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# Geopolymer production for conservation-restoration using Sicilian raw materials: feasibility studies

G Barone<sup>1\*</sup>, M C Caggiani<sup>1</sup>, A Coccato<sup>1</sup>, C Finocchiaro<sup>1</sup>, M Fugazzotto<sup>1,2</sup>, G Lanzafame<sup>1</sup>, R Occhipinti<sup>1</sup>, A Stroschio<sup>1</sup> and P Mazzoleni<sup>1</sup>

<sup>1</sup> Department of Biological, Geological and Environmental Sciences, University of Catania, Corso Italia 57, Catania, Italy

<sup>2</sup> Department of Humanities, University of Catania, Italy, Piazza Dante 32, Catania, Italy

\*E-mail: gbarone@unict.it

**Abstract.** In the last decades, particular attention has been aimed to innovative materials class with high-tech features to apply in conservation-restoration of Cultural Heritage, ensuring both aesthetic compatibility and adequate properties with regards to the original rock substrate. AGM for CuHe project aims to valorise Sicilian raw materials, natural and industrial by-products, for the development of alkali-activated materials, as geopolymers. These materials are produced by the activation of an aluminosilicate precursors in alkaline environment. Volcanic raw materials (volcanic ash, volcanic paleo-soils and pumice) and ceramic industrial waste were mixed with an alkaline solution and cured at room temperature. In some cases, small quantities of metakaolin were added to the mixture to increase the reactivity of the precursors. In order to obtain the geopolymeric reaction, the precursors need to be fully characterized. A similar approach is also applied to the synthesized geopolymers in order to understand its behaviour in relation to the original building materials. Therefore, a multi-analytical approach is proposed: chemical and mineralogical studies (XRF and XRD), combined with spectroscopic (FT-IR) and morphological (SEM and  $\mu$ CT) analyses. These preliminary results confirm the feasibility of this eco-friendly class of materials using the proposed local raw materials.

## 1. Introduction

In the framework of the Italian National Research Program “Advanced Green Materials for Cultural Heritage”, local raw materials, as well as industrial wastes are being used as precursors for geopolymers (GP).

These materials have been recently proposed in the field of conservation-restoration interventions on built heritage in substitution to traditional mortars and to Portland cement [1–4]. Historical buildings in Sicily are characterized by brick, as well as stone structures, showing black (vulcanites) and whitish (Hyblean calcarenites) colors respectively. Moreover, mortars and plasters made using the local volcanic materials show the same hues and, in addition, a typical brick-red color which is due to the use of oxidized paleo-soils, locally named *ghiara*, as aggregates. The project aims at developing advanced, smart and high-tech products for use in high-seismic risk areas, by using the same local raw materials used in the first place for buildings and monuments. Geopolymers are versatile materials that are chemically and mineralogically compatible with traditional stone substrates. Moreover, their properties



can be tailored according to the needs (blocks, mortars, plasters, etc.), in terms of viscosity, setting time, porosity, mechanical strength [1–4].

These products represent an innovative approach in terms of recycling and sustainability, since their production is carried at low temperature, involves the re-use of waste material from human activity and produces low emission of CO<sub>2</sub> and energy consumption in comparison with traditional Portland cements [3,5]. Moreover, the use of local raw materials reduces costs and CO<sub>2</sub> emissions linked to transportation. Finally, the use of colored precursors offers the possibility to obtain conservation-restoration materials that are visually similar to the original materials, yet recognizable.

Geopolymers are obtained when low-calcium reactive aluminosilicates are mixed with alkaline activators, for example sodium hydroxide and sodium silicate solutions [6]. When the silicon and aluminum contents are appropriately balanced with alkali cations and water [7,8], a geopolymeric gel will form at room temperature, through the different stages of geopolymerization reaction: dissolution of the reactive precursor, formation of oligomers, condensation of aluminosilicate units [6,7].

A multi-analytical approach is proposed to investigate the composition of the starting materials, to assess their reactivity to alkaline environment, and to optimize the formulation design. The obtained geopolymeric formulations will be then produced at a larger scale, for use in test sites. In the framework of the AGM for CuHe project, geopolymer production aims at reducing the carbon footprint and environmental impact of industrial production of conservation-restoration products, and improve the general sustainability of the intervention. The outcomes of the project encompass the development of more sustainable conservation practices, a positive impact on the industrial know-how of Sicilian companies, as well as on the tourism industry by promoting innovative fruition of cultural sites during restoration.

