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Increasing resolution in chemical mapping of geomaterials: from X-Ray Fluorescence to Laser-Induced Breakdown Spectroscopy

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Abstract

Laser-Induced Breakdown Spectroscopy (LIBS) micro-mapping is an important analytical tool for the study of geomaterials. In this work, this technique was applied, for the first time, to the analysis of alkali-activated materials and geopolymers, as well as rocks, mortars and bricks. The results obtained were compared with the ones obtained using Energy-Dispersive X-Ray Fluorescence (ED-XRF) macro-mapping and the advantages of the LIBS approach (speed, lateral and in-depth resolution, capability of light elements analysis) were highlighted.

The issues associated with the quantitative determination of the samples' composition from the analysis of the LIBS spectra were also briefly discussed.

Keywords: LIBS micro-mapping, XRF macro-mapping, geomaterials, alkali-activated materials, geopolymers, CF-LIBS, K-means

Introduction

Geomaterials, consisting in natural and artificial stones, are widely employed in different fields from civil engineering to cultural heritage [1]. They consist in rocks and various inorganic raw materials that are mixed to obtain products with specific physical properties ranging from homogenous to highly inhomogeneous systems. For example, ceramics are composed by clays and rock/mineral fragments [2], mortars are made of a binder, aggregates (sometimes reactive) and additives which can modify the mixture's properties [3-5]. Geopolymers are new green binding materials which are finding application also in the field of cultural heritage[6-8].

In the archaeological and monumental context, the characterization of geomaterials appears relevant for historical interpretation and especially for preservation purposes, where compatible materials must be identified and formulated for substituting or repairing structures. Among the methods for material characterization, microchemical analysis is essential for determining the compositional features of geomaterials and correlate this information with their physical properties and durability. Geochemical information is associated to mineralogical and petrographic analysis to obtain structural, textural and compositional characterization. In fact, each component influences the material aspects of the geomaterials, specifically aesthetical appearance and mechanical resistance but also their susceptibility to alteration or damage. With the development of new methods and portable equipment for *in situ* characterization, 2- or 3-D elemental mapping techniques have revolutionized the field of chemical analysis, usually performed on powders or on chips scanned by benchtop equipment such as XRF or SEM-EDS. These traditional approaches continue to be necessary to meet special requirements, such as analytical accuracy or the detection of some specific markers in provenance studies, or in micro-stratigraphic analysis, and so on. Otherwise, when compositional overview, identification and classification of materials, possible interactions between components and conservation state must be evaluated or monitored, *in situ* geochemical mapping might provide fundamental insights. It is the case of X-ray fluorescence (XRF) portable scanners, which allow for the acquisition of both textural and compositional information in one single map, with resolutions spanning from mm to microns, depending on the scanner's specifications, although with well-known limits in sensitivity and light elements detection typical of XRF analysis. In cultural heritages, XRF scanners - along with other imaging techniques - find their main application field in the study of artworks and painted surfaces to map pigments or alteration products [9]. However, tools as micro-XRF benchtop mapping systems are also largely employed for the study of geological materials, both for qualitative and quantitative analysis of mineral phases and textural maps [10]. When using XRF scanners, it should be considered that the XRF signal is produced in a zone corresponding to several tens of microns under the surface, the depth of this

zone depending on the composition of the material. In case of strongly inhomogeneous samples and/or in the presence of alteration or degradation surfaces, serious matrix effects can be introduced in the analysis.

Within the panorama of microchemical analytical techniques, micro-LIBS has proven to be a highly reliable method in obtaining geochemical fingerprint of geological materials, when single laser shots are acquired on samples. For instance, Harmon et al. [11] and Gottfried et al. [12] have demonstrated the suitability of the method in classifying geological materials (also from archaeological and forensic contexts) based on their LIBS spectra and statistical approaches. McMillian et al. [13] tested a method for the classification of natural rocks, gems and mineral ores using LIBS. More recently, Senesi [14] reviewed the successfully application of LIBS spectroscopy in the analysis of geomaterials, with a focus on minerals and rocks, again based on spectra and statistical analysis, while Lemiere & Harmon [15] summarized the advantages of coupling XRF and LIBS for geological surveys in the field. Technical developments of instruments evolved towards implementing scan-mode analysis, making LIBS a valuable tool for the microchemical mapping of natural and artificial stone materials, improving the range of detectable elements and the dimensional scale offered by classical XRF scanners. Pagnotta et al. [16] proposed the use of micro-LIBS mapping for the analysis of ancient Roman mortars. In 2019, Botto et al. [17] discussed the advantages of LIBS micro-mapping of geomaterials in a review paper devoted to the applications of LIBS in Cultural Heritage and Archaeology. Very recently, Jolivet et al. [18] reviewed the recent application of LIBS systems enabling to map surfaces, discussing bias and advantages of different setup, configuration, equipment properties and data processing. Herewith, relevant case studies in the field of archaeology and industry highlight the growing interest for this application and the current challenges still to explore.

In the frame of the MACh (Micro LIBS Scan Elemental Mapping: a powerful tool for Cultural Heritage studies) project, an Italian-Serbian cooperative research project funded by the Italian Minister for Foreign Affairs and International Cooperation, the micro-LIBS instrument developed at the Applied and Laser Spectroscopy Laboratory of CNR in Pisa was optimized for the analysis of geomaterials, developing a compact, transportable and economic device, able to analyze geomaterials with a strong intrinsic inhomogeneity or for the analysis of stratified samples [19]. To test the device and explore the challenges offered by the applications of micro-LIBS in the field of geological materials compared to classical XRF scanners, a set of different natural and artificial geomaterials, namely rocks, mortars, bricks, alkali-activated materials and geopolymers, have been analyzed by using both a portable XRF scanner and the micro-LIBS mapping system. The study was aimed at developing an optimized protocol for micro-destructive analysis, by integrating 2D

and 3D elemental micro-analysis. Moreover, the selected targets of natural and artificial stone materials exhibit a range of textural and compositional features providing materials for a systematic review of the potential of micro-LIBS mapping in analyzing such variety of geomaterials, also in comparison with portable XRF scanners.

The LIBS spectra were processed with the combined use of an unsupervised clustering algorithm and the Calibration-Free LIBS procedure [20]. The spectra obtained with both instruments were then compared showing advantages and drawbacks with the application of the two distinct techniques. The application of the two methods on different samples allowed obtaining a quick raw classification between geomaterials with different composition, which would be useful in the future for a better planning of sample collection for further mineral-petrographic investigations.

