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Effect of characteristics of natural zeolites on their geopolymerization

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ABSTRACT

The properties of clinoptilolite-based geopolymers are investigated with a focus on the parameters affecting the reactivity of clinoptilolite in a geopolymer binder. A complete characterization of raw materials was carried out as well as a determination of the mineralogical composition, microstructure and mechanical properties of geopolymers. The results of the investigation show that of the investigated materials, geopolymer made with clinoptilolite-bearing tuff from Bayburt has the highest compressive strength. The chemical and mineralogical characteristics of a raw material are important parameters that potentially control the geopolymeric reaction, whereas physical properties (particle size and BET specific surface area) are mainly influential at early stages of geopolymerization. Geopolymeric gel was found to be the main reaction product through characterization by XRD and SEM analysis. The geopolymer produced with the raw material from Bayburt had a narrow range of Si/Al ratios and possessed a geopolymer binder structure with an advanced nature. Lastly, in addition to clinoptilolite, feldspar has an additional effect on the geopolymeric reaction and enhances the process, especially at later ages.

1. Introduction

Portland cement production is an energy-intensive process that releases a huge amount of greenhouse gas emissions into the atmosphere, mostly CO_2. Manufacturing of 1 ton of cement production releases about 1 ton of green house gases from decarbonation of lime during clinker production [1]. Therefore, any reduction in clinker usage would have a major impact on Global warming. Recently another class of binder, which is alternative material to portland cement, generated from Si- and Al-rich materials activated in highly alkaline medium, has been developed. Geopolymers are regarded as environmentally friendly materials due to their lower CO_2 emissions compared to portland cement counterparts [2]. These materials have a potential of releasing 80–90% CO_2 generation relative to conventional cement production.

Geopolymers are a type of amorphous to semi-crystalline three-dimentional aluminosilicate polymers [3]. Essentially, geopolymerization is based on a very old technique involving a complex chemical process that results in an amorphous polymeric structure with linked SiO_4 and AlO_4 tetrahedrons. The commonly used alkaline activator is a mixture of alkali metal (Na or K) silicate or hydroxide. When the aluminosilicate source materials are activated by solutions, reactions result in the formation of binding material similar to crystalline zeolites but mostly amorphous [4–6]. Literature report that the three major steps of geopolymerization; (a) dissolution of aluminosilicate raw material in OH^- attack, (b) the diffusion of dissolved species from the particle surface to the

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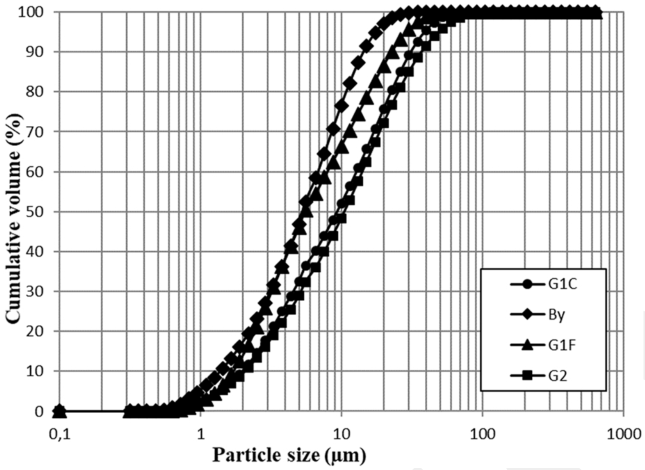

Fig. 1. Grain size distribution of the raw materials.

inter-particle space causing the condensation of oligomers into gels, (c) the hardening of the gel phase [7,8]. Geopolymers possess excellent properties, such as high compressive strength, high fire and erosion resistance, stability under chemical attack, low shrinkage, low thermal conductivity and fast setting [5,9]. Substantial research has been performed to investigate the possibility of utilizing various natural and industrial raw materials to produce geopolymers. The possible source materials have been reported as silica and alumina rich materials such as fly ash, bottom ash, metakaolin, rice husk ash, garnulated blast-furnace slag and natural pozzolans [10–14].

Studies in literature were also carried out on clinoptilolite-based geopolymers, which is the most common zeolite mineral, using different mix design formulations. In these studies, mechanical and microstructural properties of geopolymers were examined [15–19]. One of the first study is the work by Ortega et al. used calcium hydroxide to activate natural zeolite (clinoptilolite) and they found that the properties of resulting geopolymeric material depended on curing conditions, alkali concentration and the preparation method of the sample [15]. In another study, the influence of time, temperature and alkali solution on the mechanical strength of zeolite-based geopolymer was evaluated by [16]. A mixture of sodium hydroxide and sodium silicate was used for the activation of material. The authors concluded that it is possible to practice the geopolymerization of zeolitic materials. Nikolov et al. used potassium silicate solution to prepare clinoptilolite based geopolymer cured at 80 °C The highest compressive strength was 43 MPa [17]. In addition, starting material was calcined (700–1000 °C) in order to increase its reactivity. On the other hand, an application-oriented mix design optimization of zeolite-based geopolymers were reported by [18]. They used sodium silicate and sodium hydroxide solution to prepare clinoptilolite based geopolymers cured at 60 °C. Tekin used marble waste, travertine waste and quarry waste (containing clinoptilolite) to obtain sodium hydroxide geopolymers [19], which concluded that the highest compressive strength of the geopolymer composite pastes with up to 46 MPa were produced.

