Effects of calcination on structural properties and surface morphology of black volcanic ash

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Abstract
In this study, the effects of calcination on the structural properties and surface morphology of black volcanic ash were investigated. The chemical composition, texture properties, and thermal behavior of raw black volcanic ash were studied using x-ray fluorescence spectrometry, micromeritics surface area, porosity analyzer, and thermogravimetric and differential scanning calorimetry analysis, respectively. According to the thermogravimetric results, the powder of raw volcanic ash was calcined at 800, 1000, and 1100 °C. X-ray diffraction (XRD), Raman spectroscopy, and electron microscopy were employed to study the crystalline phase, mineralogical composition, and morphology of the calcinated volcanic ash. Based on the characterization of the XRD and Raman spectra, we observed that phase transformation started at 800 °C along with a change in color of volcanic ash from black to poor red. Moreover, the degree of crystallinity and peak intensity increased as the calcination temperature increased, without a significant change in the surface morphology. These findings can help in understanding the surface and bulk characteristics of black volcanic ash at high temperatures and serve to enhance their technological and economical applications.

1. Introduction
Volcanic ash is a natural material that has received attention worldwide for its industrial applications due to its physicochemical properties and abundance in the different parts of the world. Volcanic ash has promising potential applications in the various fields of science and technology, such as solar cells, catalysts, cement and concretes, insulation of construction material, lunar soil stimulants, ceramic materials, radiation shields, geopolymer materials, and adsorbents [1–11]. The possible applications of volcanic ashes mainly depend on its surface and structural properties, such as the amount of the amorphous content, porosity, surface area, mineralogy, chemical composition, and particle size distribution [12–15]. The crystal structure and chemical composition of volcanic ash depend on both eruption conditions and magma configuration, which can be an almost amorphous phase or completely crystalline structure [3, 16–19]. Therefore, the knowledge of phase transformation, morphological characteristics, and factors affecting surface and bulk characteristics of volcanic ash can help in the enhancement of its applications. Thermal effect plays an important role in many industrial applications of volcanic ash such as manufacturing ceramics which requires high temperatures (about 1100 °C). However, few reports are available in studying the effect of various temperatures on volcanic ash properties. An earlier study has investigated the thermal, structural, and ceramic properties (mechanical properties) of six different samples of volcanic ash deposits in order to use them as alternative pastes for ceramic products [4]. The samples of volcanic ash were calcined in the temperature range 1100 °C–1150 °C in order to evaluate their ceramic properties. The XRD of the raw volcanic ash showed high amounts of amorphous phase and different chemical composition such as plagioclase, olivine, pyroxene as principal minerals with high amounts of fusible elements. Therefore, the thermal properties of these volcanic ash samples vary depending on the crystalline phases and chemical composition. For example, some samples recrystallized and increased their weight due to the oxidation process, and others showed stable thermal behavior without any significant changes. After thermal
treatment of different volcanic ash samples, the XRD measurements confirmed the results of DSC showing an increase in peaks intensity with new crystallizing phases. Also, the mechanical properties of the thermally treated samples were determined and showed superior properties depending on the chemical composition and the amounts of minerals contained. Therefore, these volcanic ash samples were considered then as suitable alternative raw materials for vitrified ceramic products. Moreover, the volcanic ash samples that have high alkali content could be promising for their use also as fluxing agents. In contrast, a recent study has investigated the effects of heat treatment on the properties of volcanic ash whose minor minerals include hematite and ilmenite [20]. The raw poor red volcanic ashes were thermally treated at 800 and 1000 °C. No significant changes were detected in their structural properties. The electrical measurements also showed that the volcanic ash samples were electrically stable, so they could be used safely electrical insulation applications.

In this study, we aimed to investigate the effect of calcination temperature on crystal structural properties, and morphological characteristics of black volcanic ash. The thermal properties of raw volcanic ash were studied using thermogravimetric analysis and differential scanning calorimetry analysis (TGA-DSC). According to the thermal analysis results, the raw volcanic ash was calcined at different temperatures. The structural phases, mineralogical features, and morphological features were investigated using x-ray diffraction (XRD), Raman spectroscopy, and scanning electron microscopy (SEM), respectively. While the chemical composition characterizations were analyzed using x-ray fluorescence spectrometry (XRF). In addition, the specific surface area, and porosity properties of the black volcanic ash were determined using a micromeritics surface area and porosity analyzer.

