High-temperature phase transformations of hydroxylapatite and the formation of silicocarnotite in the hydroxylapatite–quartz–lime system studied in situ and in operando by Raman spectroscopy

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ABSTRACT

Silica-/calcium phosphate ceramics are of high interest in various aspects. On the one hand, they play an important role in medical applications due to their excellent biocompatibility. Therefore, detailed knowledge of the formation and stability properties of the high-temperature products ensures production under controlled conditions. On the other hand, they were identified as sinter deposits in industrial kilns, where it can indicate problems caused by too high combustion temperatures during the thermal combustion processes. Here, we report the results of two Raman heating studies to 1300 °C in 10 °C-steps with nano-crystalline hydroxylapatite (HAp) and tricalcium phosphate (TCP), and a Raman heating study of natural silicocarnotite (to 1200 °C, 50 °C-steps). The Raman experiments were complemented with thermal analyses. The Raman spectra of nano-crystalline HAp recorded at high temperatures revealed the stepwise loss of adsorbed water and surface-bound OH groups until 570 °C. Significant loss of structural OH started at ~770 °C and was completed at ~850 °C, when HAp transformed to β-TCP. Between ~1220 and ~1270 °C, β-TCP was found to transform to α-TCP. The room temperature Raman spectrum of silicocarnotite is characterized by an intense ν1(PO4) band at 951 ± 1 cm⁻¹ that shifts to ~930 cm⁻¹ at ~1200 °C. Using hyperspectral Raman imaging with a micrometer-scale spatial resolution, we were able to monitor in operando and in situ the solid-state reactions in the model system Ca₁₀(PO₄)₆(OH)₂-SiO₂-CaO, in particular, the formation of silicocarnotite. In these multi-phase experiments, silicocarnotite was identified at ~1150 °C. The results demonstrate that silicocarnotite can form by a reaction between β-TCP and α₁'-Ca₂SiO₄, but also between β-TCP and CaSiO₃ with additional formation of quartz.

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**Introduction**

Since the first experiment with implanted tricalcium phosphate (TCP) into animals was performed in 1920 to test its ability as a bone substitute [1], numerous studies on calcium phosphate materials have been published. This reflects the fact that calcium phosphate phases play an important role in ceramics for biomedical application due to their excellent biocompatibility, bioactivity, and osteoconductive properties (e.g., [2–11]). Furthermore, silica-/calcium phosphates have been identified in sinter residues from thermal combustion processes. As part of the debate about coal combustion, significant attention is currently being paid to alternative fuels like biomasses and sewage sludge. Several studies demonstrate the presence of calcium phosphates in biomass ashes/deposits [12], in particular, from olive pit [13–15], manure [16], agricultural and forest residues [17], and from bone material [18]. Recently, hydroxypatite (Ca_{10}(PO_4)_6(OH)_2, HAp) was found to be the most frequent mineral phase in sewage sludge ashes [19–21].

Meanwhile, HAp is the best-known calcium phosphate-based bioceramic, because its chemical compound and crystalline structure are similar to the inorganic part of bone composition [6, 22–24]. However, studies have indicated a better bioresorption of β-tricalcium phosphate (β-Ca_3(PO_4)_2, β-TCP) due to its greater solubility than HAp in physiological environments [2, 9]. Both, HAp and TCP-based materials can be prepared by several methods (e.g., precipitation, sol–gel, hydrothermal, solid-state reaction [25], and surfactant template method [26, 27]). The formation of oxyhydroapatite and oxyapatite as first steps of the phase transformation of HAp to TCP was observed by the gradually release of OH− ions at about 1000 °C [28, 29] or even above 1200 °C [30]. Other authors reported a transition temperature range between 700 and 900 °C [31]. At about 1125 °C, the metastable β-phase transforms to the first high-temperature α-phase of Ca_3(PO_4)_2 [32, 33] and at about 1450 °C to the α′-Ca_3(PO_4)_2 polymorph [32–35]. The high-temperature (HT) phase equilibria of TCP minerals were first investigated in 1959 by Nurse et al. [32] within the subsystem Ca_3(PO_4)_2-Ca_2SiO_4. Recently, highly promising studies with silicon-substituted calcium phosphates have shown that silicon is an essential trace element for bone mineralization and can improve the bioactivity of calcium phosphate materials [36–41]. The wide range of CaO, SiO_2, and P_2O_5 solid solutions varies with temperature and makes silicocarnotite (Ca_5(PO_4)_2SiO_4) [32, 34, 42–45] an excellent ceramic with great potential for medical applications [41, 45–48], which creates interest in knowledge about its synthesis conditions [35, 46, 49, 50].

Although silicocarnotite was found in basic slags rich in phosphorus centuries ago [51, 52], the natural silicocarnotite was first identified and described by Galuskin et al. [53]. The minerals of the silicocarnotite-tenselite solid solution series occur in lar- nite and gehlenite rocks of the Hatrurim Complex (Israel/Palestine). Both in nature and laboratory, silicocarnotite is commonly associated with dicalcium silicate (larnite, Ca_2SiO_4 or C_2S). The synthetic formation of silicocarnotite is described as cooling product of the so-called R phase, which is assumed to represent a solid solution between α′-Ca_3(PO_4)_2 and α-Ca_2SiO_4. An upper stability limit of about 1450 °C has been found for silicocarnotite [33–35]. Obviously, the HT behavior of silica-/calcium phosphates has attracted increasing interest due to its potential for technical and medical applications. Moreover, HAp, TCP, and silicocarnotite can serve as temperature indicators once their thermal stability fields are known, which could help kiln operators to optimize the combustion temperatures. Furthermore, this knowledge is important to ensure that the phosphate bioceramics are synthesized under optimal conditions. It follows that a detailed knowledge of the thermodynamics and kinetics of the HT reactions in the system Ca_{10}(PO_4)_6(OH)_2-SiO_2-CaO is essential in order to better understand the high-temperature behavior of silica-/calcium phosphates.

In the present study, samples of calcium oxide, quartz, and HAp were fired to about 1200 °C and the reactions were monitored in situ by confocal hyperspectral Raman imaging. The Raman spectrometer system with integrated heating stage allows to visualize mineral reactions and textures even at high temperatures with a spatial resolution of a few micrometers and without the need to quench the sample to room temperature (RT) before analyzing it [54–57]. Therefore, solid-state reactions can be studied in operando, i.e., while they are running. However, before performing the multi-phase sinter experiments, we studied the individual thermal behavior of HAp and TCP between RT and 1350 °C.
in 10 °C-steps and of a natural silicocarnotite crystal between RT and 1200 °C in 50 °C-steps, respectively, by Raman spectroscopy. The results of these experiments were, inter alia, essential to identify the different phosphate phases at high temperatures, i.e., the Raman measurements provide HT reference spectra that are needed for hyperspectral Raman imaging.

Materials and methods

Samples and sample preparation

To study the temperature behavior of silicocarnotite by Raman spectroscopy, natural silicocarnotite grains of the holotype specimen YV-415 within a silicocarnotite-bearing gehlenite from Har Parsa, Negev, were used [53]. A detailed chemical analysis and data of structure refinement of the natural silicocarnotite are given in the work of Galuskin et al. [53]. It is just noted here that the sample contains 1.85 ± 0.15 wt.% SO₃ as major impurity [53]. The polished sample, provided by the Museum of Natural History in Bern, was prepared to a sample with a diameter of 5 mm and a height of < 1 mm to minimize the temperature gradient between sample surface and thermocouple. The isochronal heating experiments with nano-crystalline HAp and TCP (©VWR, Darmstadt, Germany) were carried out with a small green body that was produced by compacting powdered precursor material into a cylinder (3 mm × 1 mm) at a pressure of 10 kPa to produce a flat surface.

The sinter experiments were carried out with cylindrical green bodies (3 mm × 1.5 mm) that were produced by compacting 20 mg of powdered precursor material. The samples were prepared from natural crystals of quartz (origin unknown), nano-crystalline HAp powder (©VWR, Darmstadt, Germany) and CaO powder (©Merck, Darmstadt, Germany). Before firing, the precursor materials were characterized and in particular checked for the occurrence of potential contaminations by ultra-fast Raman imaging using a Horiba Scientific HR800 confocal Raman spectrometer and X-ray powder diffraction measurements using a Siemens D-5000 X-ray powder diffractometer at the Institute of Geoscience of the University of Bonn, Germany. Although the CaO was stored in a furnace at 100 °C before usage, a few calcite grains could be detected, which, however, decomposed to CaO during the experiments. Traces of monetite, Ca(PO₄)OH, were identified in the nano-crystalline HAp precursor material [58], which, however, could well be excluded from the experiments. The unit cell parameters of the HAp starting material, crystallite size, and structural strain, as well as the frequency and width of the ν₁(PO₄) Raman band, are given in Table 1 for future reference and compared to literature data from nano-crystalline, stoichiometric HAp [59]. The relatively large unit cell and structural strain as well as the significantly broader ν₁(PO₄) band when compared to nano-crystalline, stoichiometric HAp [59] indicate a relatively high degree of disorder possibly related to non-stoichiometry that can be regarded as a special type of solid solution. Indeed, in some RT Raman spectra of our HAp, we observed a weak band at near 1003 cm⁻¹ that can be assigned to HPO₄²⁻ impurities [60, 61], further indicating slight non-stoichiometry of the used material. However, during heating, this band quickly disappeared.

