement for any animal husbandry as well. Other uses of the studied zeolitic rocks (e.g. as a replacement for Portland cement in concrete mixes) offer alternative prospects for the exploitation of these materials.

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Conflicts of interest. The authors declare none.

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