2. Materials and methods

The samples of black volcanic ash were collected from Harrat Khaybar, located in the western region of Saudi Arabia, which is rich with pyroclastic volcanic ash materials of different particle sizes and colors [21–23]. The samples were milled to a fine powder using a crusher unit and smoothing machine (Pulverizers agate, Rocklabs, New Zealand). Chemical analyses of the samples were performed by x-ray fluorescence (SPECTRO—EXPOS). The details regarding sample preparation and the XRF experiments are available in another study [20]. The specific surface area, particle size, and porosity properties, such as pore size and pore volume of fine volcanic ash, were measured via N₂ adsorption using the BET method with Micromeritics ASAP 2020 equipment.

To estimate the calcination temperatures of black volcanic ash, the thermal properties were performed in static air using TGA-DSC (STA 449 F3 Jupiter; NETZSCH, Germany) at a temperature ranging from room temperature up to 1300 °C, with a heating rate of 5 °C min⁻¹. According to the thermal analysis results, the raw volcanic ash was calcined in a muffle furnace at temperatures of 800, 1000, and 1100 °C, with a heating rate of 5 °C min⁻¹ for 1 h.

The chemical and mineralogical composition of the crystalline phases were determined using x-ray powder diffraction (Bruker, USA) and Cu Kα Ni-filtered radiation with a wavelength of 1.54 Å and 2θ range of 20°–70°. The surface morphologies were investigated using the SEM model JEOL 7600f (JEOL, Japan). Raman spectra of the volcanic ash samples were measured using a Raman microscope model DXR (Thermo Fisher Scientific, USA) [20].

3. Results and discussions

3.1. Chemical compositions and textural properties

The chemical compositions of the raw volcanic ash were measured using XRF. The major elements in the raw volcanic ash are Silica (SiO₂), Alumina (Al₂O₃), Iron oxide (Fe₂O₃), Calcia (CaO), Magnesia (MgO), while the minor elements are Sodium oxide (Na₂O), Potassium oxide (K₂O), Titanium Dioxide (TiO₂), Phosphorus pentoxide (P₂O₅), Manganese monoxide (MnO), and Sulfate (SO₃) as shown in table 1. Silica has the highest weight content (47.02%wt), and the black volcanic ash can be classified as scoria based on the amount of silica.

The textural properties of the raw volcanic ash, such as BET surface area, porosity, and particle size were shown in table 2. The raw powder volcanic ash presented a small BET surface area with a mesoporous structure (2–50 nm), according to the International Union of Pure and Applied Chemistry (IUPAC) convention [24–28].

| Elements      | SiO₂ | Al₂O₃ | CaO  | Fe₂O₃ | K₂O  | MgO | Na₂O | P₂O₅ | TiO₂ | SO₃ | L.O.I. |
|---------------|------|-------|------|-------|------|-----|------|------|------|-----|--------|
| wt%           | 47.02| 15.93 | 8.97 | 11.47 | 0.94 | 8.30 | 0.16 | 3.68 | 0.37 | 2.00| <0.05  | 0.18   |

Table 1. Chemical compositions of raw volcanic ash by XRF (wt%).
Lately, natural mesoporous materials have attracted much attention as promising materials with many technological applications, such as solar cells, fillers, and catalysts.

