

Shedding light onto the spectra of lime, part 2: Raman spectra of Ca and Mg carbonates, and the role of *d*-block element luminescence

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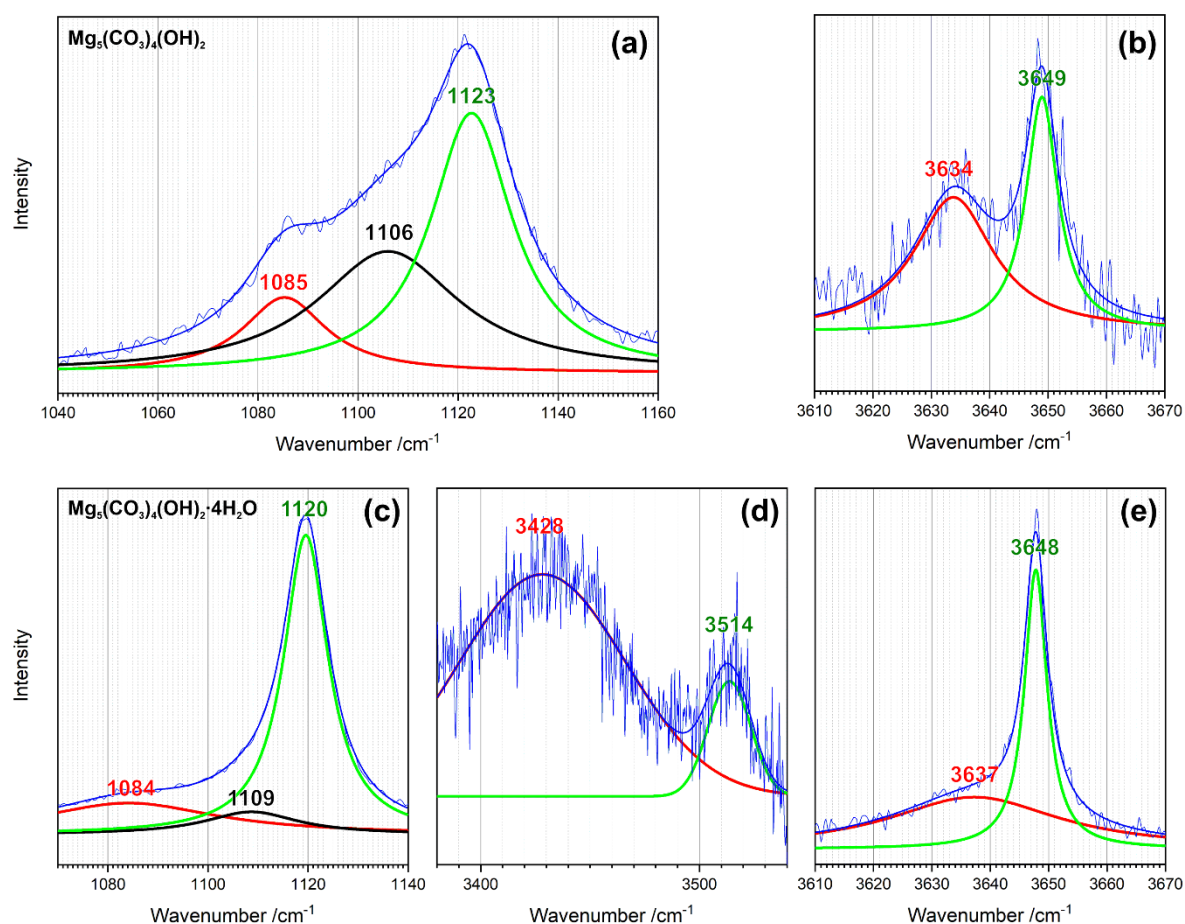


Fig. S1: Excerpts from Raman spectra of dehydrated hydromagnesite **(a, b)** (compare Fig. 1 “300°C”) and hydromagnesite **(c-e)** (compare Fig. 1 “RT” and “100°C” in the main text) acquired with a spectral resolution of 0.2-0.3 cm⁻¹ (see Experimental section for details) and deconvoluted by using linear combinations of Lorentzian functions.

