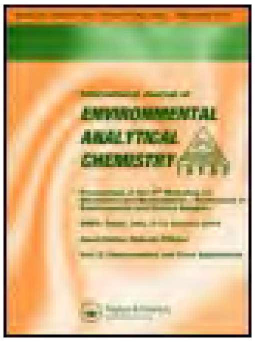

International Journal of Environmental Analytical Chemistry

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/geac20

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To cite this article: Ş. Turhan , S. Tokat , A. Kurnaz & A. Altıkulaç (2020): Distribution of elemental compositions of zeolite quarries and calculation of radiogenic heat generation, International Journal of Environmental Analytical Chemistry, DOI: 10.1080/03067319.2020.1839439

To link to this article: https://doi.org/10.1080/03067319.2020.1839439

Published online: 28 Oct 2020.

INTERNATIONAL JOURNAL OF ENVIRONMENTAL ANALYTICAL CHEMISTRY
https://doi.org/10.1080/03067319.2020.1839439

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Distribution of elemental compositions of zeolite quarries and calculation of radiogenic heat generation

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ABSTRACT

The effectiveness ofthe use of zeolites in different industrial processes depends on their physical-chemical properties that are distinctly connected to their geological deposits. In this study, major oxides, eco-toxic metals (Cr, Co, Ni, Cu, Zn, As, Zr, Cd and Pb), and rare earth (Y, La, Ce, Pr and Nd), radioactive (Th and U) and other trace elements contents of eighty-one zeolite samples collected from four different zeolite quarries in Gördes in Turkey were analysed by using energy dispersed X-ray fluorescence spectrometer. Also, pH values and SiO_2/Al_2O_3 ratios were determined for zeolite samples. In addition, radiogenic heat generation (RHG) caused by radiations emitted from uranium (U), thorium (Th) and radioactive potassium (^{40}K) in zeolite samples wereestimated.Gördes zeolite contains major oxides, on average, 75.1% SiO_2, 14.1% Al_2O_3, 3.2% K_2O, 2.4% CaO, 1.7% Fe_2O_3, 1.4% MgO, 1.3% Na_2O. The average concentration of As, Cd, Pb, Th and U analysed in zeolite samples were found as 24.8, 2.1, 47.830.1 and 6.0 $mgkg^{-1}$, respectively. According to average SiO_2/Al_2O_3 ratios, the ZO1 quarry contains middle silica zeolites while ZO2, ZO3 and ZO4 quarries contain high silica group zeolites. RHG values estimated for zeolite samples varied from 2.3 $\mu Wm^{-3}$to 4.1 μWm^{-3}.

ARTICLE HISTORY
Received 8 September 2020
Accepted 15 October 2020

KEYWORDS
Zeolite; major oxides; eco-toxic metal; uranium; thorium; radiogenic heat generation; Gördes

1. Introduction

Natural zeolites, which have become an important industrial mineral because of these properties, are widely used in environmental protection, agriculture, animal husbandry, energy, mineral-metallurgy and other industrial areas [1,2,3]. One of the most studied zeolites in basic and applied research is clinoptilolite, also known as clino zeolite.

The structure of the zeolite mineral, which is formed of hydrated natural silicates of alkali and alkaline earth elements as a result of the change of volcanic ash in the water environment millions of years ago, is very interesting and complex [4]. The primary structural units of the zeolites are SiO_4 and AlO_4 tetrahedra. These units are connected to the secondary structure units via oxygen ions to form a three-dimensional crystalline lattice structure [5]. The displacement of Si with Al defines the negative charge of the zeolite frame, which is compensated by alkali and alkaline earth metal cations. Therefore, natural zeolites appear as cation exchangers because they have a negative charge on the

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surface. Displacement in the zeolite lattice is not limited to Si-Al substitutionand Fe, B, Cr, Ge andTi atoms can also replace Si [5].The most general formula of natural zeolites with more than 50 known species is given as follows [6]:

$$(Li, Na, K)_x (Mg, Ca, Sr, Ba)_y \left[Al(x + 2y)Si_{n-(x+2y)} O_{2n}\right] \cdot m_0 H_2O \tag{1}$$

where x denotes the number of monovalent metal ions, y denotes the number of divalent metal ions, n denotes half the number of oxygen atoms, and m_0 denotes the number of water molecules.Zeolites are used in many different industrial fields as absorbers, catalysts, molecular sieves and ion-exchange materials due to their size and shape.