Briefly, published literature demonstrate that the natural clinoptilolite-based geopolymer has a potential for use as a precursor material. However, detail mineralogical characterization of whole starting material was needed. The studies concerning the effect of not only type of mineral and their content but also their quantity is prominent revealing the exact mechanism of zeolite mineral effect on the geopolymerization. In addition, previous studies have been limited to one raw material, preventing comparison of the different natures of starting materials. Variations in the chemical composition, mineralogical content and physical properties of clinoptilolite bearing tuffs have not been described in detail. Furthermore, based on our knowledge, different types of mineral impurities have a great effect on the compressive strength of resulting geopolymer. All these parameters are expected to impact the mechanical properties and microstructure of geopolymer binders. A study comparing chemically, mineralogically and physically different clinoptilolite-bearing tuffs will provide curicial data to the literature. Hence, the main aim of this study is to gain a better understanding of clinoptilolites as geopolymer material by analysing various clinoptilolites with distinct properties and correlating those properties with the compressive strength of the resulting geopolymers. Determining a relationship between the different mineralogical, physical and chemical characteristics of clinoptilolites and the mechanical properties of geopolymers is crucial to appropriate raw material selection. This work, furthermore, examines the properties of clinoptilolite-based geopolymers by focusing on the microstructural aspect.

2. Materials and methods

2.1. Materials and characterization

Pozzolanic materials from two different clinoptilolite-bearing tuff deposits formed by diagenetic alteration [20] and located in the Anatolian area of Turkey, namely Gördes (notated as G1, G2) and Bayburt (notated as BY), were used in this study. Two zeolite-bearing tuffs were formed in Neogene basin [20]. The G1 sample was ground by a ball mill to two different particle sizes (notated as G1C and

Table 1
Chemical composition and physical properties of the raw materials.

	G1C	G1F	G2	BY
Chemical Compositions (%)				
SiO_2	71.70	72.21	71.50	71.80
Al_2O_3	13.60	13.53	14.30	14.10
Fe_2O_3	1.37	1.37	1.19	0.83
CaO	4.16	4.08	4.47	3.40
MgO	1.02	1.01	1.15	0.82
K_2O	2.90	2.89	2.05	4.21
Na_2O	0.16	0.13	0.45	0.25
L.O.I.	5.09	4.78	4.89	4.59
Physical Properties				
Specific gravity	2.20	2.19	2.21	2.32
Median particlesize, µm	9.4	5.6	10.7	5.3
BET surface area, (m^2/g)	35.35	38.42	48.70	12.69

G1F) in order to determine the effect of particle size on the geopolymerization reaction. Sodium hydroxide (NaOH) with a concentration of 12 M and sodium silicate (Na_2SiO_3; 9.8% Na_2O, 27.7% SiO_2, and 62.5% H_2O by mass) were used for alkaline activation. The NaOH solution was obtained by dissolving NaOH pellets with 98% purity (foranalysis, Merck) in distilled water.

The grain size distribution of the clinoptilolite-bearing tuff samples was measured using a laser particle size analyzer (Malvern Mastersizer 2000). The grain size distributions of all samples, followed the order of BY < G1F < G1C ~ G2, are given in Fig. 1. G1 sample was ground to different fineness to examine the influence of the particle size on the geopolymeric reaction.

The composition of the investigated raw materials specified in Table 1 together with the physical properties of samples by XRF (Rigaku, ZSX Primus II). Samples G1 and G2 had very similar chemical compositions, as they were taken from different locations within the same deposit. The BY sample, on the other hand, had a somewhat different chemical composition from the other samples. It contained slightly more K_2O than the other raw materials. The specific surface area was evaluated by BET (Quantachrome Corporation, Autosorb-6**)** through nitrogen adsorption and desorption at 150 °C for 5 h [21]. The test results for BET specific surface area are also given in Table 1. G2 had the highest BET specific surface area among the studied samples, while BY had the lowest one. The fact that the BET specific surface area of samples from the Gördes region, especially sample G2, was much higher than expected is attributed to the nature of these materials. Clinoptilolite-bearing tuffs from the Gördes region were also found to have a very high BET specific surface area in a previous study by the author [22]. The samples with high BET surface areas in both studies are similar in that they both contain volcanic glass. It is thought that over-grinding of soft volcanic glass causes a marked increase in BET surface area. However, this presumption requires further investigation to verify.

A quantitative phase analysis was performed by powder X-ray diffraction (XRD). The internal standard used was α-Al_2O_3 (1 µm, Buehler Micropolish, 20 wt%). The phase formations were studied using a Panalytical X′Pert Pro device with CuKα radiation operated at 40 mA and 40 kV. Patterns were drawn a step size of 0.0179° from 3° to 80° 2θ. XRD data were analyzed using RIR/Rietveld method (TOPAS 4.2 software) [23].

Clinoptilolite-bearing tuffs were petrographically observed via Nikon polarizing microscope in order to determine the phases present in the precursor materials. The microstructure was examined using a QUANTA 400F SEM device. Semi-quantitative chemical elemental analyses were also performed using an energy dispersive X-ray spectroscopy (EDX) device. Clinoptilolite-based geopolymers were first coated with a thin Au film.