Materials and methods

Geomaterials

Natural stones, ceramics, mortars, alkali-activated materials and geopolymers have been selected for the present investigation. Natural stones include lithotypes from quartzite to breccia, covering a wide range of the occurring variability in rock texture and composition (i.e., from quite monomineralic to polymineralic systems). The stones here selected are part of a wider project aimed at creating a digital database on natural materials quarried and locally used within the Pisa district (Italy) [21]. Ceramic materials include few samples of bricks, which are largely used in building environment. The selected samples exhibit visibly different textural and compositional features due to the raw materials employed. The bricks have been collected from the archaeological complex of Massaciuccoli (Massarosa, Italy) that entails structures that have been dated between the 1st and the 2nd century BCE [22]. The analyzed mortars are laboratory replicas made by following ancient recipes based on the use of organic additives to improve workability and physical properties of the mixtures [4-5]. For the present investigation, binder type (lime), lime/aggregate ratio (1:3), aggregate type (quartz sand), water/binder ratio (0.6), and curing time (28-56 days) were kept unaltered, while different type of organics (Kaddukai, *Terminalia chebula*; Cactus, *Cactacea*; Neelamari, *Indigofera Tinctoria*) have been used, providing different proportions of fat, carbohydrate and protein, which has been demonstrated to affect the final mixtures' properties. The alkali activated materials (AAMs) and geopolymers (GP) analyzed in this work are obtained from an ongoing project aimed to formulate green materials by also recycling wastes. The scientific community agrees in indicating AAM as a "*binder obtained by a reaction between a source of alkaline metal and a silicate powder*" [23], including in this definition also geopolymer as a subset of AAMs "*where the binding phase is almost exclusively aluminosilicate and highly coordinated*"

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[23]. However, J. Davidovitshas highlighted the huge structural differences of these two materials [24]. According to Davidovits' concept geopolymer [25], the materials selected for this investigation are synthesized by the geopolymerization reaction of an amorphous super reactive metakaolin powders as precursor and a potassium-based alkaline reagent with a pH able to depolymerize the precursor structure without dissolving it. The formulation of AMMs and geopolymers couples well with the recycling of industrial wastes. For this reason, stoneware, sanitaryware, quartz composites materials and construction and demolition wastes (CDW) were used as aggregates (see Table S1).

Experimental

Samples were preliminary scanned by a portable XRF Elio ©Bruker equipped with x-y motor stage to scan surfaces up to 10 x 10 cm with a resolution of 1 mm/px. In this work, areas of 2 x 2 cm^2 were scanned on flat surfaces. On the same area, a sub-surface 1x1 cm^2 was analyzed using the optimized μ-LIBS mapping system, equipped with a double-pulse Nd:YAG laser operating at the fundamental wavelength (λ=1064 nm) and a time-integrated spectrometer coupled with a commercial microscope. The spectrometer covers a range from 200 to 900 nm with a resolution of 0.1 nm in the UV region (190-420 nm) and 0.2 nm in the VIS-IR region (410-900 nm). An external 5-joints arm allows connection of the main body of the instrument with a commercial microscope (Zeiss AXIO A1). Pairing the laser with the microscope reduces the spot of the beam up to 25-30 μm, using a 10X objective specific for the wavelength of the laser. The use of a motorized sample table, synchronized with the laser and spectrometer through dedicated software, allows to obtain elementary mappings of sample areas up to 6 cm^2 in size. The instrument is relatively small (50 cm x 130 cm x 70 cm with microscope) making the instrument easily transportable for in-situ analysis. Since the LIBS spectroscopy is based on the analysis of material ablated by a laser beam, the laser focus becomes an important parameter for a good ablation and therefore a good analysis. However, most of the samples herewith analyzed are not perfectly flat and their surface is inhomogeneous. The slight variation in the laser beam focusing leads to changes in the ablated mass, plasma temperature and plasma electron number density, which influence the intensity of the LIBS spectra and the analytical response. To minimize these effects as much as possible, the elementary intensity matrices are normalized with respect to the total intensity matrix. In this work, the crater dimension was about 20 μm in diameter and the power density was calculated at approximately 300 GW/cm^2.

Results and Discussion

Natural stones and ceramics

Among natural stone, quartzite, limestone and breccia were selected and scanned by using XRF and LIBS mapping systems, being the lithotype representative of different ranges of compositional and textural homogeneity/heterogeneity (Figure 1-2).
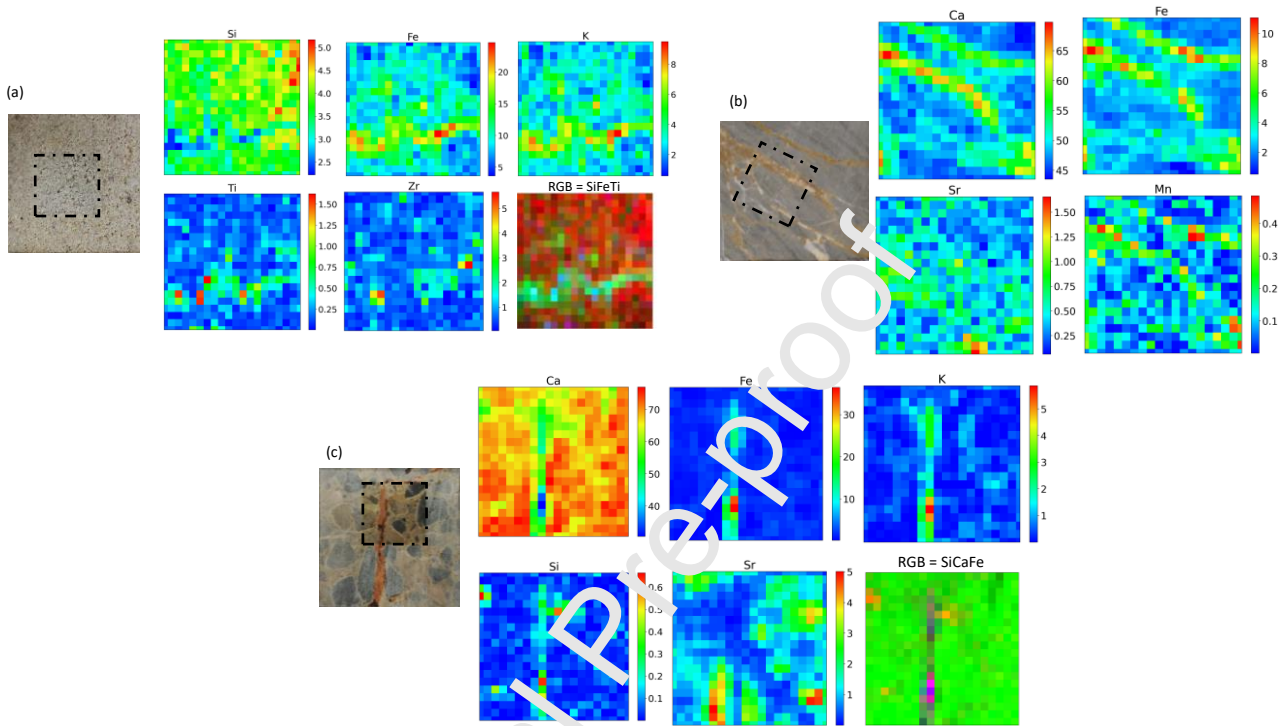

