Supporting Information

Chemo-mineralogical changes in six European monumental stones caused by cyclic isothermal treatment at 600 °C

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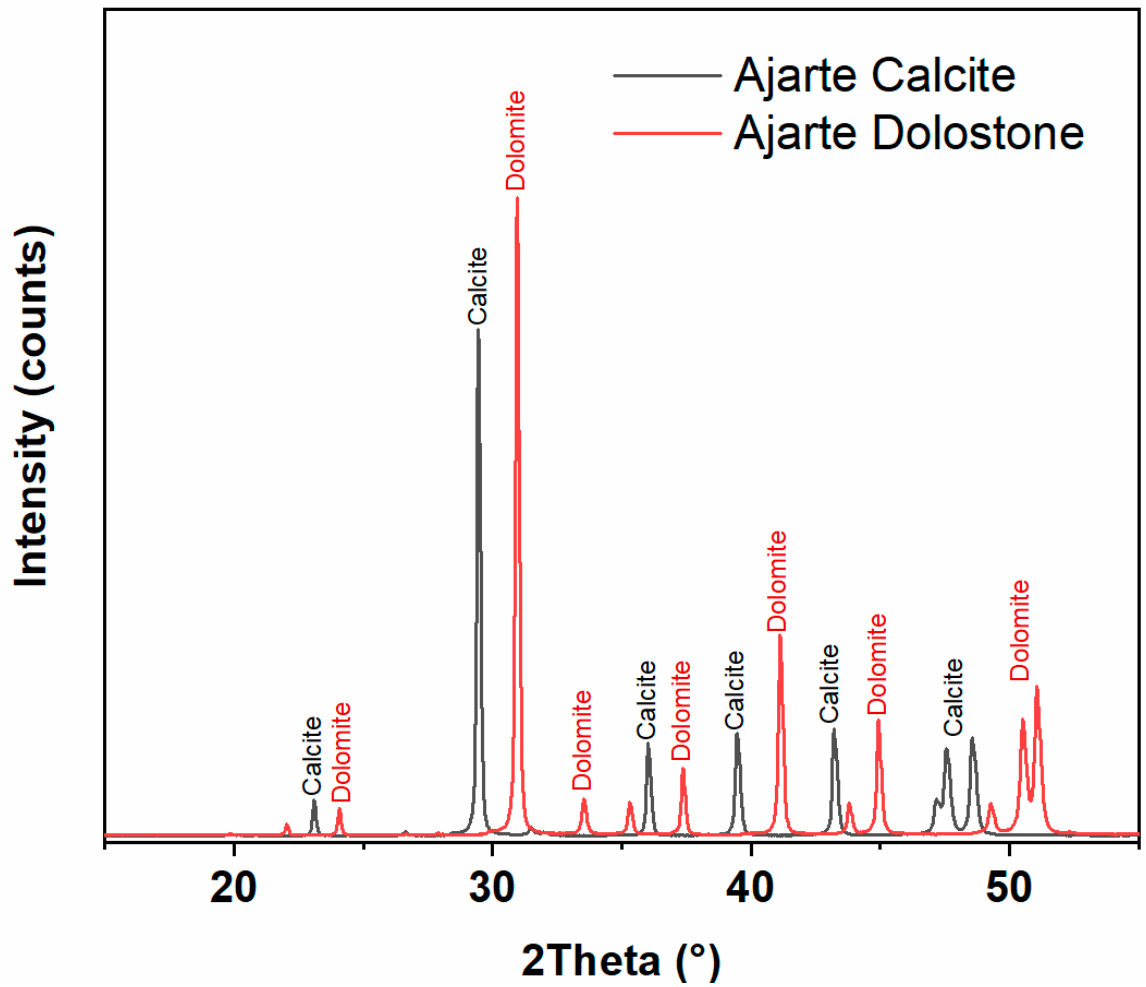


Figure S1. Mineralogical difference as analysed by XRD between Ajarte Calcite (black reflexes) and Ajarte Dolostone (red reflexes), two stone varieties quarried in the same quarry.

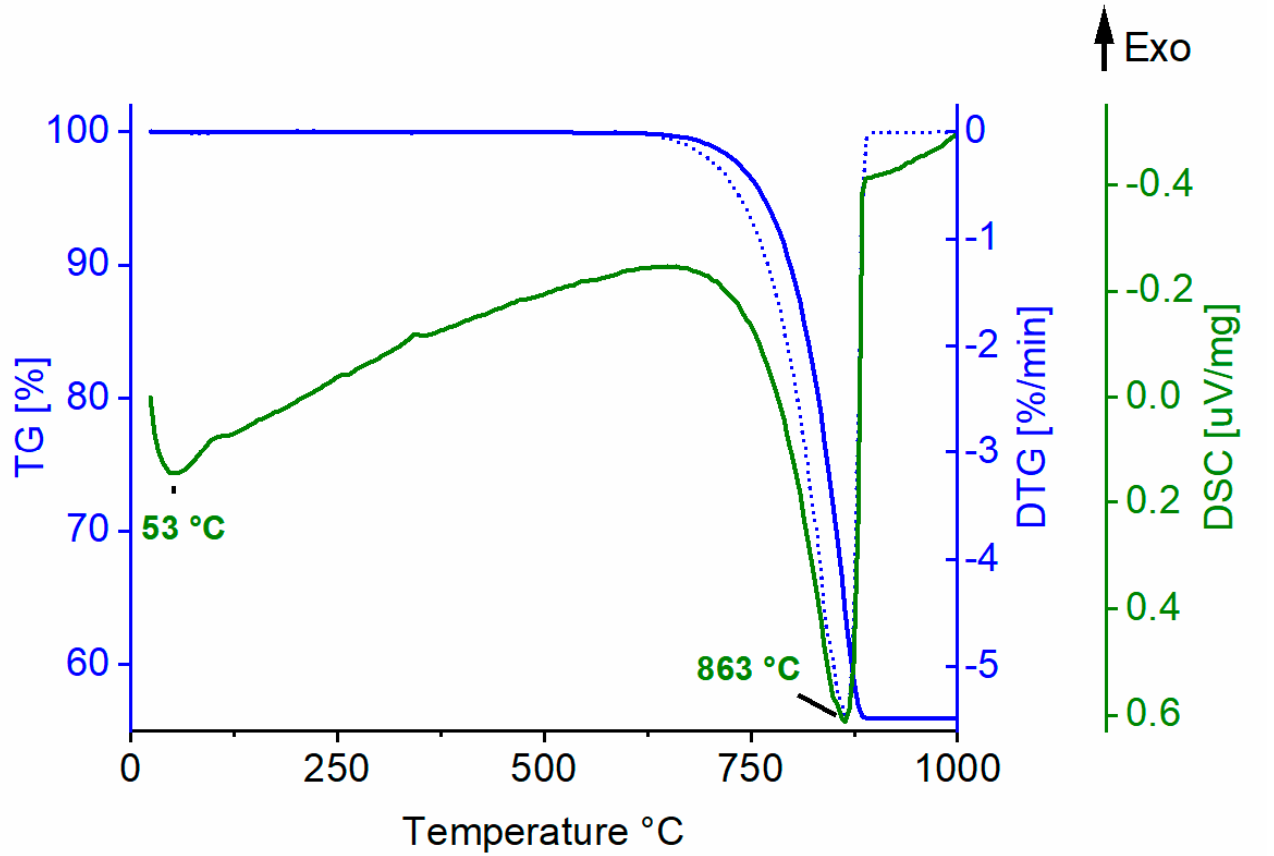


Figure S2. Simultaneous thermal analysis of Apuan Marble.

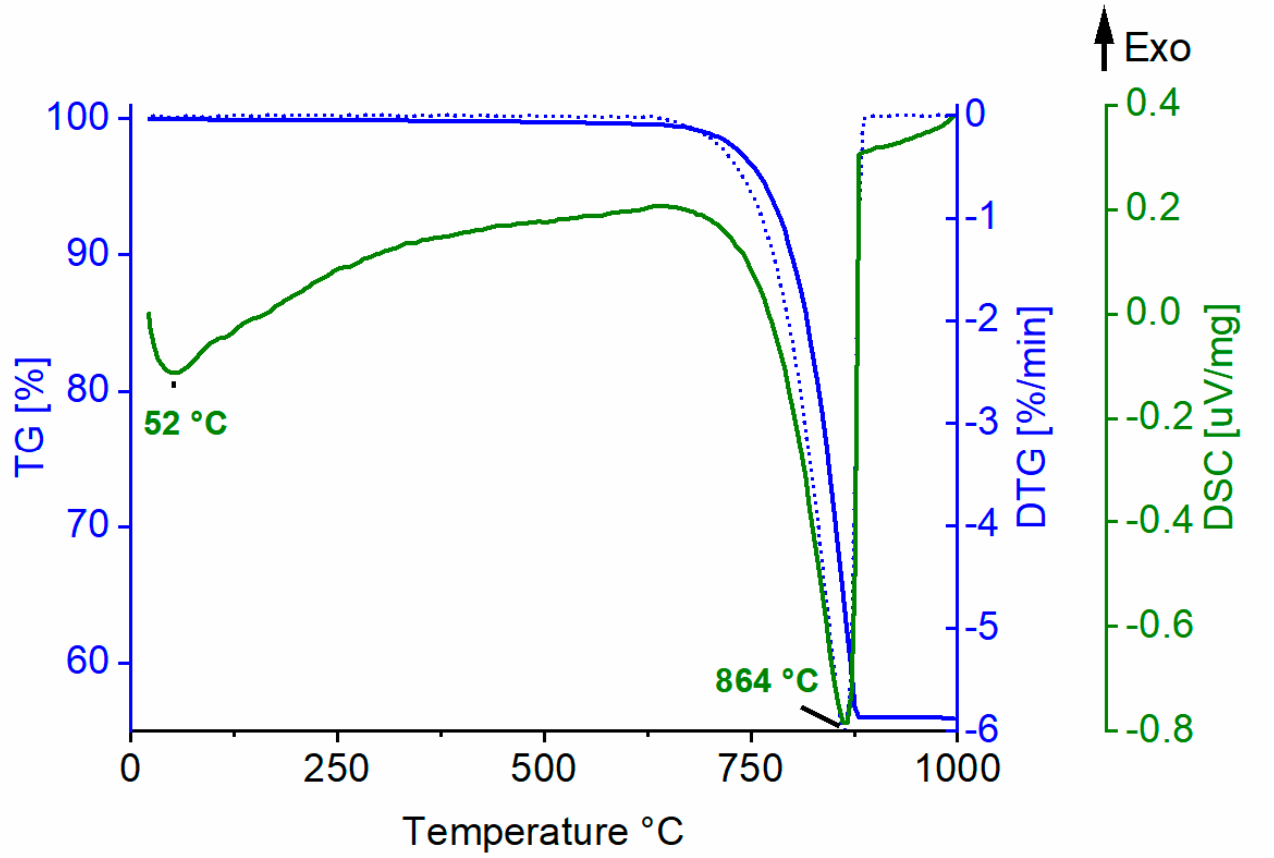


Figure S3. Simultaneous thermal analysis of St. Margarethen.

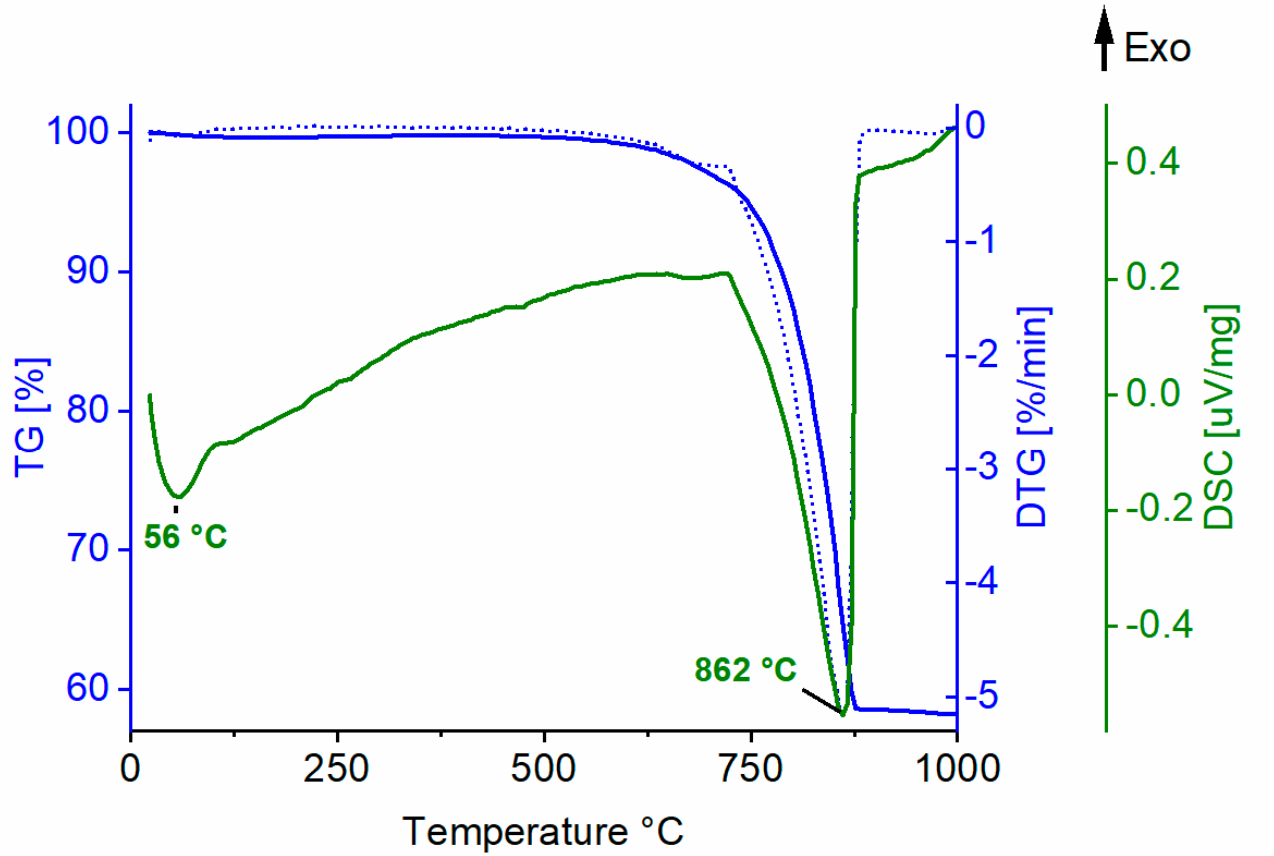


Figure S4. Simultaneous thermal analysis of Ajarte Calcite.

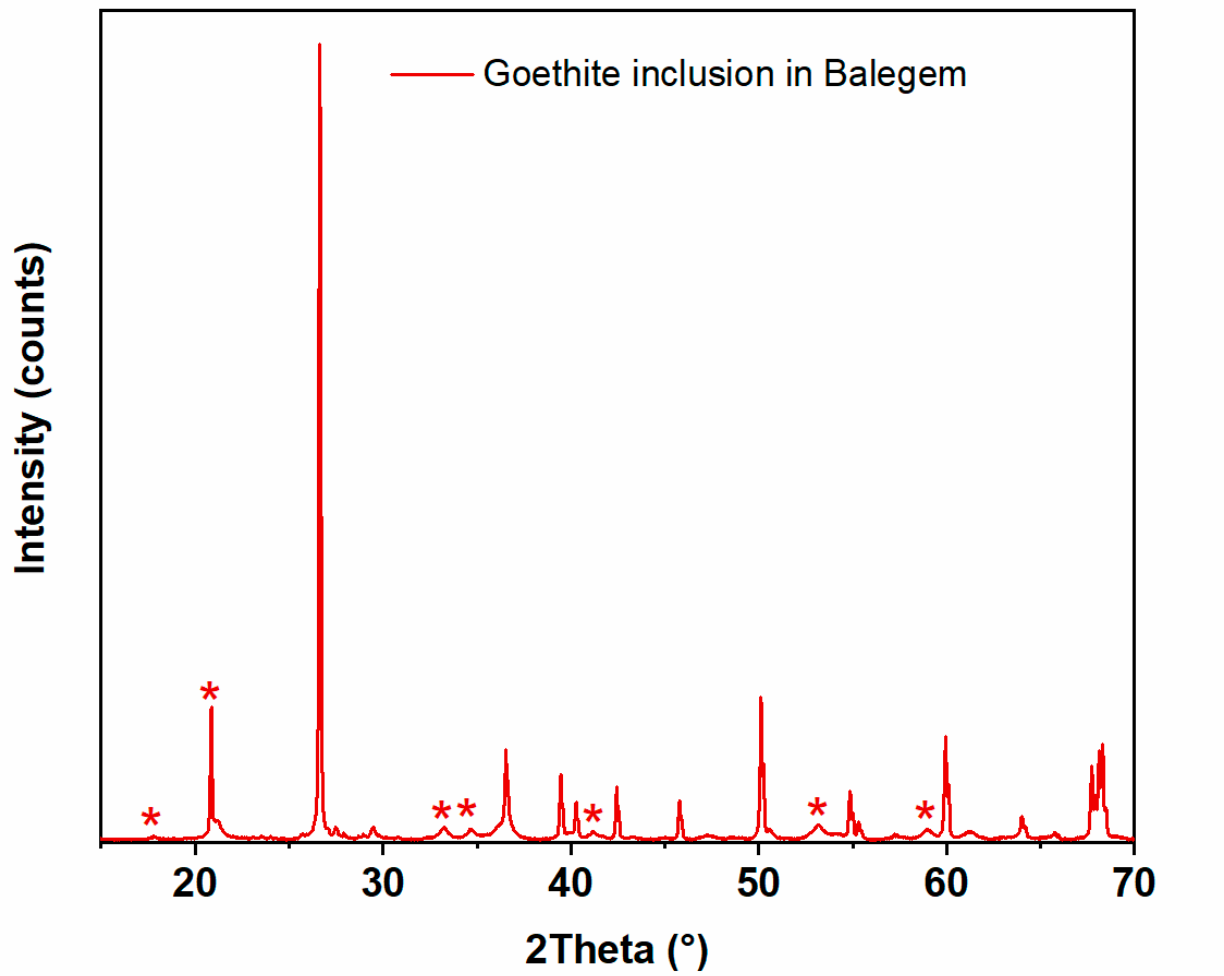


Figure S5. XRD diffractogram of goethite stone inclusion in a specimen of Balegem. Main Goethite reflexes are marked with asterisk symbols, while remaining reflexes belong to phases present in Balegem.

