Chemical imaging of historical mortars by Raman microscopy

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HIGHLIGHTS

- Chemical images with approx. 500 nm resolution were acquired by Raman microscopy.
- Clinker remnants in 19th-century Roman and Portland cement stone were analysed.
- Gypsum mortars from the Middle Ages and early 20th century were analysed as well.
- Alite, tricalciumaluminate, wollastonite, gypsum, and anhydrite were identified.
- Dedolomitisation of accessory mineral grains in gypsum mortar was visualised.

GRAPHICAL ABSTRACT
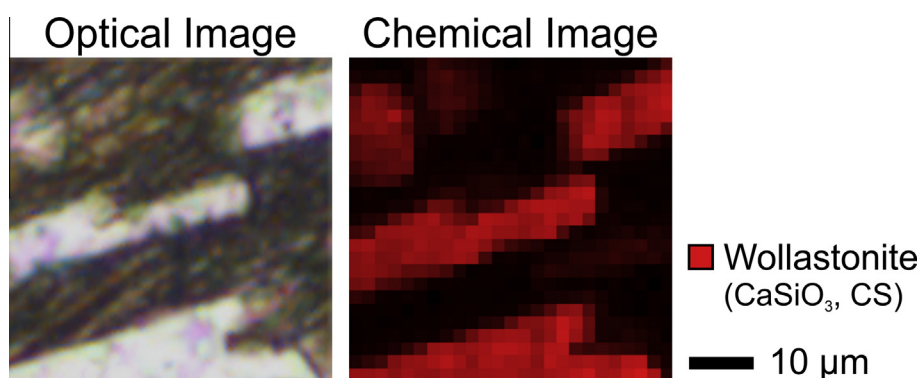
ARTICLE INFO

ABSTRACT

Raman microspectroscopic imaging was just recently introduced into the analysis of cement stone. Here, we demonstrate this approach on 19th-century Roman and Portland cement mortars and extend it to gypsum-based samples originating from a medieval stucco sculpture (high-burnt gypsum) and a stucco ornament prefabricated at the beginning of the 20th century (plaster of Paris). Furthermore, the distributions of dolomite and calcite were mapped in an accessory mineral grain with approx. 500 nm lateral resolution demonstrating the ability for studying alteration processes such as dedolomitisation. As we would like to make this approach accessible to other researchers, we discuss its present status, advantages, limitations and pitfalls.

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1. Introduction

Very generally speaking, mortars are made by mixing binder, aggregates and water. From the chemical point of view, binder and aggregate are umbrella terms for a chemically highly heterogeneous variety of materials, some of them, such as hydraulic binders, consisting of complex mixtures of inorganic phases. The chemical analysis of such complex materials can only be adequately handled by employing an arsenal of analytical methods yielding complementary information, which in combination provides insight into, for example, the type of binder, composition and provenience of the raw materials as well as heating and cooling regime during the fabrication. Historical mortars are characterised by tremendously more heterogeneous compositions than the standardised building materials employed nowadays. The use of marlstone, a natural mixture of lime and clay, for the burning of Roman cement – the first highly hydraulic

binder – intrinsically lead to varying chemical compositions of the end product, depending on the properties of the stone pit and the kiln conditions. Also the early Portland cements produced from well-defined synthetic mixtures of lime and clay in the course of the 19th century, differ from modern ordinary Portland cement (OPC), because of the lower (sub-optimal) and much more heterogeneously distributed calcination temperatures reached in the shaft kilns used at that time. Many phases found in 19th-century Portland cement occur just as intermediate reaction products in the current burning process carried out in rotary kilns, disseminated in Europe not before the turn of the century. From the chemical point of view or, more precisely, in terms of elemental composition, historical gypsum-based mortars are seemingly more simple and homogeneous, but a closer look reveals a plethora of dehydration and hydration stages, ranging from medieval high-burnt to 19th-century binder produced at much lower temperatures. Correct determination of the type of mortar preserved in historic masonry is key for the manufacture of compatible restoration materials.

So far, mainly light microscopy (including polarised light microscopy), scanning electron microscopy (SEM) – optionally combined with energy-dispersive X-ray spectroscopy (EDX) – and X-ray diffraction (XRD) were employed in the morphological and chemical analysis of historical building materials. Raman spectroscopy – an additional analytical approach – is based on inelastic scattering of light by molecules, crystals or amorphous phases and is typically performed with visible or near-infrared lasers as excitation sources. Inelastic scattering generates photons with frequencies (*i.e.*, colours), which are slightly shifted from the laser frequency. The frequency differences (expressed in wavenumbers, unit: cm^{-1}; also termed 'Raman shift') equal the frequencies of molecular or crystal lattice vibrations [1]. The set of all Raman-active vibrations (*i.e.*, the Raman spectrum) depends on the masses of the involved atoms, their distances and spatial arrangements, and is therefore a very characteristic "fingerprint" of a molecular or crystal structure. Therefore, chemical compounds (including their polymorphic forms) can be unambiguously identified by a fingerprint comparison of sample spectra with reference spectra in terms of band positions and shapes. Indeed, the "suspects" and their fingerprints have to be known in advance and thus, as described below, collection of a spectral database library of relevant phases is key for the application of this technique to building materials and part of our ongoing research. Extensive work in the determination of clinker minerals as well as hydration and carbonation products in cementitious materials was performed by Black et al.; a comprehensive – not yet complete – collection of reference spectra can be found in Ref. [2]. Examples of applications of Raman spectroscopy in the field of cultural heritage research, concerning architectural surfaces and wall paintings, are published in Refs. [3–7].