Figure 1. XRF maps collected on 2x2 cm area (pixel size 1 mm) on (a) quartzite (Guamo, LU), (b) limestone (Reth. contorta limestone, Caprona, PI) and (c) breccia (Agnano, PI), as examples. For further details on lithotypes see ref. [21]. Dotted lines mark the areas scanned by micro-LIBS.
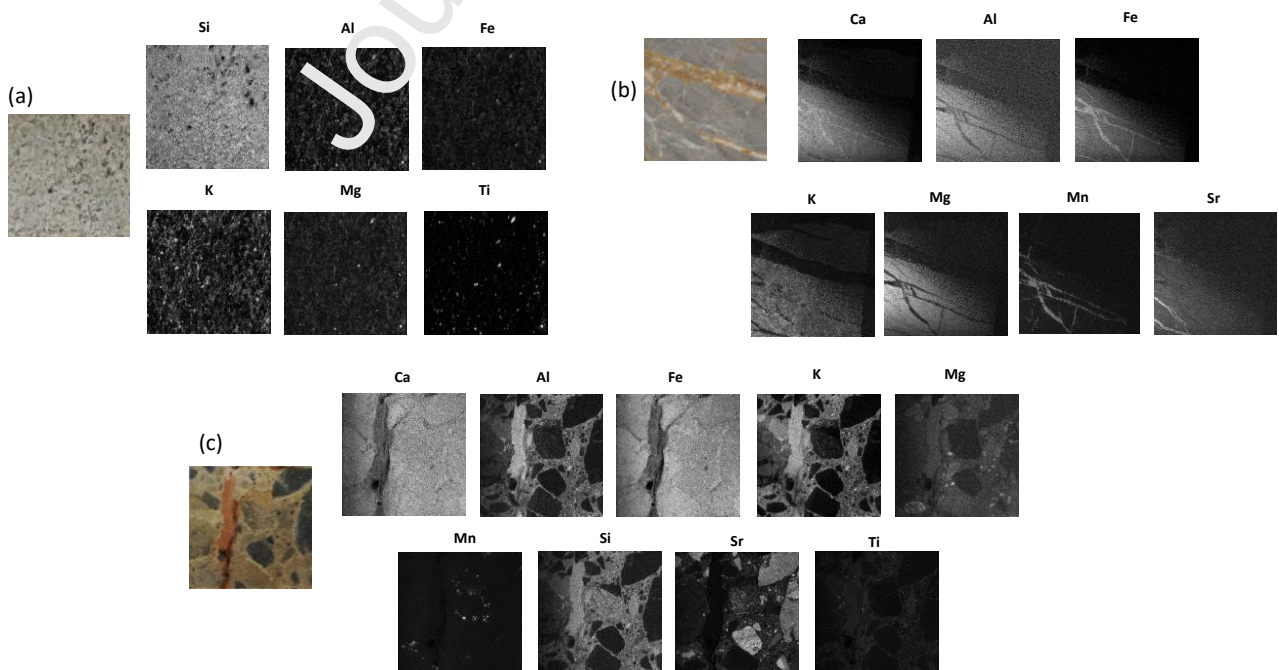
Figure 2. micro-LIBS maps on 10 mm x 10 mm (200x200 spectra with a 0,05) step subarea from XRF maps on (a) quartzite (Guamo, LU), (b) limestone (Reth. contorta limestone, Caprona, PI) and (c) breccia (Agnano, PI), as examples. For further details on lithotypes see ref. [21].

Comparative evaluations on collected maps enable discussing the figure of merits of LIBS mapping especially for highly heterogenous stone materials. In the case of quartzite and limestone, in XRF maps the distribution of chemical elements related to the constituting mineralogical phases satisfactorily, highlighting the discriminant compositional and textural features of the stones. Nevertheless, a more detailed mapping is guaranteed by LIBS analysis, determining the co-localization of elements due to minor phases, whose identity and nature can be usually fully identified only by microscope analysis. As an example, the preferred-oriented micas can be traced in quartzite by the co-localization of Al, K and Ti. In the breccia, the highly compositional and textural heterogeneity due to matrix and grains can be precisely described only by increasing spatial resolution, such as in the case of LIBS applications. Finally, as expected, the co-localization of light elements not visible in XRF spectra is easily detected by LIBS analysis, revealing the distribution of specific mineral phases.

