MINERALOGICAL, TECHNOLOGICAL AND FLUXING CHARACTERISTICS OF GRANITIC IGNEOUS ROCKS IN BIGA PENINSULA (NW TURKEY): POSSIBLE USES AS Na- AND K-FELDSPAR ALTERNATIVES FOR CERAMIC TILE PRODUCTION

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1. ABSTRACT

The Istanbul and Ukrainian clays, Aydın-Çine albite, and Düvertepe (Balıkesir, Turkey) or some local kaolins are the main components of Turkish ceramic tile products. Increasing ceramic production is leading to fast consumption of the available raw materials. On the other hand, transportation of raw materials from long distances directly cause high production costs. Thus, ceramic manufacturers are looking for local and low-cost fluxing raw materials. A research project focusing on the availability of fluxing materials was carried out on the Biga peninsula in order to find possible solutions to this problem.

A number of granitic igneous rocks which are Oligo-Miocene in age (35-19 MA) crop out in the Biga Peninsula (NW Turkey). These rocks mainly consist of I-Type granites with variable mafic mineral contents, and the mafic mineral-free leucogranite, aplogranite, granophyre, aplite and pegmatites. Whereas the pegmatites are rich in K. Feldspar (orthoclase, anorthoclase, microcline), the others are rich in Na-Feldspar (albite to oligoclase). We have investigated their fluxing characteristics and possibilities of use instead of Na-Feldspar in ceramic tile production. For this purpose, a total of 30 samples derived from the granitic rocks were characterized by optical microscopy, XRD and XRF methods, and then classified in the quartz-alkali feldspar-plagioclase (QAP) and total alkali-silica (TAS) diagrams. These studies have revealed that the granitic samples are granite, leucogranite, aplogranite, granophyric granite, aplite, pegmatite, monzonite, quartz monzonite and granodiorite.

The Biga Peninsula granitic rocks were investigated on the basis of their thermal behavior (DTA-TG), thermal expansion and sintering kinetics with water absorption, firing shrinkage. Data obtained from this study indicate that leucogranites can be used, especially, as fluxing material in variable rates instead of the common Çine-Aydın albite and show that lower-cost ceramic tile production is possible.

2. INTRODUCTION

It is widely known that a ceramic tile is composed of 40 wt.% feldspars, 40 wt.% ball clays and 10 wt.% filler materials. Therefore, feldspars are a major component of ceramic tiles. Ceramic wall and floor tile production of Turkey, for 2018, was about 335 million m^2, corresponding to 6.3 million tons of raw material. Considering the feldspar rate of 40% for this production, it is clear that the feldspar demand is approximately 2.5 million tons. Turkish ceramic companies provide the feldspars mainly from Western Turkey (Aydın, Çine, Milas regions). The major ceramic factories of Turkey are installed in the Bilecik-Söğüt and Çanakkale regions. These are far from Western Turkey feldspars, about 470 and 620 km, respectively. Therefore, long distance transportation of the feldspars causes high production costs. On the other hand, increasing usage in ceramic tile manufacturing and the high amount of feldspar exportation (nearly 6.7 million tons for 2018; IMMIB, 2019) are leading to fast consumption of the available feldspar sources.

Due to the high production costs, ceramic manufacturers demand low-cost local feldspar sources near their plants. Çanakkale Seramik Co. is also carrying out a field and lab-based research project for this purpose. In order to identify local feldspar sources, the Biga peninsula was investigated geologically. The data obtained in this study indicate that some granitic materials are suitable as alternatives to feldspar.

The use of alternative raw materials to feldspar has been studied in different regions of the world (Kayacı and Genc, 2009; Dias at al., 2017; Dondi, 2018). These are mainly "felsic/acidic" magmatic rocks, such as granite, syenite, volcanic rhyolite, dacite and their pyroclastic equivalents, which are rich in SiO_2, Al_2O_3, alkali (Na_2O, K_2O) oxides, and poor in iron and alkaline-earth oxides. Their alkali contents give rise to the fluxing character (Kingery and Bowen, 1976; Enrique at al., 1985; Klein, 2001; Sacmi, 2005; Salmang at al., 2007; Dias at al., 2017; Dondi, 2018; Zanelli at al., 2018). Due to the lower iron, MgO, MnO and TiO_2 contents, their firing colors match the requirements of ceramic manufacturers. Therefore, these rocks can be used instead of the conventional feldspars (albite, K-Feldspars).