There are significant natural zeolite reserves in the world, which are the main components of volcanic origin Cenozoic sedimentary rocks [7]. Approximately 3–3.5 million tons of zeolite in horizontally deposited tuff is extracted or produced as an important industrial mineral by open pit operation method worldwide [7].Turkey has a wide variety of mineral deposits such as chromium, copper, zinc, lead, gold, boron,feldspar, marble, perlite, pumice, sepiolite,barite clay, sand, limestone, mica, zeolite etc. due to its extremely complex geology and its location on Tethyan Metallogenic Belt [4,8].Turkey has significantly larger and richer zeolite reserves [3]. In Turkey, a well-known, the most common and important zeolite deposits are clinoptilolite and heulandite. Turkey's visible and probable zeolite (clinoptilolite and heulandite) reserve is estimated to be 345 million tonnes [9]. Turkey's most important reserves of clinoptilolite and heulanditeare located in Gördes (Manisa) and Bigadiç (Balıkesir) in Turkey's western Anatolia region [3]. In 2008, Turkey produced 100,000 tons of zeolite [7]. There are open quarries in the Gördes region that produce a wide range of natural zeolite products, which export to more than forty-five countries. Gördes zeolites are used in agriculture and water treatment, especially in animal feed additives in Turkey [10].The chemical composition of zeolites plays an important role in the synthesis, characterisation, and more effective use of zeolites. For this reason, it is important that the major, minor, and trace element distributions of zeolite quarries are accurately and precisely determined and updated over time. Although there are many studies on the absorbent, catalyst, ion exchange, and molecular sieve properties ofGördes zeolites used in different industrial sectors [11,12,13,14,15,16,17,18,19,20,21], a few studies wereperformed to determine the elemental distribution of zeolite quarries [7,22,23,24,25,26].Özen [7] investigatedthe pozzolanic and mineralogical properties of clinoptilolite, mordenite,and analcime zeolite samples. Diaz and Peraza [22] analysed the concentrations of 38 elements in zeolite samples collected from four Cuban zeolite deposits using instrumental neutron activation analysis (INAA) and X-ray fluorescence (XRF) spectrometric method.They suggested that the use of Cuban natural zeolites containing high toxic elements such as As, Hg, U, etc. should be restricted in agriculture and pharmaceutical and sugar industries.Bilgin [24] analysed oxides (SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O,K_2O) in the four zeolite samples collected from four different zeolite fields from Gördes (Manisa) region using XRD and microscope.Albayrak [25] examined mineralogical, chemical and thermal analysis-gravimetric properties of zeolite samples collected from Manisa Gördes region by using XRD, SEM and DTA-TGA techniques. Kurudireket al. [26]performed the elemental analysis of a zeolite (clinoptilolite) sample obtained from Manisa Gördes zeolite by using a wavelength dispersed X-ray fluorescence (WDXRF) spectrometer.

According to our literature research, there is no detailed study on the determination of the elemental distribution of zeolite quarries in the Gördes region and estimation of radiogenic heat generation from the zeolite sample. The aim of this study is to determine the pH values and chemical distributions of zeolite samples collected from four commercially operated zeolite quarries in the Gördes and to estimate the radiogenic heat generated by ionising radiation (alpha-, beta- and gamma-ray) emitted from the elements of uranium (U), thorium (Th) and radioactive potassium (^{40}K) in the zeolite samples.

2. Experimental

2.1. Sample collectionand preparation

Gördes zeolitic tuff located is in the north-east of Manisa province in the Western Anatolia of Turkey [7]. The continental Neogene sedimentary succession in the Gördes is 2000 m [7]. Zeolite mineral formation is observedin nearly 2/3 of the tuffs in Miocene piles.80% of these tuffs are comprised of heulandite and clinoptilolite [3].A representative number of zeolite samples were collected from each of the four zeolite quarries (ZO1, ZO2, ZO3, and

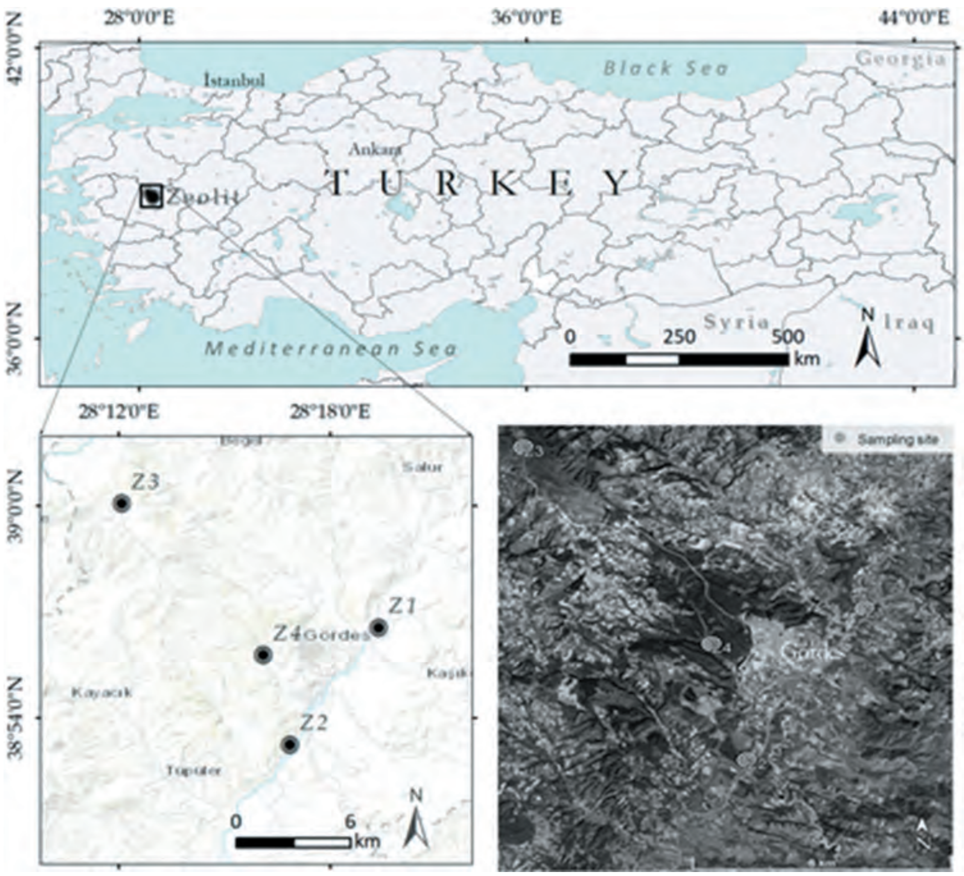

Figure 1. Location of zeolite quarries.