## 2. Raw materials

In this study, we assess the suitability of local georesources and of waste materials as geopolymer precursors: on the one hand, volcanic products, on the other, non-toxic waste from local sources. More in details, the raw materials used are:

- Volcanic ash, the finer fraction (< 2 mm) of particles erupted during explosive activity. It falls down on roads and is considered a waste material, stocked in landfills with high management costs.
- Volcanic paleo-soils, locally named “ghiara”, widely used in Catania architecture in XVII and XVIII centuries as aggregate for the production of mortars and plasters.
- Pumice (Porticello, Aeolian Islands), a highly siliceous pyroclastic product with a characteristic “foamy” structure that is due to the simultaneous, and very rapid, depressurization and consequent cooling of the magma, generated by explosive eruptions.
- Industrial ceramic waste, linked to tiles manufacturing by local industries.

All these resources were sampled, cleaned and dried before dry milling (<75 μm). They all have an aluminosilicate composition and amorphous moieties, which are both necessary for the production of geopolymers. Therefore, a multi-analytical approach is used, which includes chemical, mineralogical, structural and microstructural characterization of the raw materials.

Moreover, commercial metakaolin has been added to geopolymers formulations.

Alkali activation was performed using appropriate mixtures of sodium hydroxide (8 M) and sodium silicate (*waterglass*) solutions.

### 2.1. Chemical characterization

The chemical composition of the precursors plays a significant role in the design of geopolymeric binders formulations. Portable X-ray fluorescence (PXRF) was used in this study to obtain a preliminary chemical composition of the raw materials. PXRF can be performed *in situ*, as an alternative to the more usual destructive methods based on X-rays, without any sample preparation [9]. Moreover, low costs and short analysis times are additional advantages. In detail, for this study, analyses were performed in air with a Bruker Tracer IV-SD system equipped with an Rh target X-ray tube with Pd slits and a Silicon Drift Detector (SDD). 60 s live time accumulations were collected.

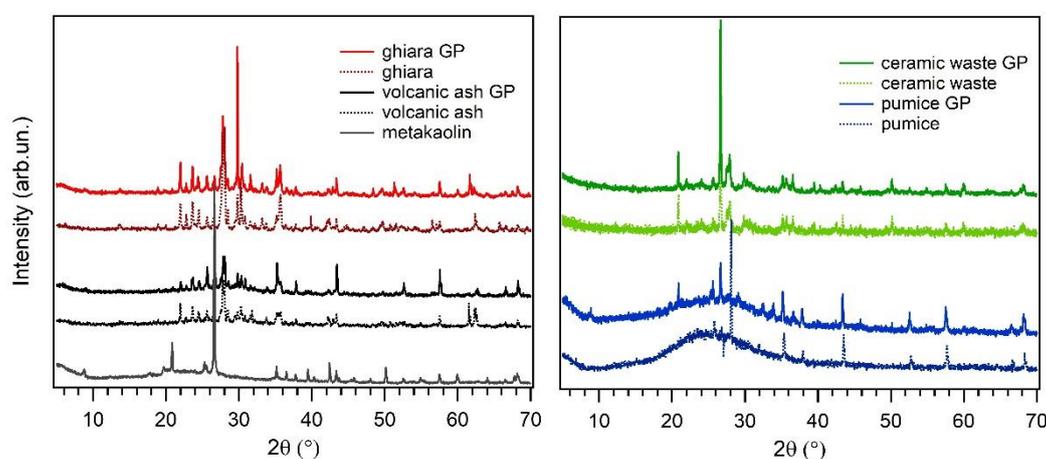
Qualitative data were obtained by means of the S1PXRF software, while the abundances of the major elements by means of PyMCA software [10], which is based on fundamental parameters, considering the Tracer IV-SD specification and the measurement setup. Table 1 shows the average composition for all the raw materials.

