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Quantification of Transient Quartz with the Optical Dilatometer

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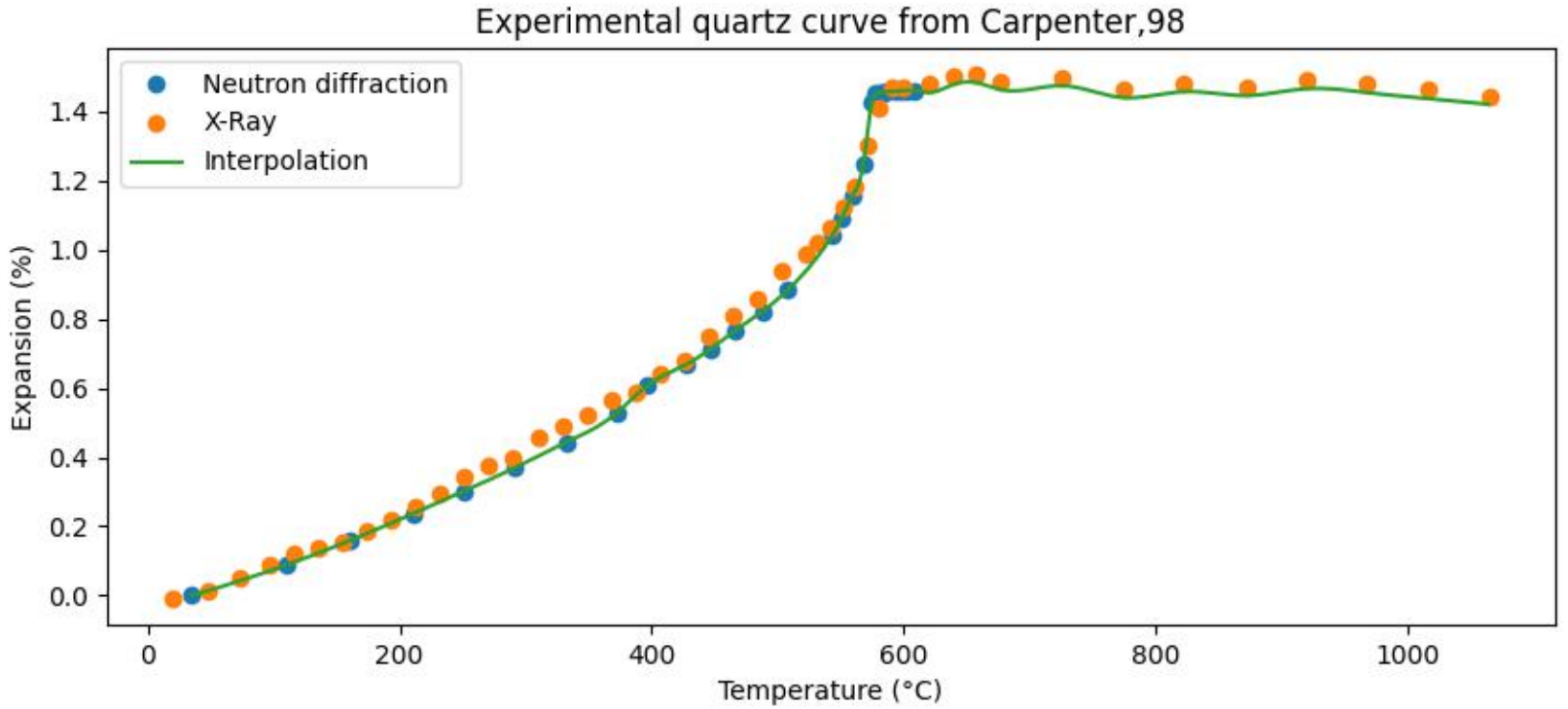
Expert Lab Service is a boutique of ceramic engineering solutions, materials analysis services and **tailor-made laboratory instruments**.

The Quartz Transition problem

Quartz Transition between α→β crystal structures happens at 575°C and is characterize by a strong exponential expansion followed by a slightly declining plateau [Carpenter,98].



The Quartz Transition problem

Quartz coming from cheap sands is a major component of tiles, sanitaryware and many ceramics. This huge transition can cause significant stress inside of the material, especially during cooling.