2.2. Geopolymer synthesis

The geopolymers were prepared by mixing alkaline activators with precursor materials. Alkaline activators were preferred based on our previous studies that demonstrate good results [24]. The clinoptilolite-bearing tuffs and an alkaline activators were mixed for 3 min in order to synthesize geopolymers. A sodium silicate/sodium hydroxide ratio of 1.5 and tuff/activator ratio of 1.5 were used. The pastes prepared from these solutions were cast in 50 × 50 × 50 mm cube molds. The specimens were removed from the molds, covered with a thin film of polyethylene to avoid water evaporation and then heat cured in an oven at 50 °C (7, 28, and 56 days) as the procedure followed by [16].

The compressive strength of the geopolymers was measured with Utest 6410 type testing machine at a loading rate of 6 Ns^{-1} (load cell = 10 kN) after 7, 28 and 56 days. The compressive strength results were presented as the average of six measurements. The results were calculated as the average of three measurements. Besides, the small pieces of crushed zeolite-based geopolymers at 28 days were examined for microstructural analysis.

3. Results and discussion

3.1. Raw material characterization

Optical microscope investigation demonstrated that G1 sample includes minor amount of quartz and biotite. Fine-grained G2 sample exhibit glassy texture and quartz. Depending on the routine method by point-counting in thin section, the glassy content of G2

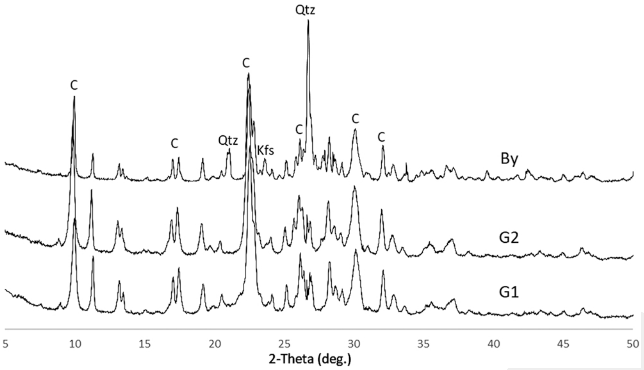

Fig. 2. XRD patterns of the raw materials (C: clinoptilolite; Kfs: K-feldspar; Qtz: quartz).

Table 2
Quantitative mineralogical composition of the clinoptilolite-bearing tuffs determined by powder XRD.

Mineral	G1	G2	BY
Clinoptilolite	**93**	**68**	**65**
Cristobalite	1		
Plagioclase	2		
K-feldspar			21
Quartz	2	4	14
Calcite			
Mica	2		
Amorphous		28	
Total	100	100	100

is designated approximately 20%. In sample BY, authigenic K-feldspars are determined by colorless, low relief and prismatic in shape. BY sample also contains considerable amount of quartz.

Fig. 2 demonstrate the XRD patterns of three raw materials examined. As shown in Fig. 2, all the sample consists of clinoptilolite clearly as a zeolite phase. XRD analysis also indicated that the zeolite sample BY contains quartz and K-feldspar as crystalline phases in addition to clinoptilolite.

The nature and quantity of the phases in each source materials are summarized in Table 2. As seen in Table 2, clinoptilolite content is 93%. G2 and BY samples have clinoptilolite contents 68% and 65%, respectively. In sample G2, a considerable amount of amorphous phase, which is stated as volcanic glass from petrographic analysis, were also detected (Table 2). In sample BY, K-feldspar (21%) and quartz (14%) are detected.

The clinoptilolite-bearing tuffs were subjected to scanning electron microscopy (SEM) to determine the zeolite phases present in tuffs and their morphologies, microstructures as well as semiquantitative elemental compositions. The resulting micrographs and corresponding EDX results of the points indicated in figures are shown in Fig. 3. G1 sample includes euhedral prismatic to tabular clinoptilolite crystals, some 1–3 μm wide and 1–2 μm long (Fig. 3a). In the G2 sample, euhedral clinoptilolite crystals as much as 3 μm long are present (Fig. 3b). BY sample, on the other hand, displays masses of anhedral to subhedral clinoptilolite aggregates (Fig. 3c). Samples G1 and G2 had similar Si/Al ratios of 6.09 and 6.21, respectively. Clinoptilolites acquired from the Bayburt region (BY) had a lower Si/Al ratio (5.21) than G1 and G2. In addition, the G2 sample had the highest K and Ca values.

3.2. Compressive strength of geopolymer pastes

The mechanical development of the clinoptilolite-based geopolymers are shown in Fig. 4 with the error bars (7, 28, and 56 days of age). Compressive strengths of samples increased remarkably from 7 days to 28 days whereas the strength development was relatively lower from 28 days to 56 days, especially for the clinoptilolite-bearing tuffs other than BY. Geopolymer pastes with BY exhibited the highest compressive strength at all test ages. It especially showed a significantly higher compressive strength when compared to the others. In order to elucidate the effects of chemical, mineralogical and physical characteristics of clinoptilolite-bearing tuffs on mechanical development of geopolymer pastes, comparative evaluations can be made for each characteristics separately.