**Table 1.** Chemical composition (wt%) of all the aluminosilicates precursors, from PXRF analyses; Na<sub>2</sub>O and MgO contents are not reported due to their high analytical error.

	Al	Si	P	K	Ca	Ti	Mn	Fe
<b>Volcanic ash</b>	14.71	54.86	0.45	2.04	12.44	1.47	0.23	13.80
<b>Ghiara</b>	27.60	50.52	0.63	1.67	6.77	1.46	0.21	11.15
<b>Ceramic waste</b>	21.44	61.67	0.21	2.22	9.08	0.74	0.11	4.54
<b>Pumice</b>	14.59	75.46	0.11	4.97	2.70	0.43	0.11	1.62
<b>Metakaolin</b>	34.03	58.56	0.20	0.69	2.08	1.88	0.00	2.57

## 2.2. Mineralogical characterization

X-ray diffraction (XRD) analyses were performed on the powdered raw materials and relative geopolymers through Rietveld refinement in order to quantify the crystalline and amorphous contents (Figure 1). In detail, for this study, a Siemens D5000 diffractometer, with Cu-K $\alpha$  radiation and Ni filter, in the 2 $\theta$  range 3-70°, using a step size of 0.02°, a counting time of 5s for step, divergence and anti-scatter slits of 1° and receiving slit of 0.2 mm was used. The quantitative data were obtained with Rietveld method using GSASII software [11]. The amorphous and crystalline phases abundance was calculated by means of internal corundum standard addition [12].



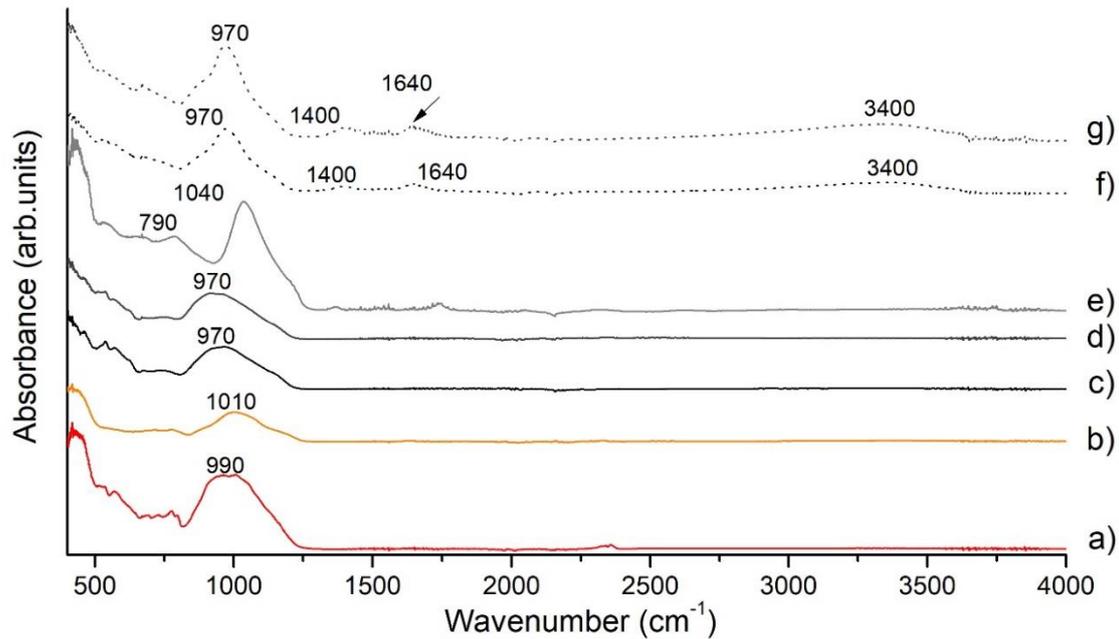
**Figure 1.** X-ray diffractograms of raw materials (dotted lines) and relative geopolymers (full lines).

## 2.3. Structural characterization

Attenuated Total Reflection Fourier-Transform Infrared Spectroscopy (FT-IR-ATR) was employed in order to exploit its high performance in the identification of chemical bonds in the structure of materials with rapid measurements.