In this study, the Biga peninsula felsic/acidic magmatic rocks are classified, based on their chemical, mineralogy and petrographical features, and their fluxing characteristics, together with their use as alternatives to feldspars, are investigated.

3. GEOLOGICAL SETTING

The Biga peninsula is characterized by a Triassic and older metamorphic basement and its sedimentary and volcanic cover of Jurassic to the recent period. This region was subjected to severe magmatic activity during the Eocene to Miocene and produced plutonic rocks and their volcanic counterparts (Genç, 1998; Yılmaz at al., 2001; Ersoy at al., 2017) (Fig 1). Plutonic rocks, Oligo-Miocene in age, are the main subject of this study. Their locations are indicated in Figure 1. These are epizonal intrusive rocks which were intruded into the basement rocks as well as the cover rocks older than the lower Miocene. The volcanic rocks related to the plutonic ones are acidic to intermediate rocks, such as rhyolite, dacite and andesitic lavas and tuffs. All these rocks were formed during the extensional tectonic regime of the NW Turkey from late Oligocene to early Miocene (Okay and Satır, 2000).

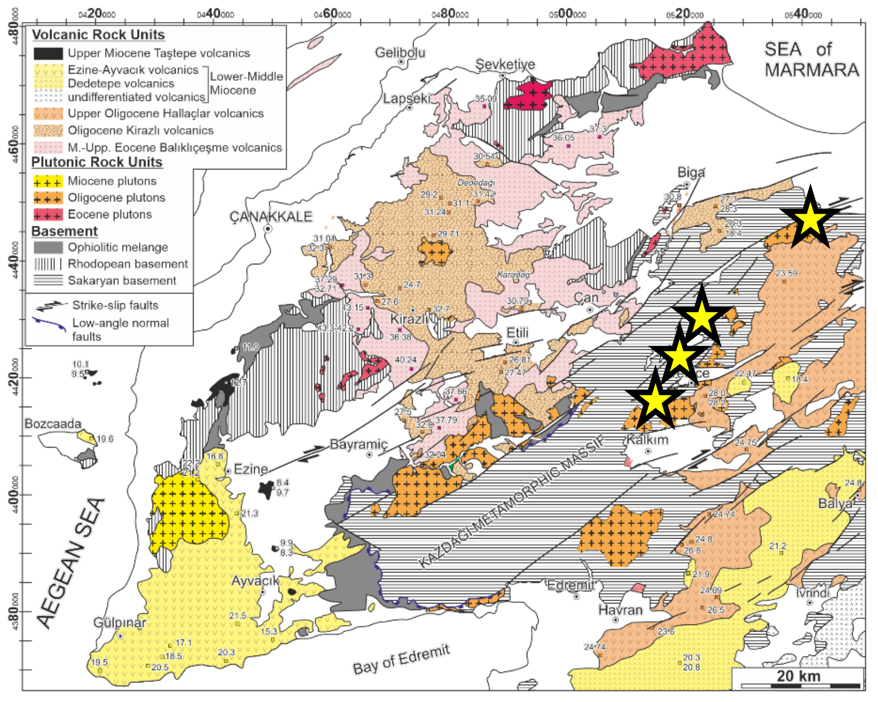

***Figure 1**. Simplified geology map of the Biga peninsula and the location of the Oligo-Miocene plutonic rocks (yellow stars) (after Ersoy at al., 2017).*

4. MATERIAL AND METHODS

A total of 30 samples were derived from the leucogranite and pegmatitic rocks from the Biga Peninsula (NW Turkey). All the experiments were done at the labs of the R&D Center of Çanakkaleseramik Co. The chemical compositions of the raw materials were determined by X-ray fluorescence (XRF) spectrometer (Panalytical Axios). X-ray powder diffraction (XRD) patterns were recorded at room temperature with a PANalytical X'Pert Pro MPD diffractometer using CuKα radiation and the X'Celerator Detector on diffracted beam. The software High Score Plus (v.6.0) for peak identification and automated search-match was used to analyze the resulting diffraction patterns. The quantitative analyses were carried out by the combined Rietveld-Reference Intensity Ratio (R.I.R) method as explained by Young (1995). Thermal analysis was performed with a Setaram Labsys EVO model DTA-TG-DSC instrument.