Experimental details

To study (i) the formation temperature of silicocarnotite, (ii) the decomposition mechanism(s) of HAp to TCP and potential other products, and (iii) the phase transformation of β-TCP to α-TCP, heating experiments of pure materials and four sintering experiments in the Ca₁₀(PO₄)₆(OH)₂-SiO₂-CaO system were carried out at temperatures of up to 1190 ± 5 °C (Table 2). The experiments were performed using a LINKAM TS 1500 heating stage (Linkam Scientific Instruments, Surrey, UK) that was mounted onto the automated x–y–z stage below the microscope objective of the Raman microscope. Due to the height and the volume of the sample cylinder, a strong temperature gradient unavoidably occurs within the furnace. This gradient was empirically determined by a procedure that is described in detail by Stange et al. [54].

Two types of sinter experiments with two different mixtures of HAp, quartz, and lime were performed (Table 2). The first chosen weight ratio 4:2:1 corresponds to the stoichiometry of silicocarnotite. In addition, two experiments were carried out with the weight ratio of 1:1:1 to investigate the dependence of silicocarnotite nucleation and growth on bulk phase composition and quenching effects. In the in situ experiments TQC-1 and TQC-2, the samples were
fired to high temperatures with a heating rate of 10 °C/min. Immediately, after reaching the respective temperature, two in situ Raman images were subsequently taken. Then, the sample was fired and measured in 50 °C-steps until the maximum temperature was reached. After recording the last image at the maximum temperature, the sample was cooled down to RT with a cooling rate of 10 °C/min and a last Raman image was recorded. In experiment TQC-3, the effect of quenching was studied. After recording a Raman image at the firing temperature, the sample was cooled to RT with a cooling rate of 10 °C/min. At RT, a Raman image was recorded before firing the sample to the next temperature step. We note that the images acquired at RT form the basis for the interpretation of conventional sintering experiments, in which the sample has to be quenched at RT before analysis.

**Raman spectroscopy**

The Raman measurements were carried out using two different Raman spectrometer (Horiba Scientific HR800/HR800 Evolution, Kyōto, Japan) both equipped with an electron-multiplier charge-coupled device (CCD) detector, an Olympus BX41 microscope, and a 2 W Nd:YVO₄ (\(\lambda = 532.11\) nm) and a Nd:YAG (\(\lambda = 532.09\) nm) laser, respectively. A 50 × long-working distance objective with a numerical aperture (NA) of 0.5, a grating with 600 grooves/}

| Table 1 | X-ray diffraction and Raman data from the HAp starting material, including the lattice parameters, \(a_0\) and \(c_0\), the unit cell volume, \(V_0\), lattice strain, and the crystallite size obtained from a Williamson–Hall analysis in comparison with literature data for nano-crystalline, stoichiometric HAp [59] |
| --- | --- | --- |
| **X-ray diffraction data** | Nano-crystalline HAp (this study) | Nano-crystalline, stoichiometric HAp [59] |
| \(a_0\) (Å) | 9.4321 (4) | 9.4217 (2) |
| \(c_0\) (Å) | 6.8947 (4) | 6.8841 (3) |
| \(V_0\) (Å³) | 531.21 (4) | 529.22 (3) |
| Lattice strain | 0.0025 (4) | 0.0021 (2) |
| Crystallite size (nm) | 106 (28) | 190 (54) |
| **Raman \(v_1(\text{PO}_4)\) band parameters** | | |
| Frequency (cm\(^{-1}\)) | 962.1 (4) | 962.36 (1) |
| Width (cm\(^{-1}\)) | 10.7 (7) | 3.08 (1) |

*The measurements and quantitative analysis of the diffraction pattern, including Williamson–Hall analysis to estimate structural strain and crystallite size, were carried out exactly as described in Asjadi et al. [59]. Note that the authors accidentally mixed up the slope and intercept from the Williamson–Hall analysis, as they are in the same order of magnitude. The corrected values for the strain and crystallite size are given here. Numbers in brackets represent the standard deviation and refer to the last digits.

| Table 2 | Experimental conditions |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Exp | HAp:Qz:CaO (wt.%) | Type of experiment | \(T_{\text{range}}\) (°C) | \(T_{\text{steps}}\) (°C) | \(T_{\text{rate}}\) (°C/min) | Acquisition time (s) | Recording time (h) |
| Silicocarnotite | In situ point analysis | 30–1200 | 50 | \(\uparrow\) \(\downarrow\) | 100 | – |
| Hydroxylapatite | In situ point analysis | 30–1350 | 10 | \(\uparrow\) \(\downarrow\) | 100 | – |
| Tricalcium phosphate | In situ point analysis | 30–1350 | 10 | \(\uparrow\) \(\downarrow\) | 100 | – |
| TQC-4:2:1 | In situ imaging | 820–1190 | 50 | \(\uparrow\) \(\downarrow\) | 0.5 (SWIFT) | 2 × 2 (4)* |
| TQC-1:1:1 | In situ imaging | 960–1190 | 50 | \(\uparrow\) \(\downarrow\) | 0.5 (SWIFT) | 2 × 2 (4)* |
| TQC-1:1:1 | In situ imaging / quench | 960–1190 | 50 | \(\uparrow\) \(\downarrow\) | 0.5 (SWIFT) | 2 × 2 (4)* |

* During a dwell time of 4 h, two Raman images with a recording time of about 2 h were recorded.
mm, and a 100 µm spectrometer entrance slit was used for all measurements. With this setting, the spectral resolution of all measurements was 3.5 cm⁻¹, as given by the width of a Ne line at 1707.36 cm⁻¹ and 1707.06 cm⁻¹, respectively. To correct for any spectrometer shift during long-time measurements, the intense Ne line was continuously monitored as “internal” frequency standard in all spectra [54, 62, 63]. The linearity of the spectrometer was regularly calibrated using the Rayleigh line and the fundamental band of a silicon standard at 520.7 cm⁻¹. During the heating studies, single crystal spectra were acquired for 100 s at each temperature step. For the sinter experiments, in situ hyperspectral Raman images were recorded from an area of 100 × 100 µm² with a 1 µm step size (100 × 100 µm² = 10,000 pixel per image) in x and y direction. At each step, a Raman spectrum was recorded for 0.5 s. Due to temperature- and reaction-related shrinkage or expansion effects, the sampling area can strongly shift during cooling and heating. Therefore, at HT 100 × 100 µm²-sized and at RT, 160 × 160 µm²-sized images were taken so that the same area could be analyzed at all temperature steps. The focus was reset before each image was taken in order to compensate for these effects using the autofocus function of the instrument that is based on a high precision piezo translator and feedback signal to automatically track and optimize the laser focus on the sample to achieve the optimal Raman signal-to-noise ratio. The best achievable lateral and axial (depth) resolution of the Raman measurements with the focus at the sample surface is usually estimated from the theoretical diffraction limit given by $d_l \approx 1.22\lambda/NA$ and $d_a \approx 4\lambda/NA^2$, yielding 1.3 and 8.5 µm in our case, respectively. However, the real lateral and axial resolution may rather be in the order of $d_l \approx 2$ µm and $d_a \approx 15$ µm, respectively [54, 57]. It is important to note that the axial resolution at the surface also depends on the absorption properties of the material investigated. Generally, for the phases of interest, about 50% of the Raman intensity is lost within the first 10 to 20 µm [57].

**Hyperspectral Raman imaging**

The data reduction and generation of hyperspectral false-color Raman images is based on the classic least-squares (CLS) fitting procedure [54, 55, 57]. In general, mineral phases are identified by the characteristic positions and relative intensities of their fundamental Raman bands. With an increasing temperature, the Raman bands of mineral phases usually shift individually to lower wavenumbers and their linewidth (full width of half-maximum) increases. Additionally, the black body radiation of the samples increases during firing and reduces the signal-to-noise ratio. The identification of minerals at high temperatures is further complicated by the fact that reference Raman spectral databases, such as, e.g., the RRUFF database [63], only contain RT spectra that usually differ significantly from their high-temperature (HT) counterparts. Therefore, the HT Raman spectra of relevant mineral phases were collected to build an in-house data base for the identification of mineral phases in multi-component systems at high temperatures and as reference spectra to be used as input data for the CLS analysis. The semi-quantitative mineral fractions of an imaged area were calculated by averaging the CLS fractions of all 10,000 spectra.

We note that the accuracy of the absolute mineral fractions is influenced by (i) crystal orientation, (ii) grain size, (iii) the temperature dependence of band position and linewidth, and (iv) the relative Raman scattering cross-sections of the mineral phases. Moreover, it has to be noted that we analyzed a relatively small area at the surface that is not necessarily representative for the entire green body. However, hyperspectral Raman imaging delivers 2-dimensional in situ information about the formation and decomposition of distinct phases and their textural relationship without the necessity of quenching the sample to RT. Moreover, Raman images can be taken during heating and cooling with a high-temperature, time, and spatial resolution. Note that all images created by our working group are shown in consistent colors.