It was performed on the powders of raw materials, used as precursors for the geopolymerization process using a Thermo Fisher Scientific 380 Infrared spectrometer (Nicolet), the spectra were collected at room temperature in the 400-4000 cm<sup>-1</sup> range, with 4 cm<sup>-1</sup> resolution. The ATR spectra of all the considered raw materials (Figure 2a-e) show the typical aluminosilicate structure with the broad band

between 800 and 1300  $\text{cm}^{-1}$  enveloping different T-O-T (T=Si or Al) contributions of amorphous and crystalline phases [6,13,14].



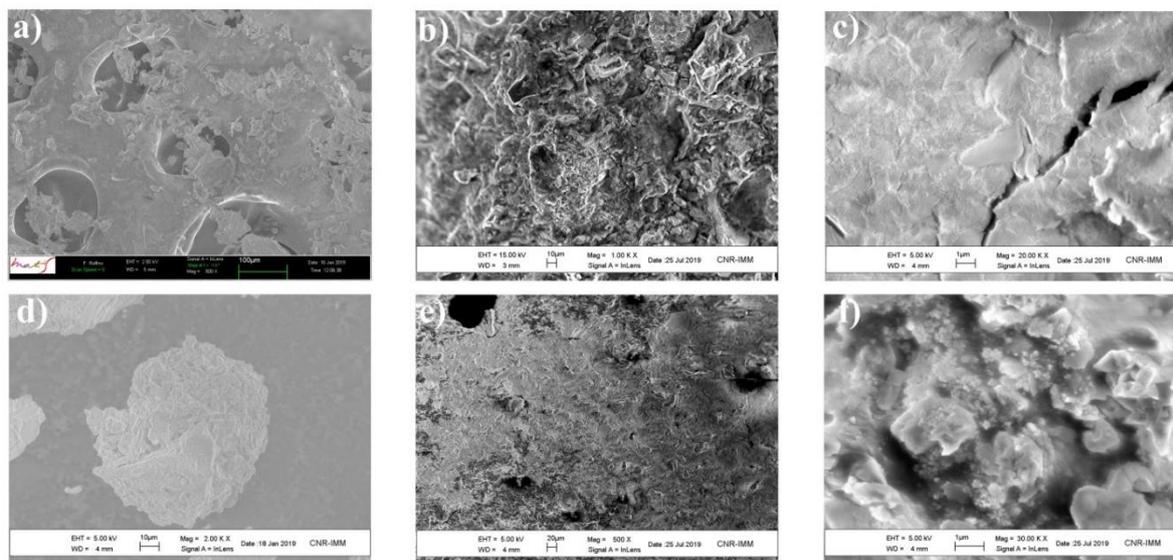
**Figure 2.** FTIR-ATR spectra of powdered raw materials (a: ceramic waste; b: pumice; c: ghiara; d volcanic ash; e: metakaolin) and of geopolymers synthesized with ghiara (f) or volcanic ash (g) with 20 wt% metakaolin addition.

#### 2.4. Microstructural characterization

In this study, a Field Emission Scanning Electron Microscope (SEM) (Zeiss FEG-SEM Supra 25 Microscope) was employed to investigate samples texture from micrometric to nanometric scale. Images were collected by InLens mode using a working distance of 3/4 mm with an acceleration voltage of 20 kV and 30 kV. Analyses of the morphological features were performed on raw materials as well as on fracture surfaces of the geopolymers, covered using a gold sputter coater (8 nm thickness).

The microscopic understanding of both raw materials and “geopolymeric gel” is not straightforward, since most analyses have been performed on binders synthesized from multicomponent resources such as natural rocks or industrial waste materials which contain a large number of unreacted phases in the gel [15-17].

Volcanic ash and ghiara (Figure 3a and d) show similar texture, both containing volcanic glass. The microstructure is extremely inhomogeneous and the particles are angular and semi-angular with different sizes and shapes. Voids (Figure 3a), typically present in volcanic scoria-type grains, have dimension varying from 100 to 10  $\mu\text{m}$ . Smaller particles in ghiara sample (Figure 3d) show agglomerations to form coarse grains which can be attributed to the milling process.