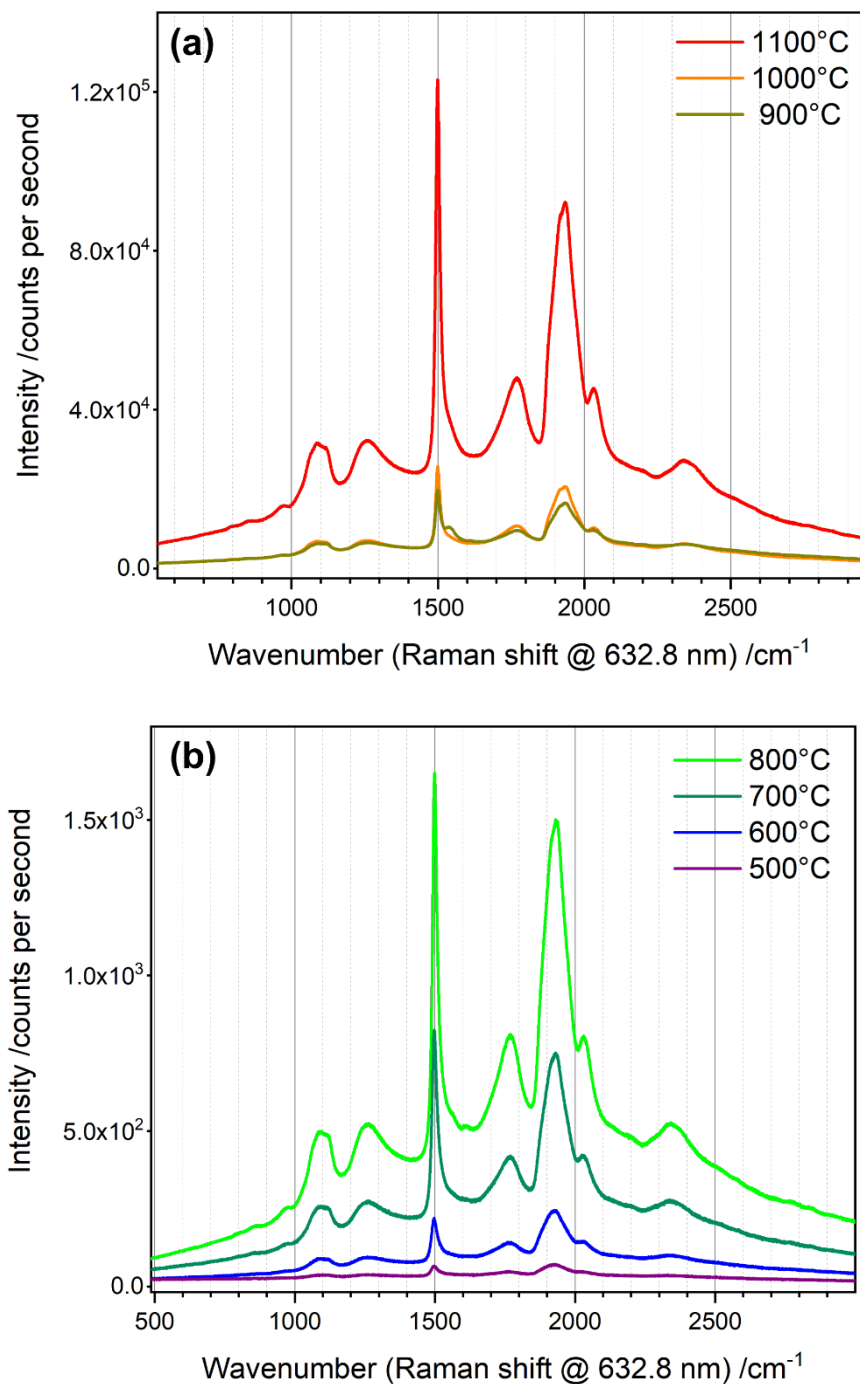


Fig. S2: Luminescence emission spectra of MgO synthesised by calcination of 5 g hydromagnesite in a laboratory furnace at the mentioned temperatures for 4 h. The different intensity scales of (a) and (b) consider the variations in intensity over approximately four orders of magnitude.

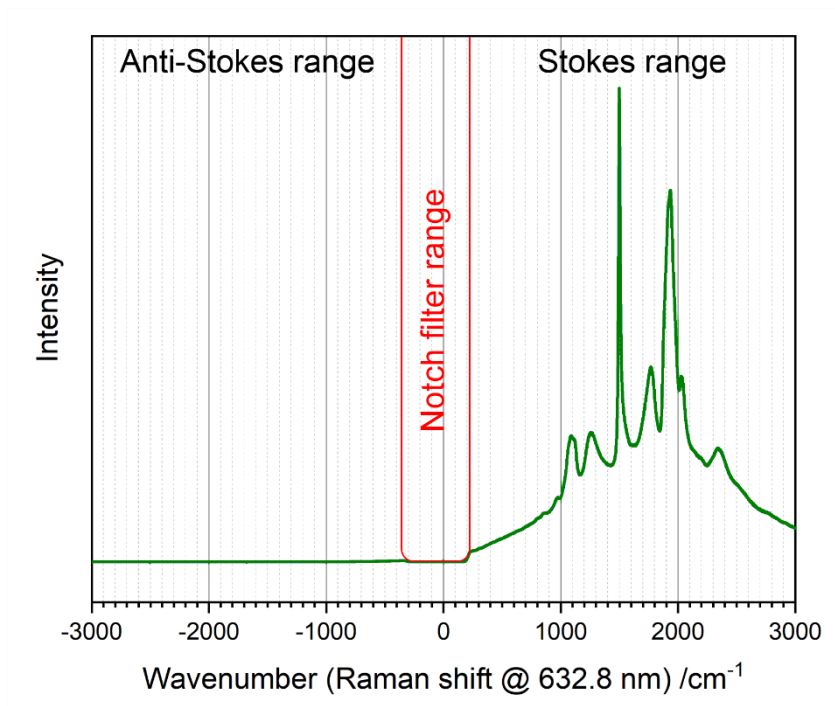


Fig. S3: Stokes/anti-Stokes test revealing the origin of the shown spectral pattern from luminescence.