**Heating experiments**

The green body of compacted HAp powder was fired from 30 to 1350 ± 5 °C in 10 °C-steps. At each temperature step, a spectrum was recorded from the same spot in the wavenumber range of 100–4000 cm⁻¹. A slight shift due to specimen expansion is possible, but not relevant since the material is homogeneous. After cooling down to RT, the same sample was fired from 30 to 1350 ± 5 °C in 10 °C-steps in order to record HT Raman spectra of
TCP between 100 and 1730 cm\(^{-1}\). The natural silicocarnotite sample was fired from 30 to 100 ± 5 °C and further until 1200 ± 5 °C in 50 °C-steps. Due to very small size of the silicocarnotite grains (< 5 µm) within the gehlenite matrix, an automated measurement at the same spot was not reliably possible and the analysis was performed manually at different spots.

For quantitative analysis, the RT Raman spectra of silicocarnotite, HAp, and TCP were least-squares fitted using an appropriate number of Gauss-Lorentz functions along with a cubic background function in the frequency range from 100 to 1200 cm\(^{-1}\). Spectra of HAp and TCP taken above 30 °C were fitted between 850 and 1200 cm\(^{-1}\) and additionally between 3400 and 4000 cm\(^{-1}\) in the case of HAp. A 5th order polynomial background function in the wavenumber range from 700 to 1200 cm\(^{-1}\) was used to correct the spectra of silicocarnotite taken above 30 °C. Before any fitting, the spectra were corrected for any spectrometer shift during long-time measurements using the Ne emission line at 1707.36 cm\(^{-1}\) and 1707.06 cm\(^{-1}\), respectively, that was fitted using a Gauss function. The reported Raman frequencies are usually precise within ± 0.02 to ± 0.2 cm\(^{-1}\), but for weak and broad bands, particular those measured at high temperatures, we estimated a precision in the order of ± 0.3 to ± 1.2 cm\(^{-1}\) from multiple measurements. Spectrum fitting was performed using the LabSpec 6.4.4.15 (Horiba Scientific, Kyōto, Japan) software.

**Thermogravimetric and differential thermal analysis (TG/DTA)**

Two thermogravimetric and differential thermal analyses (TG/DTA) were carried out using a NETZSCH STA-449F3 system coupled with a 403 Aéolos Quadro quadrupole mass spectrometer (NETZSCH, Selb, Germany) at the RWE Power AG, Niederaußem, Germany. The measurements of the HAp sample were performed at a constant heating/cooling rate of 10 °C/min using an open corundum crucible in air. The scanning temperature range was from RT to 1350 °C (HAp) and to 1500 °C (β-TCP). The temperature measurement is typically accurate within ± 1 °C at low temperatures and accurate with ± 5 °C at high temperatures (> 800 °C). Both measurements were performed one after the other. The TG curve during the first firing experiment shows the loss of OH\(^-\) ions, while the DTA results can be used to determine crystallization and phase transformation temperatures, here in particular the HAp to β-TCP, β-TCP to α-TCP, and α-TCP to z'-TCP transitions.

**Results**

**Room-temperature (RT) Raman spectrum of silicocarnotite**

Silicocarnotite (Ca\(_5\)(PO\(_4\))\(_2\)SiO\(_4\)) and ternesite (Ca\(_5\)(SiO\(_4\))\(_2\)SO\(_4\)) represent the phosphate- and sulfate-containing end member of a solid solution series. Both minerals are isotypic and crystallize in the space group \(Pnma\) (\(D\(^{17}_{2h}\)\), i.e., no. 62 [42]). A group theoretical analysis yields the following irreducible representation for optical modes in the silicocarnotite structure:

\[
\Gamma_{\text{optic}} = 35A_g + 31A_u + 31B_{1g} + 34B_{1u} + 35B_{2g} + 30B_{2u} + 31B_{3g} + 34B_{3u}
\]  

(1)

From these, the \(A_g\), \(B_{1g}\), \(B_{2g}\), and \(B_{3g}\) modes are Raman active, i.e., 132 (8d: 108, 4c: 24) Raman bands are expected. There exist two types of PO\(_4\) and SiO\(_4\) tetrahedra on the mirror plane (MO\(_4\)) and those in general positions (GO\(_4\)). Both tetrahedra types are connected with Ca\(^{2+}\) ions, which are coordinated by three oxygen atoms in the case of MO\(_4\) and by four oxygen atoms in the case of GO\(_4\) [42, 53].

Figure 1 shows a Raman spectrum of the natural silicocarnotite sample recorded at RT. A least-squares fit of 49 Raman bands and a 3rd order polynomial background to the data in the frequency range of 100–1200 cm\(^{-1}\) yielded a good agreement between the measured and fitted sum spectrum (reduced \(X^2 = 0.2\)). 83 Raman bands remain undetected may be caused by hidden bands as part of broader bands due to limitations in the spectral resolution or too weak to be detected with the chosen analytical parameters.

Between 100 and 280 cm\(^{-1}\), 12 of 21 lattice modes of Ca\(^{2+}\) rotational and translational modes can be identified. The group of bands between 300 and 500 cm\(^{-1}\) can be attributed to the \(v_2(PO_4)\) and \(v_2(SiO_4)\) bending modes [53, 56, 64–66]. The weak bands located at 498, 528, and 534 cm\(^{-1}\) may be assigned to the anti-symmetric \(v_4( SiO_4)\) bending modes, as the \(v_4( SiO_4)\) modes in the ternesite structure vibrate with similar frequencies [56]. The bands
at frequencies higher than 800 cm\(^{-1}\) can be assigned to the internal symmetric and anti-symmetric stretching vibrations of both tetrahedral units. The bands at 876 and 899 cm\(^{-1}\) and those at frequencies larger than 1025 cm\(^{-1}\) correspond to the \(v_3\) stretching modes of the SiO\(_4\) and PO\(_4\) tetrahedra, respectively [56, 64, 66–68]. The most intense Raman band is located at 952 cm\(^{-1}\) and the second most intense band near 845 cm\(^{-1}\), which can be unequivocally assigned to the symmetric \(v_1\)(PO\(_4\)) and \(v_1\)(SiO\(_4\)) modes, respectively. As the sample is of natural origin and of the ternesite-silicocarnotite solid solution series, the \(v_1\)(SO\(_4\)) mode can be additionally identified at 1005 cm\(^{-1}\) [53, 56]. Note that the \(v_1\)(PO\(_4\)) band is slightly asymmetric toward the higher frequency side. This is reflected by the fact that a second function, centered at 961 cm\(^{-1}\), is needed to satisfactorily fit the band profile in this frequency range. In addition, it should be mentioned that the \(v_1\)(PO\(_4\)) band was identified within a frequency range from 950 to 952 cm\(^{-1}\) measured at different localities on the analyzed grain, yielding an average \(v_1\)(PO\(_4\)) frequency of 951 ± 1 cm\(^{-1}\).

### High-temperature (HT) Raman spectra of silicocarnotite

Here, we present the first in situ, high-temperature (HT) Raman spectra from natural silicocarnotite crystals. In the following, we will focus on the analysis of the temperature behavior of the most intense \(v_1\) bands of the SiO\(_4\) and PO\(_4\) units. These Raman bands are of great interest, as they can be used as fingerprint bands for the identification of silicocarnotite at RT, but also at high temperatures. Figure 2a presents a stacked plot of 21 Raman spectra, which were recorded between 30 and 1200 ± 1 °C in approximately 50 °C-steps.

During firing, all observable bands, including the \(v_1\)(SiO\(_4\)) and \(v_1\)(PO\(_4\)) bands, become broader and generally shift to lower frequencies. The FWHM values for both \(v_1\) modes increase with increasing temperature and are listed in Table 5 in Appendix. All identified bands remain detectable during the entire heating process, with the exception of the \(v_1\)(SO\(_4\)) band that disappears between 1000 and 1050 °C. The ratio between the intensity of the \(v_1\)(SO\(_4\)) and the \(v_1\)(PO\(_4\)) band tends to fall to zero at about 1050 °C (3.9). By plotting the fitted band...
positions of \(v_1(PO_4)\) and \(v_1(SiO_4)\) as a function of temperature, a different temperature dependence of the two modes becomes evident, as the \(v_1(PO_4)\) mode shows a slightly larger frequency shift with increasing temperature than the \(v_1(SiO_4)\) band (Fig. 2b). From 30 to 1200 ± 1 °C, the \(v_1(PO_4)\) and \(v_1(SiO_4)\) bands shifted about 20 wavenumbers in respect to an experimental error of ± 0.02 and ± 0.3 cm\(^{-1}\) at RT and at 1200 °C, respectively, for the \(v_1(PO_4)\) band and an experimental error of ± 0.3 and ± 1.2 cm\(^{-1}\) at RT and at 1200 °C, respectively, for the \(v_1(SiO_4)\) mode. Interestingly, the ratio of the \(v_1\) band intensities did not significantly change with increasing temperature (\(A_{v_1(PO_4)}/A_{v_1(SiO_4)}\) ≈ 4.8), reflecting a particular temperature stability of silicocarnotite.