### 3.2. Thermal properties

The calcination process is a thermal treatment applied to ores and other solid materials which is an important process that leads to structural transformations such as decomposition, phase transition, oxidation, hydroxylation, surface reconstruction, or the removal of a volatile fraction \[29–32\]. The calcination normally occurs at temperatures lower than the melting point of the materials. Therefore, thermal analyses were performed on the powdered volcanic ash. Figure 1 shows the TGA-DSC curves of raw volcanic ash that were performed using a heating rate of 5 °C min\(^{-1}\). As shown by the TGA curve, the raw volcanic ash is almost thermally stable up to 1300 °C, with a small increase in weight of about 0.3%. The gain in the weight could be referred to as an oxidation phenomenon. No peaks were exhibited by the DSC curve up to 700 °C, indicating that there is no important transformation at this temperature. Above 700 °C, the exothermic peaks were exhibited at 835, 1040, and 1185 °C and could be attributed to the oxidation or phenomenon \[4\]. The strong endothermal peak at 1226 °C is attributed to the melting point of raw volcanic ash.

According to the thermal analysis results, temperatures of 800, 1000, and 1100 °C were selected for the calcination treatment. Four samples of volcanic ash (raw, 800, 1000, and 1100 °C) were investigated using XRD, SEM, and Raman spectroscopy.

### 3.3. Structural and morphological properties

The crystal structure and mineral properties of volcanic ash samples were studied by XRD. Figure 2 shows the XRD patterns of raw, 800, 1000, and 1100 °C volcanic ash samples.

The XRD pattern of the raw volcanic ash presented a significant amount of an amorphous glass phase, estimated based on the broad pozzolanicity hump (2θ = 21°–38°) with a few characteristic peaks of crystalline phases \[33\]. These peaks could be ascribed to the presence of iron oxide phases such as magnetite (Fe\(_3\)O\(_4\)). They also presented crystal phases of plagioclase (Ca\(_{Al_2}Si_2O_8\)) such as albite (Na\(_2\)Al\(_2\)Si\(_3\)O\(_8\)) and/or anorthite \[19, 33, 34–37\].

The XRD pattern of the volcanic ash sample heated at 800 °C indicated that the existing peaks increased in intensity and became sharper than those of the raw sample. Moreover, new crystallizing phases appeared, such as

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**Table 2.** The BET surface area, porosity, and particle size of raw black powder volcanic ash.

| Surface properties | Raw powder volcanic ash |
|--------------------|-------------------------|
| Surface Area (m\(^2\) g\(^{-1}\)) | 0.954 |
| Pore Volume (cm\(^3\) g\(^{-1}\)) | 0.0024 |
| Pore Size (nm) | 9.88 |
| Nanoparticle Size (nm) | 6291 |

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**Figure 1.** Thermal analysis of the raw black volcanic ash. The blue line represents the TGA curve, while the black line represents the DSC curve.
hematite ($\alpha$-Fe$_2$O$_3$), ilmenite (FeTiO$_3$) and pargasite (NaCa$_2$Mg$_4$Al$_3$Si$_6$O$_{22}$(OH)$_2$), with a change in color from black to poor red. These changes could be attributed to the recrystallization of the minerals, oxidation of magnetite or other iron oxides, and transformation into hematite, which has a red color. As the calcination temperature increased, the XRD peaks became sharper, and the intensity of the hematite and other mineral phases increased, indicating an improvement in the crystallization of the hematite and other mineral phases. Similarities were confirmed between the XRD spectra of the raw sample and the peaks of the calcinated samples. However, due to the complexity of the chemical compositions of volcanic ash, the spectrum of probable minerals will be expanding during calcination. Moreover, the interference among the peaks of mineral phases tends to complicate the interpretation. Therefore, we used the Raman technique to confirm the XRD results, which is a useful technique for defining the mineralogy of composite materials.

Raman spectra of raw and calcinated volcanic ash samples are shown in figure 3. The Raman spectra of the raw sample showed only a few broad peaks, and this result could be due to the amount of amorphous content in the volcanic ash. These peaks could be attributed to a complex composition mixture of the mineral phases, such as ilmenite, pargasite, and albite.

As seen in figure 3, the Raman spectra of calcination samples are different from the spectra of the raw sample. It shows new peaks, and the existing broad peaks become sharper with a significant increase in the intensities as.
The calcination temperature increases. The characteristic peaks of hematite and albite start to appear at 800 °C and become sharp, and their intensity increases as the calcination temperature increases to 1200 °C. These results can be attributed to the recrystallization of the mineral, oxidization of magnetite or other iron oxides, and transformation into hematite.