ZO4) operated in Gördes as shown in Figure 1.Samples were collected by random sampling method. The samples collected from eighty-one sampling locations were brought to the sample preparation laboratory and dried. The samples were dried at 110°C for five hours. The samples were then pulverised using a grinderto match the calibrated powder geometry in the EDXRF spectrometer. 5 grams of each sample were taken and homogenised with an agate mortar.

2.2. Measurement of pH and elemental concentrations

The following procedure was used for the pH measurement of each zeolite sample: 10 g of air-dried zeolite sample was placed into a 50-mL beaker. 25 mL of distilled water was added to the beaker and left for 24 hours. The pH was then measured using a pH metre (LaMotte 5 series).

Analyses of the major, minor and traceelements in the zeolite samples were carried out by using a benchtop ED-XRF spectrometer (Spectro Xepos). The EDXRF spectrometerwas equipped with a thick binary Pd/Coend-window tube(50 W, 60 kV) and a Peltier cooled Si drift detector (large detector area (30 mm^2 and active area 20 mm^2) [27]. The detector's spectral resolution (FWHM) is small to 130 eV for Mn K_α.The spectrometerhas a HAPG polariser to improve the sensitivity to elements in the Na–Cl range and a bandpass filter to improve the performance for element detection in K–Mn range. The EDXRF spectrometer optimises the excitation using polarisation and secondary targets. It has an autosampler for up to 12 items and software modules. The target changer with up to eight polarisation and secondary targets offers many different excitation conditions, ensuring the optimal determination of all elements from K to U [27]. The EDXRF spectrometer employs sophisticated calibration techniques such as 'standardless' calibration, usually based on the Fundamental Parameters (FP) method. Soil certified reference material (NIST SRM 2709) was used for the quality assurance for the EDXRF system. The analysis procedures were completed by placing the sample cups prepared for each zeolite sample into the automatic sampler and counting them once for two hours. The overall uncertainty of the analytical procedure is between 4% and 15%.

2.3. Radiogenic heat generation

Heat generation and flow are the main characteristics of the Earth's crust. Thereare two main sources of the internal heat of the earth: the first source is the cooling of the Earth and the second source is the long-lived [28]. The thermal structure and evolution of the continents depend largely on the amount and distribution of radioactive heat sources in the Earth's crust [29]. The heat generated caused by radioactive decay in rocks is of main importance in understanding the Earth's thermal history and interpreting the continental heat flux data. Therefore, radiogenic heat generation from natural radiation in the Earth's crust is the main parameter that determines the thermal structure of the continental crust. Radiogenic decay of the radionuclides which are member of the natural radioactive series of uranium (^{238}U with a half-life of 4.5 10^9 y), actinium (^{235}U with a half-life of 0.71 10^9 y), and thorium (^{232}Th with a half-life of 14.1 10^9 y) and potassium (^{40}K with a half-life of 1.3 × 10^9 y) provides the largest internal source of heat (more than 98% of present-day heat generation) [29]. ^{40}K is a naturally occurring radioactive isotope of the common element potassium (^{39}K), which represents about 2.4% by weight of the Earth's crust. It has an atomic percent abundance of 0.0117%.The kinetic energy of ionising radiations (α-, β-, γ and X-rays) was absorbed in rocks and soils and converted into heat. In general, the radiogenic heat generation rate (*RHG* in μWm^{-3}) of any rock is estimated by the following formula [30]:

$$RHG = 10^{-5} \cdot \rho \cdot (9.52 \cdot C_U + 2.56 \cdot C_{Th} + 3.45 \cdot C_K) \quad (2)$$

where$\rho$is the bulk density of the zeolite (in kgm^{-3}),C_U, $C_{Th}$and $C_K$are the concentration of uranium (in $mgkg^{-1}$), thorium (in $mgkg^{-1}$) and potassium (%) measured in the zeolite samples, respectively.

3. Results and discussion

3.1. Oxide contents of zeolite quarries

The pH values of Gördes clinoptilolite varied from 6.8 (slightly acid) to 8.0 (slightly alkaline), with an average of 7.4 (slightly alkaline). The average pH value of ZO1, ZO2, ZO3 and ZO4 quarry was measured as 7.4 (6.8–8.0), 7.6 (7.5–7.7), 7.5 (6.5–7.7) and 7.3 (7.0–7.7), respectively. Descriptive statistical information on the oxide content of Gördes zeoliteis given in Table 1.The comparison of the average oxide concentration of Gördes zeolite with those in the literature is given in Table 2.Descriptive statistical information on the oxides analysed in Gördes zeolite quarries is given in Table 3.As can be seen from Table 1, the oxides contained in the analysed zeolite samples are listed in order: $SiO_2 > Al_2O_3 > K_2O > CaO > Fe_2O_3 > MgO > Na_2O > TiO_2 > SrO > P_2O_5 > MnO$.The concentrations of SO_3 analysed only in the zeolite samples from the ZO1 quarry varied from 0.29 to 0.37% with an average of 0.34%.

The concentrations of SiO_2analyzed in Gördes zeolite samples varied from 52.6 to 78.8% with an average of 75.1%. The average SiO_2 level is approximately 40% higher than the Earth's crust average of 53.5% [31]. The average concentration of SiO_2 ZO3, ZO1, ZO2 and ZO4 was found as 77.7%, 76.9%, 74.8% and 73.0%, respectively.The average SiO_2 level is consistent with the values measured for Gördes and Ukraine zeolite in the literature, but it is greater than the average SiO_2 concentration of Bigadiç zeolite. The concentrations of Al_2O_3 analyzed in Gördes zeolite samples varied from 9.3 to 16.3% with an average of 14.1%. The

Table 1. Descriptive statistical data for major and minor oxides in the Gördes zeolite.