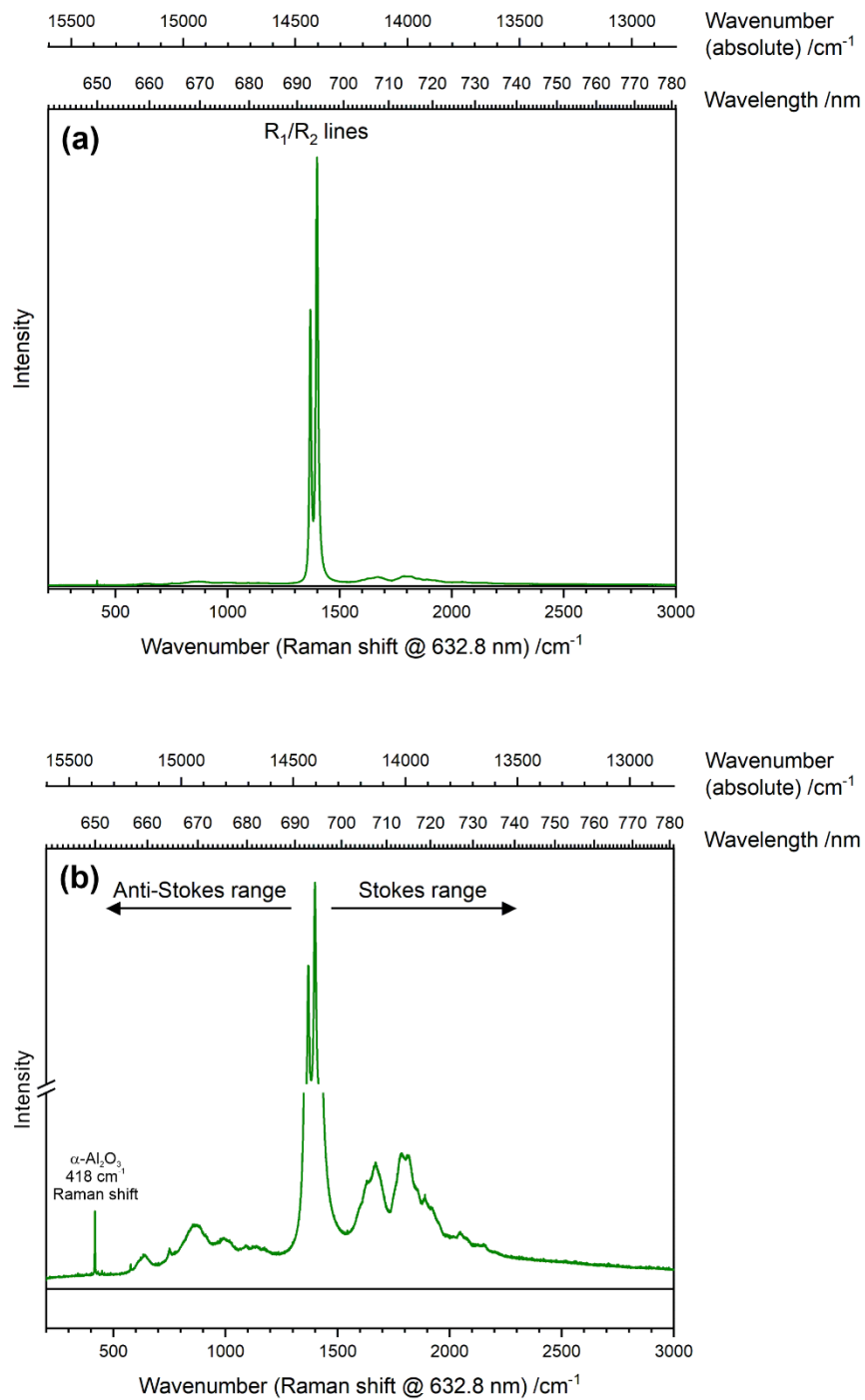


Fig. S4: Ruby luminescence of $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$ emitted by a sapphire disk. While (a) shows the well-known spectroscopic pattern dominated by the sharp R_1 and R_2 lines, the axis break in (b) enables a closer look at the vibrational side bands. The spectrum also contains the most prominent Raman band of corundum.