Cooling in industrial plants takes a long segment of furnaces just to ease this transition.

How to measure the amount of quartz?

The determination of quartz in raw materials or unfired ceramic bodies would be the first step towards mitigating this problem, but it requires and expensive X-ray mineralogical analysis.

A fired sample would need to be crushed into fine powder to be analyzed.

Another approach would be to use SEM/EDAX to determine the quartz content on a sample's surface.

The present study investigates the possibility of determining the quartz content of a fired and unfired ceramic body from its thermal expansion curve.

The early attempt of [Shüller,88] is revisited using modern mathematical approaches.

Quantification of Transient Quartz

The method relies on the abrupt phase change between α→β and beta quartz. The hypothesis is that **the quantity of quartz can be inferred from the magnitude of its transition** with respect to the otherwise linearly expanding material: thus the name *transient quartz.*

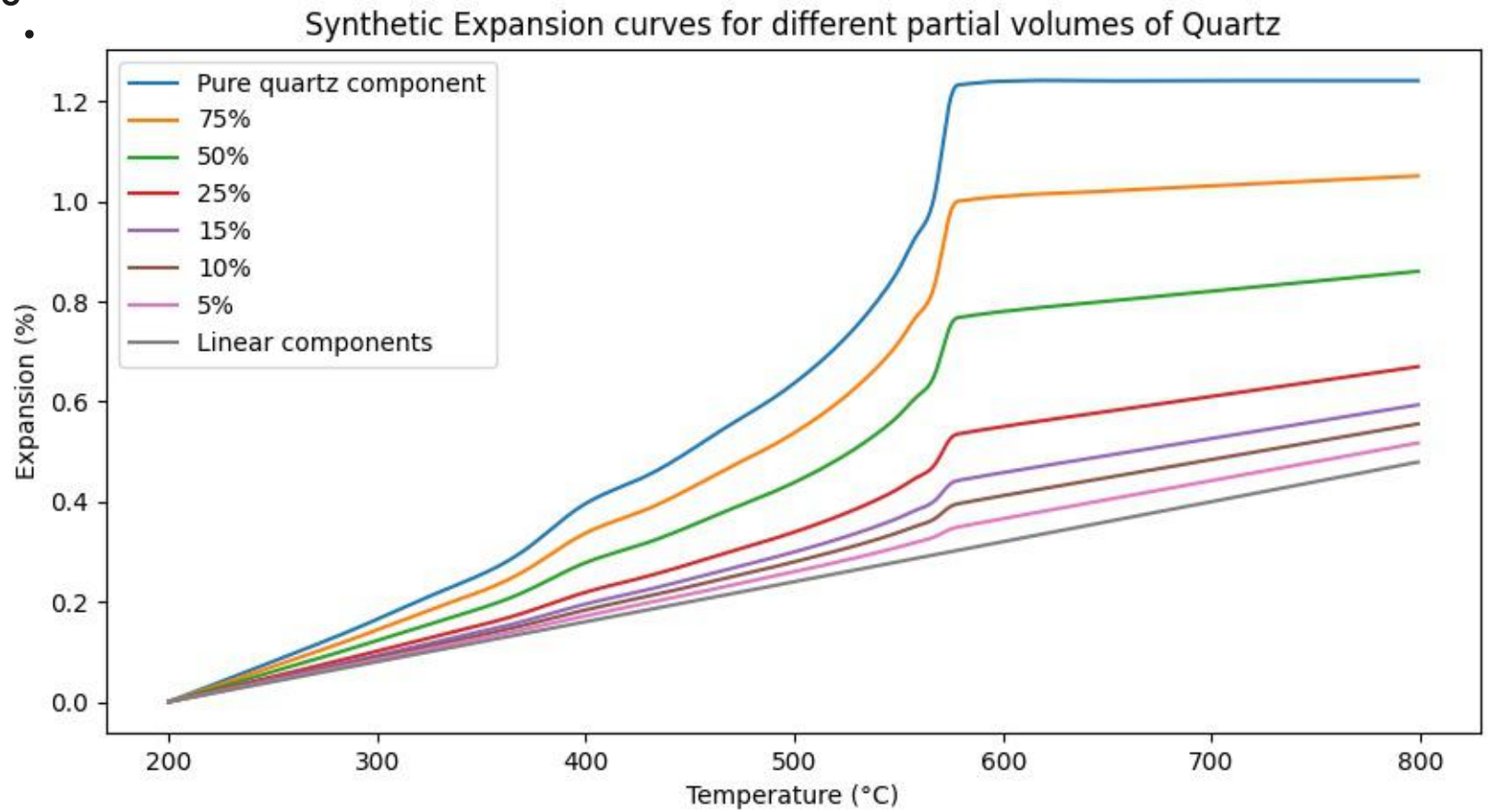
The expansion curve of a material (d) is considered as a combination of linearly expanding materials ($\alpha_{1..n}$) and the experimental pure quartz curve Q(T) multiplied by its fractional volume V_Q:

$$d(T) = V_Q Q(T) + \sum_0^n V_i \alpha_i T = V_Q Q(T) + (1 - V_Q)\,\bar{\alpha} T$$

Each component multiplied by its volumetric fraction V_Q. It can then be simplified as 2 componets: one quarz, one linear.

Synthetic curves

The following curves are generated according to the simplified 2-component model and a weighted mean linear coefficient of 8e-6/K°.



Post-transition removal (PTR) method

The simplest method to obtain the partial volume of quartz from one of the previous synthetic curves is to:

1. Perform a linear regression past the transition temperature.

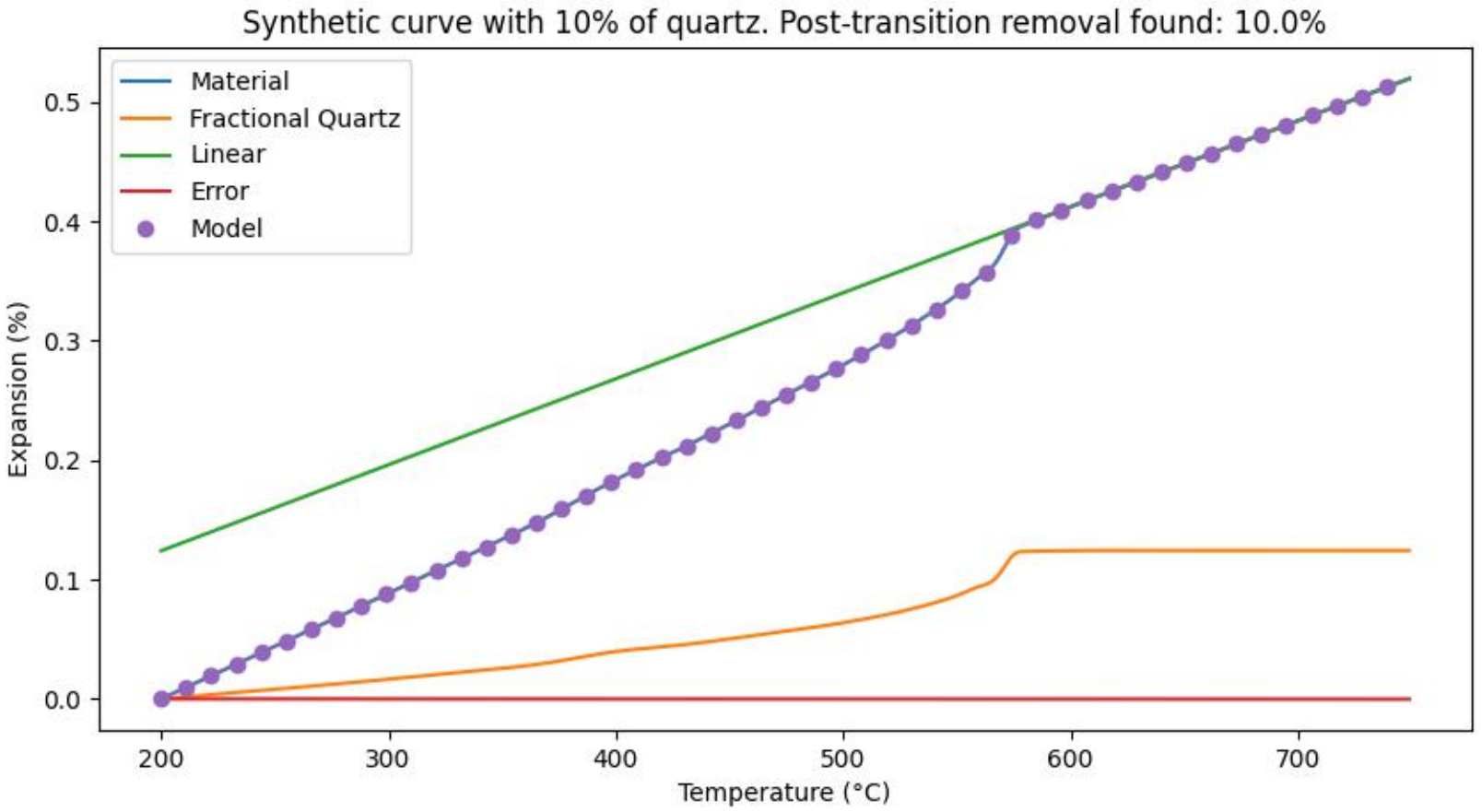
$$d(T) = \alpha T, T > 620$$

2. Remove the line fit from the whole synthetic curve, obtaining a residual curve: $res(T) = d(T) - \alpha T$

3. Calculate the partial volume as a ratio between the remaining expansion at a post-transition T (eg: 620°C) and the pure quartz expansion.