In ceramics' studies (e.g., bricks) the determination of the composition of the raw materials is relevant for provenance studies, similarly to natural stones. In Figure 3 a typical example of different manufactures identified by the color of the ceramic paste is shown. It is well known that bright red pastes are usually obtained with Fe-rich clays. On the other hand, the whitening of ceramics can be obtained in different ways (e.g., adding calcium, using Ca-rich clays, or using salts [26]). Mapping bricks represents an easy way for detecting the main components of the samples and obtaining a better understanding on the raw materials used, even in a preliminary investigation phase. In this specific case, XRF maps are quite informative regarding the composition of the clay used for the manufacture, namely Fe-rich and Ca-rich, respectively. For further details on aplastic fraction or specific textural features, micro-LIBS might improve knowledge on the ceramic fabric. As an example, the processing of LIBS maps by using Self-Organizing Maps (SOM) segmentation methods [27] can provide a classification of different mineral particles in the ceramics, enabling the discrimination among aplastic fragment naturally occurring in the raw materials, inclusions and secondary precipitated phases (see Figure 1 in [27]).
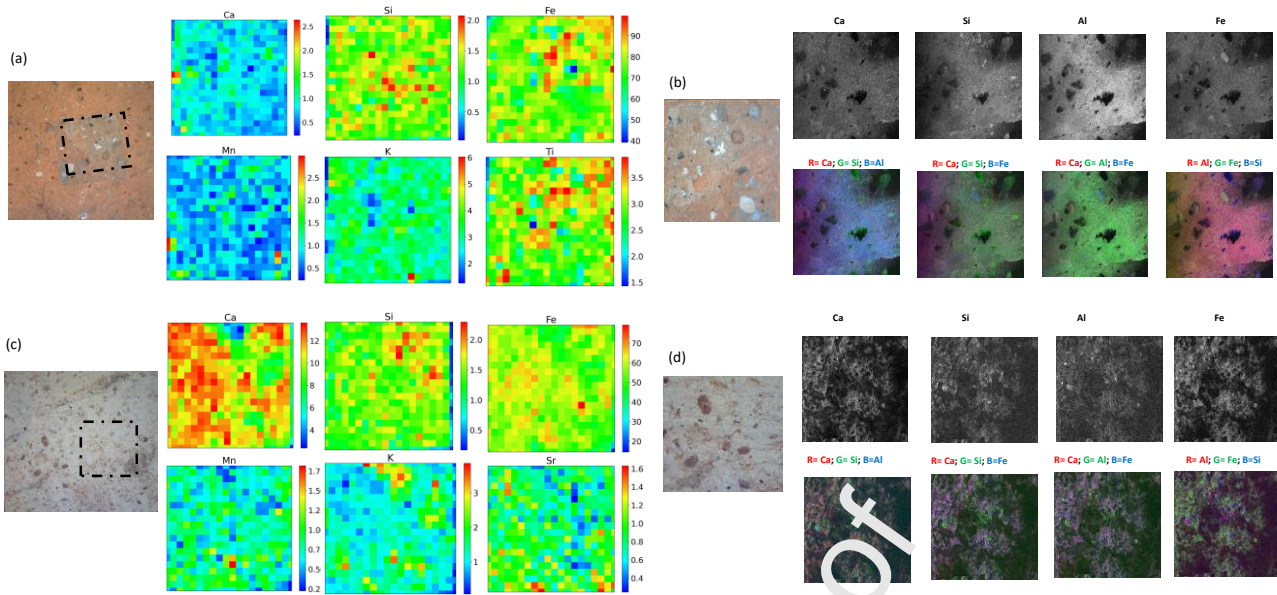
Figure 3. (a,c) XRF and (b,d) micro-LIBS maps on two bricks as examples of Fe-rich and Ca-rich clay paste. The scanned area were 2x2 cm for XRF and 10 mm x 10 mm (200x200 spectra with a 0,05 step) for LIBS

In archaeological contexts, the elemental mapping of stones and ceramics is useful for characterizing the composition of raw materials and establishing their provenance. The screening done by combining non-destructive (XRF) and micro-destructive (LIBS) portable instrumentation is particularly suitable for in situ applications and for the quick gathering of data, useful for a first evaluation of geochemical features. A two steps protocol, with a first assessment of materials' composition and a targeted sampling for further detailed laboratory analysis, is appropriate when dealing with ancient artefacts of historical and cultural interest.

Organic mortars, alkali-activated materials and geopolymers

Lime mortars are among the oldest type of building materials. Their use is attested with various recipes through countries, involving the use and the exploitation of different raw materials. In some locations (e.g., India, Turkey, China, etc.) organic additives such as plant and animal extracts are attested in ancient recipes credibly added to improve their mechanical performances. Herbs, fruits and natural extracts were mixed in water, fermented for a few days and the fermented organics along with water were added to the mortar mixture. However, the role of organics in the improvement of the mechanical and physical properties of the mortars is still not completely understood. Preliminary studies revealed that the interaction with lime matrix of carbohydrates, proteins, and fats in the organic part determine a forced carbonation and the precipitation of new phases (carbonate polymorphs and oxalates), resulting in enhanced mechanical and physical properties [4-5]. Such mixtures are highly inhomogeneous materials, so that a detailed compositional analysis at micro-scale is not a straightforward issue. In this perspective, micro-

elemental LIBS images offer interesting advantages with respect to other methodologies, such as the simplicity and the ability to make fast measurements without sample pre-treatment. Looking at the micro-LIBS maps collected on a selection of organic mortars, it is interesting to discuss the relative homogeneity in the distribution of the constitutive chemical elements. In fact, despite the different phase composition and physical-mechanical properties (see Figure S1 and Table S2), no clear difference in the elemental distribution is evidenced (Figure 4); in the selected samples, Ca and Fe are co-localized in the binder, while silica is mainly in the aggregate fraction. Trying to find discriminating criteria, some clues can be provided by a detailed inspection of micro-LIBS maps collected on organic mortars, whose textural features cannot be otherwise appreciated by XRF elemental mapping (Figure S2). In this kind of mixtures, physical properties are mainly imprinted by their structure, namely the spatial relation among grains and binder fraction determined by the addition of specific organics, even keeping unaltered component ratios. On the contrary, when different physical properties are imprinted by lime typology (e.g., aerial vs hydraulic) or by the occurrence of reactive aggregates (*e.g.*, pozzolanic materials or volcanic ashes) micro-LIBS can provide interesting information about the compositional markers discriminating between different recipes. In fact, the difference between aerial and hydraulic mortars can be evidenced looking at RGB micro-LIBS maps considering relevant chemical elements such as Al, Si and Ca (see Fig. 3 in [19]). For hydraulic systems obtained by the addition of reactive aggregates, the hydraulic index can be qualitatively evaluated and estimated looking at LIBS maps processed by using simple statistical methods such as Principal Component Analysis (see for example Figure 4 in [28]), withgood reliability when compared with quantitative SEM-EDS analysis.
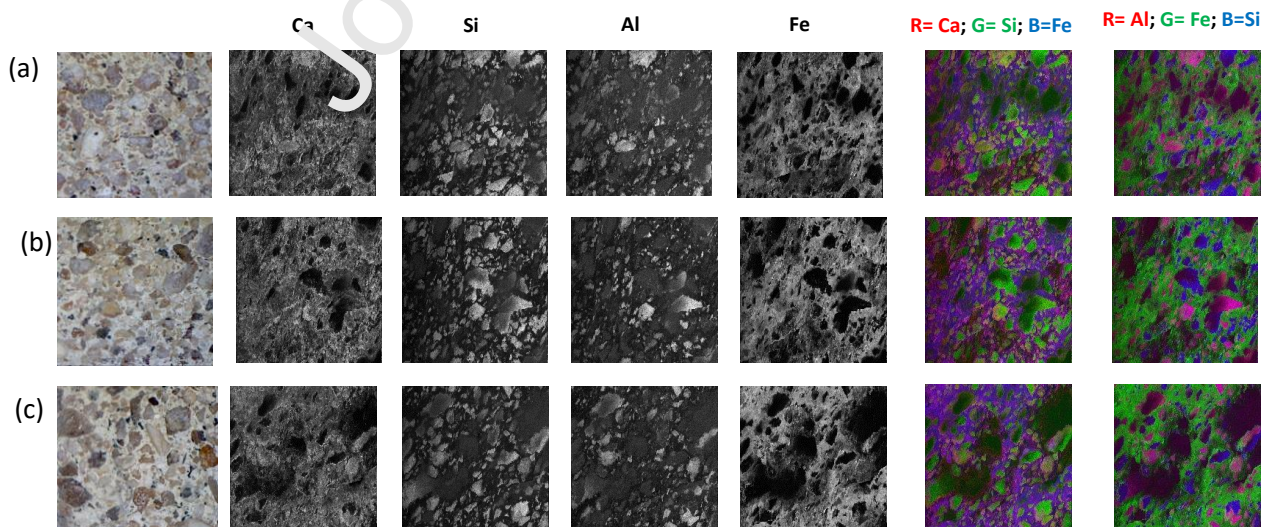