The peaks located at about 1333, 602, 404, 288 and 223 cm$^{-1}$ were attributed to the hematite phase [38, 39]. The characteristic peaks of the albite located at about 540–460, 288, and 162 cm$^{-1}$ [40, 41]. The peak at 672 cm$^{-1}$ corresponds to ilmenite [39, 42], and the peaks at 672 cm$^{-1}$ and 223 cm$^{-1}$ correspond to pargasite [39, 42]. The results of the Raman spectra are consistent with those obtained using XRD and DSC. In contrast, a recent study has investigated the effects of calcination on the structural and electrical properties of crystalline volcanic ash at different temperatures [20]. The XRD and Raman spectra showed no differences between the raw and treated samples, with stability in electric and dielectric properties. Hence, this behavior makes that type of volcanic ash suitable for electrical insulation applications. Thus, we can summarize that the effect of calcination on the properties of volcanic ash varies with the crystalline phase and chemical composition.

The surface morphologies of raw and calcinated volcanic ash samples at different temperatures were examined using SEM. Figures 4(a)–(d) show the SEM micrographs of raw and calcined volcanic ash at temperatures of 800, 1000, and 1100 °C. As seen in figure 4(a), the particles of raw volcanic ash showed small aggregates and some fragments without specific shapes that are nano/micro-sized. The calcinated samples at temperatures of 800, 1000, and 1100 °C showed that the particles and fragments of volcanic ash had started accumulating with each other (figure 4(c)). Generally, no significant changes were observed between the surface morphologies of the raw sample and the calcinated samples.

4. Conclusion

In conclusion, the effect of calcination on the structural properties and surface morphology of black volcanic ash was investigated. According to the thermogravimetric analysis results, the raw volcanic ash powder was calcined at 800, 1000, and 1100 °C. The XRD and Raman spectra of the calcinated samples showed a phase...
transformation along with a change in the color of volcanic ash from black to poor red, due to the iron oxidation process. Moreover, the degree of crystallinity and peak intensity increased as the calcination temperature increased. However, no significant changes were detected in the surface morphology of the black volcanic ash when treated at high temperatures. From these results, the behavior of volcanic ash with calcination at high temperatures can be better understood, which will lead to the enhancement of the technological and economic applications of volcanic ash.