**HT Raman spectroscopy of hydroxylapatite (HAp) and tricalcium phosphate (TCP)**

The thermal decomposition of HAp can principally be followed by the release of structural hydroxyl groups that vibrate with a characteristic frequency of 3572 cm\(^{-1}\) at RT \([64, 67]\). However, at RT, this band is hardly detectable in the Raman spectrum of the pressed nano-crystalline HAp tablet prepared for the heating study, as it is overlain by intense and broad OH bands between 3520 and 4000 cm\(^{-1}\) (Fig. 3a). We note here, however, that these bands are not observed in spectra of the loose HAp powder on a glass slide, so the \(\nu(OH)_{HAp}\) band can be clearly detected. Within the heating study, the \(\nu(OH)_{HAp}\) band is first observable at temperature above 600 °C when the other water-related bands disappear (Fig. 3b). At RT, another broad intense OH band occurs near 3850 cm\(^{-1}\) that has two shoulders near 3800 cm\(^{-1}\) and 3890 cm\(^{-1}\). Two further OH bands are detectable near 3960 cm\(^{-1}\) and 3980 cm\(^{-1}\). All seven identifiable bands are labeled 1–7 from low to high frequency in Fig. 3. The temperature behavior of the intensity of the different OH bands is shown in Fig. 3c. The high frequency bands nos. 6 and 7 are the first OH bands that completely disappear during heating already at 120 °C. At about 200 °C, the OH band no. 5 disappears. The integrated intensity of OH bands nos. 2 and 4 gradually decrease between 100 and 400 °C and at 450 °C these bands also disappear. The OH band no. 3 can be detected until 570 °C. At about the same temperature, the characteristic \(\nu(OH)_{HAp}\) band can be clearly identified near 3555 cm\(^{-1}\) (Fig. 3b). From Fig. 3b and 3c, it is further evident that the integrated intensity of \(\nu(OH)_{HAp}\) is almost constant in the temperature range between 600 and 750 °C, but rapidly decreases at about 770 °C. At 810 ± 1 °C, the \(\nu(OH)_{HAp}\) band cannot be detected in the spectra anymore.

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**Figure 2** a Stacked Raman spectra (approx. 50 °C-steps) of the silicocarnotite sample recorded between 30 and 1200 ± 1 °C. b High-temperature (HT) frequencies of the \(v_1(PO_4)\) and \(v_1(SiO_4)\) bands each along with a quadratic fit (red curves, \(r^2 > 0.98\)).
In the following, an analysis on the temperature behavior of the Raman bands of the PO\(_4\) groups within HAp and TCP is presented. The most intense Raman band reflects the fully symmetric stretching motions of the PO\(_4\) units of HAp. The other internal PO\(_4\) modes are much weaker, but can also be used to quantitatively follow the decomposition of HAp to \(\beta\)-TCP and other calcium phosphates by Raman spectroscopy. The internal stretching and bending modes of the PO\(_4\) tetrahedra can be identified within the frequency range between 300 and 1200 cm\(^{-1}\) (Fig. 4).

The groups of bands with the intense bands between 430 and 590 cm\(^{-1}\) at RT can be assigned to the internal \(v_2(PO_4)\) and \(v_4(PO_4)\) bending vibrations, respectively. The most intense band is due to the symmetric stretching mode \(v_1(PO_4)\) and is located at 961 cm\(^{-1}\) at RT. The bands between 1000 and 1100 cm\(^{-1}\) can be assigned to the anti-symmetric stretching modes of PO\(_4\) tetrahedra [64, 67, 69, 70].

Plotting the fitted frequencies of the \(v_1(PO_4)\) band as a function of temperature, three local minima or short-term shifts to higher frequencies are discernible, indicating a slight shortening of the P–O bonds (Fig. 5). The first local minimum at 200 °C seems to be associated with the loss of adsorbed molecular water bound to the nano-crystalline HAp crystallites. When the temperature reaches 380 °C, the \(v_1(PO_4)\) frequency shows a second minimum that correlates roughly with a marked intensity decrease of OH band (no. 3) (Fig. 3) and may be related to the loss of surface-bound hydroxyl groups [23, 71]. Note that nano-crystallites are dominated by relaxed surface bonds, which has an impact on the vibrational properties, as, for instant, on the average P–O bond length and thus on the average frequency of the P–O vibrations. Between about 400 and 770 °C, the \(v_1(PO_4)\) band shifts to lower frequencies with a third local minimum at about 570 °C that possibly represents another stage of the loss of further distinctly surface-linked OH groups (Fig. 5). Additionally, the \(v_1(PO_4)\) and the \(v_2(PO_4)\) bands narrow and, notably, the intensity of the \(v_1(PO_4)\) band decrease within this temperature interval, while the polarizability, i.e., the Raman intensity of the \(v_3(PO_4)\) band increases (Fig. 4b). The overall number of observable Raman bands increases, reflecting a change in the crystal symmetry and the loss of hydroxyl groups. At about 400 °C, a new band is observed at about 720 cm\(^{-1}\) (HT) and another second weak band appears near 350 cm\(^{-1}\) that we assign to the pyrophosphate \(\beta\)-Ca\(_2\)P\(_2\)O\(_7\) (Ca/P < 1.5) [72–75].

At 770 °C, a very weak new band is observed at 545 cm\(^{-1}\) (HT) which increases in intensity at about 850 °C, indicating the formation of \(\beta\)-TCP [70]. A group theoretical analysis based on a rhombohedral structure (R3c) of the \(\beta\)-polymorph of TCP reveals 136...
Raman active modes, which compares with 62 Raman active modes predicted for HAp (P63/m). The number of expected Raman modes was calculated using the position parameters of the atoms obtained from crystallographic analyses for β-TCP [76] and HAp [77, 78]. Thus, more bands are expected with increasing temperature. However, due to the low intensity and large broadening of the bands at HT, the number and positions of the bands are difficult to determine. In general, also the identification of other calcium phosphates, such as β-Ca2P2O7, is very difficult as long as HT reference spectra are missing.

Between 770 and 850 °C, the positions of the bending modes change significantly (Fig. 4c). At about 810 °C, the v2(PO4) and v4(PO4) bands between 770 and 850 °C. At about 400 °C, two new bands (350 cm⁻¹, 720 cm⁻¹) occur (pink arrows). c Zoomed part of the spectrum showing the bending vibrations between 700 and 1000 °C. At about 770 °C, a new band at 545 cm⁻¹ occurs (pink arrow). See text for more details.
intensity of the \(v_2(PO_4)\) band increases with temperature increase and the intensities of the anti-symmetric modes decrease. Obviously, HAp decomposed to \(\beta\text{-TCP}, \text{H}_2\text{O}\), and as an intermediate product to \(\beta\text{-Ca}_2\text{P}_2\text{O}_7\).

The formation of \(\beta\text{-TCP}\) is further evidenced by the observation that the frequency of the \(v_1(PO_4)\) band of HAp merges at about 850 °C with the HT \(v_1(PO_4)\) frequencies observed for \(\beta\text{-TCP}\) (Fig. 6).

Figure 7 shows all Raman spectra of \(\beta\text{-TCP}\) in the frequency range of 200–1200 cm\(^{-1}\) recorded between 30 and 1260 ± 1 °C. At RT, there are two distinct bands at 948 and 969 cm\(^{-1}\) and one shoulder at about 961 cm\(^{-1}\), respectively, corresponding to \(v_1(PO_4)\) vibrations of \(\beta\text{-TCP}\) [68, 70, 75, 79], resulting from three nonequivalent PO\(_4\) units in the unit cell [76]. Interestingly, the weak band at 918 cm\(^{-1}\), that is also assigned to a \(v_1(PO_4)\) mode, does not shift significantly (± 2 cm\(^{-1}\)) until 1350 °C. The weak band located at 1089 cm\(^{-1}\) within the RT spectrum of \(\beta\text{-TCP}\) (Fig. 7) was not observed during the heating study of HAp. However, it can be clearly attributed to the \(v_3(PO_4)\) modes of \(\beta\text{-TCP}\) [70].

When \(\beta\text{-TCP}\) is fired from RT to temperatures below about 770 °C, all observable bands become broader and generally shift to lower frequencies. The evolution of the frequency of the most intense \(v_1(PO_4)\) band as a function of temperature can be approximately described by a linear function until 770 °C \((r^2 > 0.99)\). Here, the \(v_1\) band shifts visibly to lower values and remains constant between about 800 and 830 °C (Fig. 5). From Fig. 7, it is evident that the two intense \(v_1(PO_4)\) bands of \(\beta\text{-TCP}\) merge at about 850 °C indicating a degeneration of \(v_1(PO_4)\) modes. Furthermore, both 850 °C spectra of HAp and \(\beta\text{-TCP}\) as starting material show almost the same positions of PO\(_4\) modes and in each case the symmetric bending vibrations result in a stronger polarizability, i.e., higher Raman intensity, than the respective anti-symmetric bending vibrations (Fig. 6c). Above about 850 °C, both \(v_1(PO_4)\) bands exhibit the same shift \((dv/\delta T = -0.02)\) with increasing temperature (Fig. 5). At about 1220 °C, the \(v_1(PO_4)\) bands show a local minimum before the frequencies shift to a higher value of 945 cm\(^{-1}\) until 1260 °C (Figs. 5 and 7). In this temperature range, the \(\beta\)-polymorph of TCP reconstructively transformed to the \(\alpha\)-TCP polymorph. At higher temperatures, both modes cease to shift to higher frequencies until the maximum sintering temperature is finally reached.