Figure 4. micro-LIBS maps (10 mm x 10 mm) collected on organic mortars obtained by using different organics, namely (a) Kaddukai, (b) Cactus, (c) Neelamari.

Alkali-activated materials and geopolymers represent a relatively recent innovation in engineering applications. Due to the low CO_2 emissions and the low energy required for their production, a strong interest has been shown for the application of these materials as green materials substituting the conventional Portland cement (OPC). Moreover, their high performances in term of durability and compatibility extend their field of application also to Cultural Heritage, as repair mortars. Their interesting properties promoted the research of improved formulations tailored for different applications, by using diverse raw materials both as precursor and aggregates, and sometimes also recycled wastes.
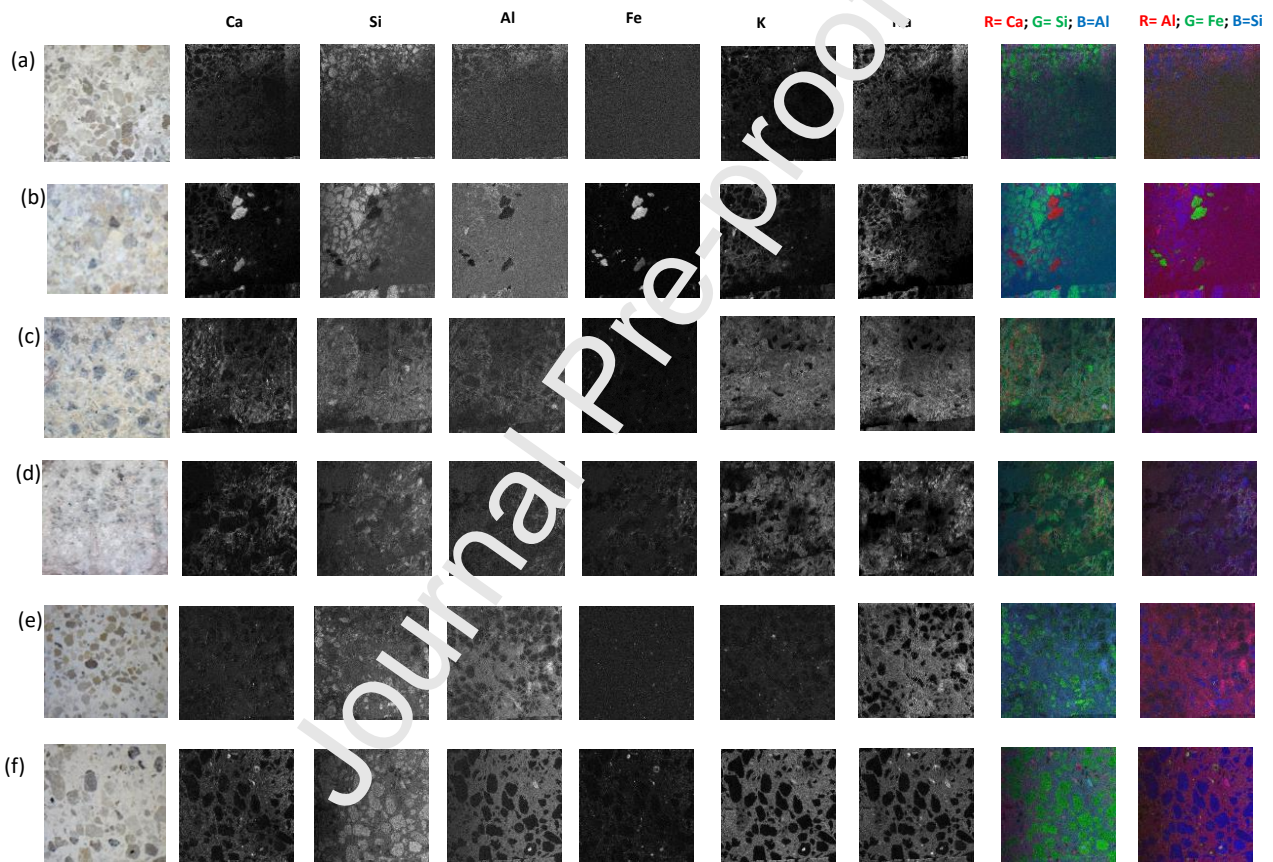

Figure 5. Alkali activated materials and geopolymer LIBS maps (10 mm x 10 mm) (a) AAM11, (b) AAM12, (c) AAM14, (d) AAM15, (e) AAM16, (f) GP1 (for compositional details see Table S1).