Raman microspectroscopic imaging (also termed 'Raman microscopy') is typically realised by step-wise movement of a sample through the laser focus employed for excitation [8]. In every step – typically ranging from several micrometres down to sub-micrometre size – the full Raman spectrum is collected, enabling the calculation of distribution maps of sample constituents in the form of colour-coded intensities of marker bands. Only few examples of Raman microscopic imaging in the analysis of building materials can be found in the literature so far, for example, the study of salts in concrete [9,10]. Examples for applications in cultural heritage research were given by Ropret et al. [11], Jallad et al. [12], Veneranda et al. [4] and Antunes et al. [13]. Recently, we introduced chemical imaging by Raman microscopy to the study of historic cement stone and proved this to be a suitable approach for the determination of the composition and for the visualisation of the distribution of the mineral phases [14,15]. The method, adept to overcome some of the limitations of the microscopic techniques or the point-spectroscopic sample characterisation used so far, provides the spatial distribution of mineral (including polymorphic) and amorphous phases, as well as crystal orientations with a sub-μm spatial resolution. It therefore adds chemical information to light microscopy images, provides phase information that is complementary to the information on purely elemental composition provided by EDX and electron microprobe measurements and extends the phase information, which is also provided by XRD (performed as a bulk analysis method) with spatial resolution. In contrast to XRD also amorphous phases can be studied by Raman microscopy. For example, amorphous carbon was previously detected in granulated blast furnace slag, found as aggregate in 19th-century cement stone [14]. Whereas the spectra of diamond and graphite are dominated by the well-known sharp bands at 1330 cm^{-1} (D band) and 1580 cm^{-1} (G band), respectively, disordered and amorphous carbon gives rise to both, D and G bands appearing strongly broadened and overlapping, but still characteristic enough to be specifically assigned to that material [16]. Furthermore, mineral components in mortars present only in amounts below the detection limit of XRD (*e.g.*, γ-Ca_2SiO_4 in Roman cement [14]) can be detected by Raman microscopy because of the micrometre-sized measurement volume of this spatially-resolved analytical approach. In contrast, individual mineral grains and in some cases not even individual remnant clinker grains can be resolved with micro-XRD instruments available on the market with typical spatial resolutions of 50 μm up to some 100 s of micrometres [17–19]. Only by using synchrotron radiation, the resolution can be improved to the lower micrometre range [20,21]. Infrared microspectroscopy, closely related and complementary to Raman microscopy, was already successfully employed for the chemical imaging of historical lime mortars [22] and for the characterisation of compounds and degradation products in paint layers [23–26]. Due to the use of infrared radiation (instead of visible light), the lateral resolution is on the order of micrometres to tens of micrometres due to the optical diffraction limit. Moreover, with a measurement range typically limited to 400–4000 cm^{-1} crystal lattice vibrations of inorganic phases (mortar binder, mineral aggregates, inorganic pigments, etc.) occurring at lower wavenumbers cannot be detected, whereas commercial Raman spectrometers provide wavenumber ranges typically starting at $\geqslant 100$ cm^{-1} and the use of special notch filters offers access to even lower vibrational frequencies.

For these reasons, we expect that Raman microscopy in the future can valuably extend the arsenal of techniques applied in the analysis of both historic and contemporary building materials. In this communication we demonstrate its application to two types of historic cement binders and extend our approach to gypsum based mortars, *i.e.* medieval high-burnt gypsum and stucco from the 19th century, demonstrating the capability to map distributions of different hydration stages of calcium sulphate. Furthermore, slight changes in band positions enabling to distinguish dolomite and calcite provide the basis for an imaging study of dedolomitisation in an accessory mineral grain. A central idea of this communication is to make researchers from the field of construction and building materials aware of this relatively new analytical approach and its actual status and capabilities. Therefore, we show how Raman microscopy can be used to add chemical information to optical microscopy images by demonstrating the tracking of the same features by both approaches in a remnant Roman cement clinker grain including the mineral wollastonite, but also discuss typical limitations and pitfalls of this approach – such as interfering fluorescence and Raman signals from embedding resins – as well as strategies to overcome them.