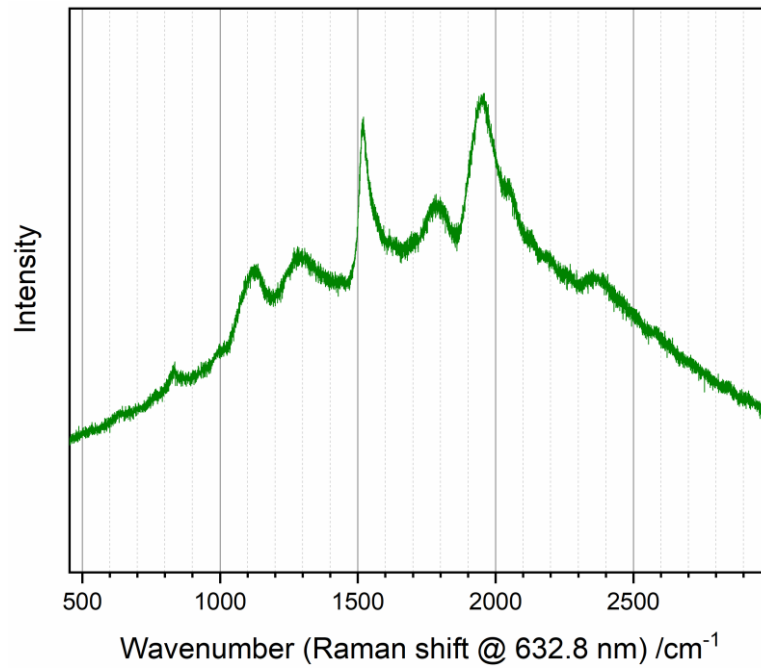


Fig. S5: Locally observed lime luminescence emission triggered in CaO by mixing 5 g highly pure CaCO₃ (≥ 99%; magnesium content specified as ≤ 0.02%) with 25 mg Cr₂O₃ prior to calcination at 1100°C.

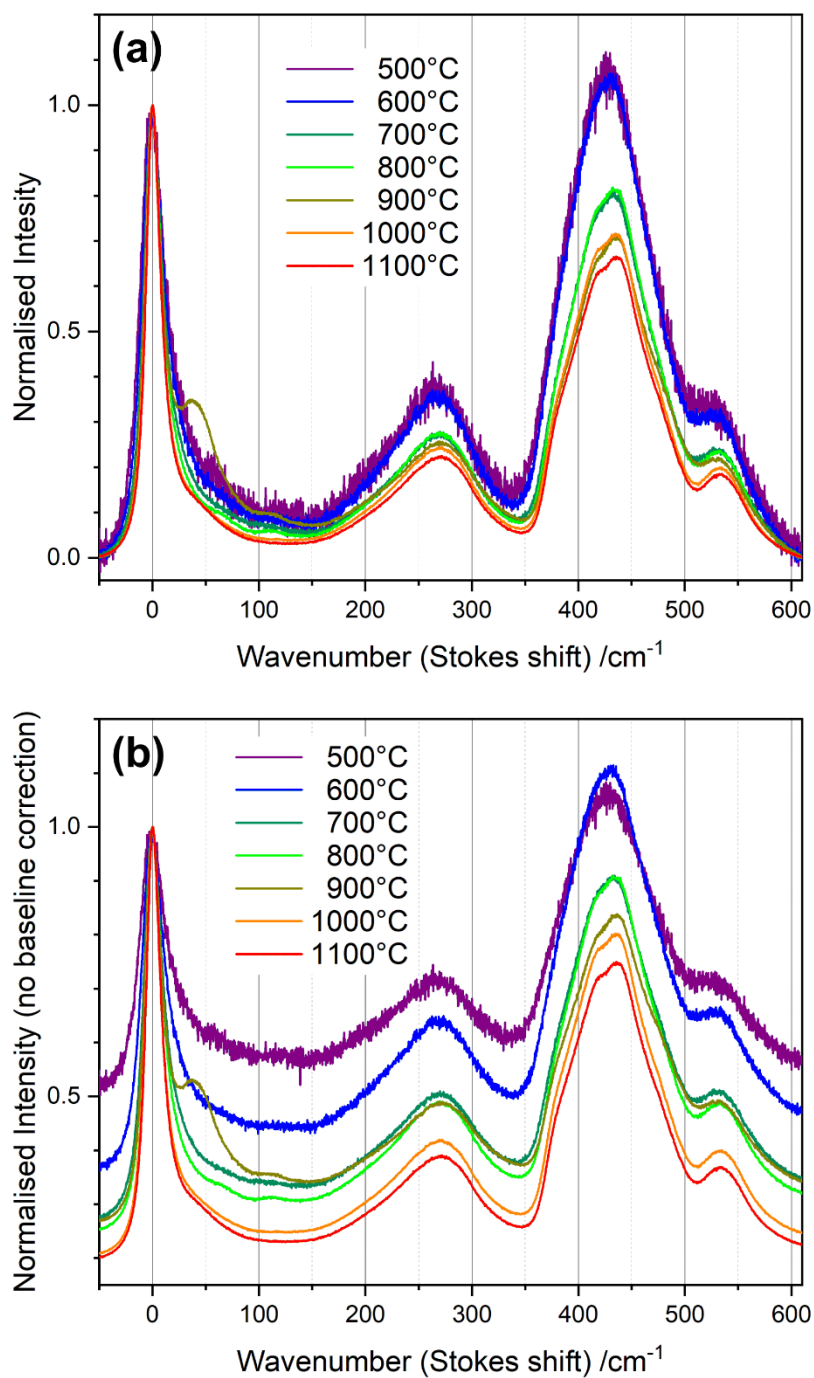


Fig. S6: (a) Baseline-corrected (line across the shown spectral range) and normalised ($\text{Intensity}(R) := 1$) luminescence spectra of MgO synthesised by calcination of hydromagnesite (see Fig. S2) showing trends in intensity ratios of R line and vibrational sidebands, and (b) normalised spectra without prior baseline correction revealing relative intensity variations of the underlying broadband luminescence.