	The concentration of oxides (%)								
Oxide	Average	SE[a]	Median	SD[a]	Kurtosis	Skewness	Min	Max	N
Na_2O	1.328	0.027	1.341	0.241	−0.553	−0.291	0.723	1.817	81
MgO	1.392	0.050	1.213	0.452	−0.593	0.753	0.581	2.361	81
Al_2O_3	14.119	0.163	14.570	1.465	0.446	−0.973	9.337	16.340	81
SiO_2	75.064	0.564	77.410	5.073	3.951	−1.901	52.630	78.830	81
P_2O_5	0.036	0.002	0.029	0.015	−0.091	1.084	0.016	0.072	81
K_2O	3.166	0.067	3.444	0.606	−0.631	−0.778	1.895	4.061	81
CaO	2.446	0.067	2.394	0.600	3.356	1.845	1.616	4.343	81
TiO_2	0.090	0.002	0.092	0.015	−0.006	−0.326	0.054	0.121	81
MnO	0.032	0.001	0.029	0.009	−0.669	0.545	0.017	0.053	81
Fe_2O_3	1.687	0.034	1.656	0.302	−0.895	−0.186	1.095	2.195	81
SrO	0.039	0.002	0.032	0.022	2.919	1.998	0.017	0.106	81

[a]SE: standard error, SD: standard deviation

Table 2. Comparison of average oxide concentrations of Gördes zeolite with literature values.

	The concentration of oxides (%)								
Quarry code	Average	SE	Median	SD	Kurtosis	Skewness	Min	Max	N
ZO1									
Na_2O	1.481	0.041	1.523	0.130	−0.788	−0.431	1.272	1.678	10
MgO	2.175	0.033	2.186	0.105	−0.528	0.116	2.031	2.361	
Al_2O_3	15.583	0.153	15.685	0.483	−0.704	−0.324	14.840	16.340	
SiO_2	76.899	0.127	77.025	0.403	−1.875	−0.273	76.350	77.370	
P_2O_5	0.065	0.002	0.066	0.005	−1.440	−0.320	0.057	0.072	
K_2O	2.399	0.046	2.394	0.146	−0.988	−0.119	2.166	2.606	
CaO	2.084	0.069	1.997	0.220	−1.172	0.686	1.800	2.394	
TiO_2	0.064	0.002	0.062	0.008	−1.100	0.406	0.054	0.077	
MnO	0.027	0.002	0.029	0.006	−0.687	−0.475	0.018	0.036	
Fe_2O_3	1.554	0.043	1.578	0.135	−1.055	−0.513	1.347	1.722	
SrO	0.094	0.003	0.094	0.010	−0.291	−0.517	0.076	0.106	
SO_3	0.338	0.008	0.337	0.026	−0.637	−0.501	0.290	0.366	
ZO2									
Na_2O	1.287	0.088	1.355	0.279	−0.702	−0.813	0.808	1.537	10
MgO	1.976	0.089	2.070	0.281	0.733	−1.368	1.410	2.191	
Al_2O_3	13.910	0.532	14.540	1.682	1.297	−1.532	10.350	15.100	
SiO_2	74.797	1.834	77.430	5.799	3.499	−2.085	60.890	77.550	
P_2O_5	0.053	0.002	0.051	0.005	−0.091	0.962	0.048	0.063	
K_2O	2.072	0.061	1.997	0.194	−2.231	0.261	1.895	2.313	
CaO	3.859	0.133	3.730	0.421	−2.323	0.178	3.453	4.343	
TiO_2	0.105	0.004	0.103	0.013	−2.329	0.122	0.092	0.121	
MnO	0.034	0.001	0.033	0.005	−2.217	0.144	0.029	0.040	
Fe_2O_3	1.275	0.057	1.249	0.180	−2.433	0.073	1.104	1.488	
SrO	0.044	0.002	0.043	0.008	−2.530	0.021	0.036	0.052	
ZO3									
Na_2O	1.241	0.050	1.195	0.244	0.257	0.304	0.723	1.817	24
MgO	1.357	0.033	1.407	0.163	−0.041	−0.697	0.945	1.597	
Al_2O_3	14.050	0.192	14.150	0.940	3.992	−1.786	11.350	15.230	
SiO_2	77.664	0.582	78.465	2.852	9.560	−3.254	67.540	78.830	
P_2O_5	0.034	0.001	0.033	0.005	−0.960	0.526	0.028	0.042	
K_2O	3.614	0.064	3.706	0.314	−0.106	−0.740	2.927	4.061	
CaO	2.166	0.058	2.206	0.282	−0.749	−0.323	1.616	2.595	
TiO_2	0.099	0.002	0.100	0.010	1.508	−0.970	0.073	0.115	
MnO	0.043	0.001	0.043	0.006	−0.395	−0.205	0.029	0.053	
Fe_2O_3	1.536	0.037	1.566	0.183	0.598	−0.471	1.095	1.926	
SrO	0.027	0.001	0.027	0.006	−0.407	0.460	0.017	0.039	
ZO4									
Na_2O	1.354	0.038	1.435	0.233	−0.832	−0.176	0.813	1.772	37
MgO	1.045	0.025	1.094	0.154	0.327	−0.687	0.581	1.260	
Al_2O_3	13.824	0.272	14.590	1.654	−0.547	−0.564	9.337	15.970	
SiO_2	72.954	0.952	77.170	5.789	2.306	−1.298	52.630	77.780	
P_2O_5	0.024	0.000	0.024	0.002	6.067	−1.264	0.016	0.029	
K_2O	3.379	0.041	3.487	0.249	2.113	−1.603	2.574	3.606	
CaO	2.344	0.032	2.436	0.196	1.461	−1.535	1.765	2.512	
TiO_2	0.087	0.001	0.088	0.008	0.502	−0.853	0.065	0.101	
MnO	0.025	0.001	0.025	0.005	3.118	1.212	0.017	0.041	
Fe_2O_3	1.933	0.032	2.004	0.196	0.662	−1.220	1.428	2.195	
SrO	0.031	0.001	0.032	0.004	0.075	−1.003	0.022	0.035	

