

Contents lists available at ScienceDirect

Applied Clay Science



journal homepage: www.elsevier.com/locate/clay

Research Paper

An integrated micro- and nano-scale investigation of green aluminosilicate materials: New insight into the gel network after natural weathering

Maria Cristina Caggiani^a, Roberta Occhipinti^a, Germana Barone^a, Giuseppe Cultrone^b, Paolo Mazzoleni^{a,*}

^a Department of Biological, Geological and Environmental Sciences, University of Catania, Italy

^b Department of Mineralogy and Petrology, Faculty of Sciences, University of Granada, Spain

ARTICLE INFO	A B S T R A C T		
Keywords: Geopolymers HRTEM Gel network Weathering Nano-structures	The microstructures of most of the geopolymers synthesized from different starting materials are composed of a mixture of (semi)-crystalline and amorphous phases. In this work we aim to investigate in dept the nanoscale morphology and composition of the gel phase of two volcanic- (Mt. Etna, Sicily) and metakaolin-based geopolymers. The main technique used is high-resolution transmission electron microscopy (HRTEM), with energy dispersive X-ray compositional analysis (STEM-EDS) and selected area electron diffraction (SAED). The results were compared with those obtained on a larger scale. For the first time, a focus at the micro- and nanoscale of geopolymers synthesized with these binary mixtures was achieved. The effect of weathering on the geopolymer network, the crystalline phases and the chemical composition was also evaluated showing, with the convergence of the results of complementary methods, that environmental exposure affects the products made with one type		

of precursor (ghiara) more than the other (volcanic ash).

1. Introduction

Geopolymerization, a relatively recent method rooted in ancient principles, has emerged in recent years as a potential solution to various environmental challenges (Shi et al., 2019; Palomo et al., 2021). This process involves the chemistry of alkali-activated inorganic binders, constituting a class of cementitious materials formed by the reaction between silica-rich and alumina-rich solids with alkali salt solutions: it yields a blend of gels and crystalline compounds, that finally solidify into a robust new matrix (Provis and Van Deventer, 2009; Palomo et al., 2014). Geopolymers structure is generally composed of tetrahedral aluminate and silicate units linked by oxygen atoms. The negative charge of Al^{3+} in IV-fold coordination is balanced by ions such as Na⁺, K⁺, and Li⁺ (Davidovits, 1991; Barbosa and MacKenzie, 2003; O'Connor et al., 2010). Geopolymers can be synthesized from naturally occurring materials (such as metakaolin) or industrial by-products (such as fly ash, slag), through an alkali-activated process. They possess remarkable engineering properties, including high compressive strength, durability, and resistance to chemical attack, making them attractive alternatives to traditional cement-based materials (Bernal et al., 2016; Coppola et al., 2020).

Among the various sources of aluminosilicates for geopolymer synthesis, volcanic materials have attracted considerable interest due to their abundance and chemical compositions (they are rich in aluminosilicate compounds) (Lemougna et al., 2018) and they do not require thermal pre-processing. Pyroclastic materials, including volcanic ash, tuff, and other volcanic by-products, are widely distributed in different regions worldwide due to common volcanic activities (Hossain, 2005; Leonelli et al., 2007; Kamseu et al., 2009; Takeda et al., 2014; Seyfi et al., 2015). These pyroclastic deposits offer several advantages, including easy accessibility and low-cost mining methods. Unlike traditional open-pit quarrying methods used for clay mining, the

Abbreviations: BSE, Back-Scattered Electrons; C-A-S-H, Calcium Alumino-Silicate Hydrate; FTIR-ATR, Fourier Transform Infrared-Attenuated Total Reflectance; GM20, Ghiara-Metakaolin geopolymer; GM20w, Ghiara-Metakaolin geopolymer after weathering; GP, Geopolymer; HAADF, High-Angle Annular Dark-Field; HRTEM, High-Resolution Transmission Electron Microscopy; L/S, Liquid to Solid ratio; MK, Metakaolin; MK_GP, Metakaolin Geopolymer; N-A-S-H, Sodium Alumino-Silicate Hydrate; SAED, Selected Area Electron Diffraction; SE, Secondary Electrons; SH, Sodium Hydroxide; SS, Sodium Silicate; S(T)EM-EDS, Scanning-(Transmission) Electron Microscopy-Energy Dispersive X-ray Spectroscopy; VG, Volcanic glass; VM20, Volcanic ash-Metakaolin geopolymer; VM20w, Volcanic ash-Metakaolin geopolymer after weathering; XRPD, X-ray Powder Diffraction.