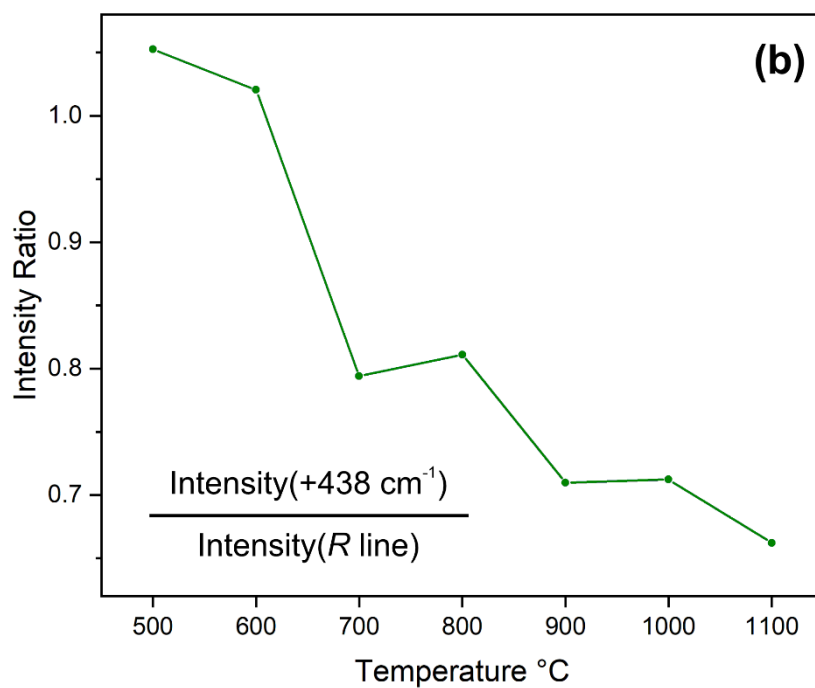
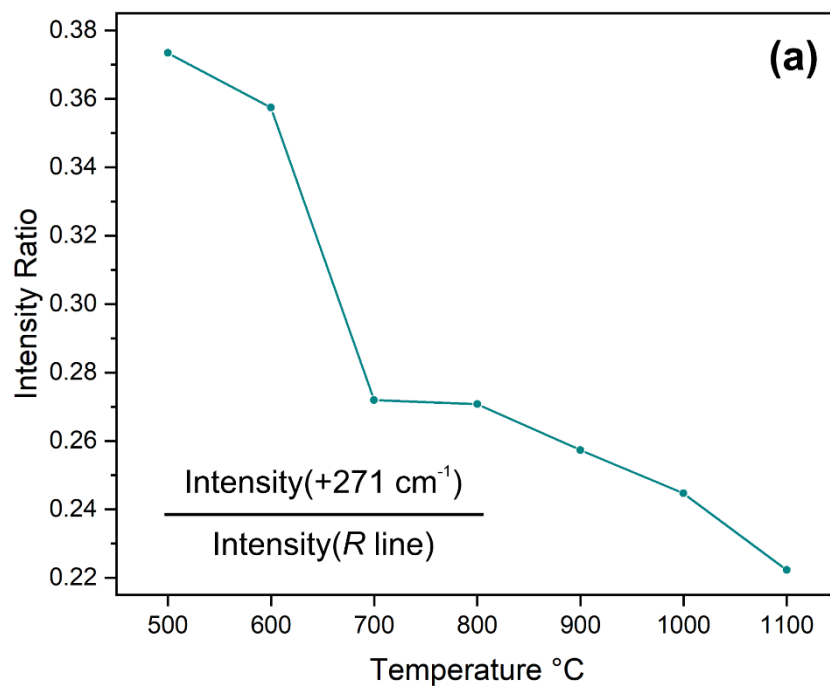


Fig. S7: Ratios of the luminescence band intensities Stokes-shifted by (a) 271 cm⁻¹ or (b) 438 cm⁻¹ from the *R* line, respectively, and the *R* line intensity as functions of calcination temperature (derived from Fig. S6).