**Figure 3.** SEM micrographs of: a) volcanic ash raw material; b) volcanic ash-based geopolymer; c) same as b, at higher magnification; d) ghiara raw material; e) ghiara-based geopolymer; f) same as e, at higher magnification. Scale bars and magnification are shown in each image.

### 3. Geopolymers

The study of geopolymers needs to explore the microscopic structure of the gel at a multi-scale level, from the nanometric to the millimetric size. A multi-analytical approach is therefore needed, partially overlapping with the one used for raw materials, which encompasses XRD characterization coupled with Rietveld refinement, FT-IR analyses, SEM imaging and Synchrotron-Radiation Microtomography (SR- $\mu$ CT).

As it concerns formulations design, the considered volcanic precursors are aluminium-poor (see Table 1) and they appear to be poorly reactive in alkaline environment, especially at room temperature. It has been proven that a small addition (10 to 30 wt%) of metakaolin to the mixture is sufficient to overcome this limit [15]. In this study, binary mixtures of metakaolin with volcanic ash, ghiara and pumice have been used for geopolymer formulation in order to enhance their reactivity to alkaline activation.

XRD analyses were performed on geopolymer samples after 28 days of curing in order to investigate the crystalline and the amorphous phases, and to compare them with the corresponding raw materials. The Rietveld refinement, in particular, allowed to determine the quantitative variation of these phases and consequently to establish the disappearance, decrease and change of crystalline phases and the amorphous content increase. Even though the different formulations show some variability, it is evident that the amorphous content increases in the geopolymers to the expenses of crystalline silicates (e.g. quartz, anorthite, diopside). In volcanic ash and ghiara based geopolymers, the formation of zeolites and calcite can also be appreciated. In pumice-based geopolymers, trona, a sodium carbonate hydrate, is observed as well.

The results of the ATR investigation carried out on geopolymers synthesized starting from ghiara and volcanic ash with 20 wt% of metakaolin are shown in Figure 2f-g. The broad bands around 1640 and 3400  $\text{cm}^{-1}$  are indicative of the presence of water in the geopolymers, being respectively ascribed to H-O-H bending and to OH asymmetric stretching vibrations of molecular water [3,16]; furthermore, the band at around 1400  $\text{cm}^{-1}$  could be attributed to the presence of carbonates. The position of the broad aluminosilicate band is shifted towards lower wavenumbers in the geopolymers (970  $\text{cm}^{-1}$ ) with respect to metakaolin (1040  $\text{cm}^{-1}$ ). However, the understanding of the formation of amorphous gel phases, and

the relationship between the raw materials' (ghiara/volcanic ash, metakaolin) main ATR signal and that of the respective geopolymers requires bands deconvolution [16].

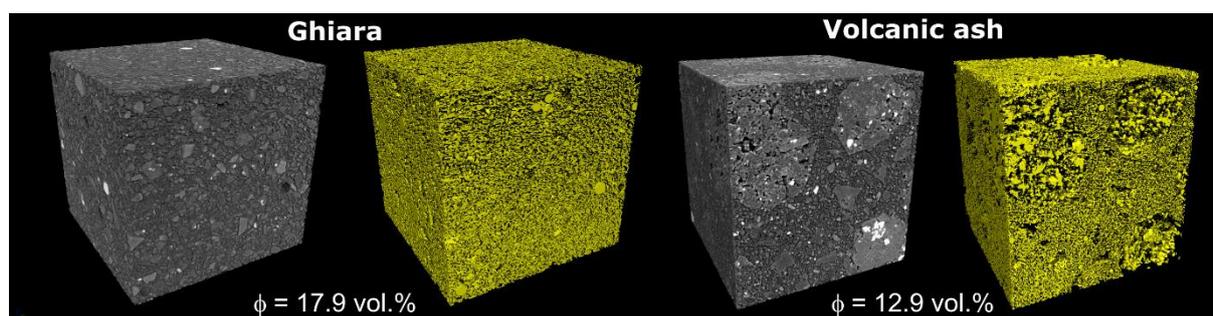
SEM observations allowed to investigate the medium to long-range ordering (tens to hundreds of nanometres). This analysis allows identifying regions of the binder that are named "geopolymeric gel" [16,18] and to study pore morphology and unreacted regions of the sample.