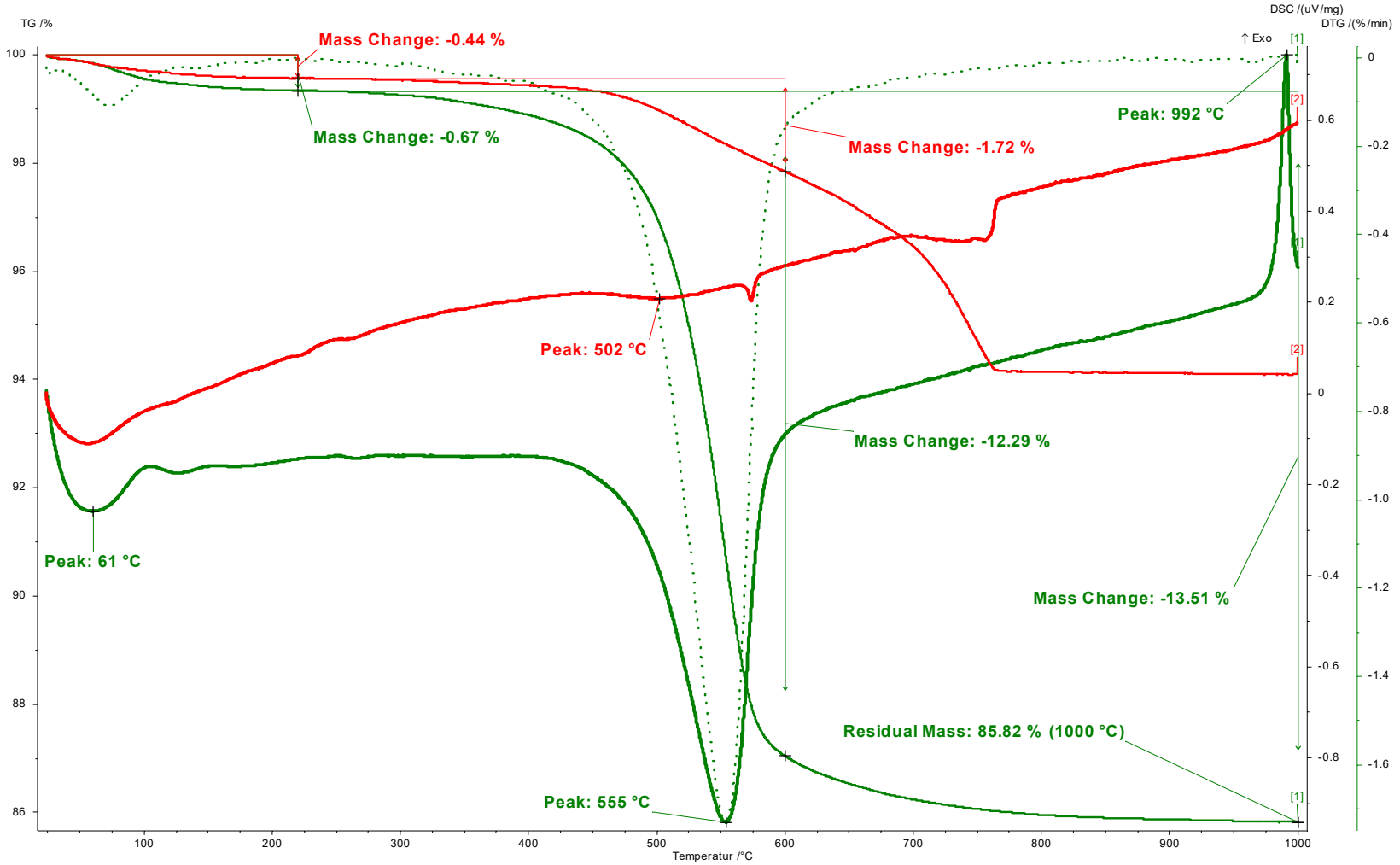


Figure S6. Comparison between Schlaitdorf (red curves) and KGa-2 Kaolinite (green curves) as analysed with simultaneous thermal analysis.

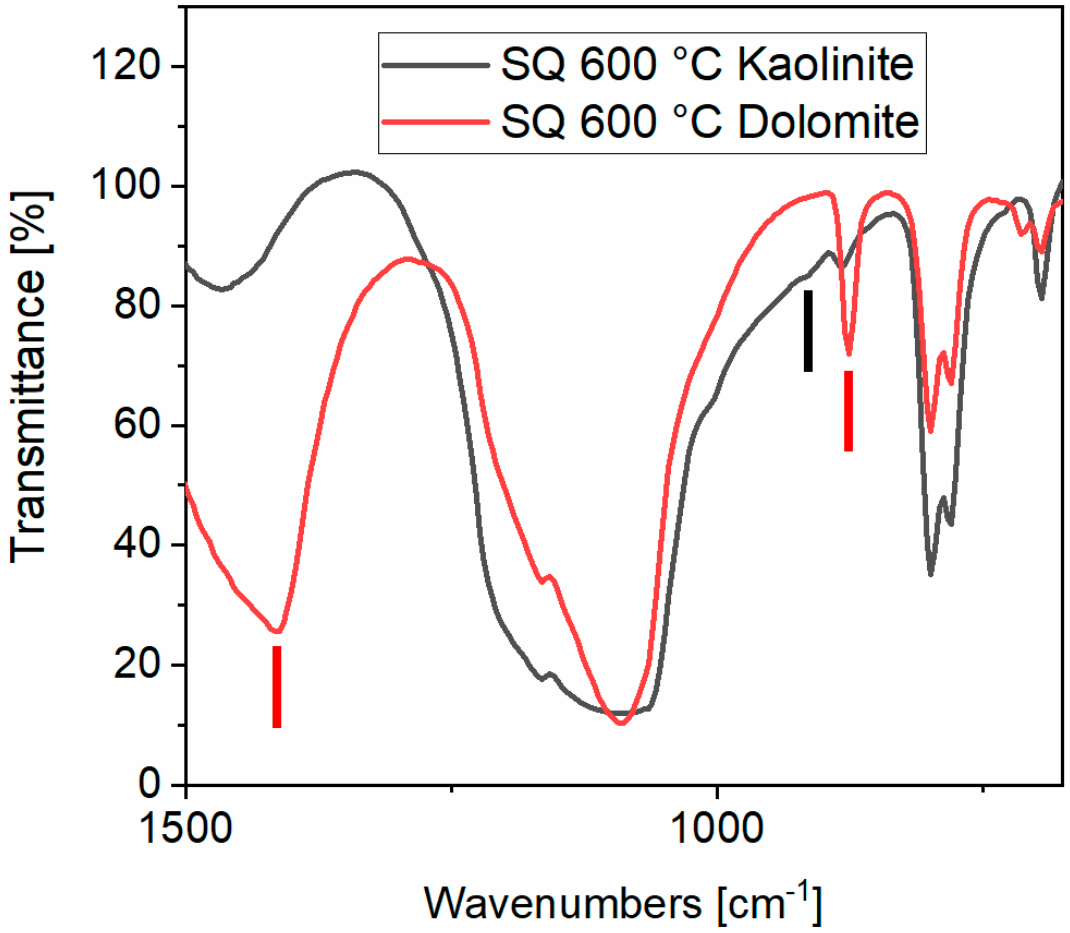


Figure S7a. Schlaitdorf analysed by means of Fourier-transform infrared spectroscopy after cycling isothermal treatment at 600°C. The 913 cm^{-1} shoulder marked with a black line indicates the presence of kaolinite, while the red marked vibrations at 1415 and 875 cm^{-1} implies the presence of dolomite.

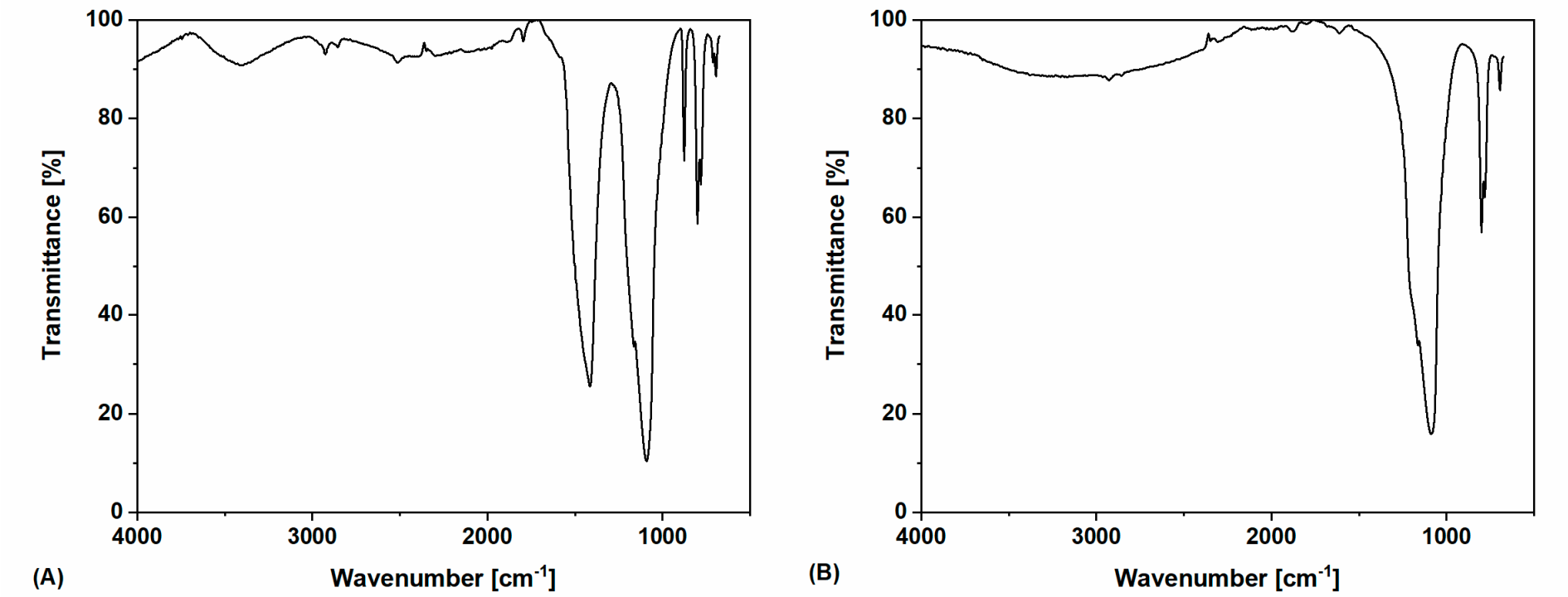


Figure S7b. Fourier-transform infrared spectra of Schlaitdorf after 10h of isothermal treatment at 600°C exhibiting a presence of dolomite (**a**) and no presence of dolomite nor kaolinite (**b**)

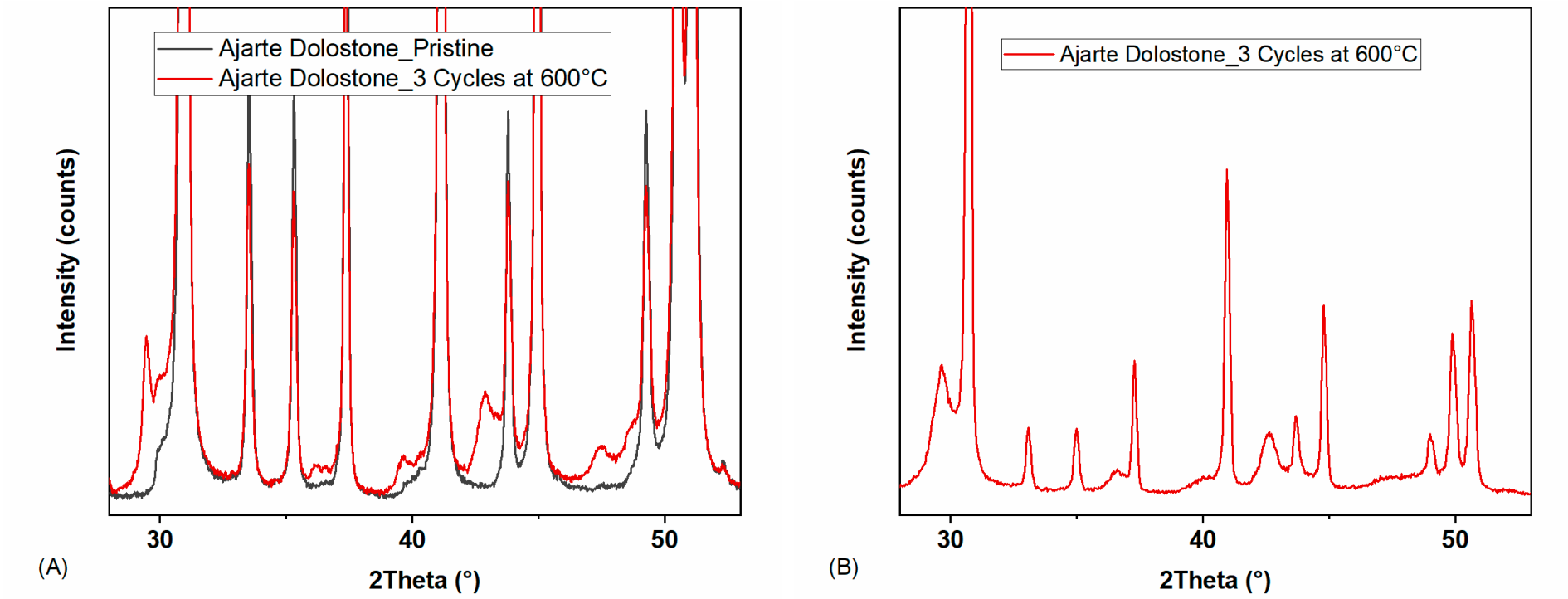


Figure S8. XRD diffractogram of (**a**) Ajarte Dolostone collected before (black reflexes) and after cyclic isothermal treatment at 600°C (red reflexes) and (**b**) same stone vareity as analysed with in-situ XRD after the 3rd cycle of isothermal treatment at 600°C. Please note that within the latter diffractogram some crystal planes have more or less intensity as the samples are in solid form and not grinded finely as it is usual for powdered XRD analysis. According to Rietveld refinement the phases present after three cycles at isothermal treatment at 600°C amount to: Dolomite 63 %, Calcium Magnesium Carbonate 27 % and Magnesium Oxide 10 %.

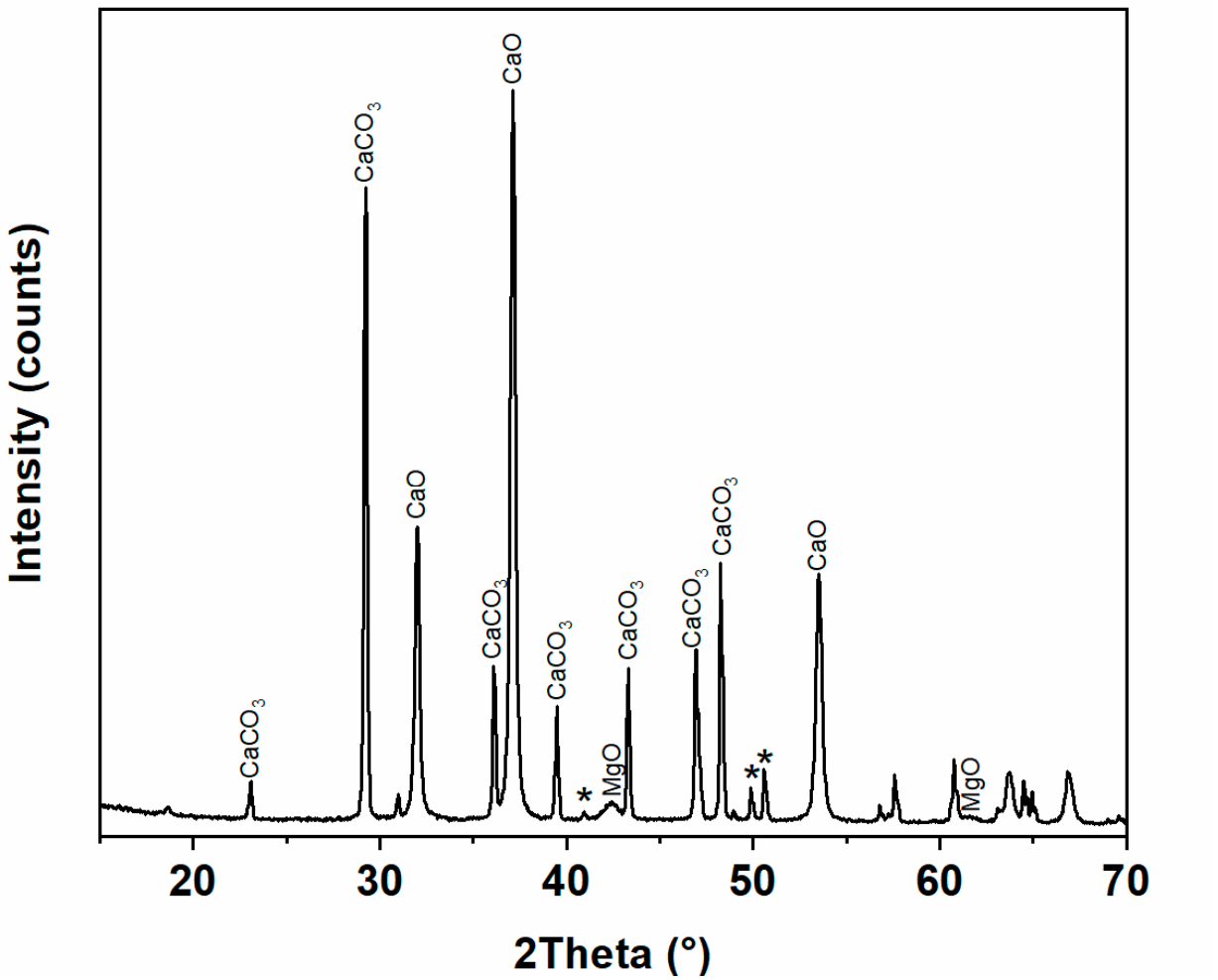


Figure S9. XRD diffractogram of the dolomite vein on Apuan Marble after cyclic isothermal treatment at 600°C. Main phases are indicated by chemical formula while the remaining dolomite is marked with asterisk symbols. According to Rietveld refinement the phases present after three cycles at isothermal treatment at 600°C amount to: Calcite 36.5%, Calcium Oxide 53.2%, Periclase 4.8% and Dolomite 5.5%.