Technological tests of the samples were also carried out to investigate the sintering behaviors. After applying the size reduction, the samples were prepared at 6% moisture content. Then, the sample was sieved through a 3 mm sieve after which the granules were obtained in the laboratory. The granules were pressed, obtaining 5-cm diameter tablets at 325 kg/cm^2. After that, the tablets were dried and sintered in porcelain tile conditions, that is at 1180°C for 45 minutes. After thermal treatments, water absorption of the samples (ISO 10545-3); linear shrinkage, i.e. the difference in the length of the test specimen before and after firing (ISO 10545-2); and the color values were measured with a Minolta 3600 d Colorimeter. Different leucogranites and pegmatitic rocks was used in body recipes as 10 (wt.%), 20, 30 and 40 proportions instead of the alkaline raw materials (i.e. albites). New recipes were fired and their technological features such as firing shrinkage, water absorption and color (L, a, b) values were measured. In addition to sintering behavior, new formed phases in the fired bodies and their microstructures were investigated using a non-contact dilatometer and XRD.

5. RESULTS

5.1. RAW MATERIAL CHARACTERIZATION (PETROGRAPHY, XRD, XRF)

The Biga peninsula granitic rocks consist of a series of plutonic rocks. Some of them are biotite and hornblende granite and granodiorites. Their high amount of mafic minerals is problematic for ceramic production due to their high iron and magnesium contents. In contrast, leucogranites without mafic minerals were found suitable for ceramic manufacturing. The leucogranites are classified on the Streckeisen (1967) plot as monzonite to granite, rarely granodiorite (Fig 2). Their main mineral paragenesis is as follows: quartz + K-Feldspar + Plagioclase (albite to oligoclase) ± microcline ± mica. Based on the magmatic textures, these rocks are described as common leucogranite, granophyre, aplogranite, aplite and pegmatite. The total alkali – Silica plot derived from the chemical analysis (Table 1) and the Streckeisen diagram combination are shown in Fig 2. This composite plot shows that the chemical and mineralogical results support each other.

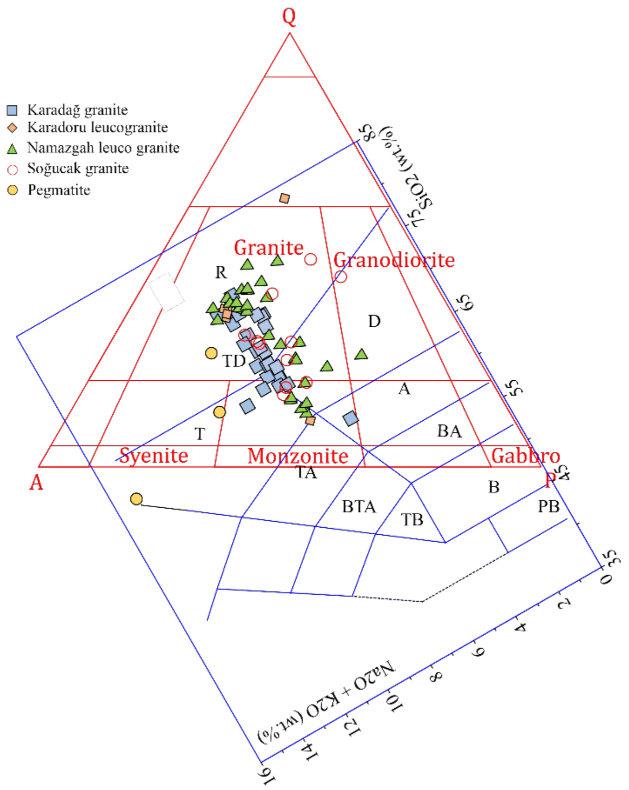

Fig 2. *Mineralogical and chemical classification of the Biga leucogranites and pegmatites on the Streckeisen (1967) and total alkali – silica plot (TAS) (Le Bas at al., 1986) combination.*