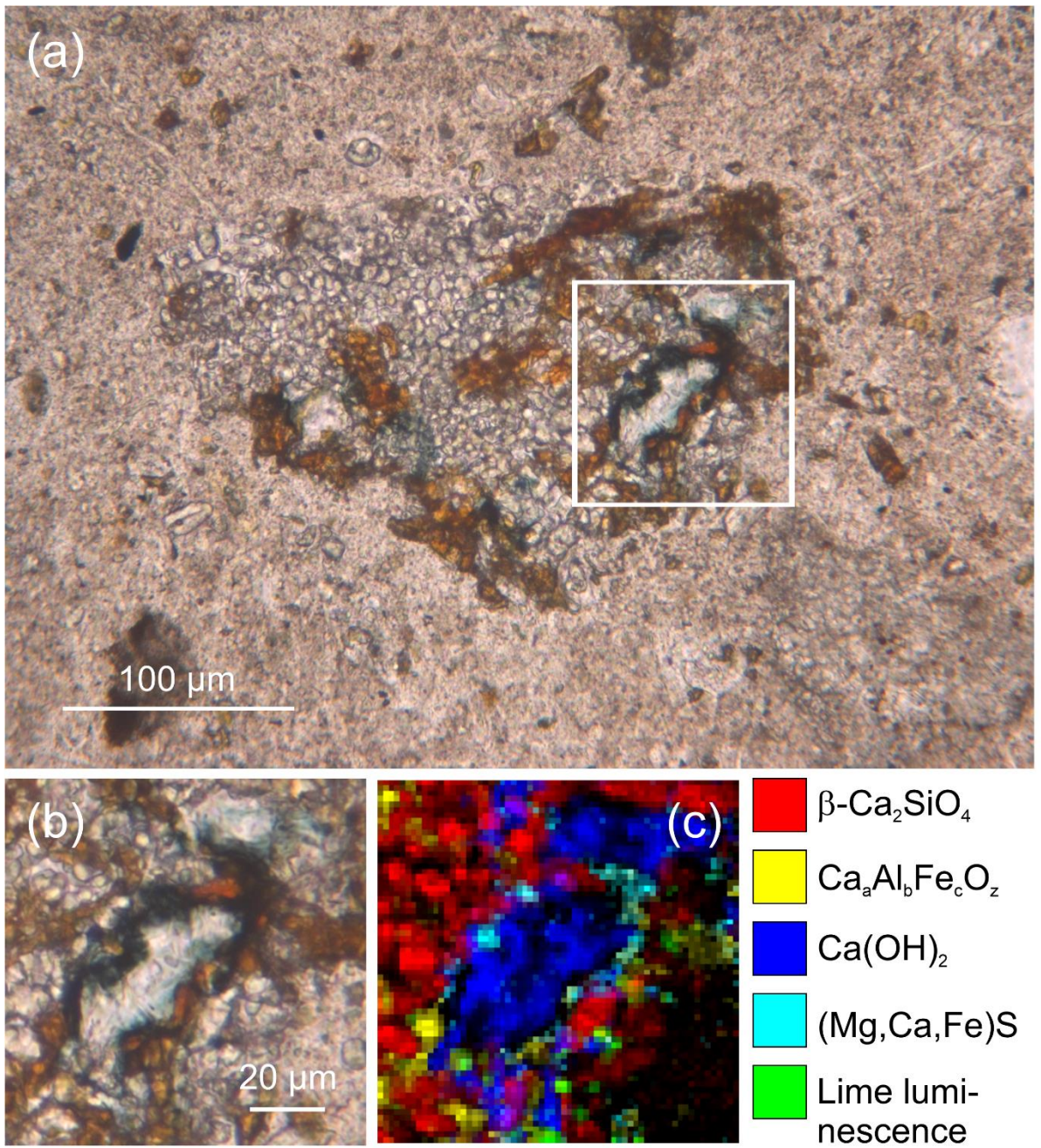


Fig. S8: Transmitted light micrographs **(a, b)** and Raman/luminescence map **(c)** of an unhydrated binder remnant in a meso Portland cement stone. In contrast to Fig. 5 in the main text, the stoichiometry of the calcium aluminoferrite phase $\text{Ca}_a\text{Al}_b\text{Fe}_c\text{O}_z$ ($z = a + (3/2)b + (3/2)c$) varies, revealing a solid-solution series between C_4AF ($\text{Ca}_2\text{AlFeO}_5$) and $\text{C}_6\text{A}_2\text{F}$ ($\text{Ca}_6\text{Al}_4\text{Fe}_2\text{O}_{15}$).