* Corresponding author.

https://doi.org/10.1016/j.clay.2025.107742

Received 18 October 2024; Received in revised form 30 January 2025; Accepted 31 January 2025

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E-mail address: paolo.mazzoleni@unict.it (P. Mazzoleni).

extraction of pyroclastic materials has limited negative environmental impact (Leonelli et al., 2007; Demirdag et al., 2008; Lemougna et al., 2011). Research has shown that these materials can serve as effective precursors for the synthesis of geopolymers with desirable properties. Volcanic ashes are utilized either as primary source of aluminosilicate material (Bondar et al., 2011; Lemougna et al., 2011; Tchakoute et al., 2013; Djobo et al., 2016a) or in combination with metakaolin (Ngouloure et al., 2024: Tchakoute Kouamo et al., 2012: Barone et al., 2020, 2021; Occhipinti et al., 2020, 2022, 2024; Slaný et al., 2023; Ijaz et al., 2024). The authors found that the incorporation of pyroclastic materials resulted in geopolymers with extensive versatility and enhanced strength and durability. Nevertheless, these properties are related to several factors such as chemical and mineralogical composition of the aluminosilicate precursor, particle size of the raw material, curing temperature, composition of the alkaline solution, and liquid-to solid ratio (Provis and Van Deventer, 2009). In general, the reactivity of volcanic ashes is significantly influenced by the amount of amorphous phases present, with higher reactivity corresponding to higher amorphous phase content (Lemougna et al., 2014; Tchakoute et al., 2015; Djon Li Ndjock et al., 2017). Volcanic ash also contains Ca and Mg, which can take part to the reaction and play the same role in the geopolymer structure, compensating the deficit of charge due to the substitution of Si⁴⁺ by Al³⁺ (Lemougna et al., 2013; Djobo et al., 2016a; Djobo et al., 2017). However, the higher silica to alumina ratio that often characterizes volcanic pyroclastic precursors can reduce reactivity. Therefore, incorporating additional sources of reactive aluminum or adjusting the mix proportions and curing methods could increase reactivity and improve final properties. This includes enhancing resistance to wet-dry cycles and reducing efflorescence in volcanic ash-based geopolymers (Najafi Kani et al., 2012; Tchakoute Kouamo et al., 2012; Yankwa Djobo et al., 2016; Occhipinti et al., 2022). Despite the increasing interest in volcanic precursor-based geopolymers, there are no studies that have specifically focused on the examination of their gel network at the nanoscale. Most of the studies on the microstructure are performed by means of SEM-EDS analyses (Djobo et al., 2017; Occhipinti et al., 2020; Finocchiaro et al., 2024). In contrast to the spherical particles of fly ash, volcanic ash particles show different morphologies, from porous to dense matrices, with distinct unreacted particles and geopolymer gel. These studies report that the microstructural characteristics and the gel chemistry of volcanic-based geopolymer binders depend on the type of aluminosilicate used and the synthesis conditions. However, there remains a need for a comprehensive understanding of the evolution of this gel network, particularly at the nanoscale, in order to bridge the knowledge gap with fly ash, slag, and/or metakaolin-based geopolymers.

So far, the authors have investigated the durability of geopolymers derived from two Sicilian volcanic precursors under the influence of environmental factors, including natural weathering processes (Occhipinti et al., 2022, 2023). The authors have investigated the mineralogical phases and the development of mechanical properties of volcanic ash- and "*ghiara*" (a volcanic paleosol)-based geopolymers - with the addition of metakaolin - before and after the atmospheric exposure. The latter can induce complex changes in the microstructure and chemical composition of geopolymeric materials, affecting their mechanical properties, pore structure, and overall stability over time.

However, as geopolymers can encompass a mixture of amorphous, semicrystalline, and crystalline phases, their mechanical properties likely derive from the combined effects of the amorphous gel phase acting as a binder and the reinforcing presence of crystalline alumino-silicate particles (Xu and Van Deventer, 2003). Thus, a comprehensive understanding of the structural characteristics of the geopolymer network is essential not only to elucidate its behavior under different conditions, but also to optimize its performance for specific applications.

The aim of this study is to understand the role that is played by the various components of the raw materials in the synthesized alkali activated systems before and after the environmental exposure. The morphology of ash-based and ghiara-based geopolymers before and after the exposure was analyzed at the nanoscale by using high resolution transmission electron microscopy (HRTEM) in comparison with that of a simpler system based on sole metakaolin. HRTEM was used in conjunction with energy dispersive X-ray compositional analysis in scanning transmission mode (STEM-EDS) and selected area electron diffraction (SAED). The analyses were focused on the gel nanostructure to highlight the presence of amorphous, crystalline, and semi/polycrystalline phases and nano-porosity. Semi-quantitative chemical analyses were carried out also by using scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS), and the results were compared with those obtained by STEM-EDS. These comparisons allowed for an evaluation of the gel type in relation to the Si/Al ratio, as well as the relative abundance of other elements such as Fe, Ca and Na. Finally, in a complementary approach, these data were correlated with infrared spectroscopy and mechanical strength results to provide a comprehensive understanding of the material properties and the effect of the weathering on the geopolymer network, such as the potential occurrence of efflorescence. The novelty and strength of this work is not only that it is one of the very few in the literature based on HRTEM for the study of geopolymers, but also that it applies this technique to binary mixtures of volcanic precursors and metakaolin, with the further advantage of evaluating the effect of natural aging on their micro- and nano-structure.