Sample characterization was carried out by the XRF and XRD methods. According to the results of the XRD analysis, quartz, and a small amount of micas such as muscovite were determined in addition to orthoclase and albite (Fig 3). The chemical and mineralogical analysis results of the samples are shown in Table 1

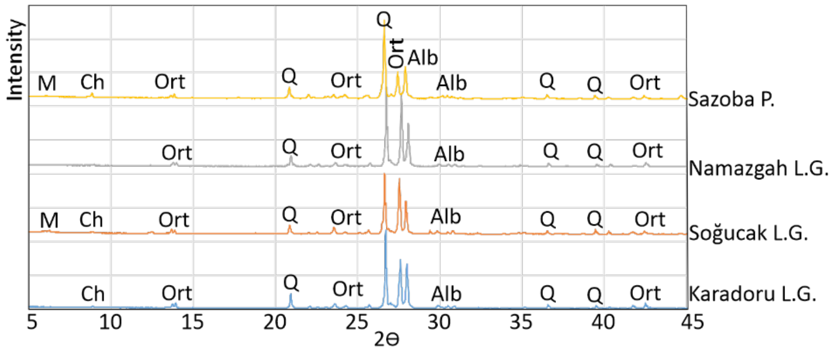

Figure 3. *XRD patterns of the Karadoru, Soğucak, Namazgah leucogranites and Sazoba Pegmatite*

	L.O.I.	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	Na_2O	K_2O
Soğucak L.G.	1.44	70.7	16.21	0.42	1.45	1.65	1.12	2.21	4.12
Karadoru L.G.	0.66	76.32	13.9	0.14	0.4	0.41	0.10	3.03	5.05
Namazgah G.	0.94	78.21	12.65	0.12	0.21	0.45	0.10	2.42	4.87
Sazoba Pegmatite	0.54	73.74	15.28	0.29	0.38	0.19	0.15	3.18	6.2
Soğucak L.G.	Q 27%, Or 30%, Alb 30%, Il 3%, Chl %8, Other 2%								
Karadoru L.G.	Q 24%, Or 39%, Alb 30%, Musc 3%, Other 4%								
Namazgah L.G.	Q 36%, Or 34%, Alb 27%, Mica 3%								
Sazoba Pegm.	Q 28%, Or 35%, Alb 30%, Mica 5%, Musc 2%								

Table 1. *Chemical (XRF) and mineralogical (XRD, Rietveld) analysis of the Biga leucogranites and the pegmatitic samples (Q: quartz, Or: Orthoclase, Alb: Albite, Musc: Muscovite, Il: Illite, Chl: Chlorite, Mica: undifferentiated micas).*

The samples were fired in the industrial roller kiln, as described above, in order to obtain the water absorption, linear firing shrinkage and color properties (Table 2). The linear shrinkage (%) at 1180°C of Soğucak leucogranite is significantly higher, and the water absorption value (%) is lower than the Karadoru and Namazgah leucogranites, and Sazoba pegmatite.

Raw Materials	Linear shrinkage (%)	Water absorption (%)	Color		
			L	a	b
Soğucak L.G.	6.68	5.34	59.19	4.98	8.69
Karadoru L.G.	2.37	18.51	84.25	2.76	5.23
Namazgah L.G.	2.77	17.77	88.94	3.29	6.10
Sazoba Pegm.	3.23	15.38	73.09	6.04	8.21

Table 2. *Technological characteristics of the Biga leucogranites and the pegmatitic samples (Max. Sintering temperature is 1180°C; furnace cycle is 45 min.).*

6. BODY FORMULATIONS

As mentioned above, the raw material characterization results obtained from these analyses indicated that leucogranitic rocks could be used as fluxing materials. In order to assess the possibility of using Biga leucogranitic and pegmatitic rocks as raw materials, these were used in a porcelain tile body. For this purpose, sixteen new bodies were designed at variable rates of alternative raw materials in replacement of Aydin-Çine albite (Table 4).

