

S2. Temperature calibration

The temperature distribution within the autoclave was determined prior to experiments and was calibrated against the temperature in the external drill hole in the top of the autoclave. In order to record the temperature distributions, three K-type thermocouples with different lengths were inserted into the autoclave. The longest thermocouple was located at the topmost position of the autoclave, while the other two were ca. 4.5 cm and 8.3 cm shorter (Figure S1). The pressure was kept at 100 MPa during temperature calibrations. A first temperature calibration was performed under “nominally isothermal conditions” with the three heating zones of the furnace set to the same temperatures and the temperature difference between the longest and shortest thermocouple (8.3 cm) was $\leq 5^\circ\text{C}$ in the calibrated temperature range (600–900 $^\circ\text{C}$), which is within the uncertainty of the temperature measurements. A second calibration was conducted under “gradient conditions” with the top and central heating zones set to equal temperatures and the bottom zone set to 250 $^\circ\text{C}$ lower. A temperature difference of 69–72 $^\circ\text{C}$ was determined between the outermost thermocouples in the autoclave. Considering the lengths of our experimental charges of ca. 7 cm, experimental charges were exposed to a temperature variation of ca. 54 $^\circ\text{C}$ over their entire length, assuming a linear temperature distribution between the individual thermocouples (Figure S1).

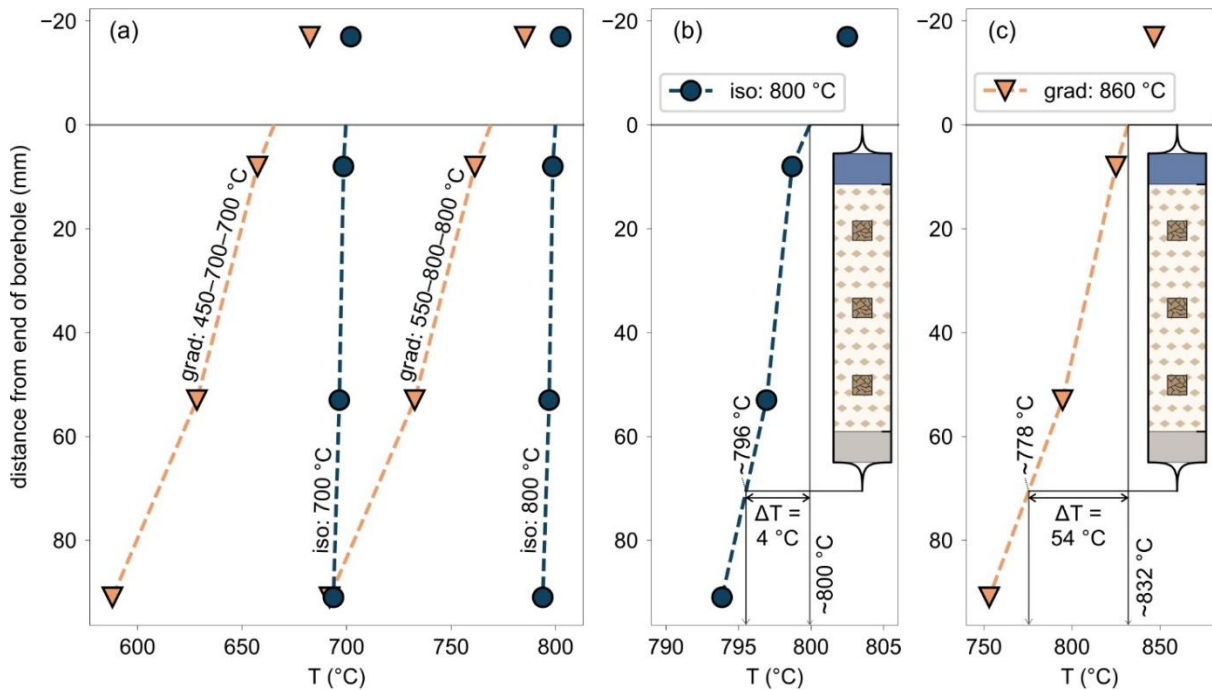


Figure S1: RH/RQ CSPV temperature calibration for nominally isothermal and for gradient conditions at 100 MPa. (a) temperature distributions in the autoclave with all heating zones set to same temperatures (isothermal, 700 $^\circ\text{C}$ and 800 $^\circ\text{C}$, blue circles) and with the lowest heating zone set 250 $^\circ\text{C}$ below the middle and top heating zones (gradient, 700–700–450 $^\circ\text{C}$ and 800–800–550 $^\circ\text{C}$, orange triangles). (b) and (c) show the approximate position of an experimental charge within the autoclave and the corresponding temperature profiles under isothermal (b) and gradient (c) conditions. The temperature distributions along a 7 cm long sample have been determined by linear interpolation between individual temperature measurements and result in a temperature difference of ca. 4 $^\circ\text{C}$ and 54 $^\circ\text{C}$ for isothermal and gradient conditions, respectively. Horizontal lines at 0 mm indicate the topmost position within the autoclave. Data points above this line were obtained from the thermocouple in the external drill hole on the top of the autoclave. Data points below the horizontal line were obtained by the three thermocouples within the autoclave. See text for details on the temperature calibration.