2. Materials and methods

2.1. Geopolymers preparation

The design of the geopolymers in this study was based on previous research conducted by (Occhipinti et al., 2022, 2023). Binary mixtures of volcanic pyroclastic residues (ash or *ghiara*) sourced from Mt. Etna (Sicily) and metakaolin (MK) were activated using an alkaline solution consisting of sodium silicate (SS with $SiO_2/Na_2O = 3.3$, supplied by Ingessil s.r.l., Italy) and 8 M sodium hydroxide (SH, supplied by Carlo Erba reagents s.r.l., Italy). The mixtures contained 20 wt% of MK; further details of the recipes are given in Table 1.

Volcanic ash and *ghiara*-based geopolymers (hereafter labelled VM20 and GM20, respectively) were cured at 25 ± 3 °C for 28 days, then three replicas of each sample were exposed to the atmospheric environment for six months and tested after the exposure (VM20w and GM20w) (Occhipinti et al., 2022, 2023).

Finally, in order to compare the binary mixture with a pure mixture, a pure MK-based geopolymer was also prepared as a standard formulation and cured at room temperature for 28 days. The formulation with metakaolin was prepared considering a SS and SH solution of 1:1 ratio. The L/S ratio was chosen based on the workability of the slurry. MK was allowed to react with this solution, in order to obtain the molar ratios reported in Table 1. The SiO₂/Al₂O₃ molar ratio provides the MK-based geopolymers with good strength (Duxson et al., 2007) and without the formation of crystalline zeolite type phases, as reported in the literature (Duxson et al., 2005).

Table 1

Composition of the geopolymers referred to weight ratio of the mixtures, including solid precursors and liquid activators and the molar ratio of SiO₂/ Al_2O_3 including precursors and alkaline activators. L/S = liquid to solid ratio where liquid refers to alkaline solution and solid to powdered precursors.

Sample	Volcanic precursor/MK (weight ratio)	Na ₂ SiO ₃ /NaOH (weight ratio)	SiO ₂ /Al ₂ O ₃ (molar ratio)	L/S ratio
VM20	80/20	1.7	4,21	0.32
GM20	80/20	1.7	3,82	0.32
MK_GP	0/100	1	2,48	0.7

2.2. Techniques

2.2.1. X-ray powder diffraction (XRPD)

X-ray powder diffraction (XRPD) patterns were recorded on a Miniflex Rigaku diffractometer equipped with a Ni filter and CuK α radiation generated at 40 kV and 15 mA. The measurement conditions were: 2 θ angular range 3° to 65°, scanning speed of 5.0°/min, step size of 0.01° 2 θ . Qualitative data were processed using BGMN/Profex 5.0 software (Doebelin and Kleeberg, 2015). Rietveld refinement was conducted by adding 5 wt% standard ZnO (BDH Laboratory Supplies) to each sample to quantify mineral phases and amorphous content. Refinement quality was assessed by visual inspection of patterns and discrepancy indices, with R-factors below 10 % indicating satisfactory results (Nguyen et al., 2021).

2.2.2. High resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy coupled with energy dispersive X-ray spectroscopy (STEM-EDS)

In order to study gel formation, micro- and nano-structural investigations were carried out by means of a HAADF Thermo Fisher Scientific TALOS F200X Transmission Electron Microscope operating at 200 kV and with a point-to-point resolution of 0.12 nm in the TEM mode and 0.19 nm in the STEM mode. Chemical analyses were obtained in STEM mode (scanning transmission electron microscopy) using the EDS (energy dispersive X-ray microscopy), with the Super-X system. Selected Area Electron Diffraction (SAED) analyses were also performed to determine the amorphous or crystalline structure at the nanoscale. A 40 μm objective aperture was used for TEM observations, while a 10 μm aperture was used for the collection of selected area electron diffraction (SAED) patterns, allowing a diffraction data collection from a 0.2 µm diameter circular area. A few tens mg of powder sample mass was dispersed in 5 ml ethanol. The dispersion was sonicated for about 3 min and the dispersed solids were fished with perforated carbon coated Cu grids. Special care was taken to avoid induced damage to the material (Egerton et al., 2004) observing its stability under the beam: it was observed that the phases present were not damaged during TEM observations. Imagej software was used to analyze and elaborate the HRTEM images.

2.2.3. Scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS)

Back-scattered electron (BSE)/Secondary Electron (SE) images and chemical analyses were conducted using a Tescan Vega LMU scanning electron microscope (SEM) equipped with an EDAX energy dispersive spectrometer (EDS). Fragments from the fracture surfaces of all samples, as flat as possible and a few millimeters thick, were placed in an oven at 100 °C overnight. They were then fixed to a support with carbon tape and coated with graphite under vacuum to make them conductive. EDS analyses (on specific spots) were conducted in BSE mode. Analyses were performed with an accelerating voltage of 20 kV, a working distance of 15 mm, and a beam current of 20 μ A. Each spot analysis was carried out over a period of 30 s. The determination of chemical composition was based on a 100 wt% oxide content on a H₂O and CO₂ free basis.