average Al_2O_3 level is lower than the Earth's crust average of 15.9% [31]. The average concentration of Al_2O_3in ZO1, ZO3, ZO2 and ZO4 was found as 15.6%, 14.1%, 13.9% and 13.8%, respectively. The average Al_2O_3 level is higher than those analysed in various zeolite samples in the literature.The concentrations of K_2O analyzed in Gördes zeolite samples varied from 1.9 to 4.1% with an average of 3.2%. The average K_2O level is approximately three times higher than the Earth's crust average of 1.1% [31]. The average concentration of

Table 3. Descriptive statistical data for major and minor oxides in the Gördes zeolitequarries.

Zeolite type	Region	Oxide concentration (%)											Reference
		Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	Fe_2O_3	TiO_2	MnO	P_2O_5	SO_3	
CLI	Turkey, Bigadiç (Balıkesir)	0.17	1.19	11	67.22	1.51	3.32	0.8	0.07	-	-	-	[34]
CLI	Turkey, Bigadiç (Balıkesir)	0.25	0.83	11.8	71.5	4.6	2.65	0.88	0.1	-	-	-	[23]
CLI	Turkey, Gördes (Manisa)	0.6	0.7	11.8	73.21	2.73	2.96	0.93	0.1	-	-	-	[23]
CLI	Ukraine	2.6	0.4	13.23	73.9	3.72	2.68	2.07	-	-	-	-	[35]
CLI	Turkey, Gördes (Manisa)	0.28	0.83	12.4	70.9	4.46	2.54	1.21	0.089	-	0.02	-	[36]
CLI+HEU	Turkey, Gördes (Manisa)	0.63	0.82	10.49	73.11	1.15	1.61	1.41	-	-	-	-	[24]
CLI+HEU		0.46	0.88	9.92	72.97	2.62	1.59	1.76	-	-	-	-	
CLI+HEU		0.22	0.69	8.78	74.26	1.9	2.62	0.92	-	-	-	-	
CHA		0.66	0.11	9.3	77.42	3.66	0.48	0.96	-	-	-	-	
CLI	Turkey, Gördes (Manisa)	0.92	0.42	12.06	71.98	4.28	1.99	0.45	-	-	0.03	0.02	[37]
CLI	Turkey, Gördes (Manisa)	0.4	0.8	11.5	74.5	2.7	3.2	1.5	-	-	-	-	[25]
CLI	Turkey, Bigadiç (Balıkesir)	0.43	1.25	11.68	71.83	3.7	3.39	1.15	0.07	0.03	-	-	[38]
CLI	Turkey, Gördes (Manisa)	0.66	0.76	11.54	67.57	4.27	2.17	1.34	-	-	-	-	[39]
CLI	Turkey, Gördes (Manisa)	0.18	0.71	11.32	75.84	3.76	2.12	0.93	0.08	0.01	-	-	[40]
CLI	Turkey, Gördes (Manisa)	0.52	1.13	13.11	69.31	2.83	2.07	-	-	-	-	0.1	[41]
CLI	Turkey, Bigadiç (Balıkesir)	0.18	1.01	9.99	64.99	1.95	3.51	-	-	-	-	-	[42]
CLI	Turkey, Gördes (Manisa)	0.69	1.58	13.61	72.09	3.49	2.64	1.91	0.102	0.07	0.06	0.3	[26]
CLI	Turkey, Gördes (Manisa) ZO1	1.48	2.17	15.58	76.9	2.4	2.08	1.55	0.06	0.03	0.07	0.34	This study
	Turkey, Gördes (Manisa) ZO2	1.29	1.98	13.91	74.8	2.07	3.86	1.28	0.11	0.03	0.05	-	
	Turkey, Gördes (Manisa) ZO3	1.24	1.36	14.05	77.66	3.61	2.17	1.54	0.1	0.04	0.03	-	
	Turkey, Gördes (Manisa) ZO4	1.35	1.04	13.82	72.95	3.38	2.34	1.93	0.09	0.03	0.02	-	