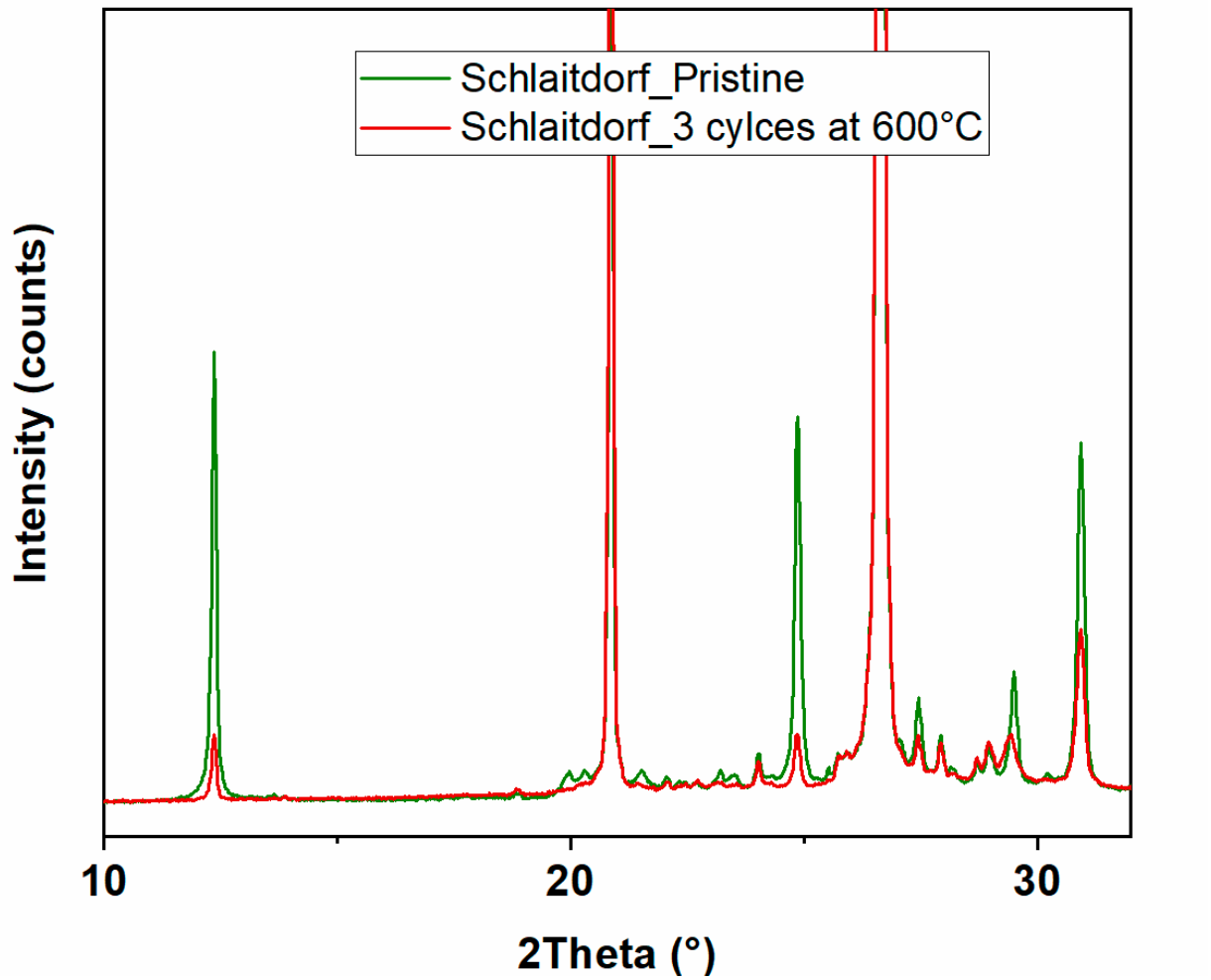


Figure S10. XRD diffractograms of Schlaitdorf as collected before and after isothermal treatment at 600°C. The reduction of kaolinite and dolomite is visible.

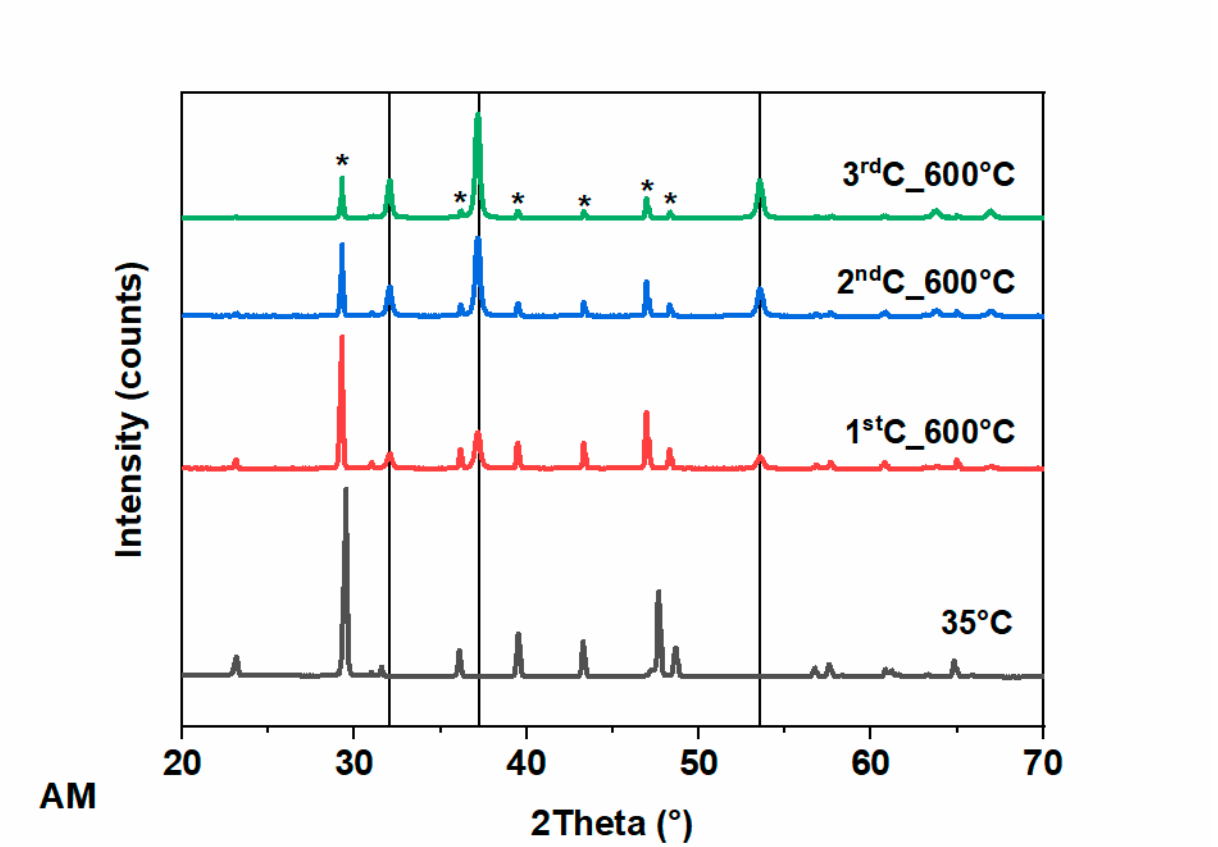


Figure S11. Diffractograms collected at 35°C and the last diffractograms (out of six) collected during the isothermal condition at 600°C per cycle exposed on Apuan Marble. The most prominent reflexes for calcite are indicated with an asterisk while the position of lime´s most prominent reflexes are shown along the line. According to Rietveld refinement the phases present after three cycles at isothermal treatment at 600°C amount to: Calcite 20.3 ±0.35%, Calcium Oxide 78.84 ±0.36% and Periclase 0.86 ±0.15%.

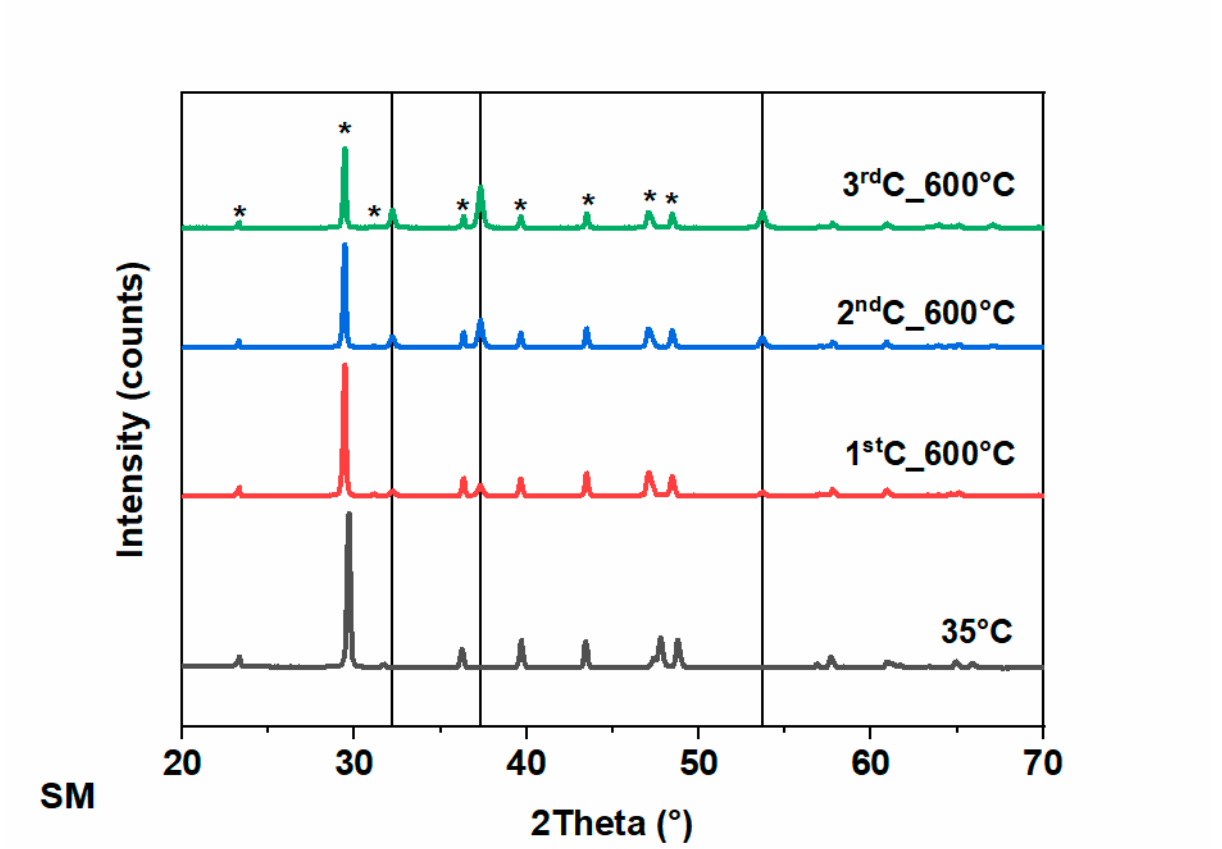


Figure S12. Diffractograms collected at 35°C and the last diffractograms (out of six) collected during the isothermal condition at 600°C per cycle exposed on St. Margarethen. The most prominent reflexes for calcite are indicated with an asterisk while the position of lime´s most prominent reflexes are shown along the line. According to Rietveld refinement the phases present after three cycles at isothermal treatment at 600°C amount to: Calcite 65.05 ±0.26% and Calcium Oxide 34.95 ±0.26%.

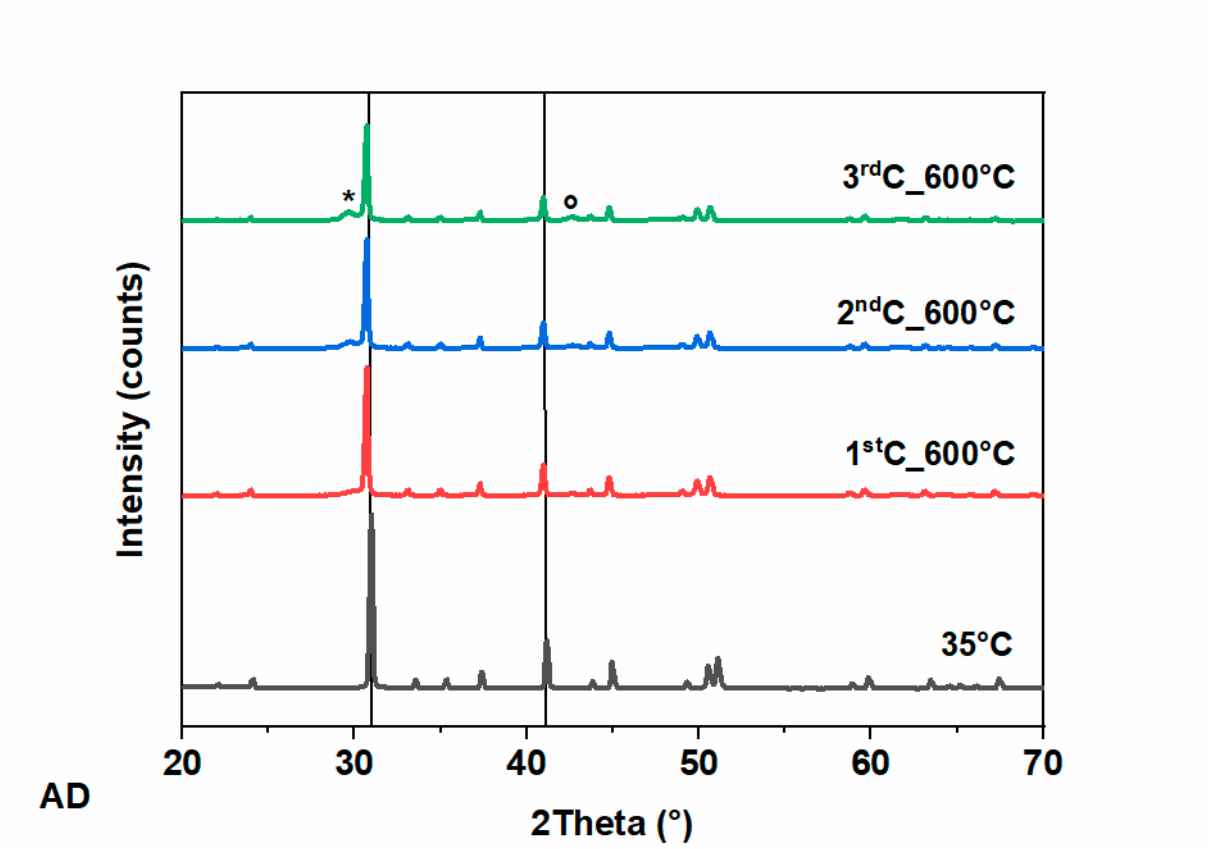


Figure S13. Diffractograms collected at 35°C and the last diffractograms (out of six) collected during the isothermal condition at 600°C per cycle exposed on Ajarte Dolostone. The most prominent reflexes for dolomite are indicated along a line while the asterisk marks a calcium magnesium carbonate phase present as a broad peak next to the dolomite peak (for more detail the reader is referred to Figure S8). A circle indicates the newly formed periclase. According to Rietveld refinement the phases present after three cycles at isothermal treatment at 600°C are: Dolomite 63.8 ±0.1%, Calcium Magnesium Carbonate 26.6 ±0.05% and Periclase 9.5 ±0.05%.

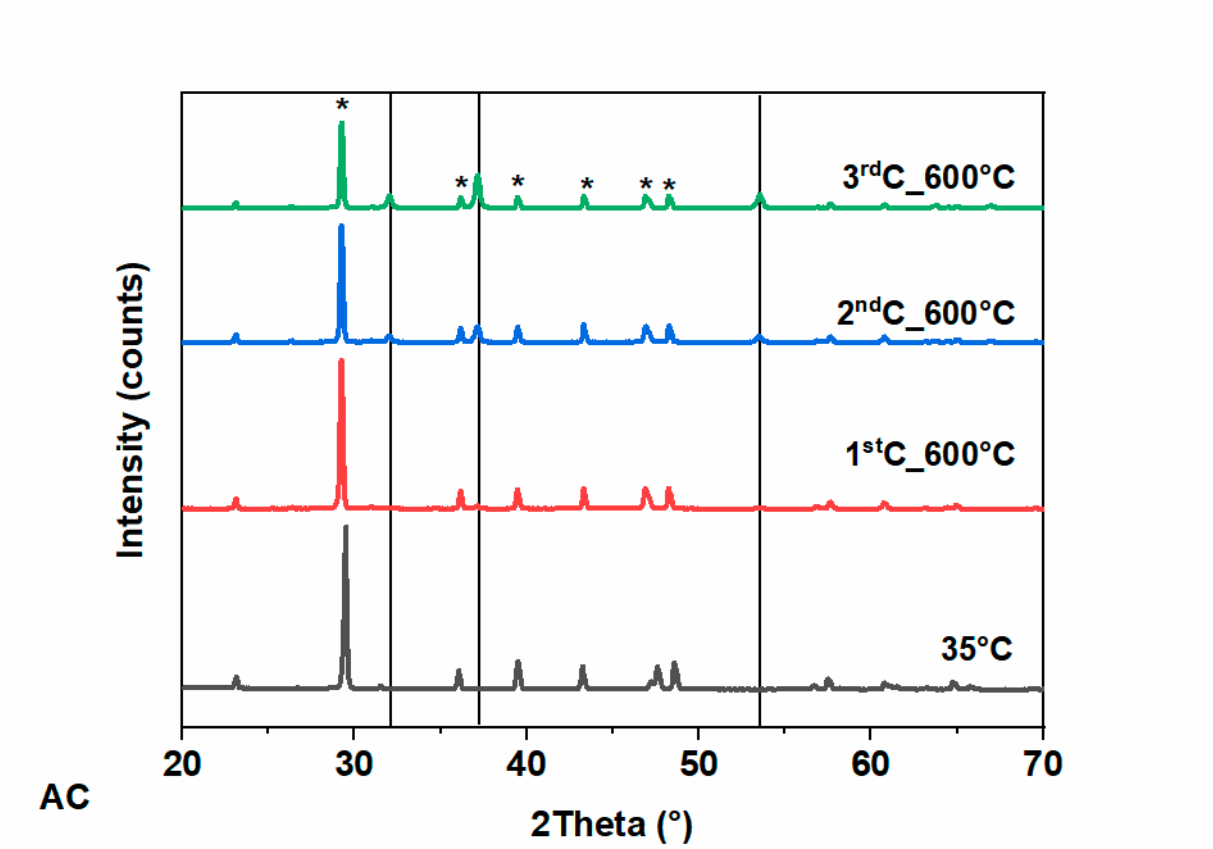


Figure S14. Diffractograms collected at 35°C and the last diffractograms (out of six) collected during the isothermal condition at 600°C per cycle exposed on Ajarte Calcite. The most prominent reflexes for calcite are indicated with an asterisk while the position of lime´s most prominent reflexes are shown along the line. According to Rietveld refinement the phases present after three cycles at isothermal treatment at 600°C are: Calcite 67.02 ±0.25% and Calcium Oxide 32.77 ±0.2%.