To evaluate the effect of particle size and BET surface area (physical characteristics) on the compressive strength performance of geopolymer pastes with clinoptilolite-bearing tuffs, it is useful to compare G1C and G1F, as these samples had similar chemical and mineralogical compositions (Tables 1 and 2) but dissimilar median particle sizes and BET specific surface areas (Fig. 1 and Table 1). Geopolymer pastes made with G1F, which had a smaller median particle size and a slightly higher BET surface area, exhibited a significantly higher compressive strength compared to pastes made with G1C at 7 days (Fig. 4). On the other hand, they showed similar strength values at later ages, suggesting that the particle size and BET specific surface area of clinoptilolite-bearing tuffs are important

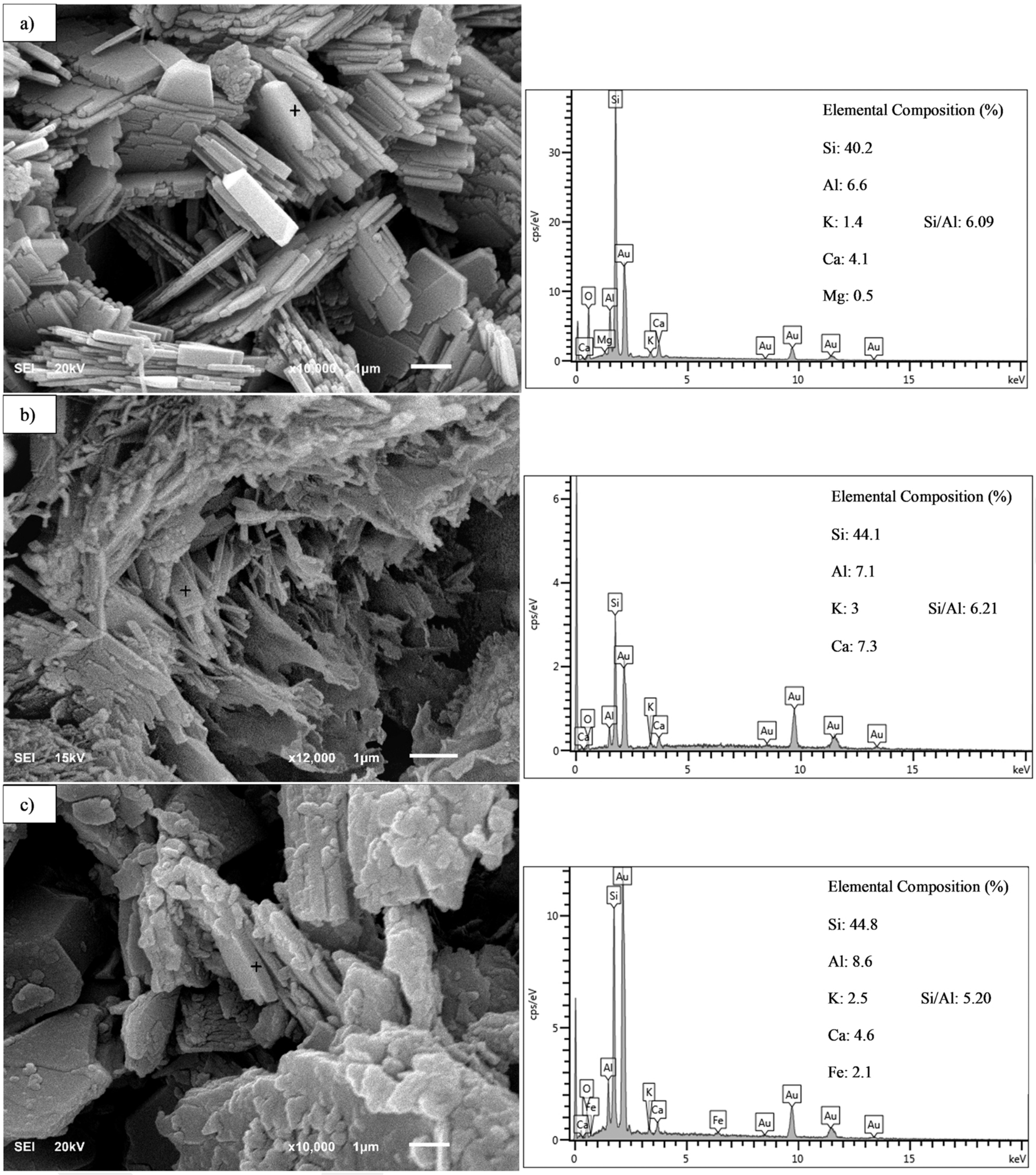

Fig. 3. SEM analyses of (a) G1, (b) G2, (c) By samples and corresponding EDX results of the points indicated in figures.

on the mechanical development of geopolymer pastes at early ages. Accordingly, the positive impact on the compressive strength of geopolymer pastes of providing a finer particle size through prolonged grinding was found to be limited at 28 and 56 days of age (Fig. 4). As stated by Deb et al. [25], the grain size of starting material plays an important effect on the mechanical development of geopolymers. The positive impact of smaller grains of clinoptilolite-bearing tuff on the early mechanical development is clarified by the rapid geopolymeric reaction of finer particles; however, at later ages, slow but progressive geopolymerization of coarser particles results in similar strength combination.