K_2O in ZO3, ZO4, ZO1 and ZO2 was found as 3.6%, 3.4%, 2.4% and 2.1%, respectively. The average K_2O level is consistent with the average K_2O concentrations measured for Gördes, Bigadiç and Ukrainian zeolites in the literature.The concentrations of CaO analysed in Gördes zeolite samples varied from 1.6 to 4.3% with an average of 2.4%. The average CaO level is approximately four times lower than the Earth's crust average of 9.4% [31]. The average concentration of CaO in ZO2, ZO4, ZO3 and ZO1 was found as 3.9%, 2.3%, 2.2% and 2.1%, respectively. The average CaO level is consistent with the average CaO concentrations measured for Gördes, Bigadiç and Ukrainian zeolites in the literature.The concentrations of Fe_2O_3analyzed in Gördes zeolite samples varied from 1.1 to 2.2% with an average of 1.7%. The average Fe_2O_3 level is approximately 50% higher than the Earth's crust average of 1.1% [31]. The average concentration of Fe_2O_3 in ZO4, ZO1, ZO3 and ZO2 was found as 1.9%, 1.6%, 1.5% and 1.3%, respectively.The average Fe_2O_3 level is consistent with the values measured for Gördes and Ukraine zeolite in the literature, but it is greater than the average Fe_2O_3 concentration of Bigadiç zeolite. The concentrations of MgO analysed in Gördes zeolite samples varied from 0.6 to 2.4% with an average of 1.4%. The average MgO level is approximately four times lower than the Earth's crust average of 5.4% [31]. The average concentration of MgO in ZO1, ZO2, ZO3 and ZO4 was found as 2.2%, 2.0%, 1.4% and 1.0%, respectively. The average MgO level is above the average MgO measured for Gördes, Bigadiç and Ukraine zeolite in the literature.The concentrations of Na_2O analysed in Gördes zeolite samples varied from 0.7 to 1.8% with an average of 1.3%. The average Na_2O level is approximately two times lower than the Earth's crust average of 2.7% [31]. The average concentration of Na_2O in ZO1, ZO4, ZO2 and ZO3 was found as 1.5%, 1.4%, 1.3% and 1.2%, respectively. The average Na_2O level is above the average Na_2O measured for Gördes, Bigadiç and Ukraine zeolite in the literature.The concentrations of TiO_2 analysed in Gördes zeolite samples varied from 0.05 to 0.12% with an average of 0.09%. The average TiO_2 level is approximately eleven times lower than the Earth's crust average of 0.97% [31]. The average concentration of TiO_2inZO2, ZO3, ZO4 and ZO1 was found as 0.11%, 0.10%, 0.09% and 0.06%, respectively. The average TiO_2 level is consistent with the average TiO_2 concentrations analyzed for Gördes, Bigadiç and Ukrainian zeolites in the literature. The concentrations of SrO analyzed in Gördes zeolite samples varied from 0.02 to 0.11% with an average of 0.04%. The average concentration of SrOin ZO1, ZO2, ZO4 and ZO3 was found as 0.09%, 0.04%, 0.03% and 0.03%, respectively. Theconcentrations of MnO analyzed in Gördes zeolite samples varied from 0.02 to 0.05% with an average of 0.03%. The average MnO level is approximately fivetimes lower than the Earth's crust average of 0.16% [31]. The average concentration of MnO inZO3, ZO2, ZO1 and ZO4 was found as 0.043%, 0.034%, 0.027% and 0.025%. The average MnO level is consistent with the average MnOconcentrations analysed for Gördes zeolites in the literature.The concentrations of P_2O_5analyzed in Gördes zeolite samples varied from 0.02 to 0.07% with an average of 0.04%.The average P_2O_5 level is approximately five times lower than the Earth's crust average of 0.19% [31]. The average concentration of P_2O_5in ZO1, ZO2, ZO3 and ZO4 was found as 0.07%, 0.05%, 0.03% and 0.02%, respectively. The average P_2O_5 level is consistent with the average P_2O_5 concentrations analyzed in Gördes zeolites in the literature.

3.2. SiO_2/Al_2O_3 ratios of zeolite quarries

The type of zeolites formed is a function of temperature, pressure, the concentration of reactive solutions, pH, activation and ageing process, and SiO_2 and $A1_2O_3$ content. Depending on the SiO_2/Al_2O_3 ratio, the zeolites can be divided or graded into three classes: low silica zeolites(Si/Al≤ 2), medium silica zeolites(2 < Si/Al≤ 5) and high

Table 4. Classification of Gördes zeolite quarries according to SiO_2/Al_2O_3 ratio.

	SiO_2/Al_2O_3 ratio		
Quarry code	Range (min-max)	Average	Class or degree
ZO1	4.7–5.2	4.9	Medium silica
ZO2	5.1–5.9	5.4	High silica
ZO3	5.2–6.0	5.5	High silica
ZO4	4.9–5.6	5.3	High silica

silica zeolites(Si/Al> 5) [32].In general, for zeolites, an increase in this parameter-causes a significant increasein parameters such as acid resistance, thermal stability, etc [33]. The SiO_2/Al_2O_3ratios of the Gördes zeolite quarries are given in Table 4. The average SiO_2/Al_2O_3 ratio of the ZO1, ZO2, ZO3 and ZO4 coded quarries were calculated as 4.9, 5.4, 5.5 and 5.3, respectively. According to these average values, it is seen that the ZO1 quarry is of medium silica grade and ZO2, ZO3 and ZO4 quarry is of high silica grade zeolite class.

3.3. Trace element contents of zeolite quarries

The concentrations of trace elements analysed in the Gördes zeolite quarries are given in Table 1.As can be seen in Table 4.1, the significant eco-toxic metals,which are primary toxic to human and environmental health, analysed in the Gördes zeolite samples are listed as Zr> Zn > Pb > As > Ni > Co > Cr> Cu> Cd according to their average concentration.The concentrations of Zranalyzed in the Gördes zeolite samples varied from 43.1 to 122.5 mgkg^{-1} with an average of 87.8 mgkg^{-1}. The average Zr level is approximatelytwo times smaller than the Earth's crust average of 170 mgkg^{-1} [31]. The averageZr concentration in ZO4, ZO1, ZO3 and ZO2 wasfound as 103.1, 81.3, 75.1 and 68.6 mgkg^{-1}, respectively.The

Table 5. The concentration of trace elements analysed in the Gördes zeolitequarries.