2.2.4. Infrared spectroscopy

Infrared spectra were acquired in Attenuated Total Reflectance -Fourier Transform Infrared mode (FTIR-ATR) using an Agilent Cary 630 (R) instrument. The range of acquisition was 4000–650 cm⁻¹, the spectral resolution was 4 cm⁻¹ and the number of scans was 64. Several areas of the bulk and external surface were analyzed for each sample, but only spectra of the bulk without the presence of salts were selected for this work. These were averaged, cut in the range 1275–790 cm⁻¹, linear baseline subtracted and normalized to the maximum intensity using LabSpec 5 software. After this treatment, the spectra were decomposed using the Fityk software.

3. Results and discussion

3.1. XRPD

The results of XRPD (Fig. 1, Table S1) show that volcanic ash and ghiara-based geopolymers before exposure have a similar mineralogical composition: amorphous phase together with plagioclase, pyroxene, and hematite and anatase crystals were revealed for both, even though, looking at quantitative data, the ghiara ones highlight a lower amount of amorphous phase in favor of plagioclase, quartz anatase and illite and a slightly higher content of hematite. All these crystalline phases are attributable to the original precursors and persist after the alkaline activation process, as also reported in previous works on the same raw materials (Barone et al., 2020; Finocchiaro et al., 2020). The exposed geopolymers of both types show the same mineralogical composition as the unexposed ones: no new secondary phases have been detected after weathering, although the presence of salts was found in previous studies by means of FTIR-ATR spectroscopy (see (Occhipinti et al., 2022) for details). After exposure, a decrease in pyroxene is highlighted for volcanic ash geopolymers, together with a slight increase in amorphous phase for both materials.

In order to better understand the possible changes at the nanoscale after weathering, HRTEM investigations were exploited to gain information from both mineralogical and elemental points of view (sections 3.2.1 and 3.2.2 respectively). Due to issues associated with particles overlapping, the distinction of partially reacted particles or crystalline phases is not always possible on the basis of morphology alone, so selected area electron diffraction (SAED) becomes important.

3.2. HRTEM

The HRTEM investigations on the VM20 and GM20 unexposed and exposed samples were carried out according to the following steps, already outlined by (Xu and Van Deventer, 2002): i) observe the micro/nano-morphology of the samples; ii) choose possible gel particles with irregular shape; iii) ascertain their amorphous or crystalline nature by performing electron diffraction on the selected particles (SAED); iv) perform EDS analyses, preferentially on amorphous particles, to study the gel composition.

In the following paragraphs, the results of the HRTEM analyses are described according to the exposed steps, and then they are compared with XRPD, SEM-EDS and FTIR-ATR results, as well as with previous structural and mechanical studies on the same samples (Occhipinti et al., 2022, 2023).

3.2.1. Morphological investigation at the nanoscale and evaluation of the crystalline phases

The SEM-SE images of the surface morphology of the samples are shown in Fig.S2. The HRTEM micrographs of VM20, VM20w GM20 and GM20w at different magnifications are respectively shown in Fig. 2 and Fig. 3. For comparison, a geopolymer using only metakaolin as precursor (MK_GP) has also been reported (Fig. 4 a and b). Morphologically, TEM observations show a heterogeneous nanostructure in the geopolymers, and different formations can be identified: geopolymer gel, semicrystalline and crystalline areas and volcanic glass particles.

Overall, there are no significant differences between the morphology of ash-based geopolymers (VM20) and *ghiara*-based ones (GM20), nor between exposed (VM20w and GM20w) and unexposed samples (VM20 and GM20).

TEM brightfield images reveal a nanostructure composed predominantly of lighter and darker zones formed by closely clustered subrounded particles with an average particle size of 15 to 40 nm. Their SAED patterns display a diffuse halo typical of amorphous material, attributable to the geopolymeric gel (Xu and Van Deventer, 2002; de Melo et al., 2017). These particles resemble those found in geopolymers based on metakaolin only, typically sub-spherical precipitates of 20–30



Fig. 1. XRPD patterns of raw materials (volcanic ash and *ghiara*) and respective geopolymers before and after environmental exposure. Au: augite; Plg: plagioclase; Hm: hematite; Qtz: quartz; Ant: anatase; Chm: chamosite; Ill: illite; Zn: Zincite (internal standard).



Fig. 2. HRTEM brightfield micrographs of unexposed and exposed volcanic ash geopolymers and electron diffraction (SAED) on selected areas of VM20 and VM20w. The point analyses of SAED patterns are indicated by numbers.

nm, representing the N-A-S-H geopolymer morphology (Autef et al., 2013b; Autef et al., 2013a; Tawfik et al., 2016; Costa et al., 2021). As in the case of metakaolin-based geopolymers, it seems that geopolymer gel precipitates also in volcanic/pozzolanic-based geopolymers mimicking the shape of the precursor particles. This phenomenon is evident here when comparing the nanostructures of our volcanic- and metakaolin-

based binary mixtures geopolymers with those of metakaolin ones, where the typical platy shape morphology of the latter is still recognizable (Figs. 2–3 vs. Fig. 4).

The formation of the geopolymers occurs through mechanisms such as surface interactions, nucleation and growth processes, and chemical bonding between gel particles and glassy phases (Van Jaarsveld and Van



Fig. 3. HRTEM brightfield micrographs of unexposed and exposed ghiara geopolymers and electron diffraction (SAED) on selected areas of GM20 and GM20w. The point analyses of SAED patterns are indicated by numbers.