In this work, micro-LIBS analysis has provided several new insights for the study of AAMs and GP. Firstly, micro-LIBS demonstrated its capability in studying and characterizing wastes, which are very frequently introduced into these mixtures. The mechanical performance of a recycled aggregate is very often worse than that of a natural aggregate. This is exactly the case of CDW. Many scholars investigated the drawbacks in using CDW for mortars formulations [29-31]. However, recycling these materials is fundamental in the circular economy scenario [32]. The use

of micro-LIBS mappings may give an important contribute to the characterization of highly heterogenous materials containing many and different components, identifying any preferential orientations of some of them and therefore foreseeing possible changes in their physical-mechanical properties. For example, micro-LIBS is capable of detecting and discriminating the CDW grains (enriched in Ca and Fe) from natural quartz grains (high silica contents), as shown in Fig. 5.b. Understanding the distribution of such components with a fast and minimally destructive method could give important information for the identification of possible structural weakness. Furthermore, for very heterogeneous materials such as CDW, it is also possible to understand what type of recycled aggregate has been used through a quick on-site analysis, without the need of sampling and laborious sample preparation.

A further interesting information can be provided by micro-LIBS mapping regarding the compositional distribution of specific chemical elements within the matrix, which would be difficult to detect with other portable instruments, especially at such high spatial resolution. For example, in AAMs containing composite materials (see Figure 5.c-d) micro-LIBS chemical maps evidenced the presence of calcium, homogeneously distributed in the matrix like a dense network. Still, raw materials used for the samples production should have very low calcium contents. Micro-LIBS can detect and map its distribution providing important insights for further detailed analyzes, for example regarding the assessment of how much Ca affects the binder structure.

Finally, in recent years, a great deal of interest in the use of AAMs and GPs has been shown in cultural heritage field [6-7], where investigation by using portable and minimally invasive equipment is often required. The in-situ characterization of repair mortars obtained by AAMs or GP formulations by using micro-LIBS would offer the possibility to quickly obtain information on the nature of the binder. For example, looking at the Figure 5.f it could be erroneously thought that the geopolymer has been formulated by using both sodium and potassium reagents. However, we know that its formulation is potassium-based. With the aid of a standard of known composition, this misinterpretation could be avoided, being able to recognize the potassic nature of the binder and attributing the Na content to minor contributes from other mixture components. A tool like micro-LIBS would therefore have an enormous impact in the study and recognition of AAMs and GPs in cultural heritage field, due to the importance that light elements such as Na have for these types of materials and due to their difficulty detection by using other methods, such as classical XRF scanners.

Quantitative Analysis

An accurate quantitative analysis of the composition of the geological materials of interest, in most of the cases, is not as important as in other applications, such as the analysis of metal alloys or

environmental samples [33]. However, in some cases, such as the one shown in figure 5.f, the quantitative information about the sample's composition might be important for determining its formulation.

The main difficulty in determining the material composition of heterogeneous samples using micro-LIBS lies in the strong dependence of the LIBS signal on the changes in the plasma parameters (ablated mass, electron temperature and number density) which, in turn, depend on changes in the sample's surface texture and composition, from one point of analysis to the other. This is an aspect of the so-called 'matrix effect', which is known to strongly affect LIBS quantitative analysis. As discussed before, normalization of the line intensity with the integral intensity of the whole LIBS spectrum may help in reducing the matrix effect, although the changes in electron temperature and number density, which affect differently the emission lines of the different elements in the sample, would not be compensated by the normalization.

A possible solution to this issue is the use of a Calibration-Free LIBS approach. This method, proposed more than 20 years ago by Ciucci et al. [20], is based on the evaluation of the plasma parameters directly from the LIBS spectrum, using the basic equations describing the emission of a plasma in Local Thermal Equilibrium [34].

In the micro-LIBS applications here reported, however, there are two difficulties to overcome for exploiting the advantages of a CF-LIBS approach. The first, specific of the instrumentation used for the analysis, is the fact that our micro-LIBS scanner is equipped with a time-integrated spectrometer (Avantes Avaspec 2048 USB, 2 ms acquisition time). Time resolution, however, is essential for the application of the CF-LIBS method, which relies on the approximation of considering the LIBS plasma in Local Thermal Equilibrium. This condition is satisfied only in a narrow temporal window after the laser pulse, hence the need for a time-resolved spectrometer, able to acquire the signal in a time interval where plasma temperature and electron number density would not vary substantially and would fulfill the LTE conditions [35].

This issue can be partially overcome considering that the intensity of the LIBS spectrum decays very quickly in time. Grifoni et al. [36] have demonstrated that with a careful choice of the acquisition delay after the laser pulse, the plasma parameters estimated from the time-integrated LIBS spectrum are equivalent to the ones obtained with a time-resolved spectrometer, with a gate of approximatively 1 μs.

The second issues is the application of the CF-LIBS algorithm to a huge number of spectra (in our analysis each map is composed by 200x200 pixels, corresponding to 40,000 LIBS spectra). To make the quantitative treatment of such an amount of data feasible, some simplification strategy should be applied. In ref. [16], Pagnotta et al. suggested to simplify the problem by segmentation of

the LIBS spectra (using the Self-Organizing Maps method) separating the sample in a limited number of mineral components. After that, the quantitative CF-LIBS analysis is performed on these components, to obtain their 'prototype' composition.

In this work, we tested a different (unsupervised) segmentation method, called K-means [37]. This approach provides the same information as the ones obtained by SOM, but it is much faster. We used the implementation of the K-means algorithm provided by the Matlab® (2022a) statistical package.

In Figure 6, we show the segmentation of the elemental maps of a sample, homogeneous for texture and composition (sample a) in Figure 1) compared to the one obtained on a very heterogeneous sample (sample c) in Figure 1). In both the cases, in the K-means algorithm a maximum number of four clusters was selected, based on the geological characteristics of the samples. In fact, only two clusters were significantly populated for sample a (corresponding to yellow and blue pixels in figure 6), while in the inhomogeneous sample (sample b) all four clusters were populated (yellow, blue, red, and cyan pixels in figure 6).
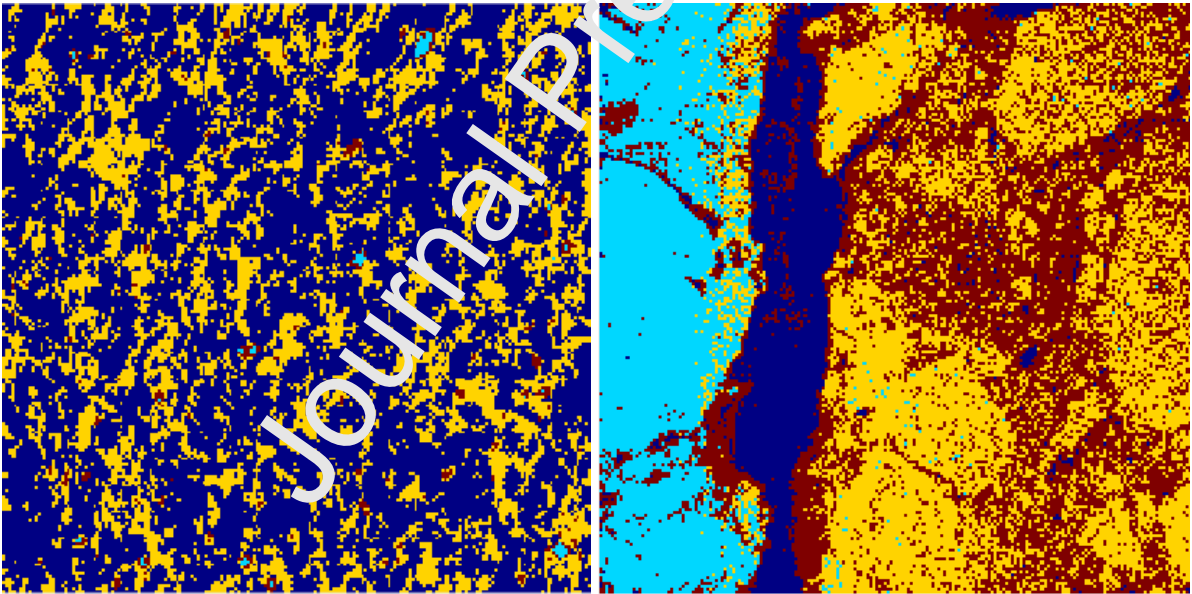