The effects of mineralogical composition, namely clinoptilolite content (purity) and types of impurities, on the mechanical development of geopolymer pastes are examined by comparing the pastes prepared with G1C, G2 and BY. Comparing the pastes made with G1C and G2 is useful for evaluating the effect of clinoptilolite content (purity), whereas the comparison of pastes made with G2 and BY is meaningful for understanding the effects of different types of mineral impurities on the compressive strength development of geopolymer pastes. As seen in Table 2, the clinoptilolite content of G1C is considerably higher than that of G2. The similar chemical compositions and median particle sizes of G1C and G2 make it reasonable to compare the effect of clinoptilolite in terms of their

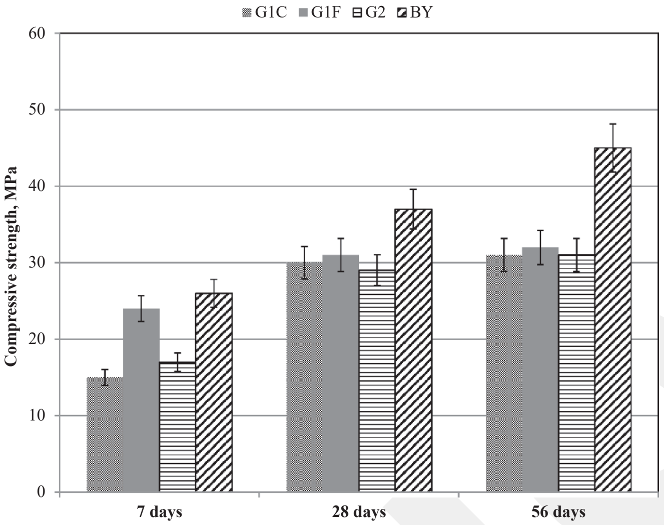

Fig. 4. 7, 28 and 56 days compressive strength of geopolymers.

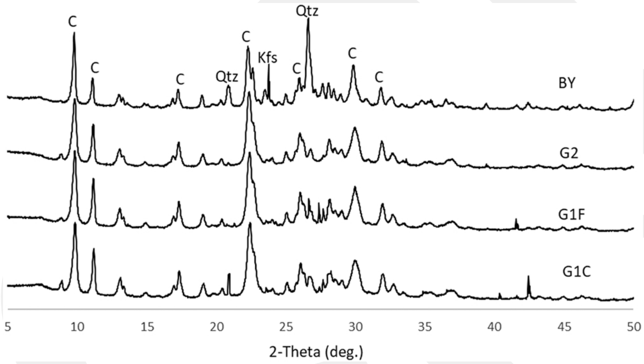

Fig. 5. XRD patterns of G1C, G1F, G2 and BY geopolymers at 28 days of hydration (C: clinoptilolite; Kfs: K-feldspar, Qtz: quartz).

mineralogical compositions. Geopolymer pastes made with G1C and G2 exhibited similar compressive strength development at both early and later ages, indicating that the presence of a high quantity of clinoptilolite does not have a major influence on the strength development of geopolymer pastes. It is also note that the amorphous phase, present in G2, does not affect the strength development of geopolymers as stated in the literature [26,27].

G2 and BY, on the other hand, which contain different impurities but similar clinoptilolite content in their mineralogical compositions, provide a useful comparison for the effect of type of impurities on compressive strength development of geopolymer pastes. G2 contains amorphous phase as a non-crystalline impurity whereas BY consists of K-feldspar and quartz as crystalline impurities. The significantly higher compressive strength of geopolymer paste with BY when compared to that with G2 at early and later ages suggests that K-feldspar in mineralogical composition of BY contributed the geopolymerization and strength development. The published literature contains reports about high ability of K-feldspar to show geopolymerization and to contribute strength due to its high dissolution tendency in alkaline solutions [12,28]. Accordingly, the highest compressive strength performance of the paste with BY, despite its significantly lower BET surface area when compared to the others (Table 1), could be attributed to its mineralogical composition containing K-feldspar as well as clinoptilolite, which enhances the geopolymerization of clinoptilolite-bearing tuff.

3.3. X-ray diffraction analysis

XRD analysis was performed to compare the phases present in the original raw materials with those present in their respective geopolymers after 28 days of curing. As seen in Fig. 5, all synthesized geopolymers display residual clinoptilolite phases as in study made by [17]. The district clinoptilolite peaks in resulted geopolymers indicates that considerable amount of clinoptilolite phases remain unreacted. However, the peak height of the partially reacted clinoptilolite present in all geopolymers decreased further in the XRD patterns of BY in comparison with the XRD patterns of the G1C, G1F and G2 samples (Fig. 4), which suggests a higher degree of geopolymerization in BY. The fact that the reacted clinoptilolite peak of the BY geopolymer is smaller than that of the G2 geopolymer