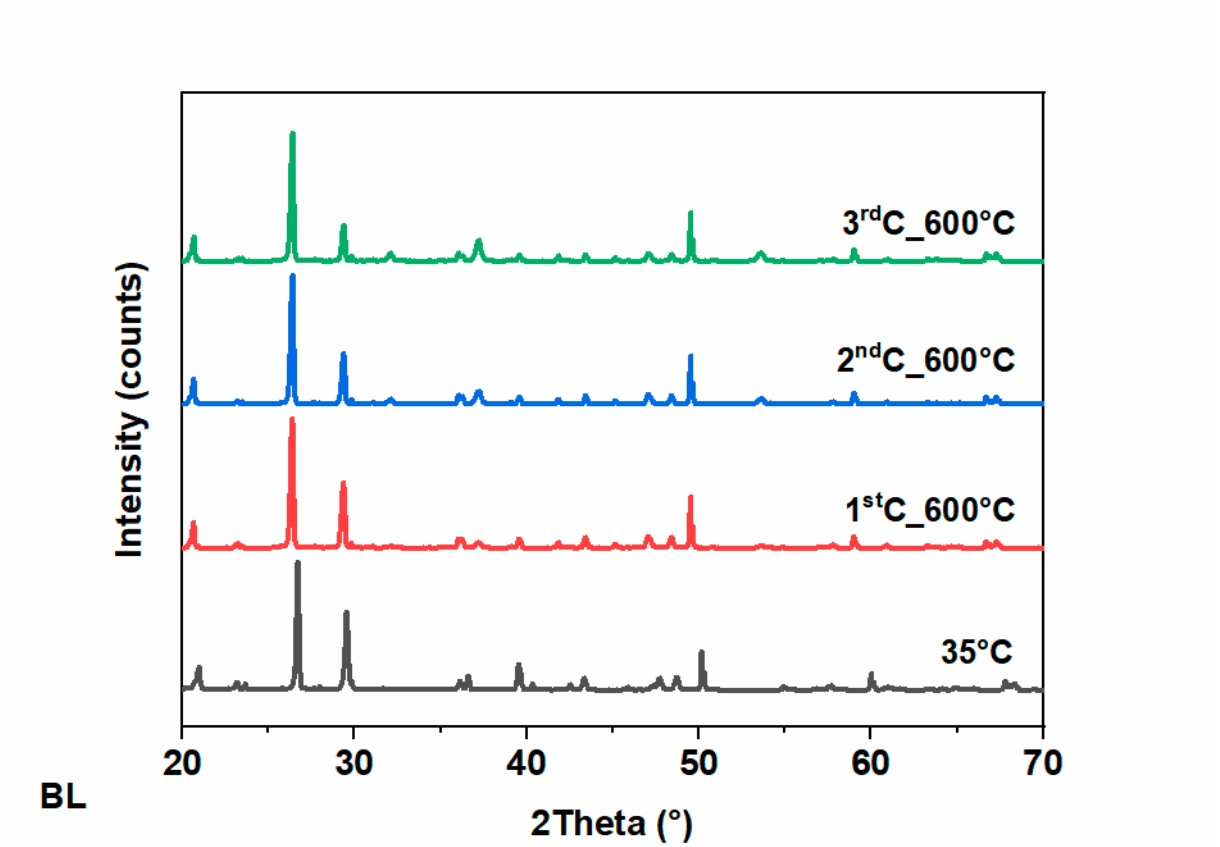


Figure S15. Diffractograms collected at 35°C and the last diffractograms (out of six) collected during the isothermal condition at 600°C per cycle exposed on Balegem. Due to the heterogeneous nature of this lithotype (relevant for fluctuations of the phases caused by thermal expansion of the surface) and the presence of too many phases (e.g., calcite, quartz, potassium feldspar and plagioclase) a reliable Rietveld refinement was not possible.

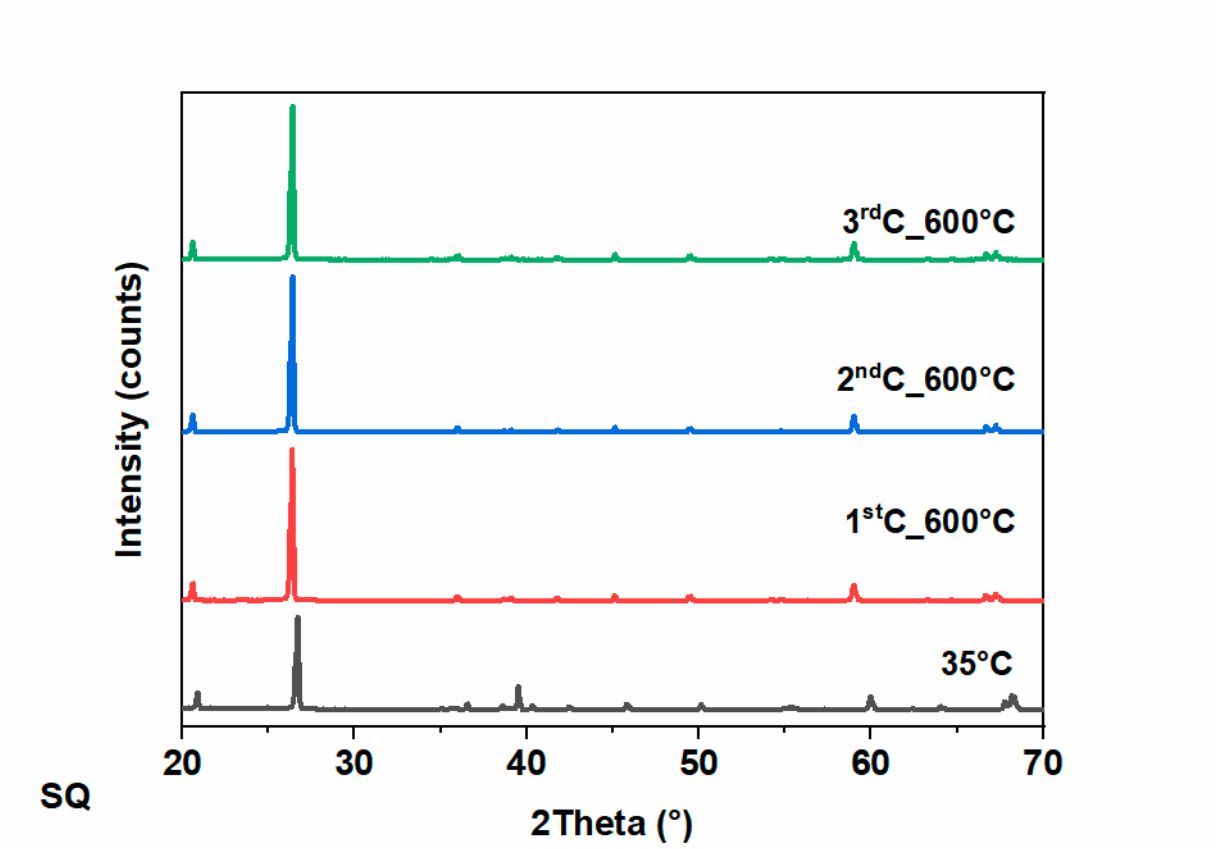


Figure S16. Diffractograms collected at 35°C and the last diffractograms (out of six) collected during the isothermal condition at 600°C per cycle exposed on Schlaitdorf. Merely the quartz inversion is observable. For more details on the reduction of kaolinite and dolomite the reader is referred to Figure S10.

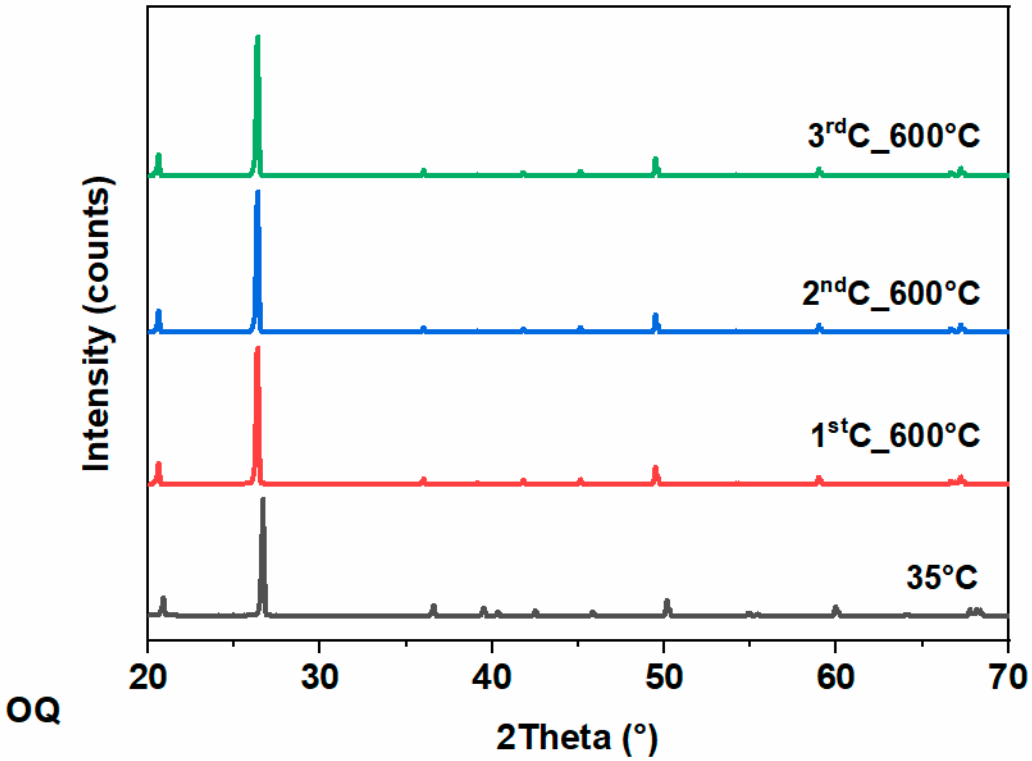
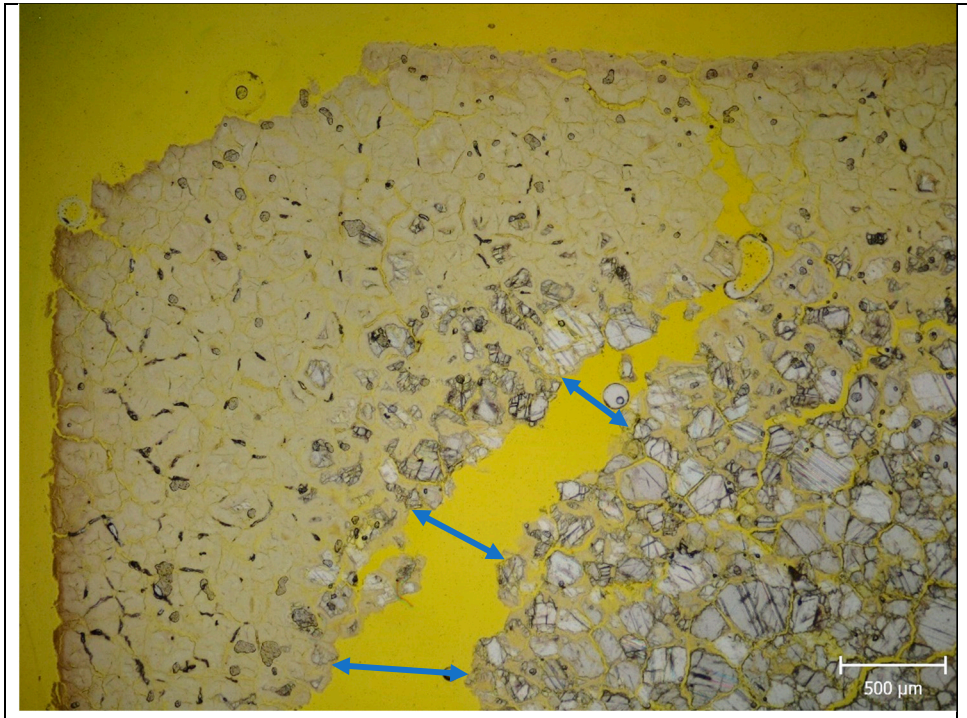
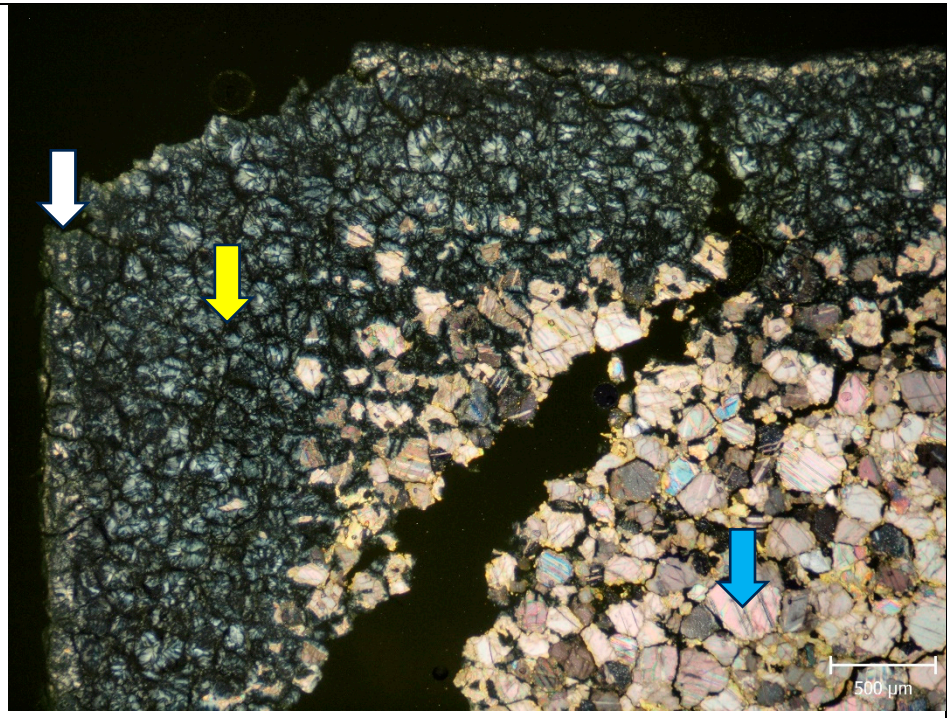


Figure S17. Diffractograms collected at 35°C and the last diffractograms (out of six) collected during the isothermal condition at 600°C per cycle exposed on Obernkirchen. Merely the quartz inversion is observable. Kaolinite is absent on the surface area analysed.



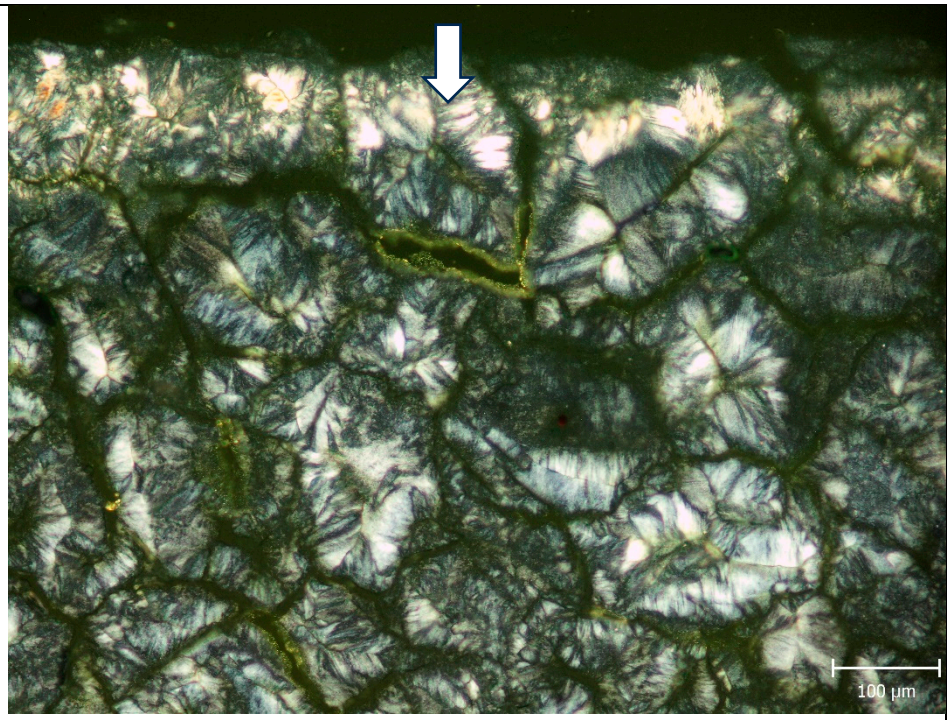
Apuan Marble 900 °C
Larger cracks (blue arrows) are formed due to the differential expansion caused by the thermal decomposition (i.e., calcite to CaO and subsequent hydration to $Ca(OH)_2$) and the volumetric changes involved in these processes (plane-polarized light, PPL).



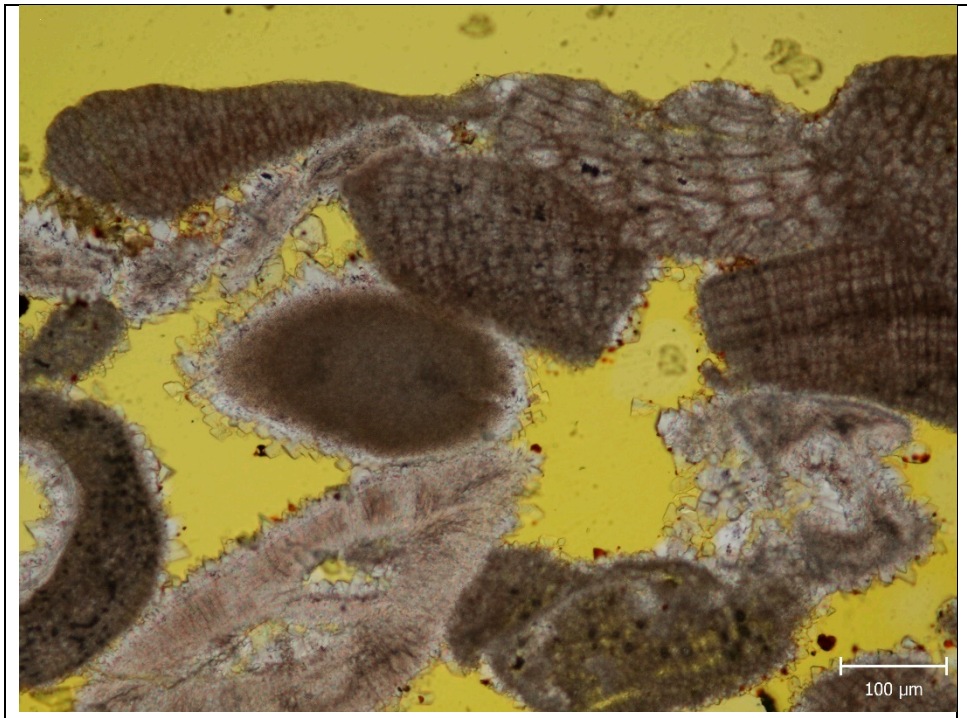
Apuan Marble 900 °C
The initiated hydration and subsequent carbonation is visible in form of a thin surface rim (white arrow) that exhibits higher order of interference colours typical for carbonates at the surface of the specimen. Below there is a thick zone made up of platy $Ca(OH)_2$ (yellow arrow). The third zone displays the "fresh" marble (blue arrow). The micrograph displays well the depth of the thermal decomposition (crossed polars, XPL).



Apuan Marble 900 °C
Detail of the thermally decomposed surface of Apuan Marble. Thermally induced intra- and intergranular microcracks are clearly visible (PPL).