Figure 6. Segmented maps of homogeneous (left) and hetherogeneous (right) samples (see figures 1 and 2 for reference)

It can be seen from the segmented maps that the homogeneous sample is made essentially of two components (yellow and blue colors in the map), while the structure of the heterogeneous sample is much more complex, with at least 4 well recognizable components that are evidenced in red, yellow, blue and cyan colors). The corresponding prototype spectra (average of the spectra corresponding to each cluster) are shown in Figure 7.
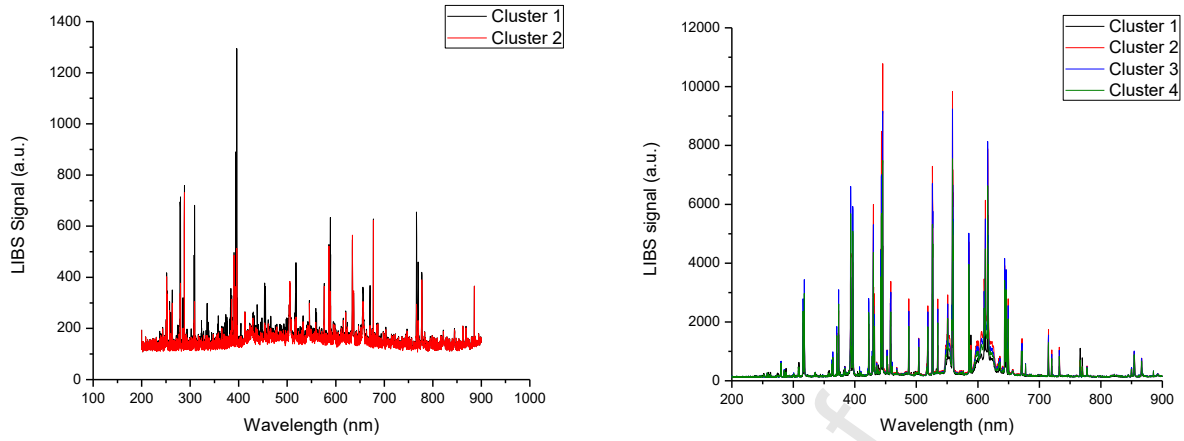
13

Figure 7. Prototype LIBS spectra of the clusters corresponding to the maps in Figure 6.
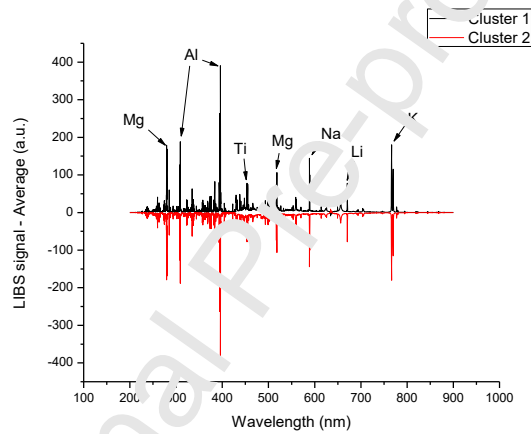

Figure 8. Difference between composition of Cluster 1 (blue points in figure 6) and Cluster 2 (yellow points in figure 6) materials (sample a)
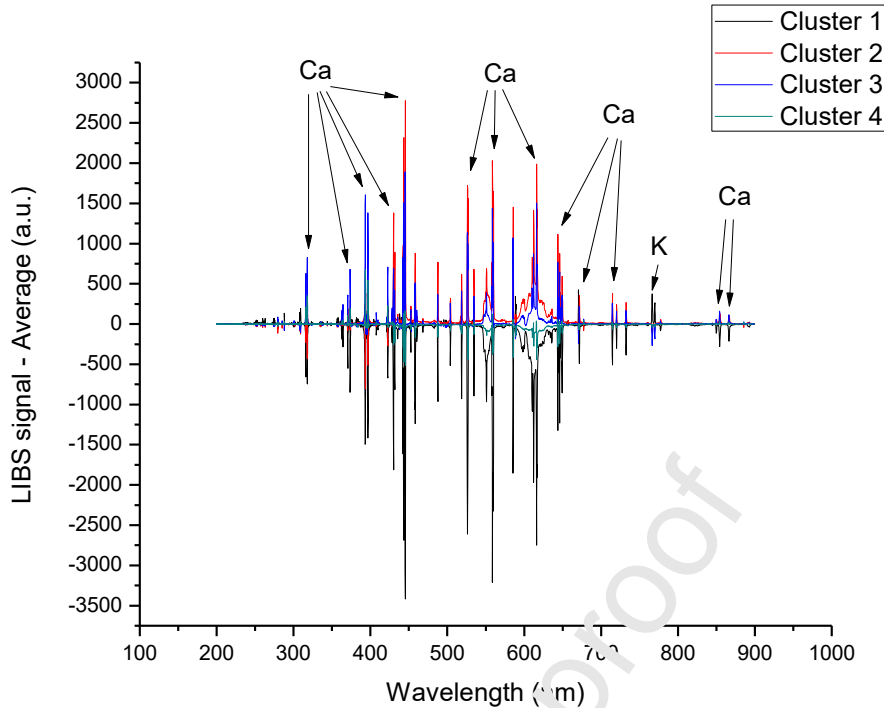
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Figure 9. Difference between composition of Cluster 1 (blue points in figure 6), Cluster 2 (cyan points in figure 6), Cluster 3 (yellow points in figure 6) and Cluster 4 (red points in figure 6) materials (sample b)