$$V_Q = (d(T) - \alpha T)/Q(T), T = 620$$

Post-transition removal (PTR) method



Optical Thermal Analysis

But how to prove that the two components (quartz+linear) can be separated, and thus the quartz reliably measured by its dilatometric curve? Firing any ceramics will consume part of the quartz, incorporating it into the glassy phase.

We choose to produce **inert mixes of Al2O3 and quartz powders**, and use out **optical dilatometer** to measure the thermal expansion.

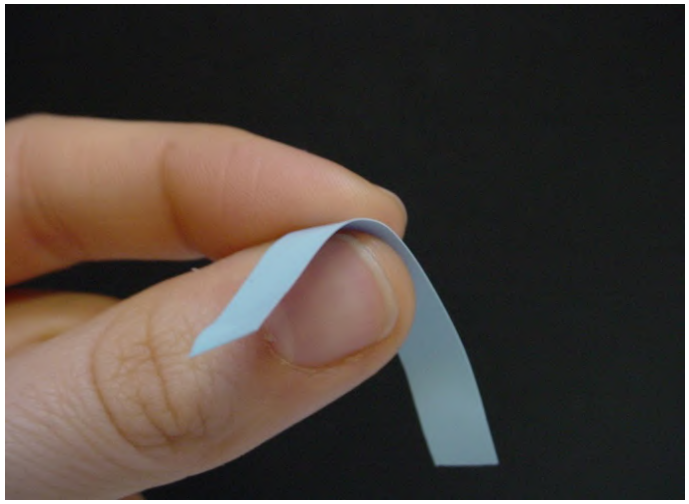
Optical thermal analysis instruments are able to measure thermophysical properties of materials **without any contact between the measurement system and the sample**.

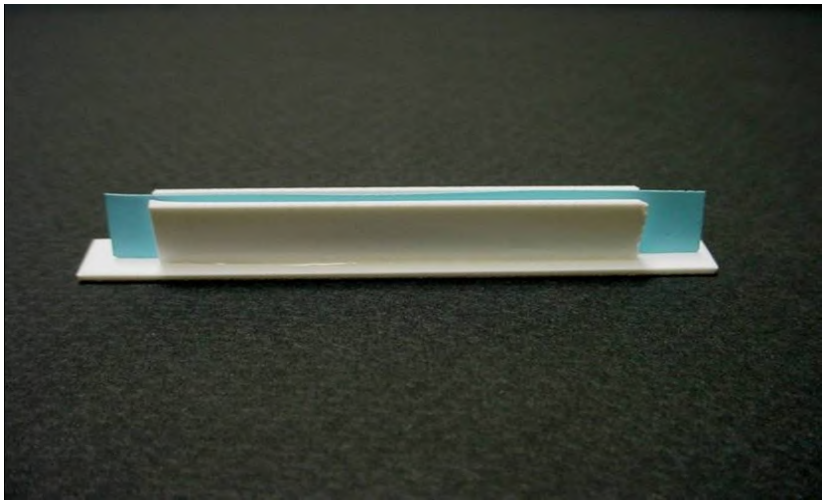
They all work by applying **computer vision techniques** to the sample's image (or some portions of it).