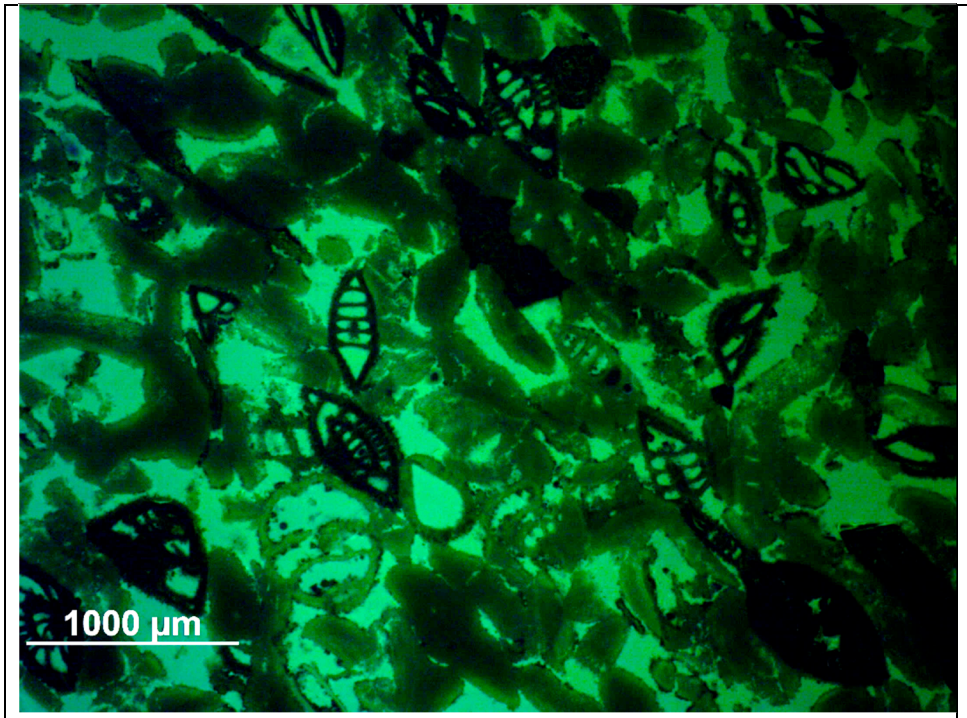
Apuan Marble 900 °C
In the image, the partly carbonated rim (arrow) and below a zone made up of $Ca(OH)_2$ is visible (XPL).



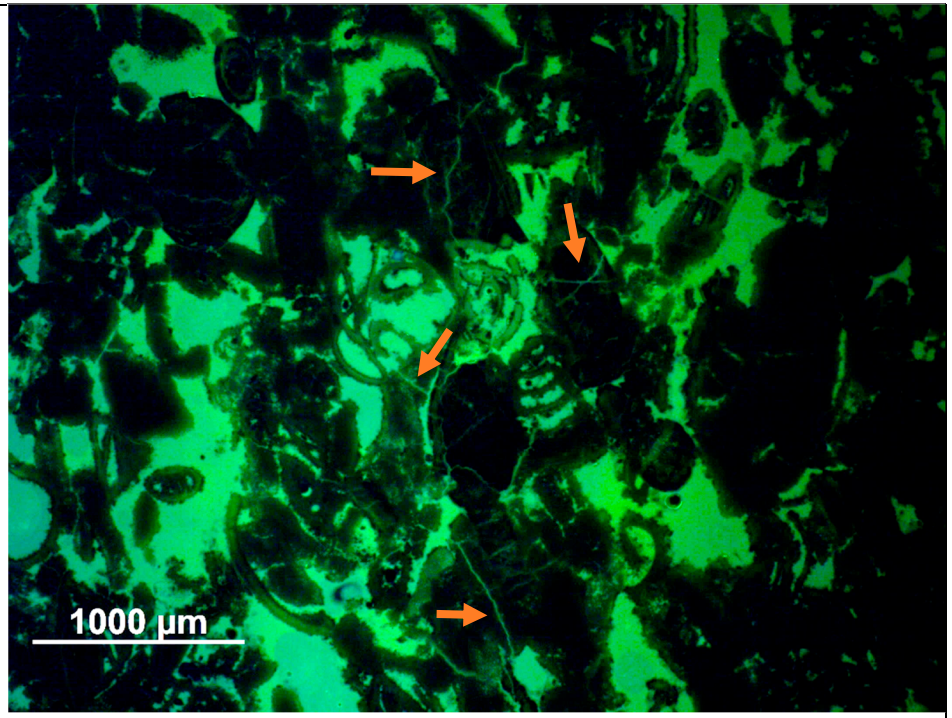
St. Margarethen 600 °C
In part, the surface appears sound and the grain contacts intact (PPL).



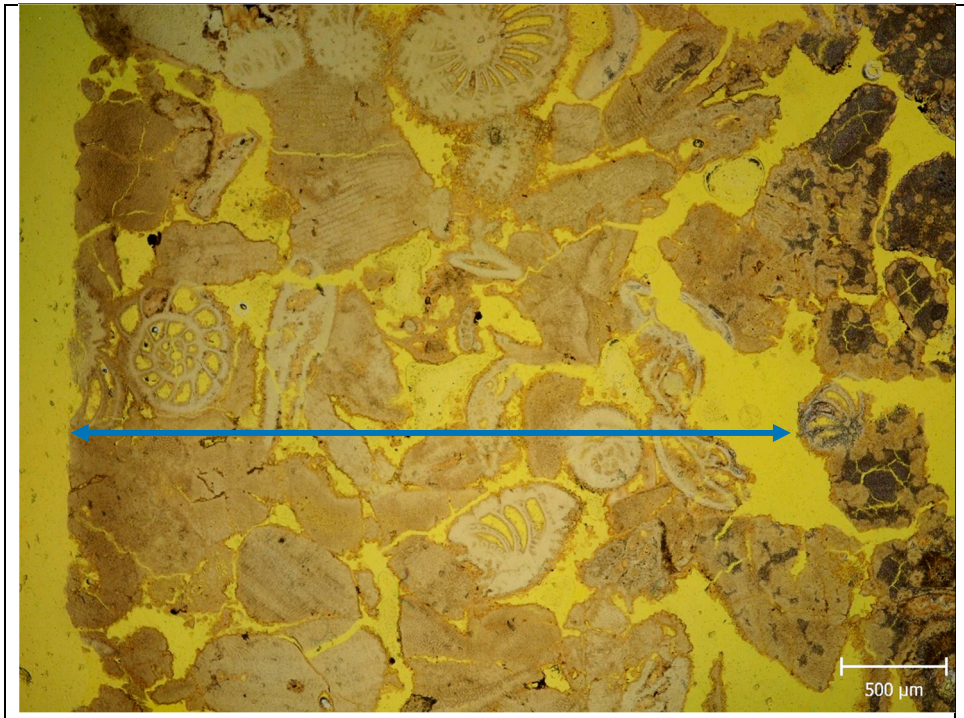
St. Margarethen 600 °C
Intragranular cracks (arrow) are visible in the micro fossils (i.e., forminifera and red algae), along intact grain-contacts.



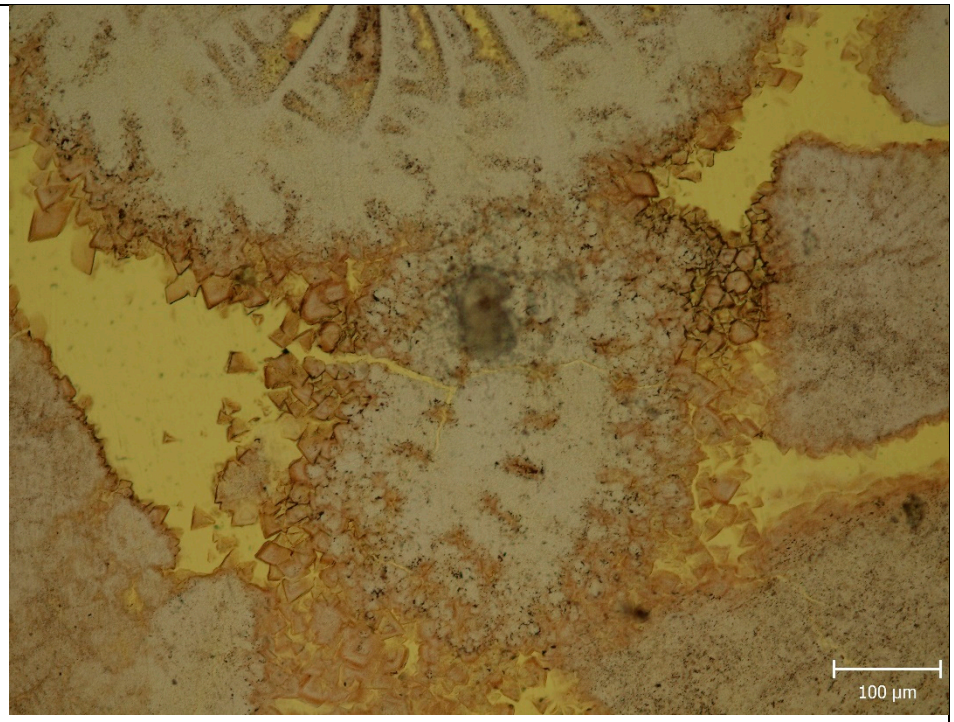
St. Margarethen pristine
Appearance of the St. Margarethen texture under UV-light in pristine condition.



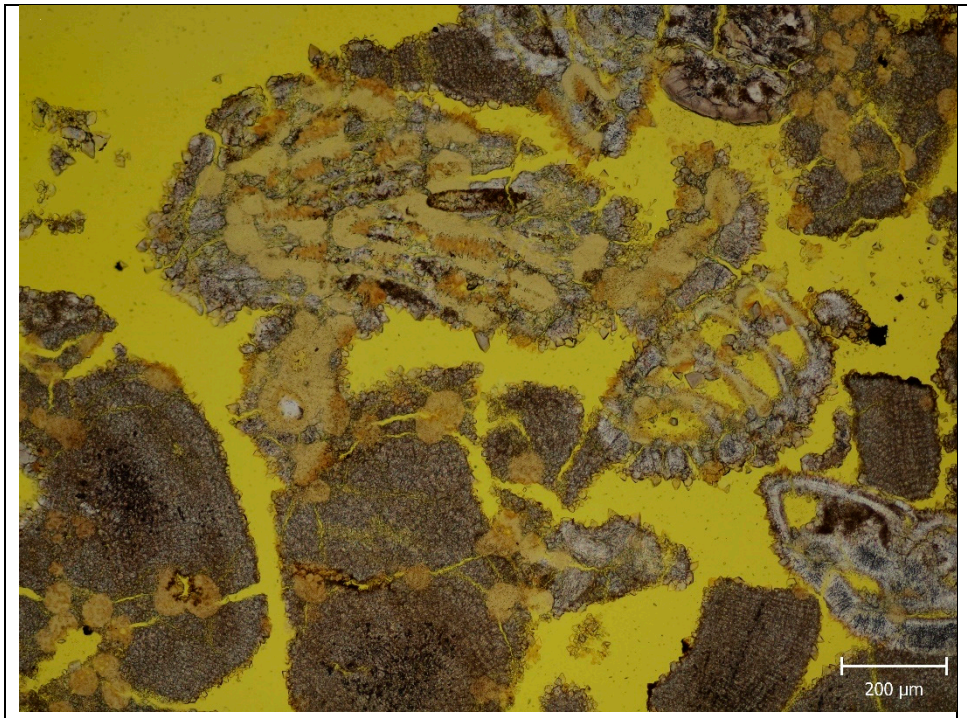
St. Margarethen 600 °C UV
Formation of intragranular microcracks is visible (arrow).



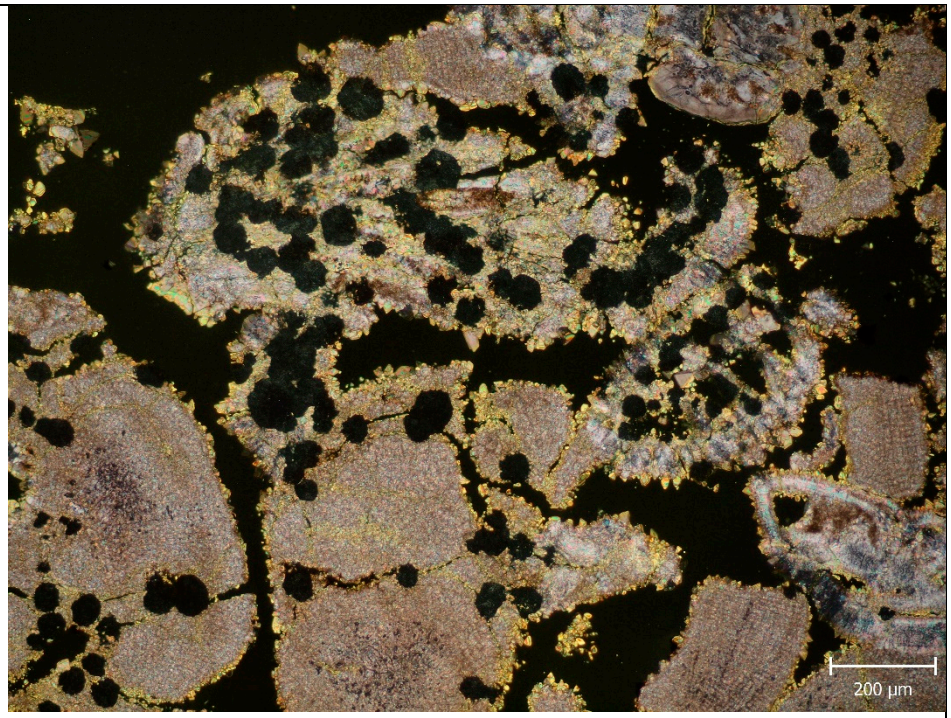
St. Margarethen 900 °C
Heating front is visible (black arrow). The micro texture of the fragments is preserved even after thermally decomposition (PPL).



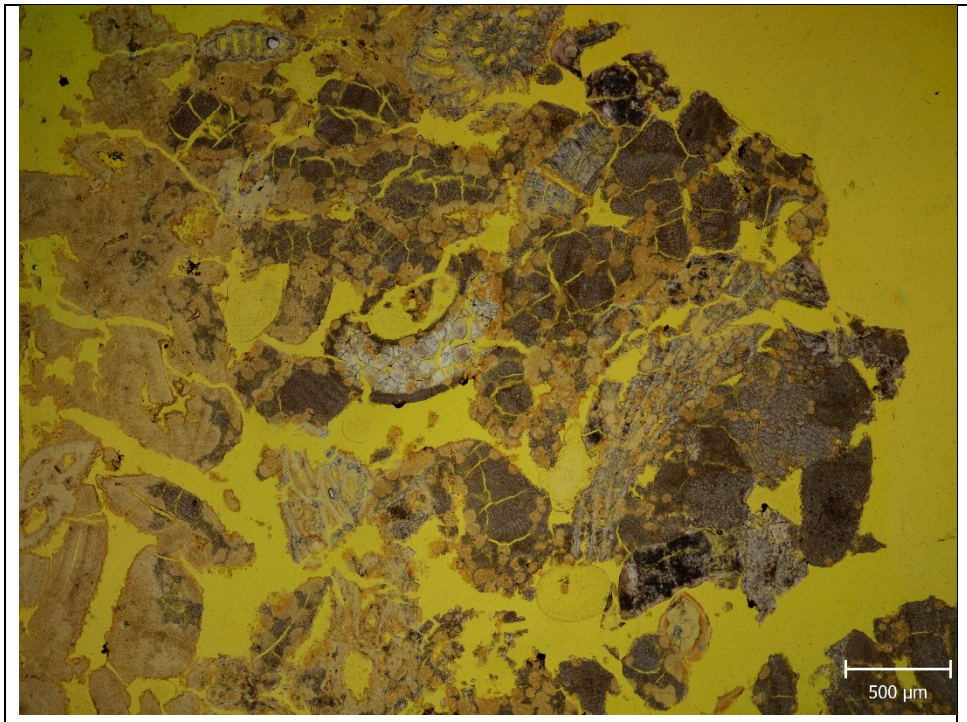
St. Margarethen 900 °C
Detail of the well-preserved shape of the micro fossils and the calcite cement-matrix despite the thermal degradation (PPL).



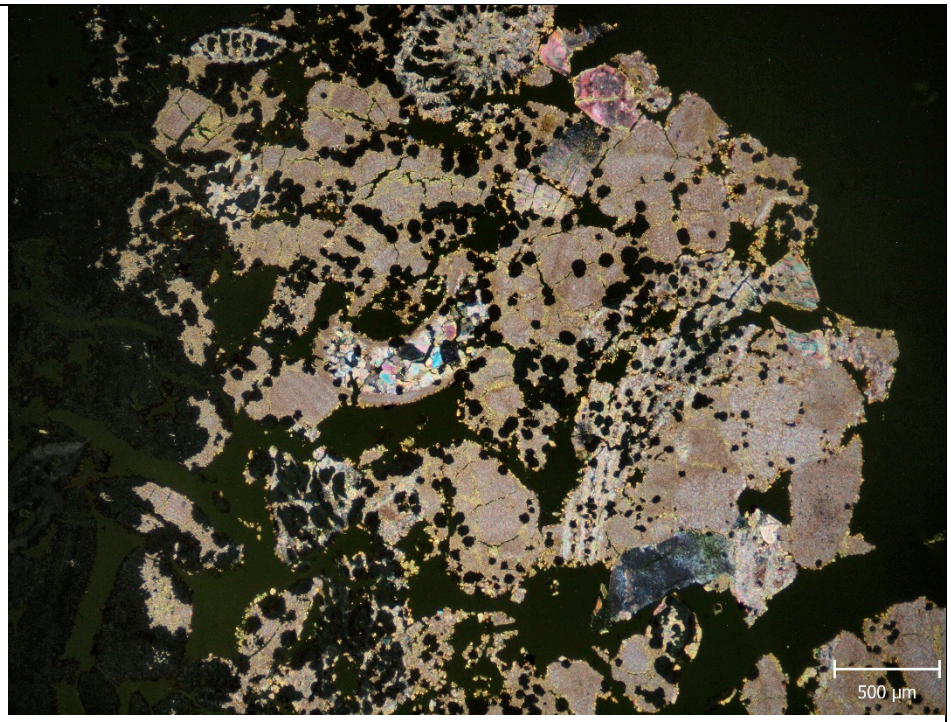
St. Margarethen 900 °C
A thermally induced pitting decomposition in form of round spots is visible. (PPL)



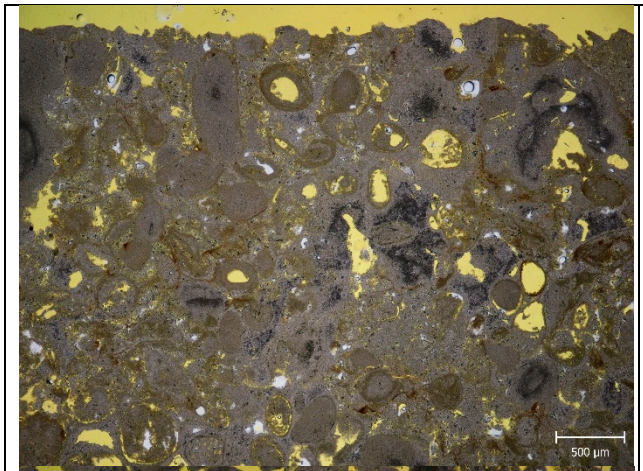
St. Margarethen 900 °C
In the cross-polarised image, the decomposed zones (i.e., spots) of the carbonate material exhibit very low order of interference colour indicating very small grain sizes. (XPL)