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References

[1] Dwyer A R and Dwyer S P 2018 US Patent No. 10,115,530Washington, DC: US Patent and Trademark Office
[2] Tchadjie J. N and Ekoku S O 2018 Enhancing the reactivity of aluminosiliccate materials toward geopolymer synthesis J. Mater. Sci. 53 1709–33
[3] Serra M F, Conconi M S, Suarez G, Aglietti E F and Rendtorff N M 2015 Volcanic ash as flux in clay based triaxial ceramic materials, effect of the firing temperature in phases and mechanical properties Ceram. Int. 41 (5, Part A) 6169–77
[4] Leonelli C, Kamezu E, Boccaccini D N, Melo U C, Rizzuti A, Billong N and Miselli P 2007 Volcanic ash as alternative raw materials for traditional vitrified ceramic products Adv Appl Ceram 106 135–41
[5] Husain A, Kupwade-Patil K, Al-Albani A F and Abdulsalam M F 2017 In situ electrochemical impedance characterization of cement paste with volcanic ash to examine early stage of hydration Constr. Build. Mater. 133 107–17
[6] Kupwade-Patil K, Al-Albani A F, Abdulsalam M F, Mao C, Bumaidad A, Palkovic S D and Büyükoztürk Ö 2016 Microstructure of cement paste with natural pozzolanic volcanic ash and Portland cement at different stages of curing Constr. Build. Mater. 113 432–41
[7] Botto I L, Barone V, Canafoglia M E, Rovere E, Violante R, González M J, Gazzoli D and Schalamuck I 2015 Pyroclasts of the explosive-effusive PCCVC volcanic eruption on the health and the environment in different zones of Villa La Angostura, Neuquen, Argentina Proc. of AUGM-DOMUS 2012, La Plata, Argentina (La Plata, Bs., Argentina) 4: 1–11
[27] Botto I L, Canafoglia M E, Gazzoli D and González M J 2013 Spectroscopic and microscopic characterization of volcanic ash from Puyehue-(Chile) eruption: preliminary approach for the application in the arsenic removal J. Spectrosc. 8 254517
[28] Villabrilé P, Vázquez P, Blanco M and Cáceres C 2002 Equilibrium adsorption of molybdosilicic acid solutions on carbon and silica: basic studies for the preparation of ecofriendly acidic catalysts J. Colloid Interf. Sci. 251 151–9
[29] Erdemdoğlu M, Birinci M, Uysal T, Porgah Tüzer E and Barry T S 2018 Mechanical activation of pyrophyllite ore for aluminum extraction by acidic leaching J. Mater. Sci. 53 13801–12
[30] Zhu W, Nakashima S, Marin E, Gu H and Pezzotti G 2020 Microscopic mapping of dopant content and its link to the structural and thermal stability of yttria-stabilized zirconia polycrystals J. Mater. Sci. 55 524–34
[31] Soni V K, Roy T, Dhara S, Choudhary G, Sharma P R and Sharma R K 2018 On the investigation of acid and surfactant modification of natural clay for photocatalytic water remediation J. Mater. Sci. 53 10095–110
[32] Blosse A 2019 Thermal behaviour of actinolite asbestos J. Mater. Sci. 54 11784–95
[33] Fares G, Alhozaimy A, Alawad O A and Al-Negheimish A 2016 Evaluation of powdered scoria rocks from various volcanic lava fields as cementitious material J. of Mater in Civil Eng. 28 04015139
[34] Akia M, Salinas N, Luna S, Medina E, Valdez A, Lopez J, Ayala J, Alcoutlabi M and Lozano K 2019 In situ synthesis of Fe3O4-reinforced carbon fiber composites as anodes in lithium-ion batteries J. Mater. Sci. 54 13479–90
[35] Poyraz S, Cook J, Liu Z, Zhang L, Nautiyal A, Hohmann B, Klamt S and Zhang X 2018 Microwave energy-based manufacturing of hollow carbon nanospheres decorated with carbon nanotubes or metal oxide nanowires J. Mater. Sci. 53 12178–89
[36] da Trindade L G, Hata G Y, Souza J C, Soares M R S, Leite E R, Pereira E C, Longo E and Mazzo T M 2020 Preparation and characterization of hematite nanoparticles-decorated zinc oxide particles (ZnO/Fe2O3) as photoelectrodes for solar cell applications J. Mater. Sci. 55 2923–36
[37] Yan X, Wu Y, Li D, Hu J, Li G, Li P, Jiang H and Zhang W 2018 Synthesis and evolution of α-Fe2O3 nanorods for enhanced visible-light-driven photocatalysis J. Mater. Sci. 53 15850–8
[38] Krolop P, Jantschke A, Gilbricht S, Nitranten K and Seifert T 2019 Mineralogical imaging for characterization of the per geijer apatite iron ores in the Kiruna District, Northern Sweden: a comparative study of mineral liberation analysis and raman imaging Minerals 9 544
[39] Frezzotti M L, Tecce F and Casagli A 2012 Raman spectroscopy for fluid inclusion analysis J. Geochem. Explor. 112 1–20
[40] Hövelmann J, Putnis A, Geisler T, Schmidt B C and Golla-Schindler U 2010 The replacement of plagioclase feldspars by albite: observations from hydrothermal experiments Contrib. Mineral. Petrol. 159 43–59
[41] Palinkás S, Wegner R, Čobič A, Palinkás L A, De Brito Barreto S, Váczi T and Bermanec V 2014 The role of magmatic and hydrothermal processes in the evolution of Be-bearing pegmatites: evidence from beryl and its breakdown products Am. Mineral. 99 424–32
[42] Rull F, Martínez-Frias J and Rodríguez-Losada J A 2007 Micro-Raman spectroscopic study of El Gasco pumice, western Spain J. Raman Sp. 38 239–44