In the laboratory tests, a typical porcelain stoneware body was reproduced with raw materials currently used by the tile manufacturing industry. This body contains ball clays (İstanbul-Şile, Turkey), quartz-feldspathic fluxes, such as sodium feldspar (Aydın-Çine, Turkey), kaolin (Çanakkale-Çan, Turkey) and porcelain wall tile waste in Kale Seramik factories (Çanakkale-Çan, Turkey) and alternative fluxes (leucogranites and pegmatite) (Çanakkale region, Turkey).

Composition	STD	S-10	S-20	S-30	S-40
Şile Clay	39	39	39	39	39
Çanakkale Kaolin	16	16	16	16	16
Tile Waste	5	5	5	5	5
Aydın-Çine albite	40	30	20	10	0
Soğucak L.G.	-	10	20	30	40
Composition	**STD**	**K-10**	**K-20**	**K-30**	**K-40**
Şile Clay	39	39	39	39	39
Çanakkale Kaolin	16	16	16	16	16
Tile Waste	5	5	5	5	5
Aydın-Çine albite	40	30	20	10	0
Karadoru L.G.	-	10	20	30	40
Composition	**STD**	**N-10**	**N-20**	**N-30**	**N-40**
Şile Clay	39	39	39	39	39
Çanakkale Kaolin	16	16	16	16	16
Tile Waste	5	5	5	5	5
Aydın-Çine albite	40	30	20	10	0
Namazgah L.G.	-	10	20	30	40
Composition	**STD**	**P-10**	**P-20**	**P-30**	**P-40**
Şile Clay	39	39	39	39	39
Çanakkale Kaolin	16	16	16	16	16
Tile Waste	5	5	5	5	5
Aydın-Çine albite	40	30	20	10	0
Sazoba Pegmatite	-	10	20	30	40

Table 4. *Formulations for porcelain tile bodies prepared from Soğucak (S), Karadoru (K), Namazgah leucogranites (N) and Sazoba Pegmatite (P) (STD: Standard body).*

7. TECHNOLOGICAL PROPERTIES

The evaluation of the results revealed that no significant unsuitability was found in the formulation of porcelain ceramic tile using the Biga leucogranites and pegmatites. Especially low water absorption (%) and high shrinkage (%) values are found in porcelain tiles that were made using Soğucak, Namazgah, Pegmatite at the rate of 20 wt.% and Karadoru leucogranite at 10 wt.% in their formulations of ceramics. However, when the alternative raw material percentages were higher than 20 wt.% (Karadoru 10 wt.%) instead of albite, it was clearly seen that water absorption increased and shrinkage decreased. In addition, the whiteness of the bodies increased with the increase in leucogranites and pegmatite (Table 5).

Compositions	Firing shrinkage (%)	Water absorption (%)	Color		
			L	a	b
STD	7.01	0.04	47.93	5.85	15.16
S-10	7.12	0.04	50.93	5.67	15.52
S-20	7.00	0.40	49.95	6.36	15.40
S-30	6.59	1.44	51.66	6.22	15.55
S-40	6.16	2.39	54.11	6.49	16.52
K-10	7.09	0.13	51.44	6.04	15.49
K-20	7.15	1.47	51.7	6.09	15.73
K-30	6.59	2.06	51.52	6.33	15.90
K-40	6.22	2.94	55.23	6.79	17.01
N-10	7.25	0.20	50.25	5.71	14.89
N-20	6.95	0.49	51.49	6.35	15.73
N-30	6.59	1.14	55.98	6.14	17.05
N-40	6.18	2.12	60.83	6.29	18.33
P-10	7.29	0.13	50.06	5.56	15.13
P-20	7.19	0.35	52.1	6.02	16.00
P-30	6.71	1.63	50.86	6.44	15.98
P-40	6.54	2.11	53.42	6.82	16.85

Table 5. *Firing behavior of the porcelain tile compositions prepared with different Alkaline Raw Materials (maximum sintering temperature was 1175 °C, and furnace cycle was 47 minutes) (STD: standard body, S, K, N, P: Soğucak, Karadoru, Namazgah and pegmatite, respectively).*

The measurement was conducted using a continuous heating rate (50 °C/min) up to 1300 °C so as to identify the sintering behavior of the formulations. According to the different formulations, the maximum sintering speed was found at different temperatures. When compared with the standard porcelain body flex point and expansion values, maximum sintering speed and expansion values for K-40 formulation was found to be at 1202 °C. Also, minimum sintering speed and expansion for the P-20 formulation was found to be at 1176 °C.