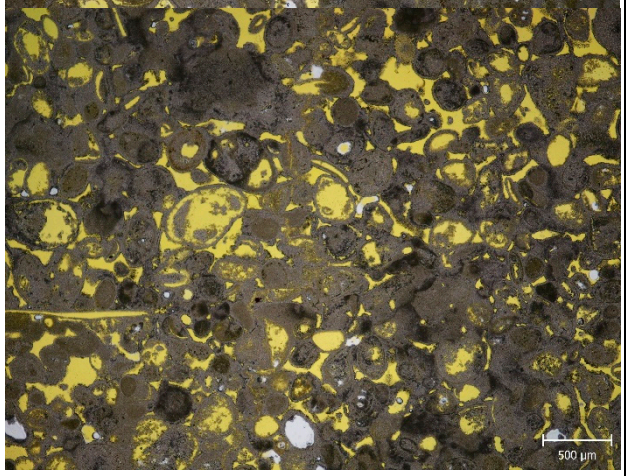


St. Margarethen 900 °C
A thermally induced pitting decomposition in form of round spots is visible. (PPL)

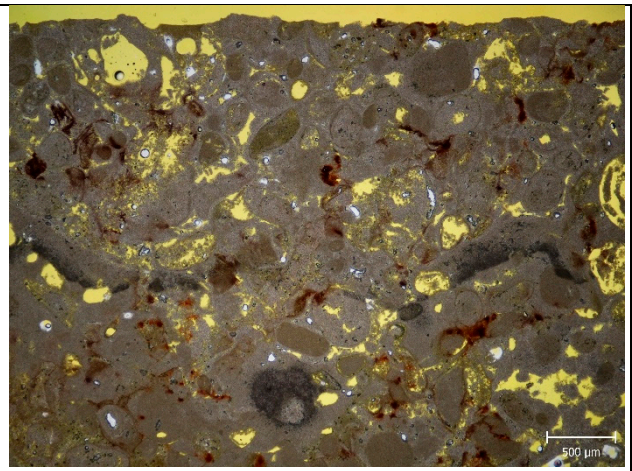


St. Margarethen 900 °C
In the cross-polarised image, the decomposed zones (i.e., spots) of the carbonate material exhibit very low order of interference colour indicating very small grain sizes. (XPL)

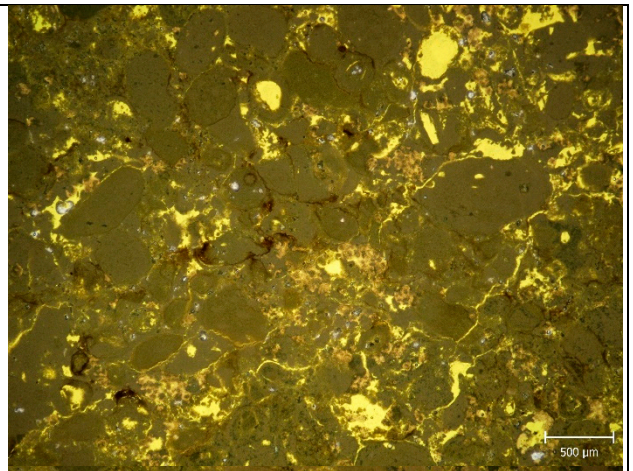


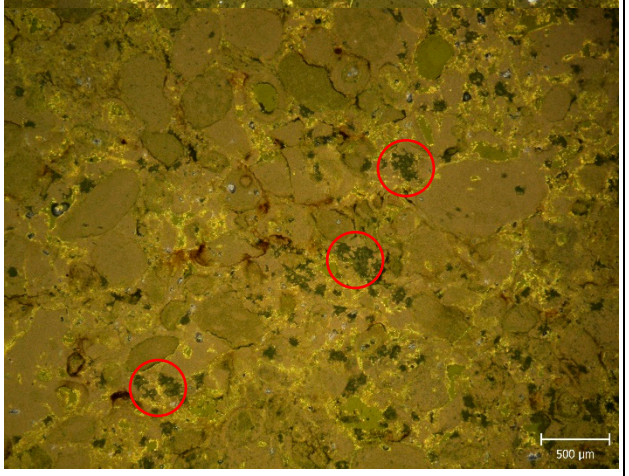


Ajarte Dolostone pristine
Detail of the pristine microstructure with black stains. Picture below shows more porous parts of the stone specimen, where the round ooids are well visible (PPL).

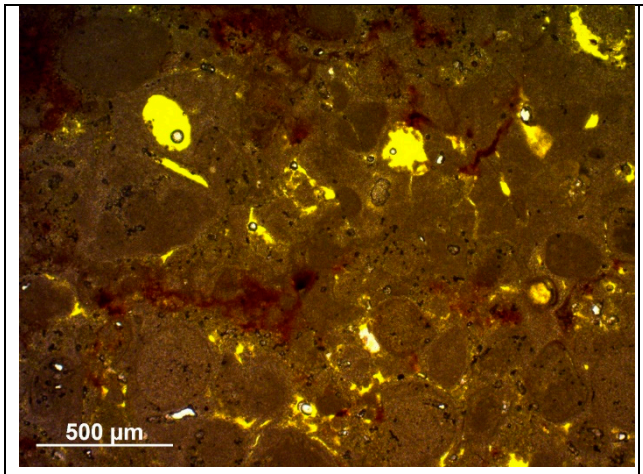
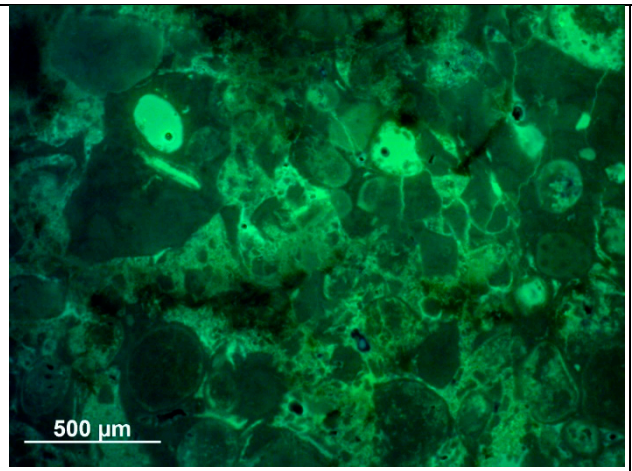
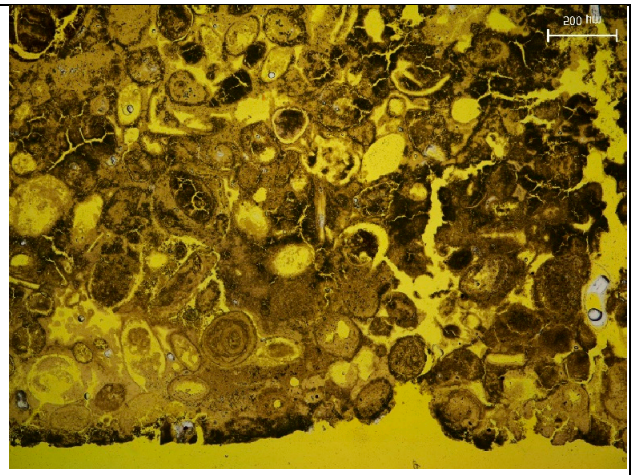


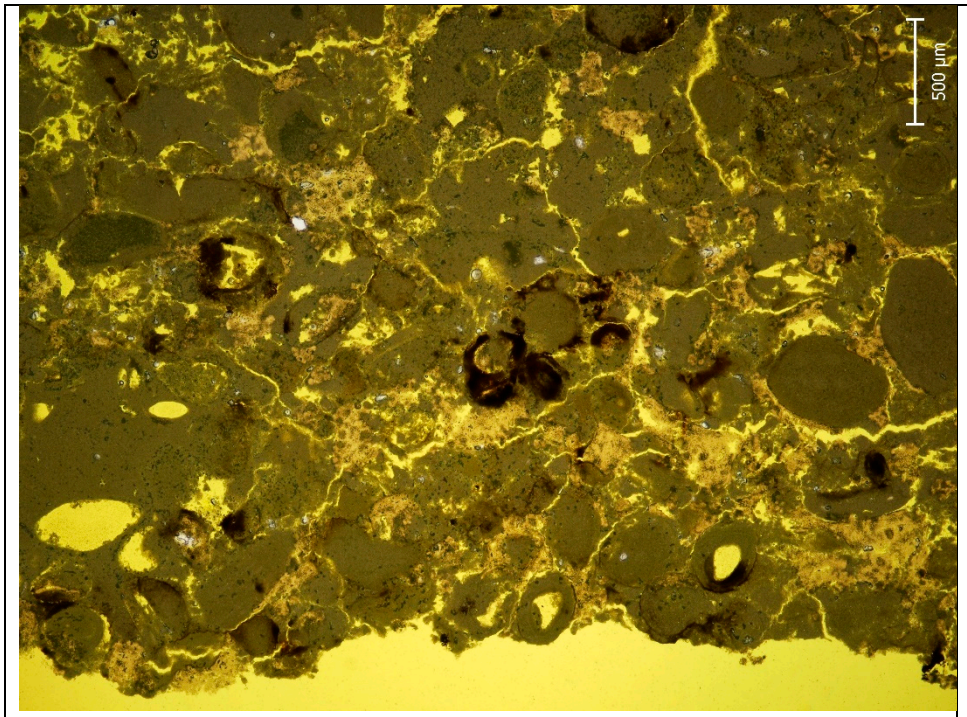
Ajarte Dolostone 600 °C
Even though the black and red stains are also evident in the sound texture, their effect is enhanced after thermal treatment (PPL).



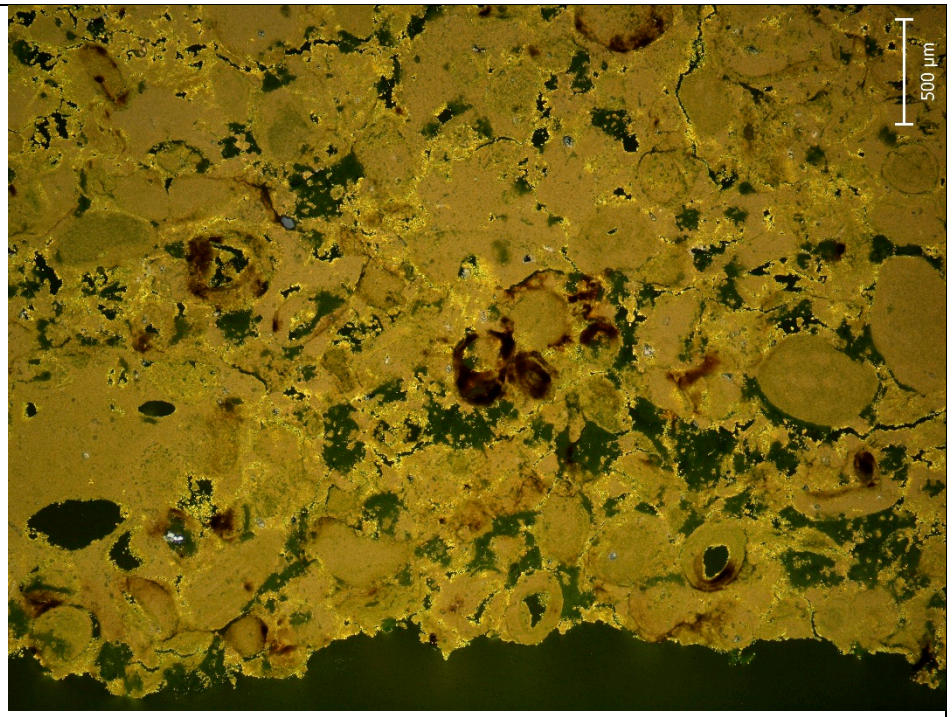


Ajarte Dolostone 900 °C
The formed microcracks are of inter- and intragranular nature but can be seen most between the round ooids and the matrix (PPL). Thermal decomposition is visible in form of blurry zones in the matrix (marked in red) (XPL).

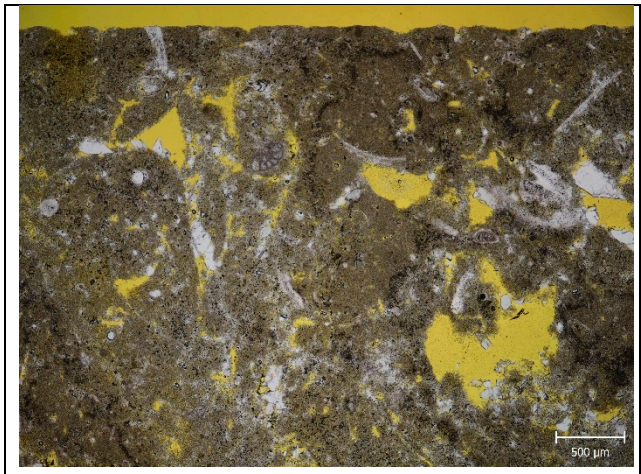
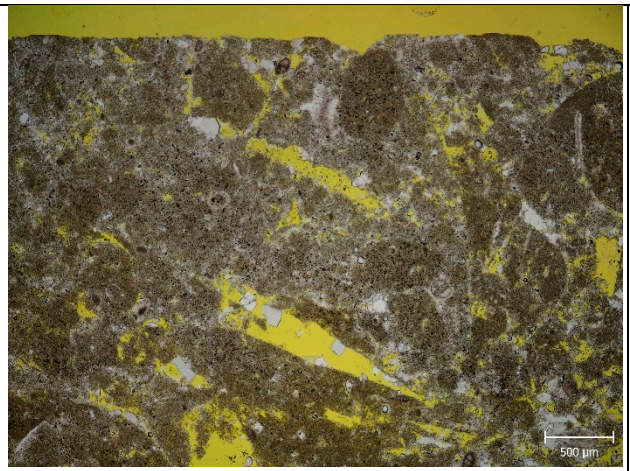
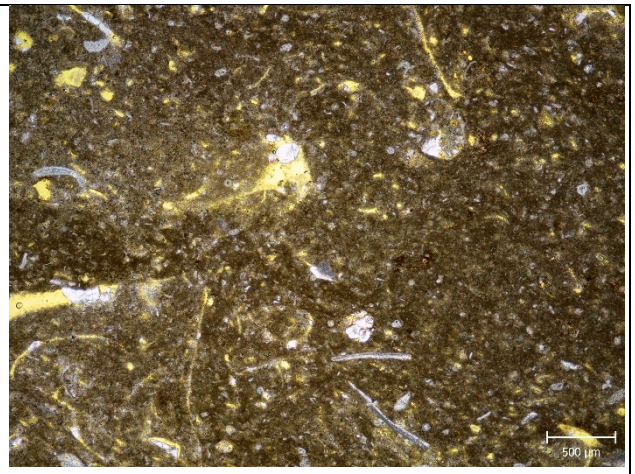
 **Ajarte Dolostone 600 °C** Induced microcracks are less visible in PPL	 **Ajarte Dolostone 600 °C** Under UV-light cracks and their distribution are clearly visible.	 **Ajarte Dolostone 900 °C** Thermal decomposition on the surface showing well-preserved ooids (PPL).

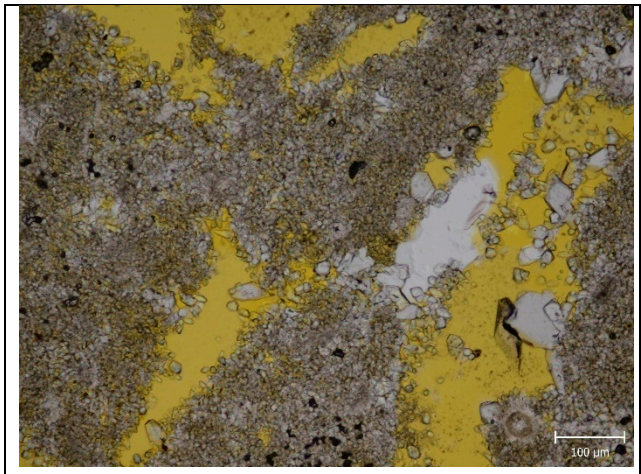
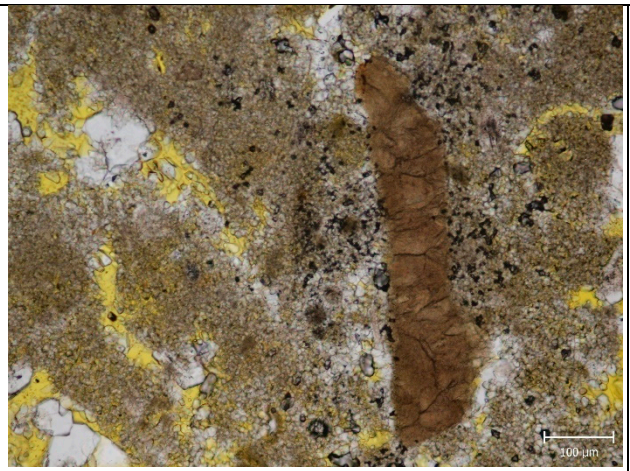
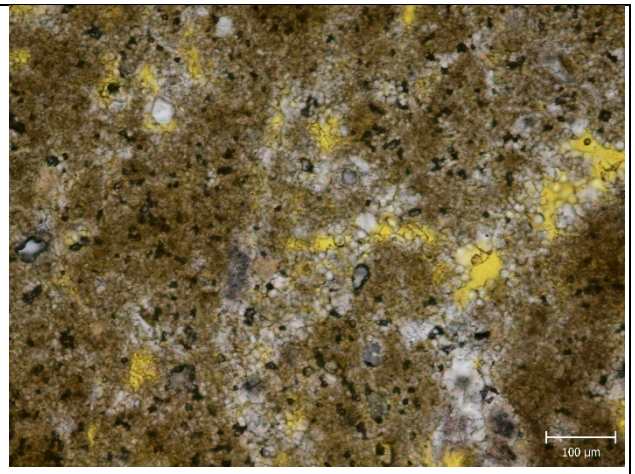


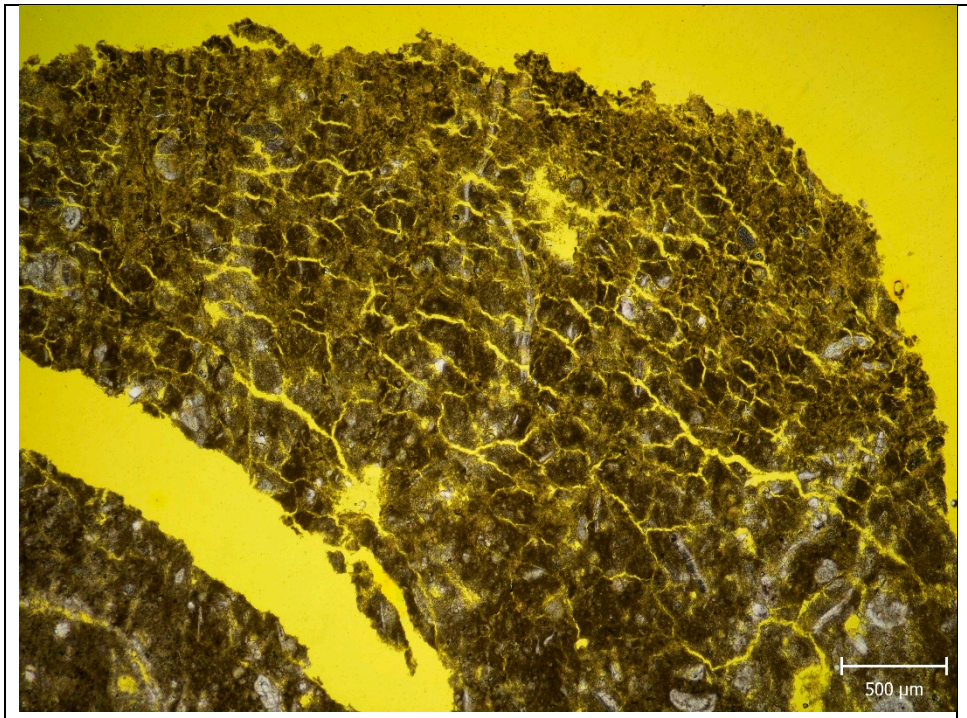
Ajarte Dolostone 900 °C
The carbonate matrix is more prone to thermal treatment than the ooids. The decomposition follows a patchy pattern with diffuse edges (i.e., blurred interfaces) (PPL).