Fig. 4. HRTEM brightfield micrographs and electron diffraction (SAED) of metakaolin based geopolymer (MK_GP). The point analyses of SAED patterns are indicated by numbers.

Deventer, 1997; Hajimohammadi et al., 2010; Hajimohammadi and van Deventer, 2016). For example, the alkali species present in the alkaline solution may preferentially adsorb to specific regions or surface features of the glassy particles, initiating the nucleation and growth of the gel phase in these areas. Thus, as the gel phase grows, it may conform to the shape and structure of the adjacent glassy particles (Fernández-Jiménez et al., 2005; Komnitsas and Zaharaki, 2007; Provis et al., 2010; Zhu et al., 2022).

Furthermore, irregularly shaped particles with sub-angular edges can also be found, as shown in Fig. 2c point 5 for VM20 sample. These morphologies may be attributed to relics of crystals from the original volcanic precursors combined with an amorphous phase, as reported by the SAED. Sharper spots are overlapped to a diffused diffraction ring, confirming the hypothesis derived from the sub-angular morphology of the area (Fig. 2c point 5). Spotted rings are clearly identifiable and are typical of the superposition of several crystals. Furthermore, a hexagonal structure can be inferred: this could be ascribed to the presence of residual metakaolin (Trusilewicz et al., 2012).

Intermediate phases resulting from an incomplete dissolution of the raw materials are common in geopolymer systems (Autef et al., 2013b; Kumar et al., 2017; de Melo et al., 2017; Costa et al., 2021), where hexagonal platy-shaped particles characteristic of unreacted metakaolin particles are clearly visible, as reported for MK_GP (Fig. 4). This phenomenon is expected in volcanic precursors-based systems due to the

presence of crystalline phases that exhibit low solubility in alkaline solutions at lower temperatures, for which reason, some particles could remain undissolved (Djobo et al., 2017).

In contrast, in ghiara-based geopolymers (Figs.3 and S3), only half of the analyzed particles showed exclusively the amorphous cloudy ring (examples in Fig. 3 points 4 to 7). Almost all the other particles present a coexistence of geopolymeric gel with residual crystalline phases, reflecting the lower amorphous content revealed by XRPD (section 3.1). This is also supported by the mechanical and structural results previously obtained on these materials, highlighting that GM20 geopolymeric gel resulted less resistant to external exposure than VM20 (Occhipinti et al., 2023). GM20w is characterized by the frequent presence of particles with a hexagonal basal SAED (Fig. S3). Just as certain crystalline or semicrystalline phases do not react in such an alkaline environment, other particles from the original volcanic precursor may not take part in the reaction. This is the case for example of elongated particles found in both ash and ghiara geopolymers (Fig. 5 a-d), which are larger in size, have sharper edges and more defined boundaries than the geopolymer particles (GP): they can be identified as volcanic glassy particles (VG) (Kawano and Tomita, 2001). Despite their amorphous nature, VG particles show low reactivity in such alkaline system (Djobo et al., 2017), although small gel particles can be found on the surface of the glassy particles in both VM20 and GM20 samples, effectively covering or locally dissolving it (Fig. 5 a-d). STEM-EDS analyses performed on



Fig. 5. HRTEM brightfield micrographs showing the different morphologies of volcanic glass and geopolymer gel and respective STEM/EDS spectra.

selected points of the volcanic glass (VG) and geopolymer (GP) particles provide evidence of their different chemical compositions. This analysis is particularly crucial given the amorphous nature of both particles. The GP particles exhibit a significantly higher Si/Al ratio (1 GP, 3 GP, and 5 GP spectra) and a higher sodium (Na) content - which can certainly be related to the N-A-S-H gel phase composition - compared to their VG counterparts (1VG and 4VG spectra). The Si/Al ratio increases in the geopolymer due to the presence of sodium silicate that leads to the formation of the N-A-S-H gel.

Therefore, the various nanostructures present in both volcanic ash and *ghiara*-based geopolymers can be distinguished based on their morphology, with gel particles located between crystalline particles, which may also act as binders, and glass particles, potentially partially covered by/reacted with the gel. This morphological distinction reflects the complexity of the geopolymer structure and highlights the multifunctional interactions between the different components within the matrix.

Concerning nano-porosity, in combination with nanoparticle components, it plays a key role in determining the overall structure and properties of the geopolymer matrix. High-Angle Annular Dark-Field (HAADF) images of both volcanic ash and *ghiara* samples before and after weathering are shown in Fig. 6 a-d. The variation in electron contrast across different regions reveals a complex and heterogeneous nanopore structure embedded within the gel matrix. This nanostructured network, with dimensions around 10–20 nm, indicates the complex arrangement of pore spaces that intricately interconnect throughout the geopolymeric material. A defined geopolymer structure made up of spherical particles separated by nano-porosity in a spongelike microstructure is typical of MK-based geopolymers and defines clusters of aluminosilicate particles measuring approximately 5–10 nm in diameter (Maitland et al., 2011). This structural feature, as also documented by (Kriven et al., 2004; Duxson et al., 2005; Bell et al., 2006; Autef et al., 2013a), represents a fully reacted geopolymer phase.