Differences in the morphology of corresponding geopolymer binders are hereafter shown based on high-resolution SEM images (Figure 3b, c, e, f). At this level of magnification (500-1000 $\times$ ), a textural feature common to both samples is the presence of micro-sized defects such as micro-voids, which may be ascribable to entrapped air and micro-cracks due to sample preparation. Both geopolymer binders contain unreacted particles bound together by geopolymeric gel. The development of an aluminosilicate gel can be observed at higher magnification (Figure 3c, f). It is characterized by a quite uniform morphology constituted by a homogeneous matrix which seems denser in volcanic ash-based geopolymer binder. The unreacted particles are loosely embedded in the matrix and they are not well distinguishable.

Geopolymers have been shown to have a microporous framework, with the characteristic pore size ranging from below 10 nm up to approximately 100  $\mu\text{m}$  [19–21], which can lead to significant complexities in the pore geometry. In general, porosity can be related to the strength of a material. Control of binder's porosity can allow tailoring properties for certain applications. For this reason, SEM analyses were not intended to be used as a method to obtain statistical information on the pore size distribution [20] because they cover a small area in 2D micrographs.

A 3D information on bigger volumes should be useful to accurately determine tortuosity and connectivity. In this respect, computed microtomography has become a powerful tool for investigating the inner structure of samples at the micron scale. In the last decades, it developed among the innovative techniques employed in the characterization of geo-materials. The advantage of this technique is that it offers a rapid and non-destructive inspection of sample textures, providing parameters not obtainable by common 2D techniques, such as 3D morphology of the phases of the material and their real abundance within the investigated volume.

For the purpose of this study, feasibility tests of SR- $\mu\text{CT}$  on selected samples were carried out at the SYRMEP beamline of the Elettra synchrotron laboratory (Trieste, Italy) by using high-resolution SR- $\mu\text{CT}$  in phase-contrast mode [22]. A polychromatic X-ray beam in transmission geometry illuminated three millimetric-sized samples. Experiments were performed with sample-to-detector = 200 mm, collecting 1800 projections over a total scan angle of 180 $^\circ$  with an exposure time of 2 s/projection. The effective pixel size of the detector was set at 1.952  $\mu\text{m}^2$ . The 2D tomographic slices were reconstructed using the Syrmep Tomo Project (STP) house software suite [23] applying a single-distance phase-retrieval algorithm [24] to improve the consistency of the morphological analysis. The virtual 3D volumes were then segmented and analyzed using the Fiji software [25]. Analyses were performed on sub-volumes extracted from the original reconstructed 3D images. Binary images of the 3D pore morphology were obtained by manual segmentation. As a preliminary investigation, the total porosity was determined (Figure 4). Three-dimensional renderings were obtained by VGStudio Max 2.2 software (Volume Graphics, Heidelberg, Germany).



**Figure 4.** 3D rendering of the investigated geopolymer samples (analysed volume = 7.41 mm<sup>3</sup>) and corresponding segmented pores phase (in yellow). The porosity  $\phi$  is reported as volume fraction %.

#### 4. Conclusions and perspectives

Locally available resources, such as pumice and ghiara, as well as waste products, such as volcanic ashes and non-toxic industrial by-products, were selected as potential aluminosilicate precursors for low-calcium alkali-activated materials, i.e. geopolymers.

The characterization of the selected raw materials allowed to optimize the design of the formulation, and to obtain geopolymeric binders with aesthetic, chemical, mineralogical, mechanical and structural compatibility with historical building materials.

The successful geopolymerization reaction is demonstrated by the increase in amorphous moieties shown by Rietveld refinement of XRD data, by the changes in the vibrational spectra, and by the observation of the gel in high-magnification electron microscopy images. Moreover, the visualization of porosity by micro-tomography is a powerful tool to understand the texture and morphological features of geopolymeric compounds.

Sicilian raw materials are suitable precursors for promising green, versatile, high-tech materials for conservation-restoration of built cultural heritage. Further studies are needed in order to assess their applicability in selected test sites, in close cooperation with local enterprises, conservators, stakeholders. Finally, particular attention will be given to positively impact the tourism industry by promoting more conscious fruition of built cultural heritage under conservation-restoration.

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