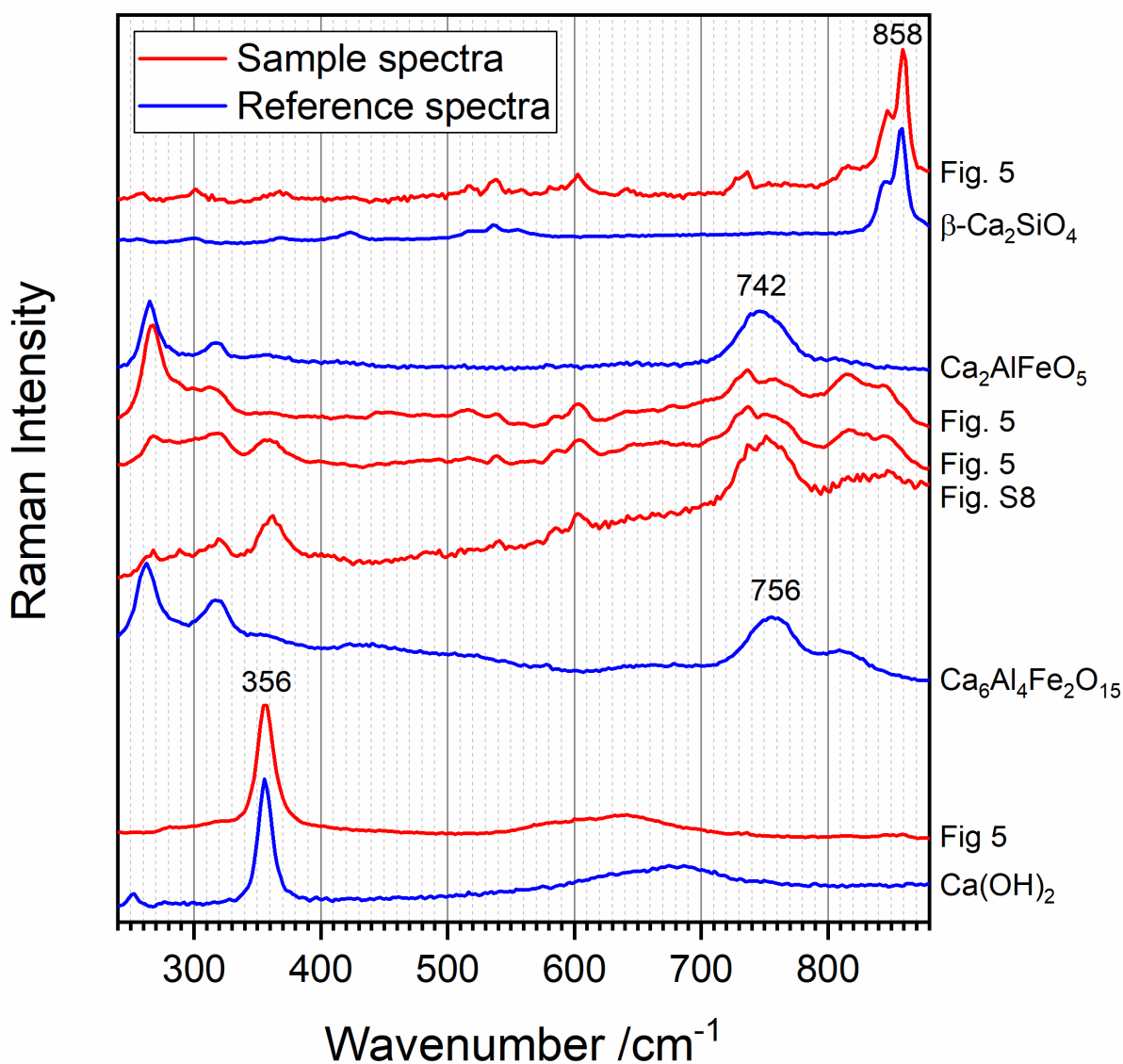


Fig. S9: Selected spectra from the Raman microspectroscopic images shown in Fig. 5 or Fig. S8, respectively, compared with reference spectra of β -Ca₂SiO₄ (β -belite), Ca₂AlFeO₅ (brownmillerite, C₄AF), Ca₆Al₄Fe₂O₁₅ (C₆A₂F),^[2,28,29] and Ca(OH)₂ (portlandite)^[1] from our own collection, confirming their assignments. As previously demonstrated^[29], the stoichiometry of the calcium aluminoferrites was determined by Gauss fitting of the broad characteristic band at 742 cm⁻¹ to 756 cm⁻¹ for exact wavenumber determination. The band position of around 742 cm⁻¹ in Fig. 5 speaks for C₄AF, while some spectra in Fig. S8 reveal this band at higher wavenumbers, speaking for members of the solid-solution series between C₄AF and C₆A₂F.