Ajarte Dolostone 900 °C
In the cross-polarised image, the effect described is more evident. The very low birefringence of these areas points to the presence of fine-grained, needle-like calcium hydroxide (XPL).

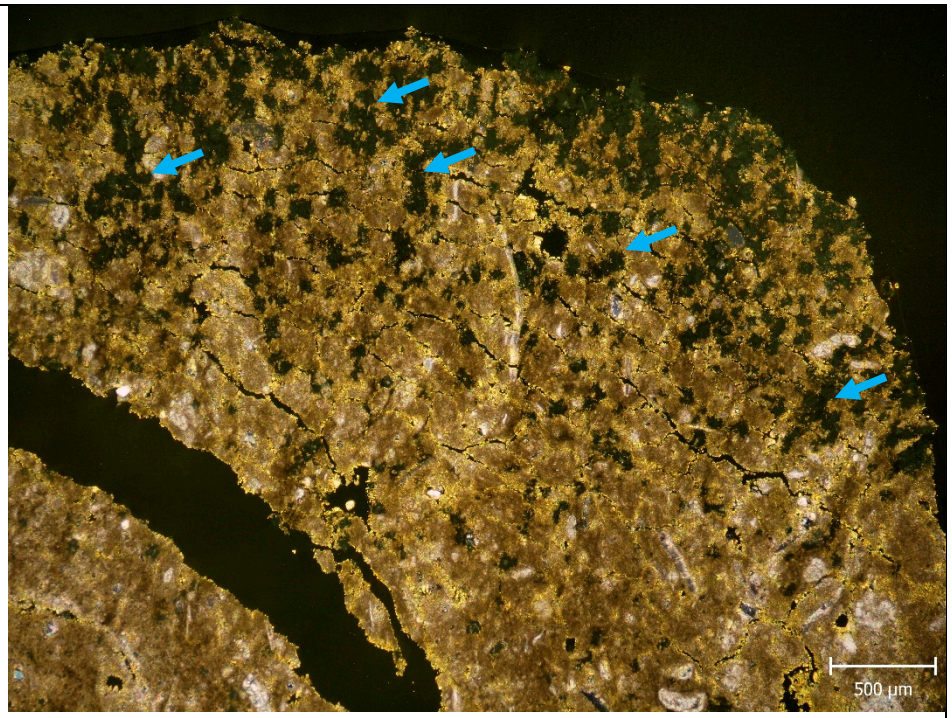
		
Ajarte Calcite pristine Pristine microstructure of the Ajarte Calcite with visible black stains of an unknown origin, which are also observable on Ajarte Dolostone (PPL).	**Ajarte Calcite 600 °C** Apart from the colour change that is also observable at the macroscopic level, no apparent changes are visible in the microstructure after thermal treatment at 600°C. The microcracks cannot be easily detected under PPL.	**Ajarte Calcite 900 °C** After thermal treatment at 900°C the texture seems densified (PPL).

		
Ajarte Calcite pristine Detail of the pristine microstructure and the brownish microcrystalline calcite matrix (PPL).	**Ajarte Calcite 600 °C** The most apparent change is the colour change, however, other than that, no evident alterations can be recorded. The few cracks observed appear rather in the calcite matrix (PPL).	**Ajarte Calcite 900 °C** A darkening of the calcite cement matrix is evident and the fabric seems densified (PPL).



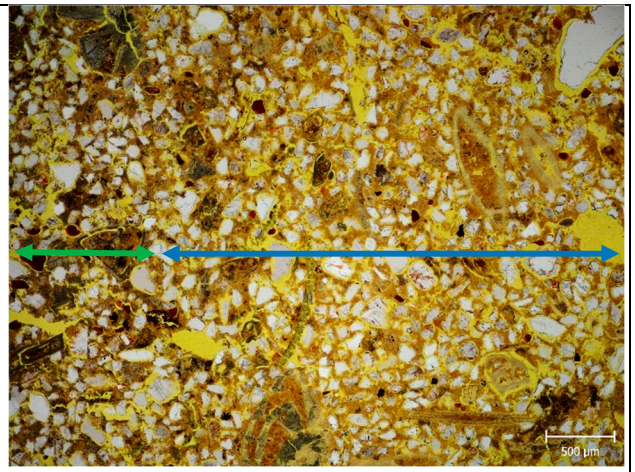
Ajarte Calcite 900 °C

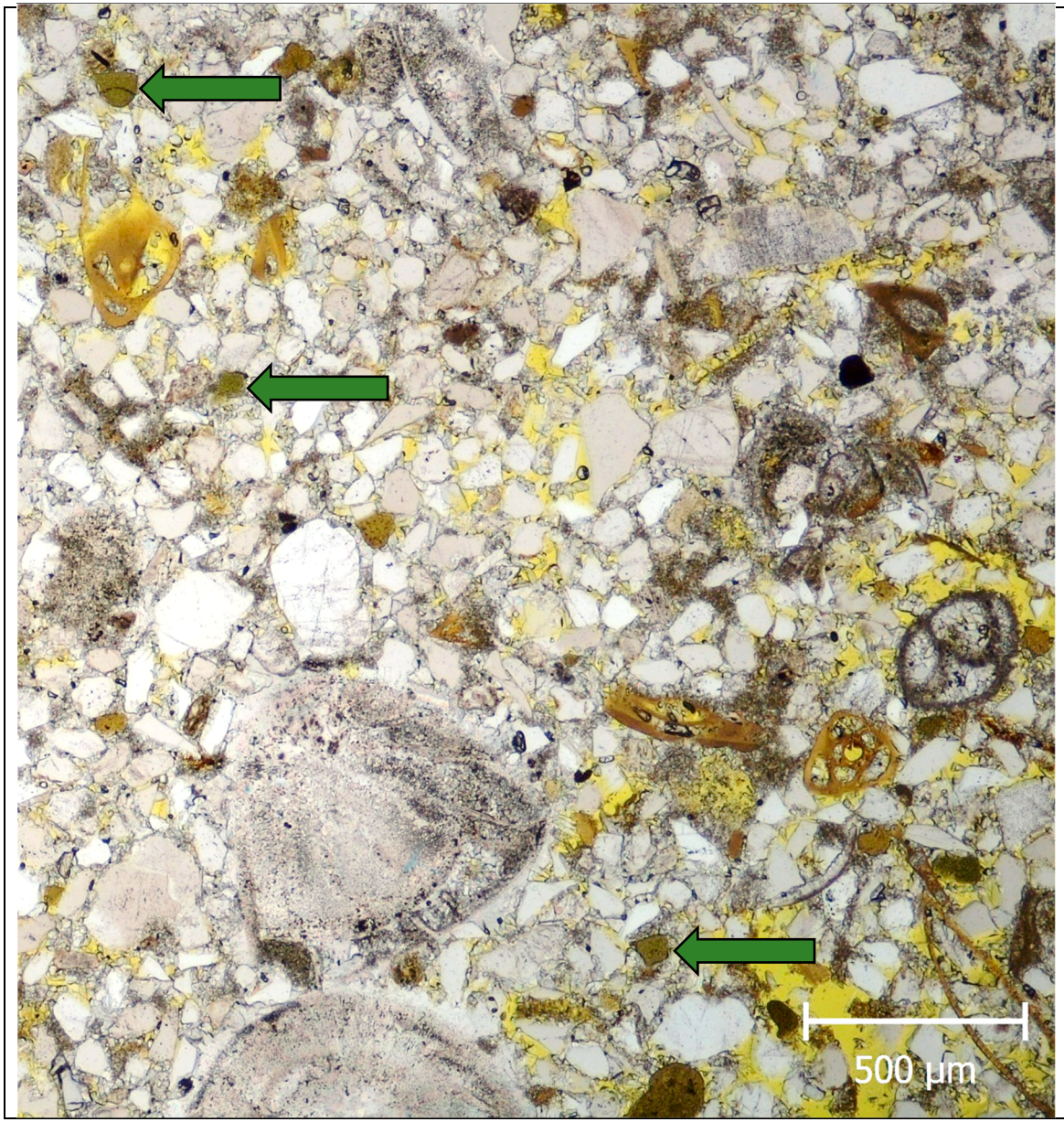
The microcracks as well as the big apparent crack are surface parallel and are a result of the differential stresses caused by the decomposition-hydration- and subsequent carbonation processes (PPL).



Ajarte Calcite 900 °C

Thermal decomposition in form of a pitting pattern with blurred edges can be observed (blue arrows) (XPL).

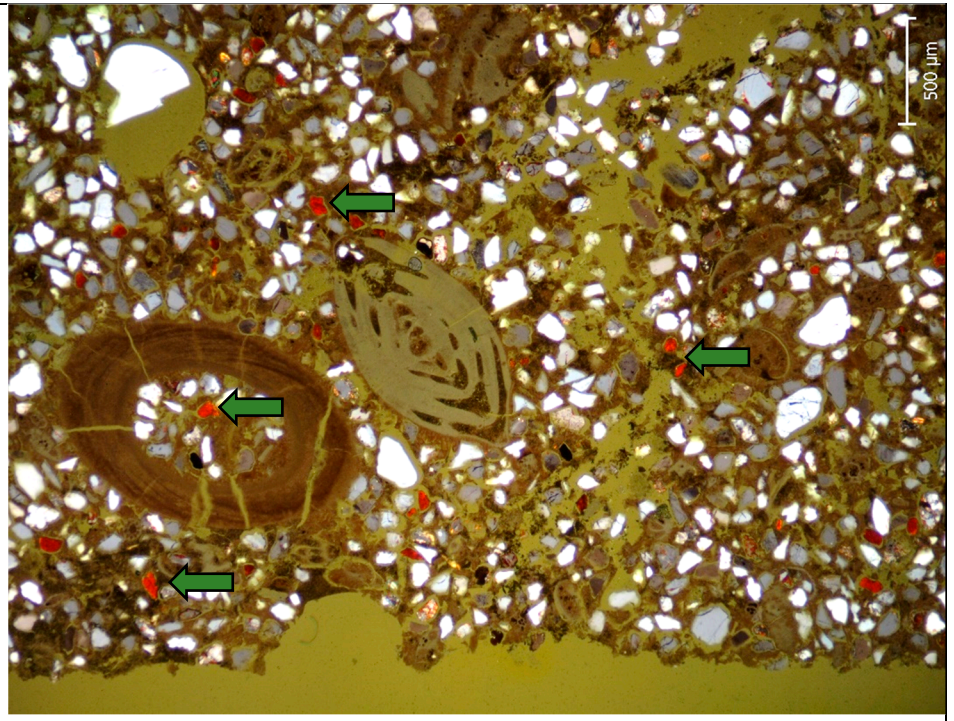
		
Balegem pristine Sound microstructure of the Balegem limestone (PPL).	**Balegem 600 °C** Changes in colour are apparent and especially the microfossils appear darker (possibly because of the finer $CaCO_3$ grain sizes). No effect of thermal decomposition is visible at the surface (PPL).	**Balegem 900 °** Thermally decomposed (blue arrow) and initially altered microstructure (green arrow) is visible. Most cracks are visible at the interface between the microfossils and the surrounding texture (PPL).



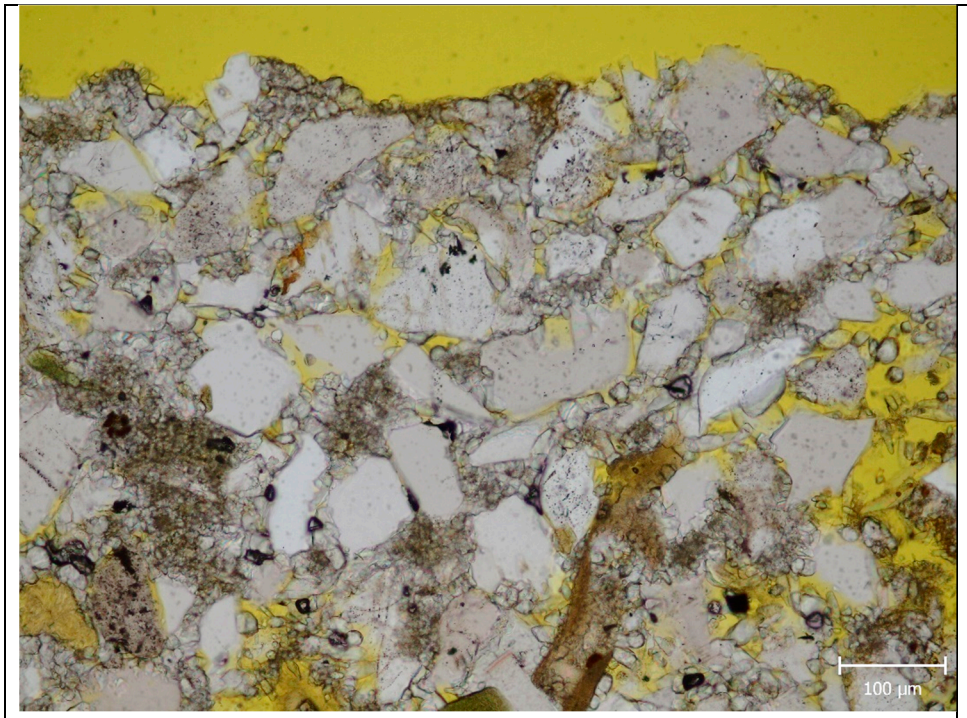
Balegem pristine
Arrows indicate the presence of glauconite (PPL).



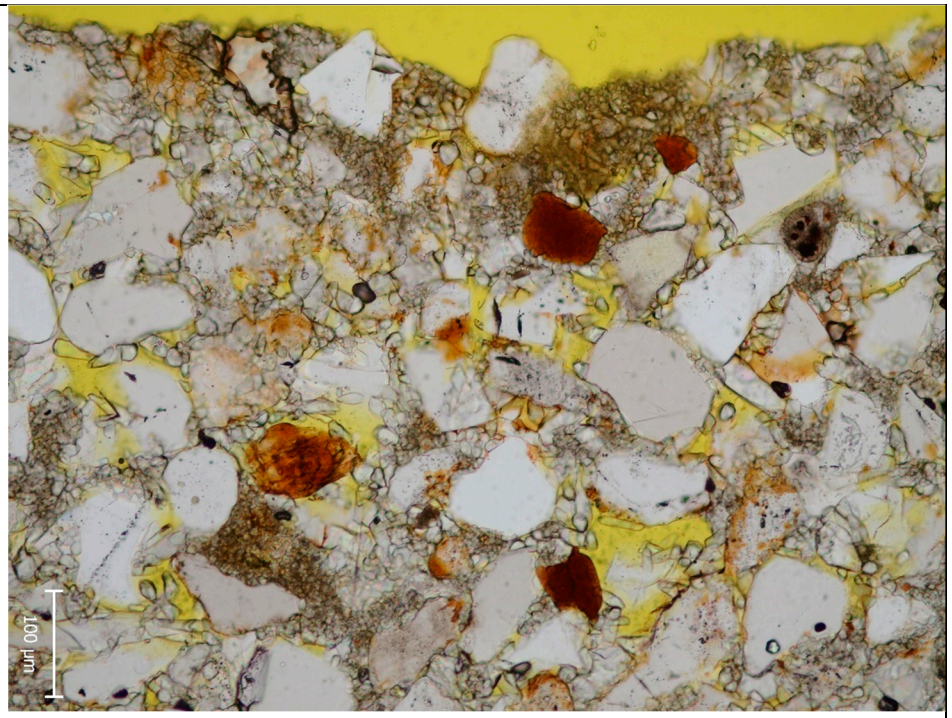
Balegem 900°C
Glauconite is turning red after the thermal treatment (PPL).



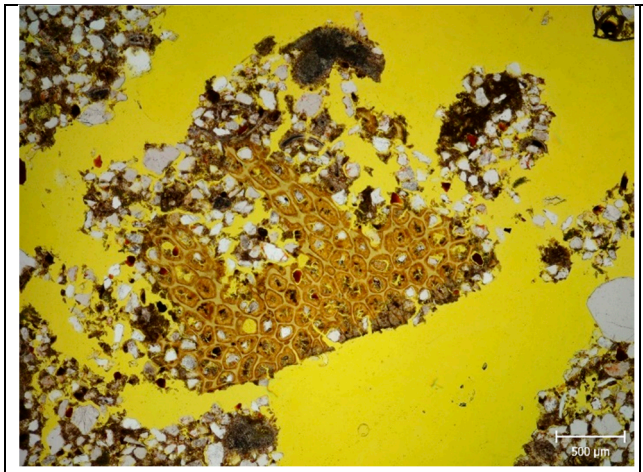
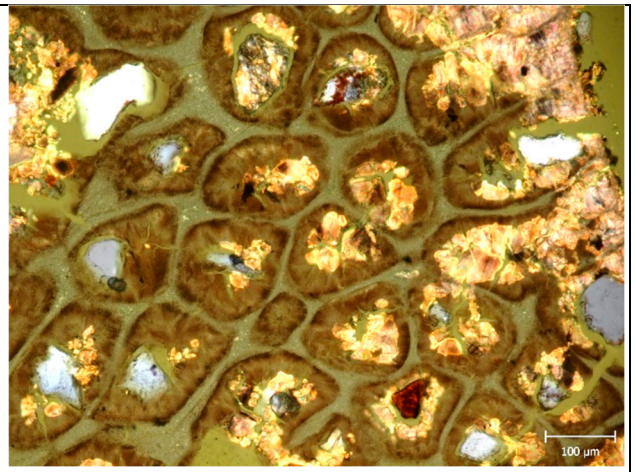
Balegem 900°C
Glauconite´s red colour is more intense in "XPL" (note that the polars are not completely crossed).