		The concentration of trace element in Gördes zeolite quarries (mgkg^{-1})											
		ZO1			ZO2			ZO3			ZO4		
Group	Element	Ave	Min	Max	Ave	Min	Max	Ave	Min	Max	Ave	Min	Max
Toxic metal	Cr	4.2	1.9	5.9	12.7	8.3	15.1	10.4	6.1	13.8	4.6	1.5	6.6
	Co	8.7	7.2	10.6	11.8	7.4	15.3	9.5	6.0	17.2	7.5	6.4	11.5
	Ni	9.2	8.0	10.4	12.9	10.7	14.5	11.2	8.5	13.1	8.4	6.2	12.9
	Cu	3.7	2.6	4.7	4.8	2.6	6.7	4.9	3.2	6.6	3.9	2.1	6.9
	Zn	35.5	29.5	40.4	31.7	25.6	36.6	43.1	31.1	56.5	75.2	37.2	140.3
	As	126.0	103.4	148.5	13.1	11.1	15.7	21.2	14.1	31.0	2.9	0.8	5.2
	Zr	81.3	62.2	90.0	68.6	53.3	79.8	75.1	43.1	100.0	103.1	77.8	122.5
	Cd	1.9	1.2	2.9	3.3	2.0	4.6	2.3	1.4	4.5	1.6	1.2	1.7
	Pb	49.1	41.0	54.6	28.8	22.8	33.6	47.2	33.6	58.3	52.9	33.7	78.6
Transition metal	V	4.3	1.3	7.7	12.2	7.8	16.0	7.2	0.5	14.6	1.5	0.5	4.7
	Nb	12.4	9.7	13.5	11.3	8.5	14.2	11.5	8.3	13.9	12.9	9.0	14.3
	Ag	3.3	1.0	6.7	7.8	7.0	8.8	4.7	1.0	9.7	2.1	1.0	5.8
	Hf	5.4	3.4	7.3	5.9	3.8	7.8	4.9	2.6	7.9	5.4	3.0	7.3
	Ta	28.0	20.9	32.5	26.4	17.3	31.8	23.4	13.7	31.9	27.9	18.5	33.3
	W	3.1	2.3	3.9	2.2	1.4	3.1	2.8	1.4	4.6	1.5	0.5	3.1
Radiotoxic actinide	Th	30.4	26.1	33.5	27.9	22.7	31.9	29.7	21.7	37.1	30.9	23.6	35.9
	U	9.5	8.0	10.7	6.4	5.5	7.5	6.3	4.9	8.3	4.9	3.3	6.3
Rare earth element	Y	21.6	19.0	23.5	21.4	18.2	24.0	17.9	14.5	21.7	10.9	9.2	14.8
	La	58.8	1.9	146.9	13.9	1.9	74.2	19.0	1.9	83.4	25.6	1.9	109.5
	Ce	33.5	1.7	146.0	15.9	1.7	95.4	21.9	1.7	132.1	19.6	1.7	108.0
	Pr	15.4	1.3	136.0	7.4	1.9	19.9	8.2	2.0	23.9	7.4	2.0	23.2
	Nd	66.4	57.7	89.9	71.9	59.2	83.9	68.0	46.2	78.6	59.8	46.0	76.8
Alkali metal	Rb	199.6	164.3	216.1	101.4	81.8	116.5	155.7	108.0	182.2	181.7	133.7	196.8
	Cs	259.8	200.5	294.3	27.2	4.0	64.9	47.1	4.0	70.6	70.7	4.0	109.0
Alkaline earth metal	Ba	1160.8	877.7	1452.0	345.4	258.5	421.8	148.5	45.6	228.4	206.8	161.3	253.0
	Sb	6.4	3.0	11.0	7.3	2.1	11.4	4.1	2.1	8.0	2.6	0.2	9.3
	Ga	16.3	12.9	18.7	14.4	10.9	17.3	15.9	11.9	19.6	15.6	11.2	17.8
	Te	8.0	2.0	14.6	12.4	8.7	16.6	5.6	2.0	10.5	2.3	0.2	13.4
Halogen	I	3.2	2.3	8.0	7.0	3.1	10.4	4.7	1.9	10.2	3.4	2.0	8.8
Post-transition metal	Sn	4.3	1.2	7.3	7.9	5.6	11.1	4.4	0.4	9.7	2.1	0.2	9.1