3.2.2. Elemental composition

Chemical data resulting from SEM-EDS and STEM-EDS on both volcanic ash- and *ghiara*-based geopolymers are plotted in the graphs of Fig. 7 and Fig. 8, respectively. The multipoint maps with the corresponding EDS results are shown in the Supplementary Materials (S4 and S5). The advantages and drawbacks of the two techniques lead us to compare the data obtained by both.

Concerning ash-based geopolymers, the chemical composition reveals that the average Si/Al ratio is 1.9 for VM20 and 2 for VM20w from SEM-EDS analyses, while 2.3 and 2.4, respectively, from STEM-EDS; overall, the results are consistent with literature data on metakaolinbased geopolymers (Si/Al > 1.80) (Duxson et al., 2007; Autef et al., 2013a). Even though they are not correlated, it is interesting to observe the variation of sodium, calcium and iron content with respect to Si/Al (Fig. 7), which is easier through SEM-EDS due to the higher number of spots analyzed. Here, sodium content is in the range of 4.18 to 12.66 wt % for most of the spots, while a few have Na < 4 wt% and also have lower Si/Al ratios, while a group of spots has much higher sodium values (20.32–46.80 wt%). It should be noted that all the latter belong to the unexposed sample. Probably, these latter analyses reflect the presence of efflorescences at microscale formed due to an excess of Na in the mixture, which is in accordance with previous results demonstrating how sodium carbonates were present in higher amounts on unexposed samples, and then leached out during atmospheric exposure (Occhipinti et al., 2023). This also explains why in the STEM-EDS analyses, where the geopolymer gel is better selected as explained in the previous paragraphs, sodium varies from 2.16 to 6.34 wt% with one outlier at 9.78 wt%, not reaching the high values of the above-mentioned group. Similarly to sodium, calcium is also divided into two groups; most of the points have SEM-EDS values between 0.3 and 4.30 wt%, while few samples show higher calcium levels (6.60-14.94 wt%), probably influenced by the intermingling of geopolymeric gel and volcanic precursor powder. STEM-EDS analyses also identify two groups for calcium abundance: 0.5-1.31 wt% and 4.3-4.7 wt%, but both are included in the lower cluster of SEM-EDS, once again leading to exclude the spots with higher SEM-EDS concentrations. Iron amount shows a positive correlation with the Si/Al ratio, suggesting a possible substitution of some aluminum in coordination IV by Fe³⁺ (Ponomar et al., 2022). However, this observation cannot be confirmed by STEM-EDS analyses, where the iron content ranges from 1.13 to 1.63 wt%. In the diagram Ca vs. Na, three distinct clusters can be distinguished, summarizing what remarked before: i) the majority of the analyzed points, falling within a relatively homogeneous group: this group displays similar SEM-EDS and STEM-EDS data, which can therefore be considered to represent the composition of a true geopolymeric gel; ii) a group with high sodium, involving only unexposed samples analyzed by SEM; iii) a group with high calcium (only unexposed samples, again data from SEM). The last two groups, as already pointed out, are most likely associated with the occurrences of salts on unexposed samples or of other minerals or volcanic glass linked to the original raw materials. The comparison of the composition of pure geopolymer gels before and after atmospheric exposure therefore reveals no significant differences for volcanic ash-based geopolymers.

Concerning *ghiara*-based geopolymers, the Si/Al ratios calculated from SEM-EDS data are on average 2.5 (GM20) and 2.1 (GM20w). Interestingly enough, these are instead 1.7 and 2.4, respectively, from STEM-EDS. Due to the better selection of gel spots with HRTEM instrumentation, the value of 1.7 seems to be more accurate. The behavior of sodium and calcium with respect to Si/Al (Fig. 8) is comparable to that observed for volcanic ash-based samples: even though there seems to be a less sharp distinction between groups with lower or higher content of these two key elements, the range of values, including the STEM-EDS data, should be taken into account for the geopolymer gel composition. Regarding iron, excluding spots with a concentration higher than 20 wt%, there is a noted positive correlation between with



Fig. 6. High angle annular dark field (HAADF) micrograph taken in STEM mode of: a) VM20, b) GM20, c) VM20w and d) GM20w. On the image with a higher magnification (d) pore sized are marked with red lines. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 7. Plot of sodium, calcium and iron content vs. the silicon/aluminum ratio and plot of the calcium vs. sodium content for unexposed and exposed volcanic ashbased samples by SEM-EDS and STEM-EDS analyses.