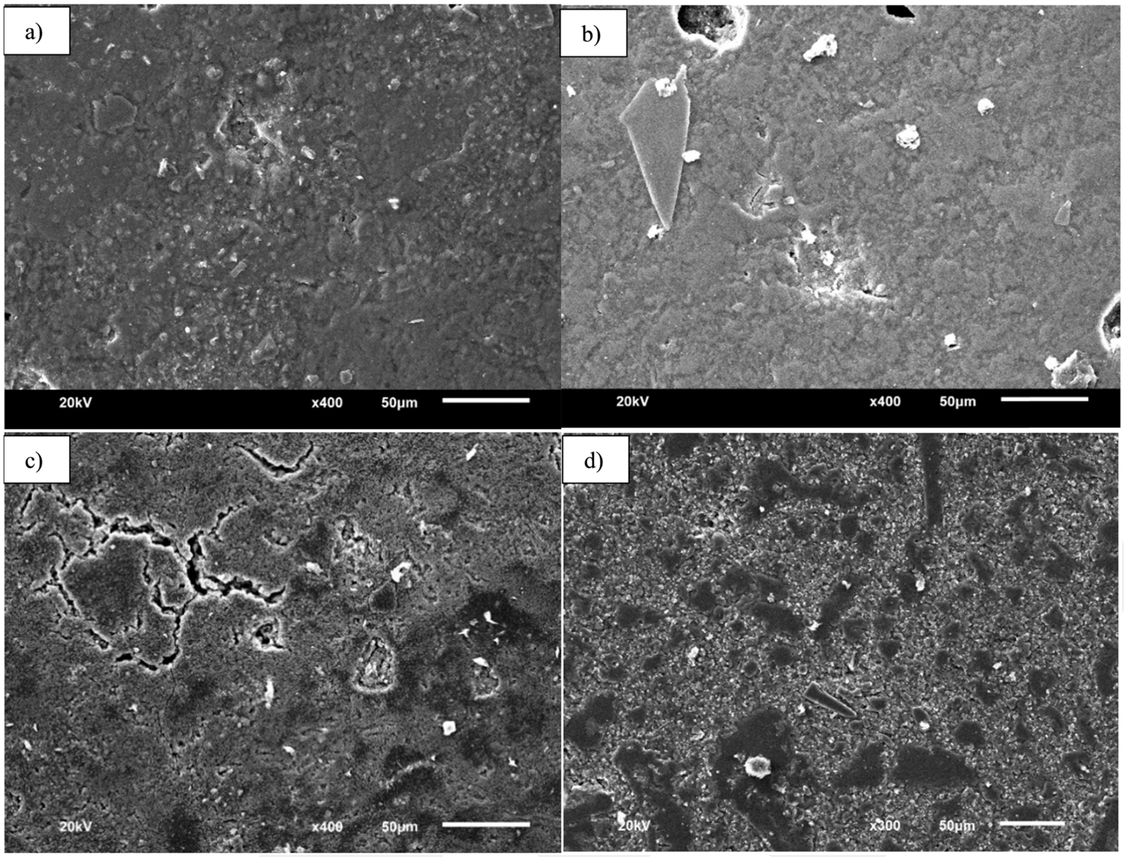

Fig. 6. SEM micrographs of (a) G1C, (b) G1F, (c) G2, (d) BY geopolymers.

despite similar original clinoptilolite contents indicates that the K-feldspar phase in BY, might somewhat contribute the reaction of clinoptilolite in the BY geopolymer. It should be noted that the peak of K-feldspar is still observed in the XRD pattern of BY geopolymer, which indicate that this phase also partially reacted during geopolymerization process. In their study, Gunasekera et al. [29] were also stated partially reacted starting material, due to the detection of remaining unreacted particle grains. The glassy phase indicated by a raised background of XRD patterns of geopolymer pastes between 25° and 35° 2-theta values is a common characteristic referring to geopolymerization products [30,31]. As seen in Fig. 5, this glassy phase is more apparent for the geopolymer paste of BY, which again indicates a relatively higher degree of geopolymerization for BY. This results also corresponds with the higher compressive strength By based geopolymer (Fig. 4).

3.4. SEM/EDX analysis

SEM micrographs showing the general microstructural features of the clinoptilolite-based geopolymers are shown in Fig. 6. It was observed that a denser microstructure with no obvious microcracks is clearly distinguished for the BY geopolymer (Fig. 6d). However, some voids and microcracks, which could decrease strength, were found in the SEM micrographs of the other geopolymers (Fig. 6a,b, c).

The microstructure of the fracture surface of geopolymers at the higher magnification and corresponding results of EDX analyses after 28 days of activation are given in Fig. 7. As seen in Fig. 7, clinoptilolite-based geopolymer acquired from Bayburt region (BY) has the densest microstructure and the most homogenous gel-like structure, which is most probably because of higher degree of gel formation. Chemical composition of gel-like structure found in the main matrix area was determined by semiquantitatively. EDX analysis of selected plots revealed that all the gel-like areas analyzed from G1C, G1F, G2 and BY geopolymers include mainly Si, Al and Na ratios and these ratios have similar chemical composition to the geopolymer gel in literature [32]. Therefore, glassy region is suggested to be a geopolymeric gel. This presumption is also supported by XRD analysis, which provides that the amorphous phase starts to appear by geopolymerization. Besides, Fig. 7 demonstrates that the existence of Na with regard to the original raw materials (Fig. 3) as a result of the chemical attack of the alkaline solution.

The results of all of the semiquantitative elemental analyses of selected spots (including spots shown in Fig. 7) taken from geopolymer gel are marked as (K+Na+Ca+Fe+Mg)/Al vs Si/Al (Fig. 8) and given in Table 3. The gel phases present in BY geopolymer are clearly different in accordance with their elemental composition (Fig. 8). The BY geopolymer, which showed the highest compressive