**Results of the thermal analyses of HAp and TCP**

Figure 8a shows the thermogravimetric measurement of the nano-crystalline HAp powder up to 1350 °C. In Table 3, we link the thermal analyses results with those from high-temperature Raman spectroscopy. The TG curve from HAp reveals a first mass loss step in the temperature range between about 100 and 200 °C (green curve) that can be explained by the loss of adsorbed water, reflected by the disappearance of
Raman bands (6) and (7). A second mass loss is observed between 200 and 380 °C. Above about 380 °C, the weight decreases rapidly until 480 °C and results in the largest mass loss of ~ 3.1 wt.% (mass loss step 3), possibly due to the loss of further surface-bound water. After this temperature, the mass decreases slowly (mass loss steps 4–6) with another step near 750 °C (mass loss step 5). Beyond 1050 °C, the sample weight remains stable at ~ 93.7% of the original weight. Figure 8a additionally shows a quadrupole mass spectrometric measurement of the molecular mass 18, corresponding to molecular water, as a function of temperature (orange curve). These data show two broad and less intense peaks at about 115 and 770 ± 1 °C and one intense peak near
The DTA curves of HAp and \( \beta \)-TCP are shown in Fig. 8b. Between RT and about 460 °C, the DTA heating curve of HAp is characterized by a broad and intense endothermic signal that can be assigned to the loss of adsorbed water and surface OH groups, also observed by Raman spectroscopy. Between 700 and 800 °C, small endothermic signals possibly can be attributed to the stepwise loss of structural OH– ions as HAp transforms to \( \beta \)-TCP. The endothermic peak observed at 1300 (onset: 1277) ± 5 °C can be assigned to the \( \beta \)-to-\( \alpha \)-TCP polymorphic phase transformation, whereas the exothermic peak at 1080 ± 5 °C observed during cooling is associated with its reverse reaction. Both the endothermic and the exothermic peak, resulting from the \( \beta \)-to-\( \alpha \)-TCP transition, have a similar peak area (\(*1535 versus *1640 \) \( \mu Vs \), respectively). A second experiment was performed until 1500 °C, but revealed no further mass loss (data not shown here).

The DTA curve of \( \beta \)-TCP shows two endothermic peaks at 1300 ± 5 °C (onset at 1287) and at 1480 (onset at 1454) ± 5 °C. The first peak reflects the \( \beta \)-to-\( \alpha \)-TCP polymorphic phase transformation and the second relates to the \( \alpha \)-to-\( \alpha \)-TCP transition. During cooling, an exothermic peak at 1450 (onset at 1444) ± 5 °C is observed, reflecting the reverse \( \alpha \)-to-\( \alpha \)-TCP transformation. The two small exothermic signals at 1270 and 1080 ± 5 °C can be attributed to the transformation of the \( \alpha \)-phase to \( \beta \)-TCP.

**Multi-phase in situ experiments (TQC-1 and TQC-2)**

In the first experiment TQC-1, the green body containing HAp, quartz, and CaO in a weight ratio 4:2:1 was fired to 820 ± 5 °C with a heating rate of 10 °C/min and then stepwise (\(*50 °C\)-steps) to 1190 ± 5 °C. Figure 9a shows extracts of four false-colored hyperspectral Raman images taken at different temperatures and dwell times. It is clearly discernible that nano-crystalline HAp transforms unevenly. At 820 ± 5 °C, the nano-crystalline HAp grains transformed to \( \beta \)-TCP only in the upper part of the imaged area. The temperature-dependent change of bending mode positions described above marks this transformation. In Fig. 9b, two spectra of the image taken at 820 ± 5 °C after a dwell time of two hours are shown in a frequency range from 300 to 750 cm\(^{-1}\). The spectrum 1 identifies HAp; however, it does not differ significantly from spectra recorded at lower temperatures, e.g., 700 ± 1 °C. The spectrum 2 can be compared to those taken at 820 ± 1 °C during the heating study of HAp and \( \beta \)-TCP, respectively. The bands at about 350 and 720 cm\(^{-1}\) (at HT) can be assigned to pyrophosphates \([72–75]\) formed by the decomposition of HAp. Within the imaged area, pyrophosphate is only visible at 820 ± 5 °C immediately after the temperature is reached. Upon further heating, the pyrophosphate concentration decreased as shown by single-phase images in Fig. 9c. After two hours at 870 ± 5 °C, the bands identifying pyrophosphate are no longer detectable in the spectra, whereas more and more \( \beta \)-TCP can be identified.
It is possible that additional β-TCP was formed by the reaction between pyrophosphate and small lime particles located below the image plane.

At 910 ± 5 °C, the spectra of HAp and β-TCP become increasingly similar and the colors in the Raman image appear blurred. Between 910 ± 5 and 1190 ± 5 °C HAp completely transformed to β-TCP, but no other phases newly crystallized within the imaged area. However, after cooling down to RT, wollastonite was found outside the investigated area, formed by a reaction between lime and quartz.

A proportional weight ratio of the phases of the green body was chosen for the in situ experiment TQC-2. False-color hyperspectral Raman images of an area 100 x 100 μm² were recorded in situ during stepwise high-temperature sintering (~ 50 °C-steps) to 1190 ± 5 °C (Fig. 10). Two images were taken in succession at each temperature. However, only representative images are shown here. At 960 ± 5 °C, all calcite was already decomposed to CaO and CO₂ as expected [57]. As in experiment TQC-1, the nanocrystalline HAp partially transformed to β-TCP and...
possibly to pyrophosphate, indicated by newly identified but very weak bands at about 350 and 720 cm\(^{-1}\) [72–75]. Moreover, the HT polymorph of dicalcium silicate (\(\alpha\_L\text{-Ca}_2\text{SiO}_4\)) crystallized at interfaces between quartz and lime and as small grains within the HAp matrix. \(\alpha\_L\text{-Ca}_2\text{SiO}_4\) likely formed by the reaction with small SiO\(_2\)/CaO particles located below the focal image plane. Between 960 and 1050 ± 5 °C, more and more \(\alpha\_L\text{-Ca}_2\text{SiO}_4\) replaced larger quartz grains (marked in Fig. 10). Furthermore, more \(\beta\)-TCP has formed from HAp. After the temperature was increased to 1100 ± 5 °C, the \(\alpha\_L\text{-Ca}_2\text{SiO}_4\) grains grew together and quartz was observed only as relics in the center of some grains. The time series images at 1150 ± 5 °C show the time-dependent formation of silicocarnotite, which could be identified after a dwell time of two hours in various spectra throughout the image area by its characteristic fundamental Raman bands near 930 and 828 cm\(^{-1}\) [68, 70, 75, 79], while \(\alpha\_L\text{-Ca}_2\text{SiO}_4\) within the imaged area completely transformed to \(\beta\)-Ca\(_2\)SiO\(_4\) (larnite) [55, 56, 65, 80] during cooling. In particular, silicocarnotite could be identified in contact with dicalcium silicate at the same location within the \(\beta\)-TCP matrix where it was also detected at HT (spectrum 2 in Figs. 10 and 11). Furthermore, silicocarnotite formed a distinct reaction rim around a large quartz grain that was preserved in the lower right of the imaged area. Notably, at RT, also wollastonite could be identified, usually in contact to silicocarnotite and larger quartz grains.

**In Situ/quench experiment TQC-3**

The experiment TQC-3 was performed using the same precursor materials as in experiments TQC-1 and TQC-2 and the same weight ratio chosen for experiment TQC-2 to study the effect of quenching on phase assemblage. After recording a 100 × 100 \(\mu\text{m}^2\)-
sized Raman image at the firing temperature, the sample was cooled to RT with a cooling rate of 10 °C/min. At RT, a 160 × 160 μm²-sized Raman image was recorded before firing to the next temperature step. Due to the shrinkage and expansion of the sample the imaged area varies slightly. Unfortunately, not all mineral reactions observed at RT could also be identified at HT.

Figure 12 shows a direct comparison of the false-color hyperspectral Raman images recorded during the high-temperature firing and the quenching steps. During firing to the first temperature step of 960 ± 5 °C, calcite was already decomposed to lime but partially recrystallized during the following quenching step due to a high CO₂ fugacity in the furnace [56]. During the next firing steps, however, no more CaO was available anymore and therefore no calcite could form during quenching to RT. At 960 ± 5 °C, dicalcium silicate (ε₁-Ca₂SiO₄) was first detected, but transformed to larnite during cooling.

**Figure 10** False-colored hyperspectral Raman images of the mineral distribution of a 100 × 100 μm² surface area of a green body containing HAp, CaO, and quartz at different temperatures and two dwell times (experiment TQC-2). The yellow arrows mark the new formed mineral phases dicalcium silicate (DC), and silicocarnotite (SC). Note that the formation of silicocarnotite started at 1150 ± 5 °C.

During the cooling process, the ε₁-phase of dicalcium silicate transformed to the β-phase (larnite). Within the yellow boxes, two average spectra were extracted (Fig. 11).
Moreover, it is evident that during the first heating step HAp only partially decomposed to $\beta$-TCP and possibly other pyrophosphates, the formation of which is suggested by the observation of a weak Raman band near 720 cm$^{-1}$ indicative for pyrophosphates [72–75]. In the course of the sintering experiment, the decomposition of HAp advanced and more and more $\alpha'_L$-$\text{Ca}_3\text{SiO}_4$/larnite crystals grew at the expense of quartz.