Fig. 8. Plot of sodium, calcium and iron content vs. the silicon/aluminum ratio and plot of the calcium vs. sodium content for unexposed and exposed ghiara-based samples by SEM-EDS and STEM-EDS analyses.

the Si/Al ratio for SEM-EDS data, again, potentially indicating a substitution of Al^{3+} (IV). In addition, a significant increase in iron is observed at constant Si/Al ratio, suggesting a potential shift towards octahedral coordination, as hypothesized by (Ponomar et al., 2022). In the case of *ghiara* products, it should be underlined that the raw material is particularly rich in iron oxides (Lanzafame et al., 2022). Once again, STEM-EDS data do not confirm this hypothesis. In the Ca vs. Na diagram, a pronounced decrease in sodium is observed in the SEM-EDS data of exposed samples, probably due to the higher amount of sodium salts present in the unexposed geopolymers: in fact, this difference is not visible in the STEM-EDS data. The most significative difference between *ghiara*-based geopolymers, strictly linked to gel composition before and after atmospheric exposure, remains the lower Si/Al ratio of GM20.

The comparison between the two techniques proves their complementarity. If, on one hand, much more spots could be analyzed with SEM and, due to the larger volume of sampling, the data could be considered more representative, though limited to a small fraction of the sample; on the other hand, although the spots analyzed by TEM were much fewer and representative of nano-sections of the samples, they could be better chosen, excluding non-amorphous zones and allowing to focus on geopolymer gel.

3.3. Relationship between elemental composition, molecular structure and mechanical properties

Therefore, taking into account the Si/Al ratios derived from STEM-EDS, it is evident that GM20 only detaches from the uniform values of 2.3–2.4 that characterize the other three geopolymers. A correlation between these ratios and the mechanical properties previously evaluated (Occhipinti et al., 2023) is not easy. It is known from the literature that the compressive strength of geopolymer paste increases as Si/Al increases (Ozer and Soyer-Uzun, 2015), even though it seems that the strength starts to decrease again after a certain threshold value, i.e. 1.5 (Wang et al., 2020) or 1.9 (Duxson et al., 2007). The three very close ratios characterizing VM20, VM20w and GM20w correspond to likewise close compressive strength values for VM20 (43.92 MPa) and GM20w (43.32 MPa), while the ratio of 1.7 for GM20, which is below the abovementioned threshold, corresponds to a stronger geopolymer (53.85 MPa). The much higher result for VM20w (63.58 MPa), instead, is not consistent with the other data.

In order to understand this inconsistency, infrared analyses were used. Salts spectra were excluded and only those of geopolymer, free of additional crystalline phases, were considered and averaged, since the aim is to study the gel composition and its relationship with the Si/Al ratio and the mechanical properties. The FTIR-ATR spectra (Fig. 9) revealed similar positions of the main aluminosilicate band (referred to the asymmetric stretching of Si-O-T) for all the four samples. This is centered around 970–975 cm⁻¹, a rather low position in accordance with infrared spectra of geopolymers synthesized from a mixture of metakaolin and volcanic scoria (Tchakoute Kouamo et al., 2012; Djobo et al., 2014, 2016b). Only ghiara-based geopolymer before atmospheric exposure show an even lower position (969 cm^{-1}) than all the others (977 cm^{-1}) : this could indicate a transformation of the gel in *ghiara*geopolymers after weathering. A link with the Si/Al ratios is besides immediately visible, with GM20 again being the only sample that differs from the others. Indeed, it is known that the main IR band positions shift towards lower wavenumbers as the Si/Al decreases (Ozer and Sover-Uzun, 2015). Furthermore, for ghiara-geopolymers, an evident loss in intensity of the main band is visible after weathering. According to (Wang et al., 2020), a larger peak area indicates a higher amount of gel and, consequently, better mechanical properties. In this case, therefore, this loss in intensity would imply a worsening of the mechanical properties, which is consistent with our previous findings (Occhipinti et al., 2022, 2023). This is also consistent with the inverted band intensity of non-exposed and exposed volcanic ash-based geopolymers, for which the compressive strength trend is opposite to that of ghiara (Occhipinti et al., 2022, 2023).

Another evidence that emerges from the complete infrared spectra in Fig. 9 concerns the low wavenumber region. Raw volcanic ash and *ghiara* spectra show a band around 735 cm⁻¹, whereas MK is at 785 cm⁻¹: these are ascribed to the stretching vibration of 6-fold coordinated $Al_{(VI)}$ –OH and 6-fold coordinated $Al_{(VI)}$ –O. In the spectra of geopolymers, instead, these bands are no longer visible and a signal around 685 cm⁻¹ appears, attributable to Si–O symmetric stretching. This demonstrates that after geopolymerization, 6-coordinated $Al_{(VI)}$ was replaced by 4-coordinated one, taking part into the framework structure (Yunsheng et al., 2010; Tchakoute Kouamo et al., 2012).

Finally, the broad band linked to hydroxyl units, both structural and from water, is also visible between 3700 and 2600 cm⁻¹, together with the band at 1645 cm⁻¹, and even when the spectra are normalized to the



Fig. 9. FTIR-ATR average spectra of the three precursors and the four geopolymers in the region 4000–650 cm^{-1} . The intensities of MK, volcanic ash and *ghiara* are divided by two for clarity.

maximum intensity, the former appears higher in the unexposed samples.