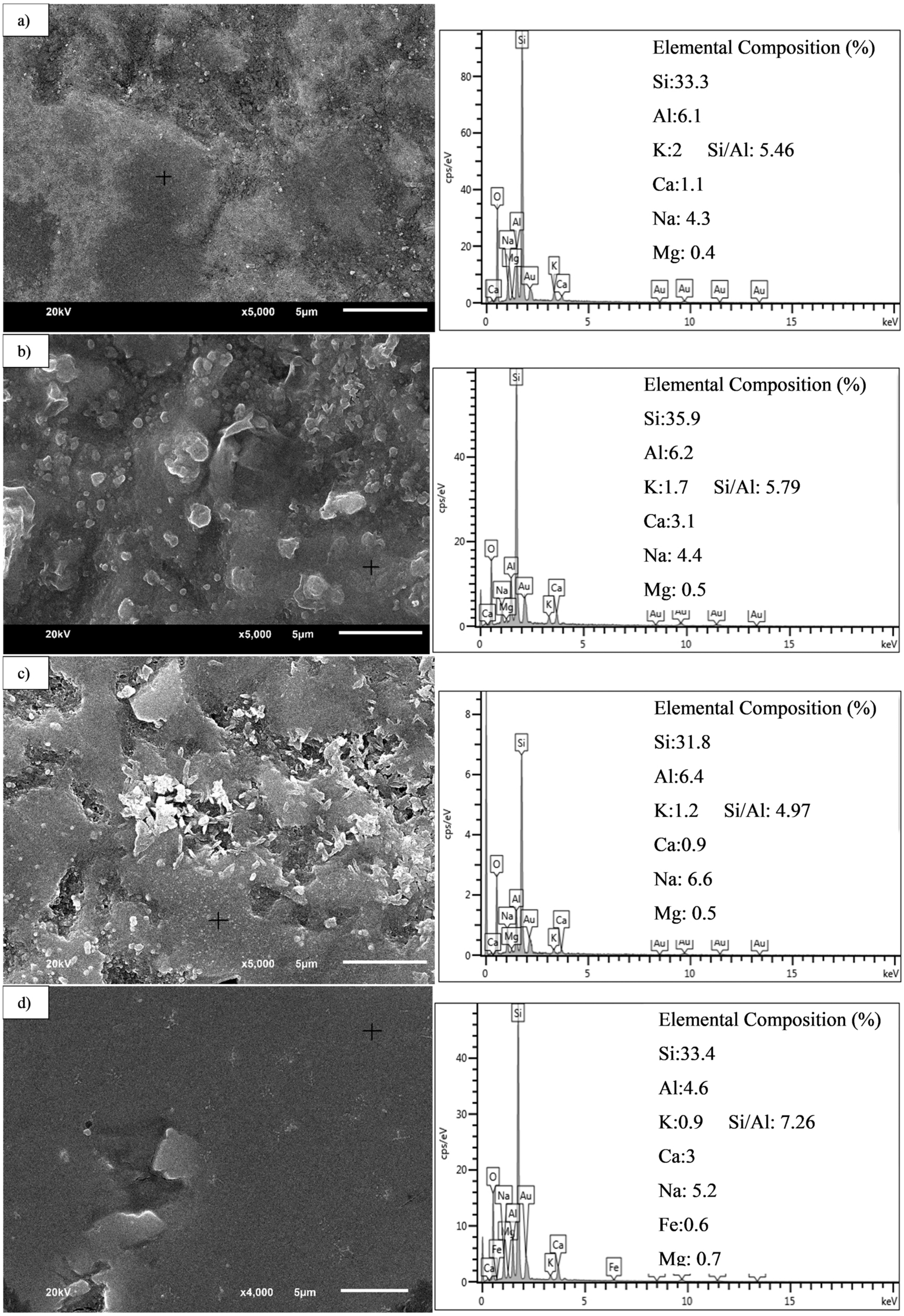

Fig. 7. SEM micrographs of (a) G1C, (b) G1F, (c) G2, (d) BY geopolymers and corresponding EDX analysis results.

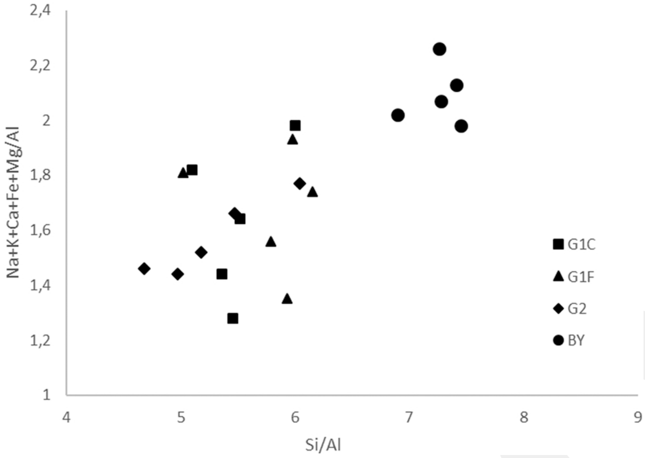

Fig. 8. EDX analysis results plotted in the axis (K+Na+Ca+Fe+Mg)/Al vs. Si/Al.

Table 3
Atomic compositions (semiquantitative) on specific points, which correspond to the spots in Fig. 7, of the geopolymer gel (A: Na+K+Ca+Fe+Mg/Si).