After heating to 1050 ± 5 °C and cooling down to RT, silicocarnotite and wollastonite were detected in contact with a large quartz grain located in the lower left of the image. About 8 vol.% silicocarnotite can be clearly identified within the 5 × 5 μm$^2$ area marked by a yellow box in Fig. 12. During the next firing/quenching step (1100 ± 5 °C) wollastonite grew at the expense of quartz, but on further firing/quenching (1150 ± 5 °C) the wollastonite content decreased while the silicocarnotite content increased as rim around the quartz grain. Interestingly, the quartz concentration seems to have remained stable and the wollastonite increased again during the last quenching from 1190 ± 5 °C.

From 1100 ± 5 °C, small silicocarnotite nuclei, surrounded by HAp/$\beta$-TCP matrix, could also be identified in various HT spectra throughout the imaged area. However, it has to be noted that due to the similarity of the spectra of silicocarnotite and $\beta$-TCP at HT, it is difficult to distinguish between these phases, in particular, if one of them occurs in low concentrations. Nevertheless, the large difference between the HT and RT silicocarnotite concentrations within the imaged area indicates that the main growth of silicocarnotite grains inside the HAp/$\beta$-TCP matrix near to larnite grains must have occurred during cooling down to RT. During firing to the next temperature steps at 1150 and 1190 ± 5 °C and quenching to RT, respectively, the formation of $\beta$-TCP from nano-crystalline HAp was advanced, which should have been already completed considering the heating study with HAp. At 1190 ± 5 °C, silicocarnotite grains became visible at HT und grew further during cooling to RT. At RT, many silicocarnotite grains were identified as rims around larger quartz grains and within the $\beta$-TCP matrix in direct contact with larnite (Fig. 12). In both experiments TQC-2 and TQC-3, the upper stability limit of silicocarnotite was not reached.

Discussion

The stability of HAp and the formation of $\beta$-TCP

HAp crystallizes in two different space groups: monoclinic ($P2_1/b$, $C_{2h}$, no. 14) and hexagonal ($P6_3/m$, $C_{6h}$, no. 176 or $P6_3$, $C_6$, no. 173, respectively). Although the monoclinic form is thought to be thermodynamically more stable, it appears that a
The hexagonal form allows atomic substitutions (e.g., Na?, Mg2?, Si2?, K?, Zn2?, Sr2?, Ba2?, Cl?, F?, CO32- [23]), balanced by disordered hydroxyl groups as also observed in bones (e.g., [22–24]). However, the structural definition of HAp is still intensively discussed with regard to the hexagonal space groups P63/m and P63, the stoichiometry of HAp, as well as to biological and theoretical considerations [23, 64, 67, 85–87]. A group theoretical analysis for the C6h factor group yields only 62 Raman active modes for space group P63/m (14Agl + 142E2g + 102E1g + 142E2g + 102E1g) [77, 78, 88], where the OH stretching mode is not involved [64]. In contrast to the C6h factor group, 110 Raman bands (22A + 22E1 + 22E2) are expected for the C6 factor group [86–89].

Using crystal structure data published by Ikoma and co-authors [90], a group theoretical analysis for the monoclinic phase reveals that 126 (63A + 63B) among 249 expected optical modes are Raman active [88]. However, the crystal symmetries P21/b, P6 3/m, and P63 are very similar and the number of expected bands differs due to the order of OH– ions, which changes during heating. We note in this context that the band near 630 cm\(^{-1}\), which has been assigned to the liberation of OH– ions within the P63 symmetry [64, 69, 87], was not observed in our Raman spectra.

In general, the temperature-dependent decomposition of nano-crystalline HAp may operate via three possible reactions, whereby TCP and other calcium phosphates are formed and H2O is released into the atmosphere:

**Figure 12** False-colored hyperspectral Raman images of the mineral distribution of a 100 x 100 µm\(^2\) surface area of a green body containing HAp, lime, and quartz at different temperatures and after cooled to room temperature (experiment TQC-3). Note that a larger area was measured at RT. The white frame marks the corresponding area at HT. The imaged area varies slightly due to the shrinkage and expansion of the sample. The yellow arrows hint to the newly formed mineral phases dicalcium silicate (DC), wollastonite (Wo), and silicocarnotite (SC) within the HAp matrix, which transformed to β-TCP during the experimental process. Dicalcium silicate crystallized in contact to lime in the expense of quartz. The high-temperature polymorph α-Ca2SiO4 crystallized to lanite during cooling to room temperature (RT) and recrystallized during firing. The formation of silicocarnotite started after cooling from 1050 ± 5 °C (8 vol.% within the 5 x 5 µm\(^2\) large yellow box) in contact to lanite and wollastonite, respectively. The crystallization of silicocarnotite within the HAp/β-TCP matrix started after cooling from 1100 ± 5 °C.
\[ \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \rightarrow 2\text{Ca}_3(\text{PO}_4)_2 + \text{Ca}_2\text{P}_2\text{O}_7 + 2\text{CaO} + \text{H}_2\text{O} \]  
\[ \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \rightarrow 2\text{Ca}_3(\text{PO}_4)_2 + \text{Ca}_4\text{P}_2\text{O}_9 + \text{H}_2\text{O} \]  
\[ \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \rightarrow 3\text{Ca}_3(\text{PO}_4)_2 + \text{CaO} + \text{H}_2\text{O} \]

In the case of Eqs. 2a and 2c, lime is also formed as an intermediate product that has only a weak second-order Raman spectrum and is thus difficult to detect [57]. The HT Raman study of pure, nano-crystalline HAp reveals significant spectral changes due to the alteration of P–O bonds within the PO4 units. By using the empirical correlation between Raman wavenumbers of PO4 tetrahedra and their P–O bond lengths in crystalline phosphates [91], we obtain a shortest bond length of 152.3 pm for the highest frequency (1076 cm\(^{-1}\)) and a longest bond length of 155.6 pm for the lowest frequency (961 cm\(^{-1}\)) of HAp. P–O bond lengths of 151.9 and 156.0 pm were calculated for \(\beta\)-TCP indicating a shortening of the P–O bond of the assigned \(v_3(\text{PO}_4)\) band and an expansion of the P–O bond of the assigned \(v_1(\text{PO}_4)\) mode during the transformation of HAp to \(\beta\)-TCP. Some authors claim a dehydration of HAp by a gradual release of its OH– ions at temperatures above 1000 °C [28–30]. However, our observations suggest a complete loss of structural OH groups between a relative narrow temperature interval already between 770 and 850 °C (Table 3). This difference in the dehydration temperature likely reflect difference in the structural state or the degree of disorder of the used HAp samples, including non-stoichiometry, which is very difficult to detect by XRD analysis alone [92–94].

Loss of hydroxyl groups bound to the surface of the HAp nano-crystals, however, occurs in distinct overlapping stages below about 600 °C. The first step is the loss of adsorbed water below 200 °C [23, 71], which can be followed by (i) the first mass loss in the TG curve and the first peak in the QM (m = 18) curve (Fig. 8), (ii) the decrease of OH bands in the frequency range 3500–4000 cm\(^{-1}\), in particular the disappearance of the OH bands (5–7) (Fig. 3a, c), and (iii) the abrupt shift to higher frequencies of the main band position of HAp during firing (Fig. 5), i.e., the average P–O bonds shortened.

Previous studies have indicated that another type of water in addition to adsorbed surface molecular water, surface, and structural OH groups occurs within the HAp structure, which has been defined as lattice water [71, 95], structural intra-crystalline water [96], structurally incorporated water [97], or dissociated water [98]. All terms refer to inner-surface-bound water that fills the empty space in the crystal lattice channels of HAp. The fact that the OH bands (2–7) are found only in the pressed tablet, but not in the powder suggests a surface-bound origin, possibly favored by the nanocrystallinity of the sample material. Thus, the OH bands (2–4) are assigned to surface-bound OH groups, which can be removed by heating to above 200 °C [96]. Indeed, these OH bands disappear in the temperature range 400–600 °C. Moreover, the TG data agree well with studies on carbonated HAp, except for an additional weight loss for CO2 [95–97]. In agreement with Pasteris and colleagues, we obtained about 3% mass loss due to the loss of structurally incorporated water [97].

The loss of surface-bound molecular water and hydroxyl groups can cause a contraction of the HAp unit cell in the a-axis dimensions [71] and possibly a reversal of the ordered hydroxyl groups [83, 99] which could be responsible for the observed spectral changes in the frequency range 300–1200 cm\(^{-1}\) between 380 and 770 °C. The position and intensity of all stretching and bending modes changed significantly (Fig. 4). At 480 °C, a monoclinic-to-hexagonal phase transition is predicted [23, 99–102], which could explain the spectral changes above 380 °C and the anomalies in our DTA analysis at about 450 °C (Fig. 8), respectively. However, the most dramatic changes occurred between 770 and 850 °C (Fig. 4), where the HAp structure broke down, leading to the formation of \(\beta\)-TCP (Eqs. 2a–c). The peak at about 770 °C in the QM (m = 18) curve indicates a release of H2O during the decomposition of HAp. At nearly the same temperature, the \(v(\text{OH})_{\text{HAp}}\) band disappears (Fig. 3c), suggesting the formation of oxyapatite (\(\text{Ca}_{10}(\text{PO}_4)_6\text{O}\)) [28]. In fact, new Raman bands at about 350 and 720 cm\(^{-1}\) (HT) can be assigned to pyrophosphates (Ca/P < 1.5) [72, 73, 103], which were produced during the transformation from HAp to \(\beta\)-TCP by changing the Ca/P ratio from 1.667 to 1.5 [74, 75].