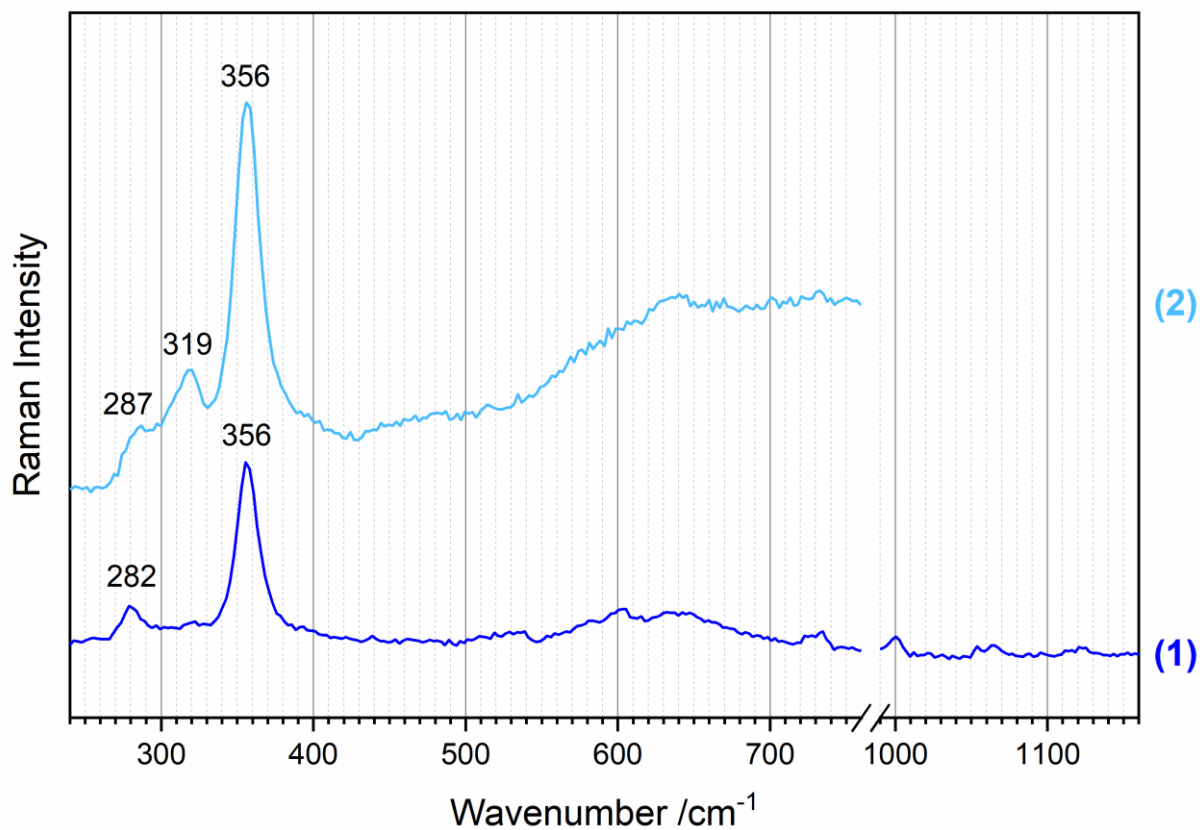


Fig. S10: Portlandite spectra acquired as part of the Raman map shown in Fig. 5 in the main text. Trace **(1)** is assigned to Ca(OH)₂ and contains an additional band discussed in the main text, while trace **(2)** reveals the spectral signature of a mixture of portlandite with (Mg,Ca,Fe)S.

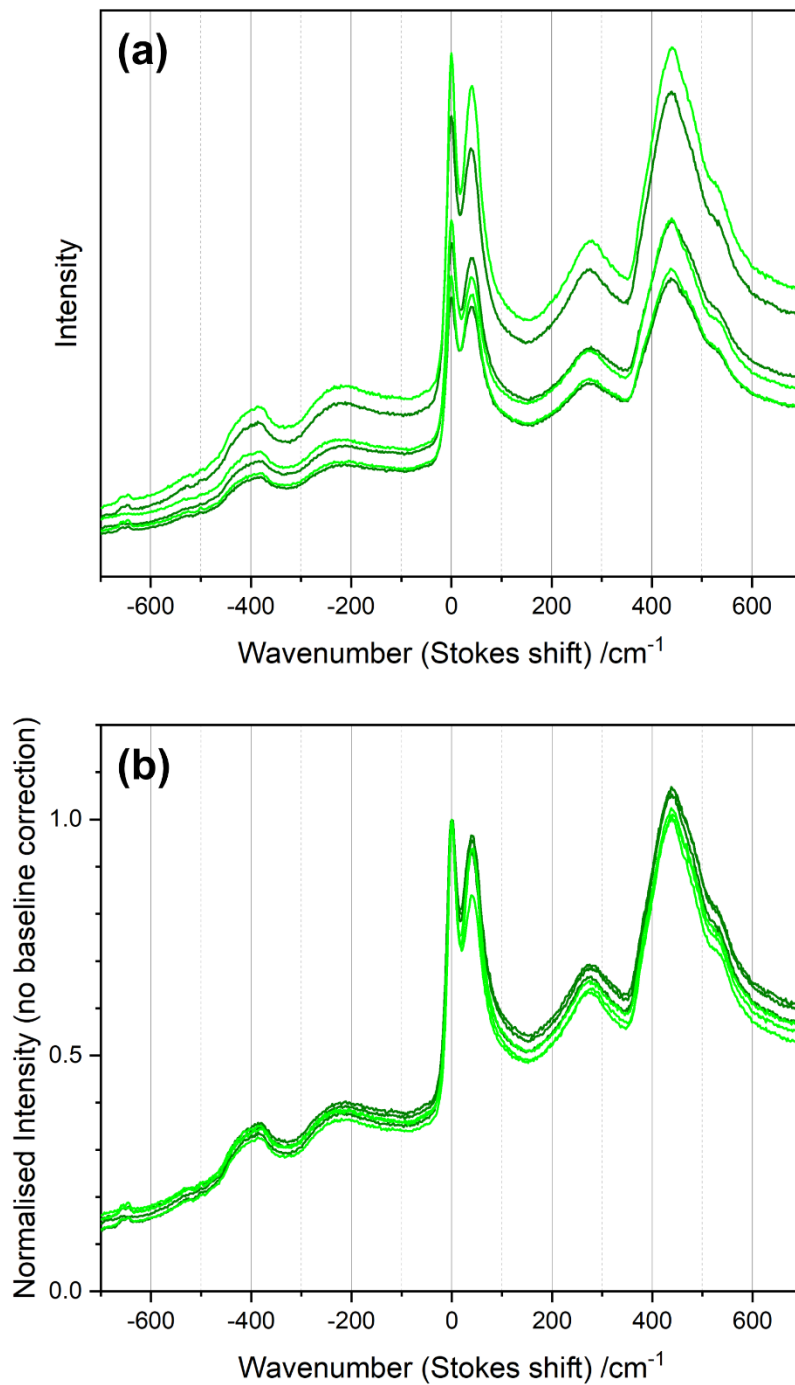


Fig. 11: Lime luminescence spectra from different spots in the Raman map shown in Fig. 5 in the main text: **(a)** shows the raw data, and in **(b)** the spectra were normalised (Intensity(R) := 1) for better comparability.