The main compositional differences between Cluster 1 and Cluster 2 materials in sample a involve the amount of Mg, Al, Ti, Na, Li and K, which are more abundant in Cluster 1 material with respect to Cluster 2. The interpretation of the spectra corresponding to the four clusters corresponding to sample b is more complex, since the main differences are associated maily to Ca (less abundant in Cluster 1, for example, which is characterized by higher quantities of K, instead). It is evident that the compositional and structural difference between sample 1 and sample 2 does not allow any quantitative comparison between them at the level of their LIBS spectra (and, consequently, of their elemental maps). However, the quantitative analysis of the spectra through the Calibration-Free method would provide results (the elemental composition of the sample) which do not depend on the nature of the samples themselves, or on experimental parameters difficult to control and stabilize, as the focussing distance and the laser energy.

Conclusion

The spatial resolution and the speed of analysis of the LIBS technique make it especially suited for elemental mapping of geomaterials. Overall, the materials selected for the present investigation exhibited a range of textural and compositional heterogeneity suitable for exploring the relationship

between grain size and spot of analyzers. Micro-LIBS mapping seems extremely competitive with respect to X-Ray Fluorescence (macro-) mapping, in terms of speed (100 ms per pixel vs. 1 second in XRF), lateral resolution (10-20 mm vs. 1 mm in XRF), in-depth resolution (about 1 mm per shot vs. several tens of microns in XRF), especially in the case of materials for which relevant textural features are usually investigated at microscale by traditional microscopy methods. Moreover, LIBS can easily detect and map light elements, unlike XRF. Despite the relative novelty of the methods proposed, the study shows how the combination of the two instruments can provide a solid method for the characterization of geomaterials. The strength of the outlined protocol is its replicability and its potential usability in streamlined analysis of a large number of samples. The combination of XRF and LIBS mapping has shown to be a reliable tool for in situ screening of various types of geomaterials, useful for gathering insightful data and sampling for further destructive analysis. In cultural heritage research, the availability of comparable and replicable data is crucial in order to gather compositional information, useful for researching on materials' provenance and for a better planning of conservation actions. LIBS micro-mapping has also demonstrated to be an important investigation tool for the study of new cathegories of geomaterials, as alkali-activated materials and geopolymers.

Acknowledgements

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Author's contributions

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We confirm that we have given due consideration to the protection of intellectual property associated with this work and that there are no impediments to publication, including the timing of publication, with respect to intellectual property. In so doing we confirm that we have followed the regulations of our institutions concerning intellectual property.

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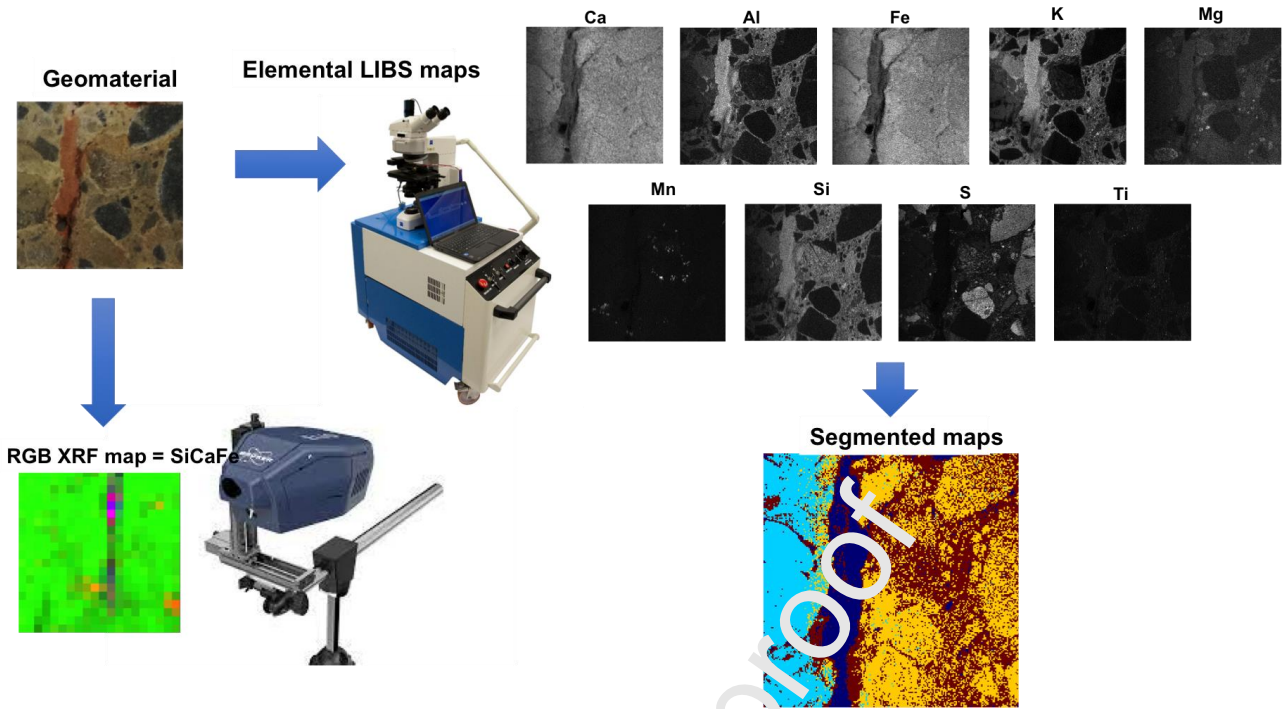Review & Editing, Visualization

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Declaration of interests

☒ 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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Declaration of interests

Geomaterial

Elemental LIBS maps

RGB XRF map = SiCaFe

Ca Al Fe K Mg

Mn Si S Ti

Segmented maps

Highlights

- XRF and LIBS mapping systems are compared for geomaterials analyses. ⌞SEP⌟

- micro-mapping LIBS was applied, for the first time, to the analysis of alkali-activated materials and geopolymers.

- Combined XRF-LIBS data strongly increased the samples characterization