Sample		Si	Al	Na	K	Ca	Fe	Mg	Si/Al	A
	1	31.11	6.1	7.9	1.9	0.9	0	0.4	5.10	1.82
	2	30.4	5.5	4.2	1.5	2.3	0.3	0.7	5.53	1.64
G1C	3	32.4	5.4	5	1.8	1.9	1.2	0.8	6.00	1.98
	4	33.3	6.1	4.3	2	1.1	0	0.4	5.46	1.28
	5	31.6	5.9	3.9	1.6	2	0.7	0.3	5.36	1.44
	6	35.9	6.2	4.4	1.7	3.1	0	0.5	5.79	1.56
	7	40.3	6.8	4.6	2.3	1.7	0	0.6	5.93	1.35
G1F	8	36.3	5.9	4.7	1.8	2	1.1	0.7	6.15	1.75
	9	32.9	5.5	5.4	1.4	2.6	0.6	0.6	5.98	1.93
	10	31.62	6.3	4.8	1.9	3.9	0	0.8	5.02	1.81
	11	31.8	6.4	6.6	1.2	0.9	0	0.5	4.97	1.44
	12	32.3	5.9	6.5	1.1	1.5	0	0.7	5.47	1.66
G2	13	32	5.3	6.1	0.9	2.1	0	0.3	6.04	1.77
	14	32.1	6.2	6	1.2	1.3	0	0.9	5.18	1.52
	15	33.7	7.2	5.9	0.9	2.9	0	0.8	4.68	1.46
	16	33.4	4.6	5.2	0.9	3	0.6	0.7	7.26	2.26
	17	35	4.7	4.9	1.7	1.5	0.6	0.6	7.45	1.98
By	18	34.1	4.6	4.5	2.9	1.6	0.5	0.3	7.41	2.13
	19	33.1	4.8	3.9	3.8	1.4	0.4	0.2	6.90	2.02
	20	33.5	4.6	7.2	1.6	0.4	0.2	0.1	7.28	2.07

Table 4
Averaged elemental compositions of geopolymeric gels given in Table 3.

Elemental Composition (%)	G1C	G1F	G2	By
Si	31.9	36.84	32.38	33.82
Al	5.8	6.14	6.2	4.66
Na	5.06	4.78	6.22	5.14
K	1.76	1.82	1.06	2.18
Ca	1.64	2.66	1.74	1.58
Fe	0.44	0.34	0	0.46
Mg	0.52	0.64	0.64	0.38
Si/Al	5.51	6	5.27	7.26
(Na+K+Ca+Fe+Mg)/Al	1.63	1.68	1.57	2.09

strength, exhibited the highest Si/Al ratios among the geopolymers examined. In addition, the chemical composition of the BY geopolymer presented a narrow range of Si/Al variation, whereas the molar ratios varied considerably for the G1C, G1F and G2 geopolymers. The constricted chemical composition of BY indicates the improved geopolymer binder structure [33,34].

Table 4 summarizes averaged elemental compositions of geopolymeric products given in Fig. 8 and Table 3. As clearly seen in Table 4, the K+Na+Ca+Fe+Mg composition of BY geopolymer is higher than G1C, G1F and G2 geopolymers due to the highest K content of BY. The presence of some alkali metals within the geopolymer is owing to the decomposition of precursor materials and replacement of these alkali metals by geopolymeric reaction [32–35]. Thus, the higher K value of BY is an implication of higher decomposition and incorporation of this alkali metal into the structure. However, the clinoptilolite contents of G2 and BY are similar, and the amount of K in clinoptilolite in BY (K: 2.5) is even lower than in G2 (K: 3) as seen in Fig. 3. According to Table 2, BY raw material also include K-feldspar in 21% wt. Therefore, it is reasonable to conclude that K-feldspar in addition to clinoptilolite might also provide extra K for reaction and enhance the geopolymerization process of BY especially at later ages. It is already stated that K from the dissolution of K-feldspar is observed to increase the mechanical strength [12]. However, it should be noted that feldspars containing different alkali metals (e.g. Na) will affect geopolymerization in different ways. For example, Gonzalez-Garcia et al. [36] reported a natural pozzolan (contain in Na rich feldspar) based geopolymer cured at 40 °C with a low compressive strength (up to 13 MPa). That is, the chemical nature of raw material, which depend on mineralogical content, is very influencial parameter that affect the geopolymerization.

4. Conclusions

In this study, the effects of chemical, physical and mineralogical characteristics of natural zeolites on their geopolymerization were investigated. Based on the experimental results, the following conclusions can be drawn;.

- Two different clinoptilolite-bearing tuff deposits namely Gördes and Bayburt have the potential for construction applications.
- From all samples, clinoptilolite-bearing tuff acquired from Bayburt region (BY) exhibited the highest compressive strength at all testing ages in geopolymer binders.
- Finer G1 (G1F) resulted in a higher early compressive strength at 7 days than the coarser one (G1C). However, fineness of natural zeolites was found to be slightly effective on compressive strength of geopolymer pastes at later ages.
- The chemical and mineralogical nature of raw materials played the most important role in strength development and microstructure of clinoptilolite based geopolymers.
- Type of impurities in mineralogical compositions of starting materials plays an important role on the mechanical development of geopolymer pastes.
- Hardened geopolymer pastes of BY exhibited considerably higher compressive strength than G1 and G2 samples especially at 28 and 56 days of curing, which could be attributed to additional contribution of K-feldspar in BY with its high dissolution tendency in alkaline medium.
- XRD analysis of hardened geopolymer pastes indicated that clinoptilolites partly decomposes during geopolymerization in a highly alkaline medium and some part of clinoptilolite phase remained unreacted.
- EDX analysis of selected plots revealed that all the gel-like areas analyzed include mainly Si, Al and Na, which are the main elements of geopolymeric gel. Advanced nature of binder structure is detected for BY geopolymer, which has a narrow range of Si/Al ratio.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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