It is important to note that Liao and co-workers [28] observed in heating and quenching experiments with a commercially available HAp sample from Merck (Darmstadt, Germany) that this HAp converts to \(\alpha\)-TCP and tetracalcium phosphate at temperatures
above 1360 °C without the formation of β-TCP as an intermediate product. Coelho and co-workers [31], on the other hand, have reported evidence from heating-quenching experiments for the formation of β-TCP in the temperature between 700 and 900 °C [31], which agrees well with our observations (Figs. 5 and 6b). We obtained a transformation temperature for the HAp to β-TCP between 800 and 810 °C (determined inflection point: 808 ± 5 °C), while the bulk decomposition starts already at 770 ± 5 °C with the loss of structural OH, which is accompanied by the formation of pyrophosphates, likely at the surface of the nano-crystallites. We note that this transformation temperature also agrees well with results of other authors, who all observed the appearance of a TCP phase at a temperature of about 800 °C for HAp samples which they also defined as a characteristic of Ca-deficient, non-stoichiometric HAp [104, 105].

Within the ternary system Ca$_3$(PO$_4$)$_2$(OH)$_2$-SiO$_2$-CaO, the breakdown of the nano-crystalline HAp and formation of β-TCP proceeded at significant higher temperatures. Although it is very difficult to distinguish HAp and β-TCP in situ at high temperatures due to spectral similarities, the changes of bending modes (Fig. 4b) can be used for the unambiguous identification of β-TCP. In experiment TQC-1, the temperature-series Raman images reveal that the decomposition of HAp started at 820 ± 5 °C and pyrophosphates were likely formed (Fig. 9). In contrast, in experiment TQC-2, where much more quartz and lime were present, β-TCP crystallized at 1050 ± 5 °C (Fig. 10). Thus, the presence of quartz and/or lime appears to decrease the rate and increase the activation energy for the thermal decomposition of HAp to β-TCP. Unexpectedly, Raman images acquired during the in situ/quench experiment (TQC-2, Fig. 12) show that, although β-TCP could clearly be identified in situ between 960 and 1100 ± 5 °C, HAp formed during quenching. It is known that α-TCP can be hydrolyzed to Ca-deficient HAp at temperatures as low as the human body temperature [60]. The hydrolysis of β-TCP with water from the furnace environment could possibly have led to the formation of Ca-deficient HAp. However, weak bands within the frequency range between 770 and 880 cm$^{-1}$ or between 1003 and 1005 cm$^{-1}$ [60, 61], as occasionally observed in the HAp starting material used here, or a distinct broadening of the $\nu_1$ band, which would indicate non-stoichiometric HAp, were not observed. In general, the observation that β-TCP was first identified at RT after cooling down from 1150 ± 5 °C indicates that a long sintering period is needed to decompose HAp at lower temperatures so to obtain β-TCP at RT.

The β- to α-TCP and the α- to α’-TCP transformation

The β- to α-TCP polymorphic phase transformation has previously been observed between 1125 and 1130 °C [32–34]. However, Serena and co-authors [35] observed that the presence of MgO stabilize the β-TCP phase, leading to a phase transition at a significantly higher temperature of 1230 °C. However, impurities (> 0.02 wt.%) could be excluded and yet both the DTA and HT Raman studies of HAp/β-TCP sample reveal a β-TCP to α-TCP transformation at temperatures above 1220 °C. The α-phase crystallizes in the monoclinic space group P2$_1$/a (C$_{2h}$ no. 14) with 24 formula units (312 atoms) per unit cell [106], reflecting the complexity of the high-temperature polymorph. A group theoretical analysis for the C$_{2h}$ factor group yields 468 Raman active modes (234A$\_g$ + 234B$\_g$) based on published crystal structure data [106]. However, due to the low intensity and large broadening of the bands at HT, the number and positions of the bands were difficult to determine. However, the significant shift of $\nu_1$(PO$_4$) to higher frequencies between 1220 and 1260 ± 1 °C clearly suggests a phase transition within this temperature range, which is further confirmed by the endothermic DTA peaks with onsets slightly above 1270 °C during heating. During cooling, the reverse reaction $\alpha \rightarrow \beta$-TCP was observed at lower temperatures than on heating. The hysteresis effect during cooling defined by the exothermic peak at 1080 °C indicates a first-order phase transition that depends on the heating and cooling rates. For the physicochemical conditions of our experiments (heating/quenching rate, holding time, composition, etc.), we can assume an upper stability temperature of 1220 ± 1 °C with a transition zone to about 1270 ± 5 °C for β-TCP, which then remained metastable during cooling to RT. In our experiments, the RT Raman spectra clearly identify the β-polymorph of TCP. We can further state that the new band at 1089 cm$^{-1}$ for the fired HAp/β-TCP matches well with the shortest P–O bond length calculated for β-TCP.

The onset of the $\alpha \rightarrow \alpha'$-TCP transformation was observed at 1454 ± 5 °C and is consistent with other
The formation of silicocarnotite

Within the ternary system HAp-SiO₂-CaO, dicalcium silicate (x′₁-C₅₂SiO₄) already formed at temperatures below 960 °C by a reaction between quartz and lime (Figs. 10 and 12). During quenching, the x′₁-phase reversibly transforms to the β-phase (larnite), as reported and discussed in detail in our previous study [56]. The identification of silicocarnotite is based on the published data on the ν₁(PO₄) and ν₁(SiO₄) frequencies, varying between 950 and 964 cm⁻¹ and 845 and 854 cm⁻¹, respectively (see Table 4).

It is well known that silicocarnotite can be synthesized by a solid-state reaction between dicalcium silicate and tricalcium phosphate as described by following equation:

\[
\text{Ca}_3(\text{PO}_4)_2 + \text{Ca}_2\text{SiO}_4 \rightarrow \text{Ca}_5(\text{PO}_4)_2\text{SiO}_4
\]

It has been proposed that a so-called R solid solution phase is formed as reaction product of the high-temperature polymorphs x′₁-C₅₂SiO₄ and x-C₅₂SiO₄ at temperatures above 1450 ± 20 °C [32–35]. During cooling down to RT, the R phase was found to transform to silicocarnotite at about 1370 °C [33] or 1310 °C [35] by DTA of stoichiometric mixtures.

The material used for the Raman heating study is the same as investigated by Galuskin and co-authors [53]. Compared to our data, the number of identified bands varies and there are some differences in band assignments. For example, the authors assigned a band at 584 cm⁻¹ to anti-symmetric bending modes of both the SiO₄ and PO₄ units, although they occur in different frequency ranges, i.e., 520–570 and 570–620 cm⁻¹, respectively [56, 64–67]. On the other hand, we can confirm that the band at 633 cm⁻¹ can be assigned to a ν₄(PO₄) mode. The bands at frequencies above 1010 cm⁻¹ can be unambiguously assigned to ν₃(PO₄) vibrations, whereas anti-symmetric stretching modes of the SiO₄ tetrahedra occur at much lower frequencies (~ 880 cm⁻¹) [56].

The ν₁(PO₄) frequency of silicocarnotite recorded at RT after quenching the multi-component experiments is in good agreement with the ν₁(PO₄) position of 951 ± 1 cm⁻¹ observed from the natural silicocarnotite sample. Using the HT reference spectra, we were able to identify silicocarnotite even at high temperatures. The time- and temperature-series Raman images of the in situ experiment TQC-2 and the in situ/quench experiment TQC-3 reveal that silicocarnotite was first identified as small grains located close to large x′₁-C₅₂SiO₄ grains within the HAp/β-TCP matrix. After cooling to RT, silicocarnotite crystallized further as rims around dicalcium silicate grains. Grains of wollastonite appear to have reacted with the adjacent β-TCP to silicocarnotite. With reference to previous results, we note that wollastonite cannot only form by a reaction between quartz and lime [e.g., 107], but could also be a breakdown product of dicalcium silicate at temperatures higher than 1020 °C [54–56, 108]. Here, we propose that silicocarnotite can form by the reaction between tricalcium phosphate and wollastonite which yields additional silica:

\[
\text{Ca}_3(\text{PO}_4)_2 + 2\text{CaSiO}_3 \xrightarrow{\text{1050°C}} \text{Ca}_5(\text{PO}_4)_2\text{SiO}_4 + \text{SiO}_2
\]

In fact, silicocarnotite and wollastonite usually occurred together in contact with large quartz grains (Figs. 10 and 12). While the wollastonite concentration decreased, the silicocarnotite content increased. It is possible that newly formed silica reacted with dicalcium silicate and new wollastonite was formed, which is confirmed by the observation that the quartz concentration remained stable (Fig. 12).