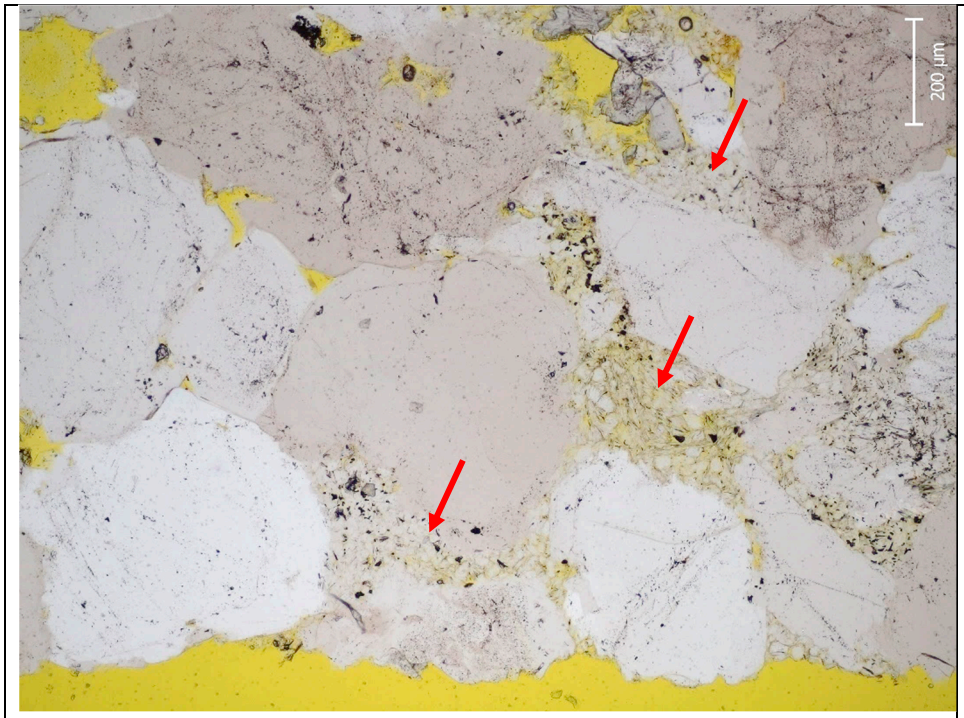


Balegem pristine
Detail of the pristine microstructure and grain boundaries (PPL).

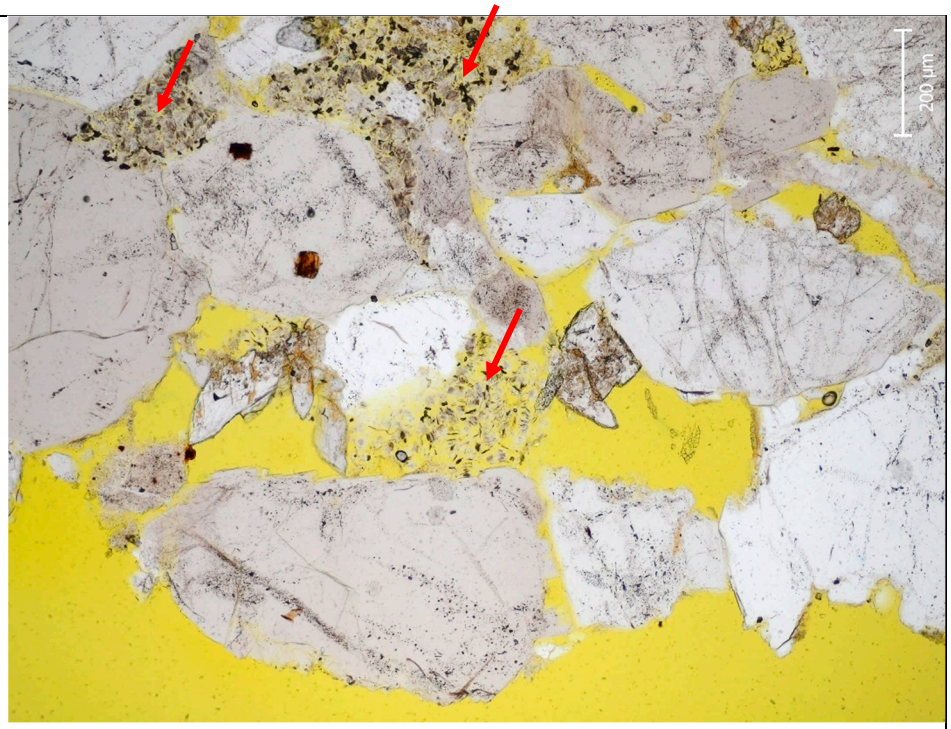


Balegem 600 °C
Colour change and a slight increase of the porosity is evident. Most probably glauconite discoloration is also present (red grains) (PPL).

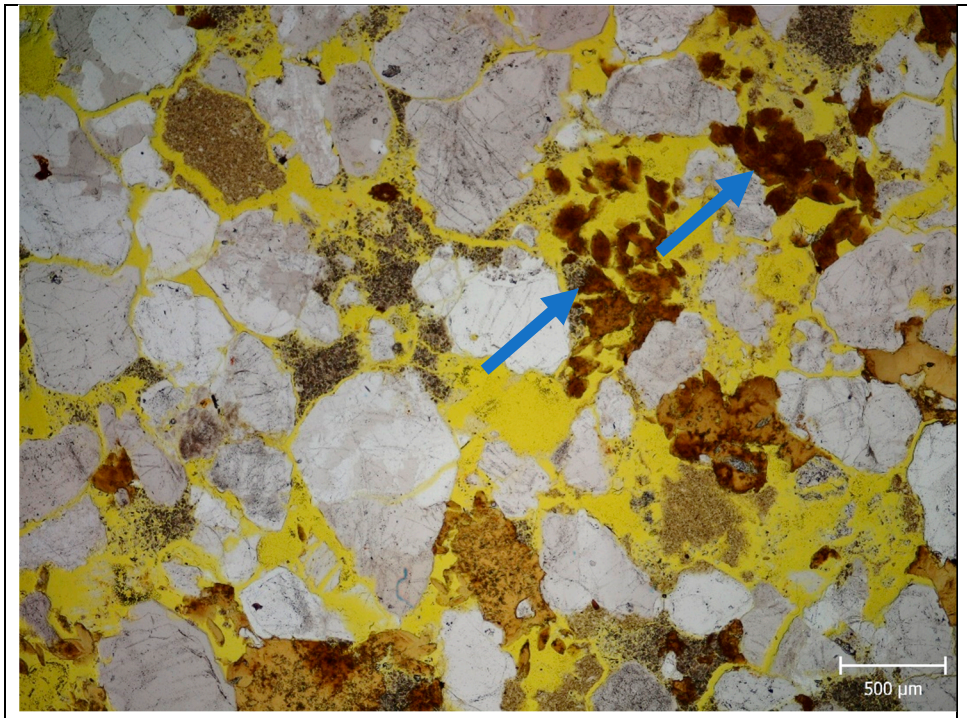
 **Balegem 900 °C** Thermal decomposition of a stone feature in form of a honeycomb pattern (centre) (PPL).	 **Balegem 900 °C** Detail of the thermally decomposed area displaying honeycomb structure (PPL).	 **Balegem 900 °C** ″XPL″ displaying different degrees of crystal grain sizes (note that the polars are not completely crossed).



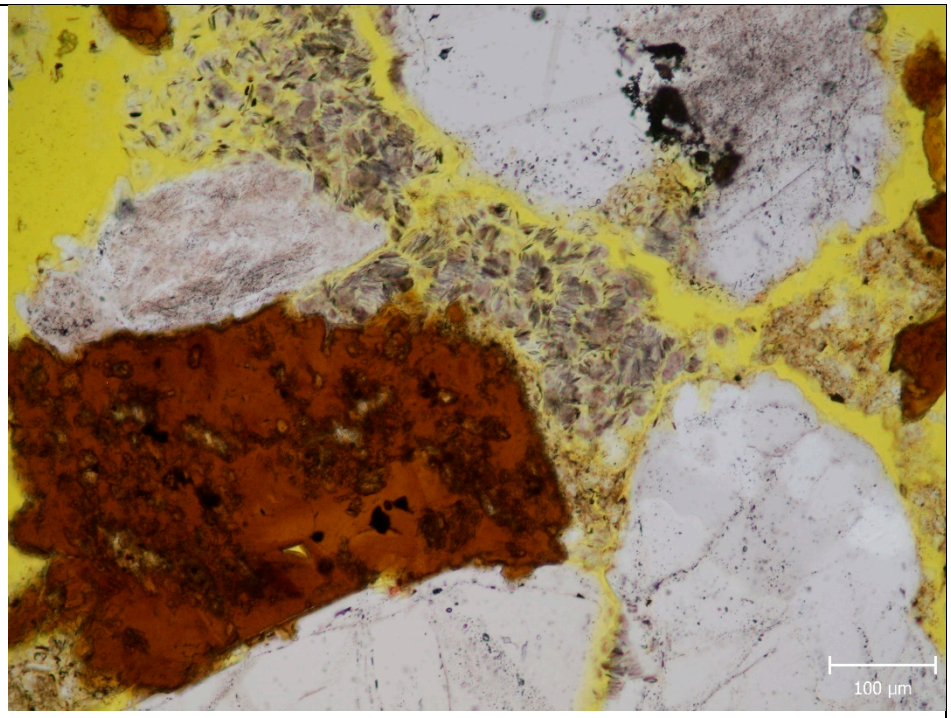
Schlaitdorf Sandstone pristine
Detail of the pristine fabric where the kaolinite appears whitish (PPL).



Schlaitdorf Sandstone 600 °C
The kaolinite is turning darker (arrows). A loss of cohesion between the grains is evident in form of a widening between the grains (PPL).



Schlaitdorf Sandstone 900 °C
Blue arrows show probably the decomposed dolomite grains based on their rhombohedral shape.



Schlaitdorf Sandstone 900 °C
Detail of the red mineral, probably dolomite.



Obernkirchen Sandstone pristine
Overview of the pristine texture (PPL).



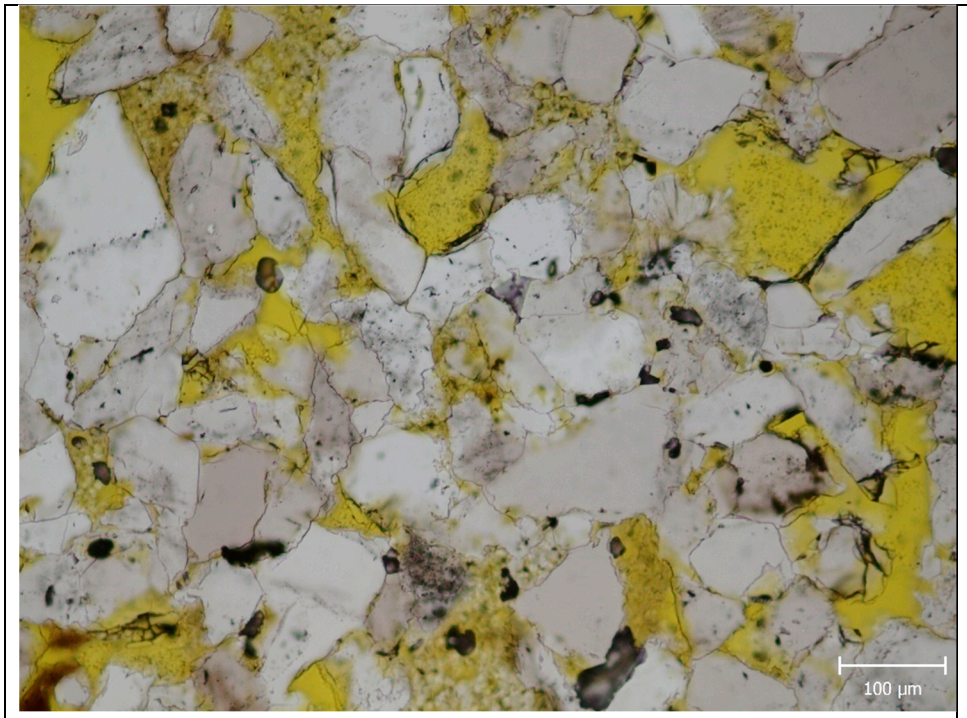
Obernkirchen Sandstone 600 °C



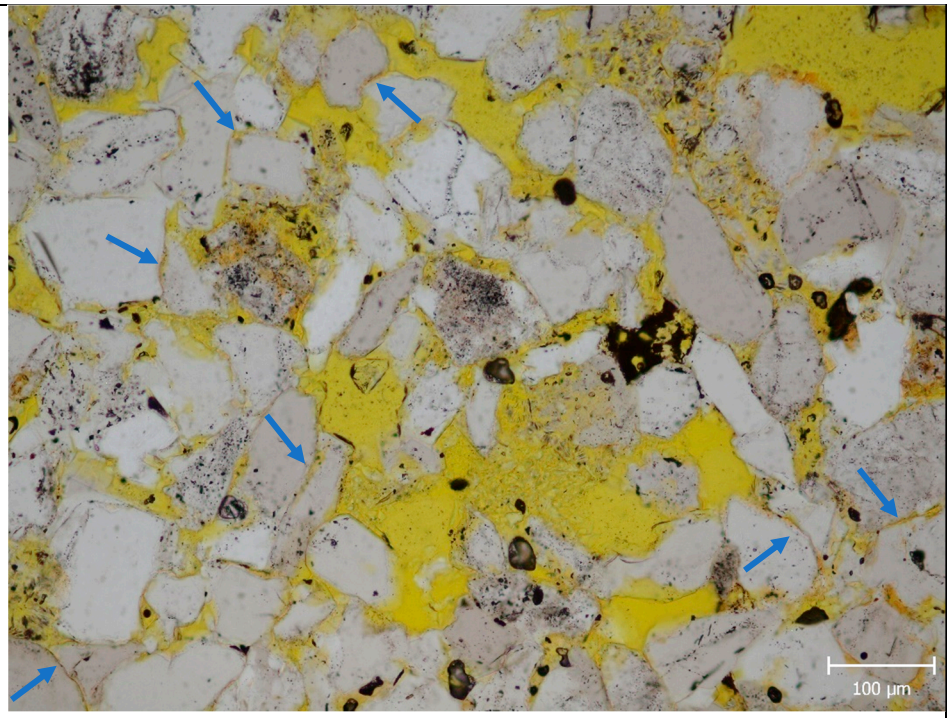
The colour change is mostly evident within the kaolinite, and it appears reddish (image below) (PPL).



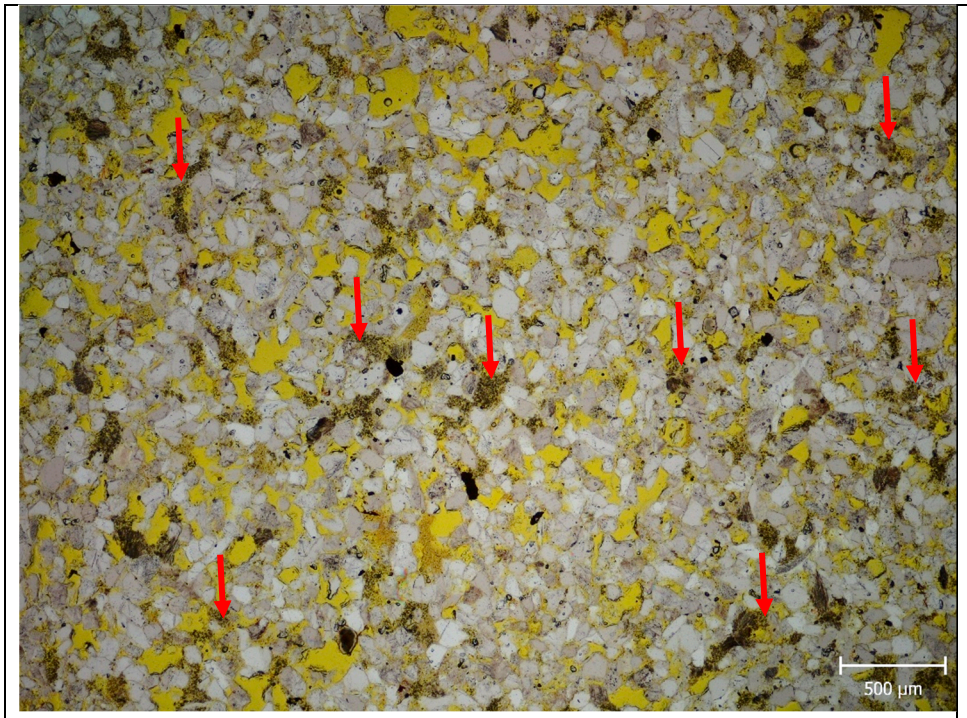
Obernkirchen Sandstone 900 °C
The colour change within the kaolinite is even more evident as it turns darker. The stone specimen remains compact after the treatment but it seems like the aggregates rearranged to form larger voids within the texture (PPL).



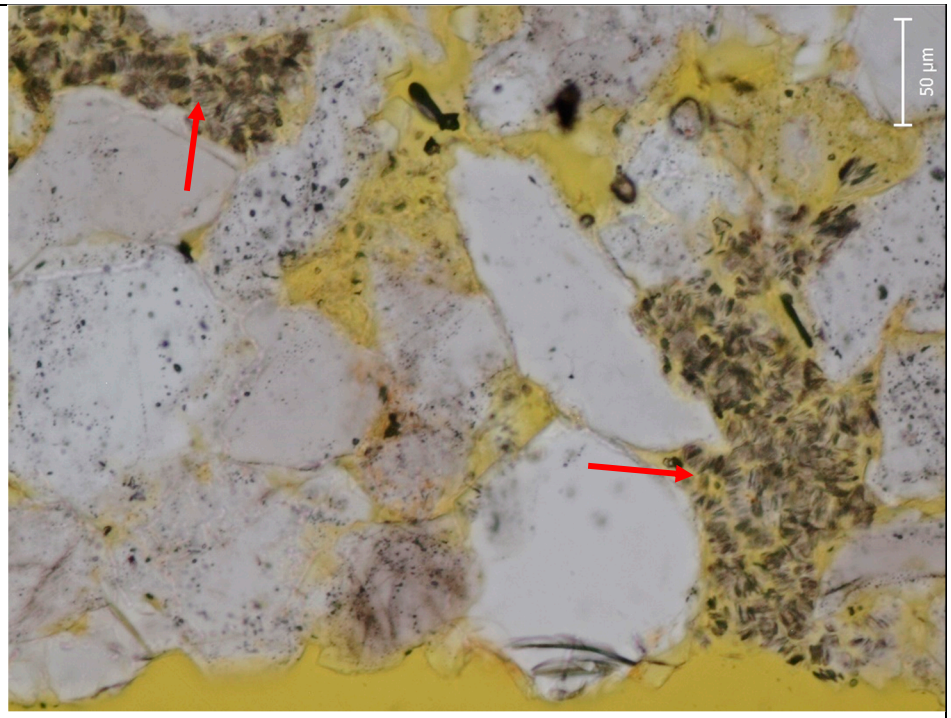
Obernkirchen Sandstone pristine
Good grain contact in the pristine fabric (PPL).



Obernkirchen Sandstone 600 °C
A widening of the grain contact is visible (PPL).



Obernkirchen Sandstone 900 °C
The colour change (arrows) within the kaolinite is visible through the whole specimen (PPL).



Obernkirchen Sandstone 900 °C
Colour change of kaolinite at the surface (arrows) (PPL).