

# Raman band widths of anhydrite II reveal the burning history of high-fired medieval gypsum mortars

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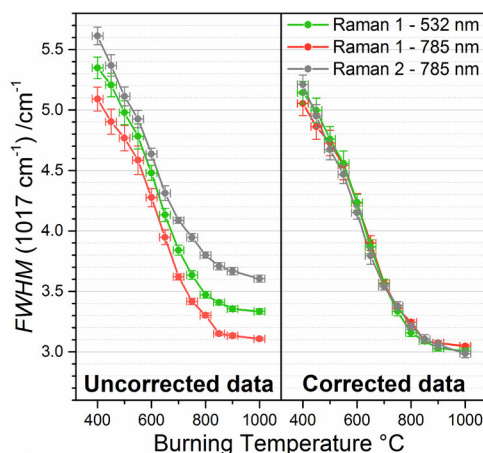
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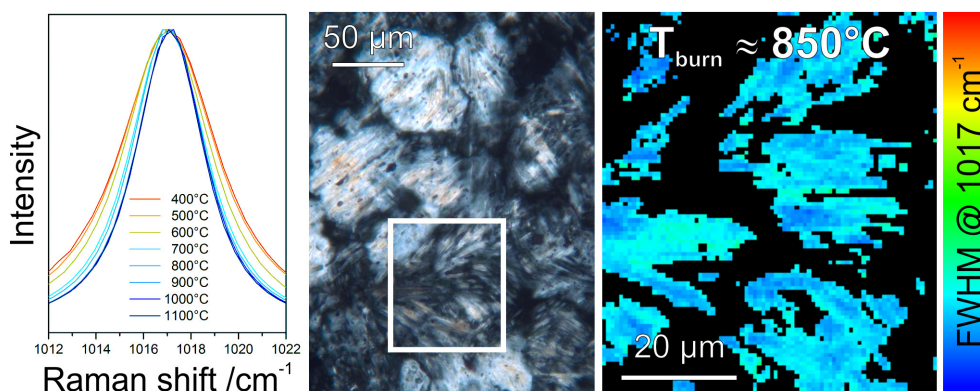
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The use of high-fired gypsum as binder for masonry and joint mortars or stuccowork in Central Europe in the Early and High Middle Ages was a regional specific as it depended on local gypsum deposits. The calcination technology possible at the time resulted in an assemblage of calcium sulphate phases dehydrated to different degrees and partly thermally damaged accessory minerals of the raw gypsum. Because of the absence of medieval textbooks, the observation of high-temperature, low-pressure mineral transformations and the correlation of phases coexisting in not hydrated binder relicts in the gypsum matrix to the mineralogy of the raw material and the burning conditions constitute the only source to the historical technological know-how.

The  $\text{CaSO}_4\text{-H}_2\text{O}$  system consists of five crystalline phases, which can be discriminated by structural analysis methods, such as Raman spectroscopy, due to obvious differences in their spectroscopic data: gypsum ( $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ ), bassanite (hemihydrate,  $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$ ), anhydrite III ( $\text{CaSO}_4$ ), anhydrite II ( $\text{CaSO}_4$ ), and anhydrite I ( $\text{CaSO}_4$ ). Only recently, it was possible to demonstrate that small spectroscopic variations exist also within the relatively large stability range of anhydrite II from approx.  $180^\circ\text{C}$  to  $1180^\circ\text{C}$ : all Raman bands narrow with increasing burning temperature applied in the synthesis from gypsum powder [1]. The determination of band widths of down to  $3 \text{ cm}^{-1}$  and differences between them of a few tenths of a wavenumber is not a trivial task. Thus, this contribution discusses peak fitting and strategies for correction of instrument-dependent band broadening [2].



**Figure 1.** Full widths at half maximum (*FWHMs*) of the most prominent band at  $1017 \text{ cm}^{-1}$  in the room-temperature Raman spectra of anhydrite II after burning from gypsum at different temperatures. Data measured with two different instruments and excitation wavelengths, and shown prior to (left) and after correction of instrument-related band broadening (right) [2].



**Figure 2.** Shape of the most prominent Raman band of anhydrite II as a function of burning temperature (left), polarised light micrograph (crossed Nicols) of a cluster of firing products in a high-fired medieval gypsum mortar (centre), and Raman band width distribution map of the highlighted area (right). The mean band *FWHM* relates to a burning temperature of approx. 850°C [3].

Raman maps of polished thin sections of gypsum mortars provide access to the burning histories of individual remnant thermal anhydrite grains and enable the discrimination of natural anhydrite originating from the gypsum deposit. This novel analytical method was applied to samples from medieval South Tyrolean stucco decorations and sculptures. Beyond that, Raman microspectroscopy was employed for following pyrometamorphic reactions in natural impurities of the raw material. In the presented examples mineral thermometry indicates process temperatures above 800°C: the breakdown of magnesium-rich chlorite led to the formation of forsterite  $Mg_2SiO_4$ , while the thermal decomposition of dolomite  $CaMg(CO_3)_2$  yielded – after hydration and carbonation – magnesite  $MgCO_3$ ,  $CaCO_3$  polymorphs and magnesian calcite. Lower burning temperatures, which leave the accessory minerals in their pristine form, can be traced by measuring the spectra of anhydrite crystalites in grains of firing products and evaluating Raman band widths. Throughout the applications of this analytical method so far, calcination temperatures ranging from approx. 600°C to 900°C were determined [3].

## Acknowledgements

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## References

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