In experiment TQC-2, silicocarnotite was first identified at 1150 ± 5 °C after a dwell time of two hours. This observation suggests that a long sintering time can activate the formation of silicocarnotite by the supply of more β-TCP by the decomposition of HAp or that the diffusion of Ca₅(PO₄)₂ into Ca₂SiO₄ appears to be very slow [35]. Quenching, in turn,

| Table 4 Published data on ν₁(PO₄) and ν₁(SiO₄) Raman frequencies of silicocarnotite at room temperature |
|-------------------------------------------------|--------|--------|--------|--------|--------|--------|
| Reference | [45]   | [35]   | [47]   | [53]   | [48]   | This study |
| ν₁(PO₄) [cm⁻¹] | 954    | 964    | 959–963 | 957    | 953    | 950–952 |
| ν₁(SiO₄) [cm⁻¹] | 847    | 854    | 854    | 880    | 845    | 845    |
seems to trigger the nucleation and growth of silicocarnotite. In experiment TQC-3, silicocarnotite was first identified at RT after cooling from $1050 \pm 5 \degree C$, i.e., about $250 \degree C$ below the expected R phase-to-silicocarnotite phase transition. Nurse and co-authors postulated that increasing the dicalcium silicate content in the starting mixture promotes the crystallization of silicocarnotite, which is accompanied by another unknown silicate phase (A phase), at lower temperatures than observed for stoichiometric mixtures [32]. However, no A phase could be identified in our experiments. Moreover, our in situ and in operando experiments show that the formation of silicocarnotite is not only possible above $1450 \degree C$ by the reaction between the high-temperature polymorphs $\alpha'$-Ca$_3$(PO$_4$)$_2$ and $\alpha$-Ca$_2$SiO$_4$, but also at significant lower temperatures (approx. $1050$–$1150 \degree C$) through either a reaction between the high-temperature polymorphs $\beta$-Ca$_3$(PO$_4$)$_2$ and $\alpha'$$_1$-Ca$_2$SiO$_4$ or from the reaction between $\beta$-Ca$_3$(PO$_4$)$_2$ and CaSiO$_3$ with additional formation of quartz.

**Conclusion**

The in situ Raman heating experiments with nano-crystalline HAp and $\beta$-TCP and the TG/DTA measurements gave new insights into the breakdown process of nano-crystalline HAp and the formation of tricalcium phosphate polymorphs, which are summarized in Table 3. The main observations are:

- The Raman spectra from a pressed, non-stoichiometric, nano-crystalline HAp sample show a number of surface-OH bands that, to the best of our knowledge, have not been reported before. Their loss is a stepwise process which is completed at about $570 \degree C$.
- Between $770$ and $850 \pm 1 \degree C$ and $1220$ to $1270 \pm 5 \degree C$, the reconstructive HAp $\rightarrow$ $\beta$-TCP and $\beta$-TCP $\rightarrow$ $\alpha$-TCP transformations, respectively, were observed for this particular sample and heating conditions.
- At a heating rate of $10 \degree C$/min, the onset temperature of the likewise reconstructive $\alpha$ $\rightarrow$ $\alpha'$-TCP transformation was observed at about $1450 \degree C$.
- With the same quenching rate, $\beta$-TCP remained metastable down to RT.

In addition, HT Raman spectra of a natural silicocarnotite sample were recorded for the first time up to $1200 \degree C$ in $50 \degree C$-steps and a heating rate of $10 \degree C$ per minute. This experiment revealed, for instance, that the position of the v$_1$(PO$_4$) band shifted from $951 \pm 1 \text{cm}^{-1}$ to approx. $930 \text{cm}^{-1}$ at $1200 \pm 1 \degree C$. The HT Raman spectra were also used to identify silicocarnotite in experiments in the ternary system Ca$_{10}$(PO$_4$)$_6$(OH)$_2$-SiO$_2$-CaO, which gave additional information about solid-state silica-/calcium phosphate reactions:

- In these experiments, the nano-crystalline HAp decomposed at higher temperatures ($960 \pm 5$–$1050 \pm 5 \degree C$), indicating that quartz and/or lime stabilize HAp during firing. Considering also literature data [28–31, 105], it appears that the stability of HAp strongly depends on its stoichiometry and associated structural disorder, the surrounding phase assemblage, and the heating and cooling paths.
- The in situ formation of silicocarnotite was observed after a dwell time of two hours in direct contact to $\alpha'$$_1$-Ca$_2$SiO$_4$ grains located within the initially nano-crystalline HAp/$\beta$-TCP matrix.
- During quenching, silicocarnotite was first identified at RT after cooling from $1050 \pm 5 \degree C$, i.e., about $250 \degree C$ below the previously observed R phase-to-silicocarnotite phase transition zone.
- Silicocarnotite crystallized in the temperature range between $1050$ and $1150 \degree C$, either from the reaction between $\beta$-Ca$_3$(PO$_4$)$_2$ and $\alpha'$$_1$-Ca$_2$SiO$_4$ or from the reaction between $\beta$-Ca$_3$(PO$_4$)$_2$ and CaSiO$_3$, which additionally involve the formation of quartz.

In conclusion, hyperspectral in situ Raman imaging is a unique tool to study high-temperature solid-state reactions in multi-component systems in situ and in operando, i.e., while the solid-state reactions are running, so the sample does not need to be quenched to RT before further investigations. In situ Raman imaging of HT reactions also offers the possibility to systematically investigate the influence of heating and cooling cycles on textural and mineralogical re-equilibration with only one single experiment and by analyzing the very same sample.
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Data availability

RT/HT Raman data are available to readers by contacting the corresponding author.

Declarations

Conflicts of interest  The authors declare no conflict of interest.

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Appendix

See Table 5.

Table 5  Observed (Raman shift), widths, given as a full width at half maximum (FWHM) and intensity ratios between the $v_1(PO_4)$ and the $v_1(SiO_4)$ modes of the silicocarnotite sample. The normalized intensity ratio of the $v_1(PO_4)$ band to the $v_1(SO_4)$ band is also given.

| $T$ (°C) | $v_1(PO_4)$ (cm$^{-1}$) | FWHM $v_1(PO_4)$ (cm$^{-1}$) | $v_1(SiO_4)$ (cm$^{-1}$) | FWHM $v_1(SiO_4)$ (cm$^{-1}$) | $v_1(PO_4)/v_1(SiO_4)$ | $v_1(PO_4)/v_1(SO_4)$ |
|----------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 30       | 950.3           | 12.1            | 843.4           | 19.1            | 5.1             | 9.7             |
| 100      | 949.4           | 12.8            | 843.2           | 17.3            | 5.4             | 9.6             |
| 150      | 948.6           | 14.0            | 842.2           | 20.7            | 5.0             | 9.0             |
| 250      | 947.9           | 14.9            | 841.1           | 19.8            | 5.6             | 7.7             |
| 300      | 946.8           | 16.2            | 840.2           | 20.9            | 5.2             | 8.2             |
| 350      | 945.9           | 16.6            | 838.7           | 21.2            | 5.3             | 7.3             |
| 400      | 945.2           | 17.3            | 838.2           | 19.1            | 5.6             | 6.5             |
| 450      | 944.7           | 18.8            | 837.7           | 23.1            | 5.5             | 7.3             |
| 500      | 944.0           | 20.6            | 837.1           | 27.1            | 4.8             | 7.6             |
| 550      | 943.0           | 20.9            | 837.0           | 28.6            | 4.4             | 5.4             |
| 600      | 942.0           | 21.8            | 835.3           | 27.2            | 4.7             | 6.7             |
| 650      | 940.6           | 22.2            | 835.0           | 28.3            | 4.5             | 6.2             |
| 700      | 939.4           | 21.1            | 834.8           | 26.9            | 4.5             | 6.1             |
| 750      | 938.5           | 22.2            | 834.5           | 27.3            | 4.6             | 5.5             |
| 800      | 937.9           | 23.4            | 833.4           | 31.5            | 4.3             | 5.7             |
| 850      | 936.8           | 24.3            | 832.6           | 31.2            | 4.1             | 6.5             |
Table 5 continued

| $T$ (°C) | $v_1$(PO$_4$) (cm$^{-1}$) | FWHM | $v_1$(PO$_4$) (cm$^{-1}$) | FWHM | $v_1$(SiO$_4$) (cm$^{-1}$) | FWHM | $v_1$(SiO$_4$) (cm$^{-1}$) | Intensity ratio | Intensity ratio (norm.) | $v_1$(PO$_4$)/$v_1$(SO$_4$) |
|---------|-------------------------|-------|-------------------------|-------|-------------------------|-------|-------------------------|---------------|----------------------------|----------------------|
| 900     | 936.3                   | 24.6  | 831.9                   | 31.7  | 4.4                     | 7.5   |                         |               |                            |                      |
| 950     | 935.6                   | 26.3  | 830.9                   | 29.1  | 4.4                     | 6.8   |                         |               |                            |                      |
| 1000    | 934.5                   | 26.0  | 830.6                   | 34.6  | 4.2                     | 5.9   |                         |               |                            |                      |
| 1050    | 934.2                   | 28.8  | 829.6                   | 31.0  | 4.5                     | 3.9   |                         |               |                            |                      |
| 1150    | 930.9                   | 29.6  | 826.9                   | 38.4  | 4.6                     | 0     |                         |               |                            |                      |
| 1200    | 929.8                   | 30.9  | 824.5                   | 45.6  | 3.4                     | 0     |                         |               |                            |                      |

$\frac{\delta v}{\delta T} = -0.0127, \frac{\delta \text{FWHM}}{\delta T} = 0.0156, \frac{\delta v}{\delta T} = -0.0104, \frac{\delta \text{FWHM}}{\delta T} = 0.0186, r^2 > 0.99, r^2 > 0.98, r^2 > 0.98, r^2 > 0.85$

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