To further investigate the role of OH group linked to silicon atoms, the spectra were cut in the region of interest $(1275-790 \text{ cm}^{-1})$, baseline subtracted, normalized to the maximum intensity and decomposed. The results are shown in Fig. 10. The almost constant position of the main band for three spectra over four is confirmed, but the presence of further signals under the envelope induced some reflections. The band between 1042 and 1049 cm⁻¹ for ash-geopolymers and around 1065 cm⁻¹ for *ghiara* ones surely accounts for the MK component in the precursors' mixture (Tchakoute Kouamo et al., 2012; Djobo et al., 2014, 2016b). On the other hand, it can also be linked to a N-A-S-H component of the gel, which adds to the C-(A)-S-H one in a lower position, giving the resulting

band shape after the complete 28 days maturation (Garcia-Lodeiro et al., 2011). This is consistent with the graph shown in Fig. S6 from which it emerges that most of the gel compositions spots fall in the N,C-A-S-H field. Furthermore, the band included between 885 and 895 cm⁻¹ must be carefully considered. It is assigned in the literature to Si-O stretching and OH bending (Si-OH) and the presence of these units in the geopolymers is known to reduce the degree of polycondensation reaction, which in turn decreases the mechanical strength (Lee and Van Deventer, 2003; Yunsheng et al., 2010; Tchakoute Kouamo et al., 2012; Djobo et al., 2014). The area of this spectral component was therefore considered in relation to the total area of the band and plotted against the compressive strength values for the four samples, taken from (Occhipinti et al., 2023). A linear correlation is evident (Fig. 10),



Fig. 10. decomposed FTIR-ATR spectra of the four products in the region $1275-790 \text{ cm}^{-1}$ and plot of the ca. 890 cm^{-1} band area normalized to the total area, against compressive strength values taken from (Occhipinti et al., 2023).

confirming a worsening of the mechanical performance of *ghiara*-geopolymers after exposure, which is also consistent with the abovementioned position shift and intensity reduction of the main aluminosilicate band.

4. Conclusions

This work allowed an in-depth investigation of the geopolymer network at the micro- and nanoscale, never before described for products derived from binary mixtures of volcanic based materials and metakaolin, with the further addition of natural weathering assessment. This was done with two levels of comparison: 1) two products obtained with two different volcanic precursors originated from Mt. Etna, i.e. volcanic ash and *ghiara* paleosol (both associated with metakaolin); 2) the same products as such or after exposure to the atmospheric environment.

Firstly, through HRTEM investigations, interesting observations could be made on the morphology of the geopolymer gel itself when observed at the nanoscale, distinguishing gel from (partially) unreacted particles and observing how the forming gel mimics the precursor's particle shape.

Furthermore, the use of HRTEM was essential to determine whether the gel underwent significant changes after weathering at the nanoscale, both from mineralogical and elemental points of view, in line with previous structural observations and mechanical performances. It was confirmed that *ghiara*-based products are more affected by atmospheric exposure than those ash-based. This conclusion was finally obtained by the convergence of the complementary techniques within the approach adopted. GM20w was in fact the product with the more pronounced change in the Si/Al ratio (STEM-EDS), with a lower content in amorphous phase with respect to VM20w (XRPD), with the higher presence of salts on the respective unexposed sample (SEM-EDS), with the more important shift of aluminosilicate infrared band simultaneously to its intensity loss (FTIR-ATR) and with the higher increase in Si-OH units (i. e. decrease in compressive strength; FTIR-ATR coupled with mechanical performance).

VM20w, instead, showed less marked or even opposite behavior, therefore we can finally conclude that with this work we gave an important confirmation to the possible use of "ash-based + metakaolin" geopolymers with the future perspective of promoting their use as high performance advanced green materials in outdoor applications.

Future perspectives will concern the role of iron and the N,C-A-S-H nature of both gels emerging from the SEM and STEM-EDS analyses, studying HRTEM elemental maps of samples with different amounts of Ca-additive.

CRediT authorship contribution statement

Maria Cristina Caggiani: Writing – review & editing, Writing – original draft, Methodology, Investigation, Data curation, Conceptualization. Roberta Occhipinti: Writing – review & editing, Writing – original draft, Methodology, Investigation, Data curation. Germana Barone: Writing – review & editing, Writing – original draft, Supervision, Project administration, Methodology, Funding acquisition. Giuseppe Cultrone: Writing – review & editing, Writing – original draft, Supervision, Investigation, Data curation. Paolo Mazzoleni: Writing – review & editing, Writing – original draft, Supervision, Project administration, Data curation. Paolo Mazzoleni: Writing – review & editing, Writing – original draft, Supervision, Funding acquisition, Data curation, Conceptualization.

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.

Acknowledgements

The work of Roberta Occhipinti, Germana Barone and Paolo Mazzoleni has been supported by MUR in the framework of PNRR Mission 4, Component 2, Investment 1.3 under project CHANGES. The research of Maria Cristina Caggiani has been supported by Attraction and International Mobility (AIM1833071; CUP E66C18001310007) project and 2017POCSICILIA1/5/5.4/9.2.3/AVV6.22/0001 (CUP G6110002200095).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.clay.2025.107742.

Data availability

Data will be made available on request.

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