Recipes		**Flex (°C) / Expansion (%)**	**Recipes**		**Flex (°C) / Expansion (%)**
Soğucak L.G.	S-10	1207 / -3.67	Namazgah L.G.	N-10	1178 / -3.19
	S-20	1178 / -3.32		N-20	1189 / -3.53
	S-30	1183 / -3.13		N-30	1191 / -3.71
	S-40	1194 / -3.28		N-40	1169 / -2.87
Karadoru L.G.	K-10	1171 / -2.90	Sazoba P.	P-10	1176 / -3.07
	K-20	1183 / -3.19		P-20	1176 / -3.02
	K-30	1194 / -3.12		P-30	1193 / -3.31
	K-40	1202 / -3.77		P-40	1192 / -3.13

Table 6. *Sintering behavior of the different body formulations (standard porcelain tile value is: flex: 1169 °C, expansion: -3.25%).*

8. PHASE ANALYSIS AND TECHNOLOGICAL ASPECTS

The produced porcelain tiles were investigated for their mineral phases by XRD. These studies revealed that the crystalline phases were residual quartz, albite, orthoclase, together with a small amount of newly crystallized mullite. From the intensity of the XRD peak results, it is evident that the ratio of relict feldspar decreased from 10 to 40 for each formulation (Fig 4). This is due to the fact that leucogranites and the pegmatite have lower feldspar contents compared to the Aydın-Çine albites.

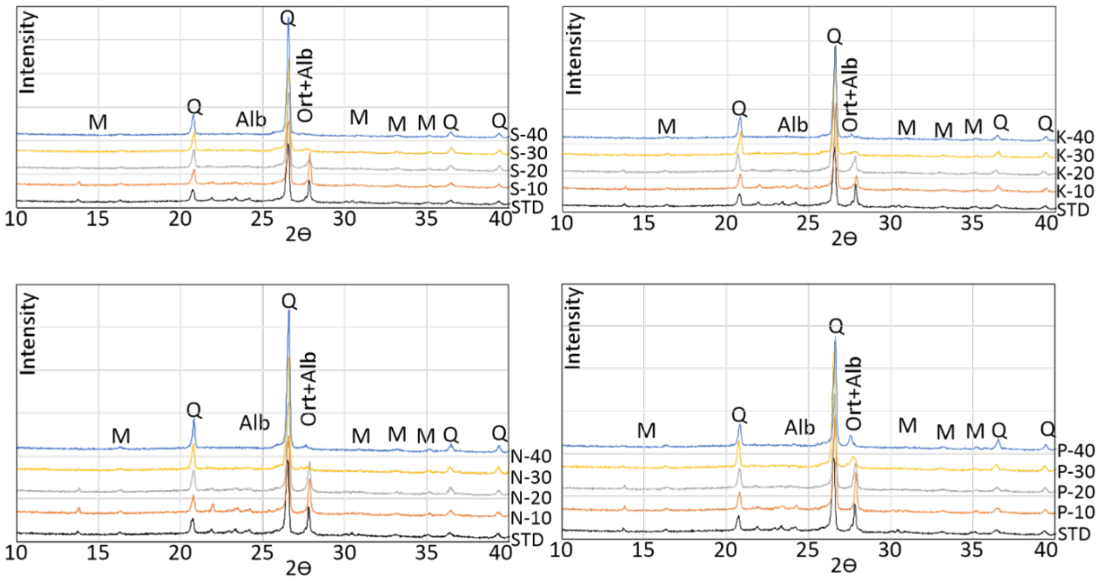

Figure 2. *Fired XRD patterns and mineral phases determined of the recipes and standard body.*

9. CONCLUSIONS

All these findings show that the Biga leucogranites and pegmatite can be used as alternatives to Na-Feldspar and used in porcelain tile production as a fluxing material in different rates and conditions. Usage of these and similar local raw materials will reduce the amount of raw materials supplied far from the plants and also reduce their transportation costs. On the other hand, it will promote the use of leucogranites and pegmatitic rocks, which are not used currently, as potential ceramic raw materials.

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