concentrations of Znanalyzed in the Gördes zeolite samples varied from 25.6 to140.3 mgkg^{-1} with an average of 55.5 mgkg^{-1}. The average Zn level is approximately1.5 times smaller than the Earth's crust average of 83 mgkg^{-1} [31]. The average Zn concentration inZO4, ZO3, ZO1 and ZO2 wasfound as 75.2, 43.1, 35.5 and 31.7 mgkg^{-1}, respectively.The concentrations of Pbanalyzed in the Gördes zeolite samples varied from 22.8 to 78.6 mgkg^{-1} with an average of 47.8 mgkg^{-1}. The average Pb level is approximately three times higher than the Earth's crust average of 16 mgkg^{-1} [31]. The averagePb concentration inZO4, ZO1, ZO3 and ZO2 wasfoundas 52.9, 49.1, 47.2 and 28.8mgkg^{-1}, respectively.The concentrations of Asanalyzed in the Gördes zeolite samples varied from 0.8 to 148.5 mgkg^{-1} with an average of 24.8 mgkg^{-1}. The average As level is approximately fifteen times higher than the Earth's crust average of 1.7 mgkg^{-1} [31]. The averageAsconcentration inZO1, ZO3, ZO2 and ZO4 wasfound as 126.0, 21.2, 13.1 and 2.9mgkg^{-1}, respectively.The concentrations of Nianalyzed in the Gördes zeolite samples varied from 6.2 to 14.5 mgkg^{-1} with an average of 9.9 mgkg^{-1}. The average Ni level is approximately six times lower than the Earth's crust average of 58 mgkg^{-1} [31]. The averageNi concentration inZO2, ZO3, ZO1 and ZO4 wasfound as 12.9, 11.2, 9.2 and 8.4mgkg^{-1}, respectively.The concentrations of Coanalyzed in the Gördes zeolite samples varied from 6.0 to 17.2mgkg^{-1} with an average of 8.8 mgkg^{-1}. The average Co level is approximately twotimes lower than the Earth's crust average of 18 mgkg^{-1} [31]. The averageCo concentration inZO2, ZO3, ZO1 and ZO4 wasfound as 11.8, 9.5, 8.7 and 7.5 mgkg^{-1}, respectively.The concentrations of Cranalyzed in the Gördes zeolite samples varied from 1.5 to 15.1mgkg^{-1} with an average of 7.3 mgkg^{-1}. The average Cr level is approximately eleventimes lower than the Earth's crust average of 83 mgkg^{-1} [31]. The averageCr concentration inZO2, ZO3, ZO4 and ZO1 wasfound as 12.7, 10.4, 4.6 and 4.2 mgkg^{-1},respectively.The concentrations of Cuanalyzed in the Gördes zeolite samples varied from 2.1 to 6.9mgkg^{-1} with an average of 4.3 mgkg^{-1}. The average Cu level is approximately eleventimes lower than the Earth's crust average of 47 mgkg^{-1} [31]. The averageCu concentration inZO3, ZO2, ZO4 and ZO1 wasfound as 4.9, 4.8, 3.9 and 3.7 mgkg^{-1},respectively.The concentrations of Cdanalyzed in the Gördes zeolite samples varied from 1.2 to 4.6mgkg^{-1} with an average of 2.1 mgkg^{-1}. The average Cd level is approximately sixteentimes higher than the Earth'scrust average of 0.13 mgkg^{-1} [31]. The averageCd concentration inZO2, ZO3, ZO1 and ZO4 wasfound as 3.3, 2.3, 1.9 and 1.6 mgkg^{-1},respectively.

The concentrations of Thanalyzed in the Gördes zeolite samples varied from 21.7 to 37.1 mgkg^{-1} with an average of 30.1 mgkg^{-1}. The average Th level is approximately twotimes higher than the Earth's crust average of 13 mgkg^{-1} [31]. The averageTh concentration inZO4, ZO1, ZO3 and ZO2 wasfoundas30.9, 30.4, 29.7 and 27.9 mgkg^{-1}, respectively.The concentrations of Uanalyzed in the Gördes zeolite samples varied from 3.3 to 10.7mgkg^{-1} with an average of 6.0 mgkg^{-1}. The average U level is approximately twotimeshigher than the Earth's crust average of 2.5 mgkg^{-1} [31]. The averageU concentration inZO1, ZO2, ZO3 and ZO4 wasfound as 9.5, 6.4, 6.3 and 4.9 mgkg^{-1},respectively.

3.4. Radiogenic heat generation from zeolite samples

Radiogenic heat generation (RHG) caused by the Gördes zeolite samples varied from 2.3to 4.1 µWm^{-3} with an average of 3 µWm^{-3}. The averageRHG values for ZO1, ZO3, ZO2 and ZO4quarry were estimated as 3.7 (3.2–4.1)µWm^{-3}, 3.19 (2.4–3.9)µWm^{-3}, 2 (2.5–3.3) µWm^{-3} and 2.8 (2.3–3.3) µWm^{-3},respectively.

4. Conclusions

This study is the first detailed study in which twelve oxides (Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, K_2O, CaO, TiO_2, MnO, Fe_2O_3, SrO and SO_3) and 30trace elements (Cr, Co, Ni, Cu, Zn, As, Zr, Cd, Pb, Th, U, V, Nb, Ag, Hf, Ta, W, Y, La, Ce, Pr, Nd, Ba, Sb, Ga, Te, Rb, Cs, I and Sn)contained in eighty-one zeolite samples collected from commercially operated zeolite quarries in Gördes were analysed by the EDXRF spectrometric method.As a result, it was found that Gördes zeolite contained high levels of toxic arsenic, cadmium and lead, and radiotoxic thorium and uranium, which are harmful for human and environmental health.Erionite, a zeolite type is known to cause mesothelioma disease which is a dangerous and rare form of lung cancer such as asbestos, especially in the Nevşehir (Turkey) region. Also, as mentioned above, Gördes zeolites include toxic metals and radiotoxic elements. In this context, the following points are recommended:

(1) to check whether these measures have been taken in these quarries, as it is of vital importance for workers working in the health and safety of workers for both the extraction of the zeolite mineral and for workers working in the crushing and screening phase and (2) zeolites from zeolite quarries containing lower toxic heavy metal and radiotoxic elements should be used for feed additive, water treatment, soil amendmentin agriculture and building raw materials in construction industry in Turkey.

Acknowledgments

This study is carried out within the framework of a master thesis conducted at Kastamonu University and supported by The Scientific Research Projects Coordinator of Kastamonu University (Research Project codded of KÜ-HIZDES/2019-51).

Disclosure statement

No potential conflict of interest was reported by the authors.

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