Measurable properties: coefficient of thermal expansion, melting point, elastic tensions, plastic deformation, contact angle, surface tension, viscosity estimation.

Seeing > Touching

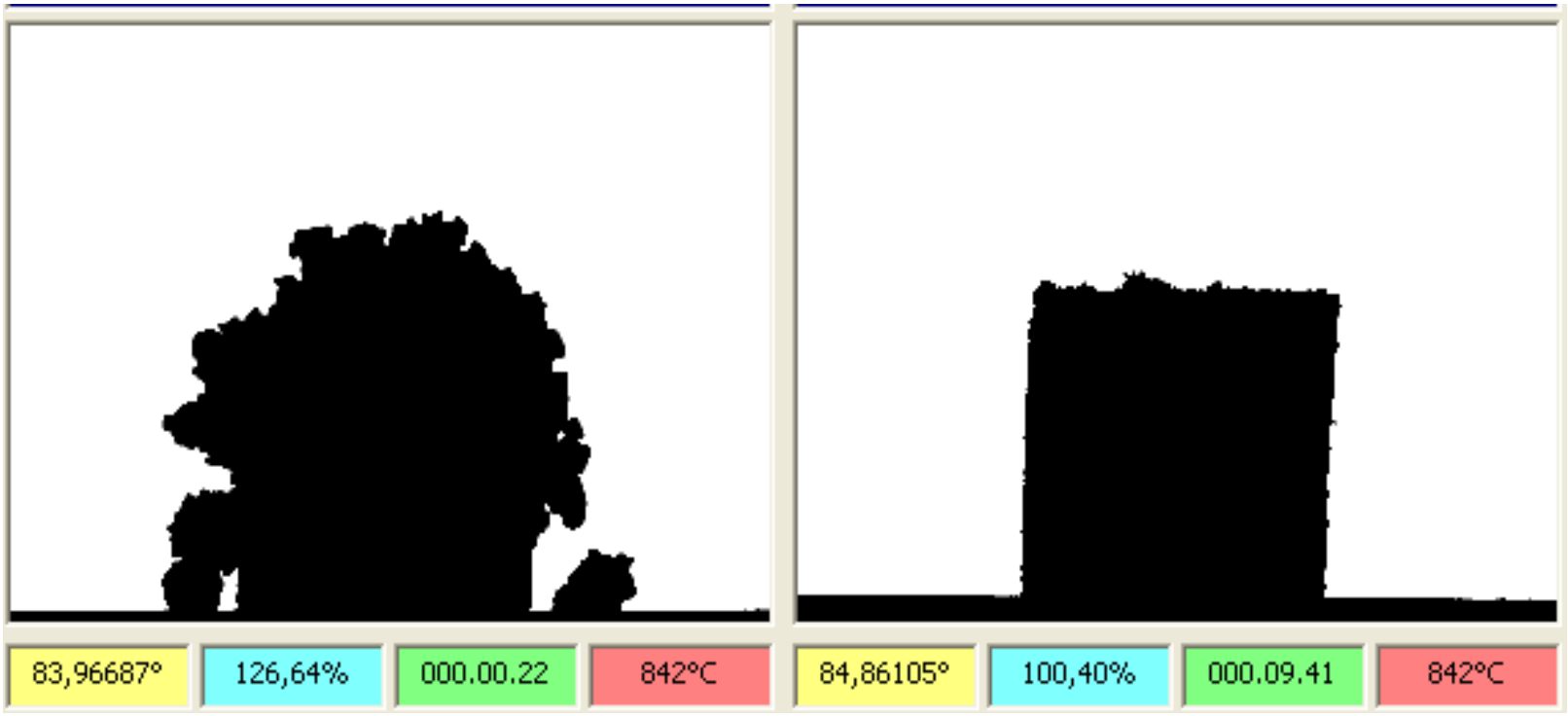
Being contactless, we avoid most of the interference of the instrument on the sample.





Kinetics > Equilibrium

The instrument does not heat up during the measurement. This allows to observe the sample behavior with very fast heating rates.



Materials > Standards

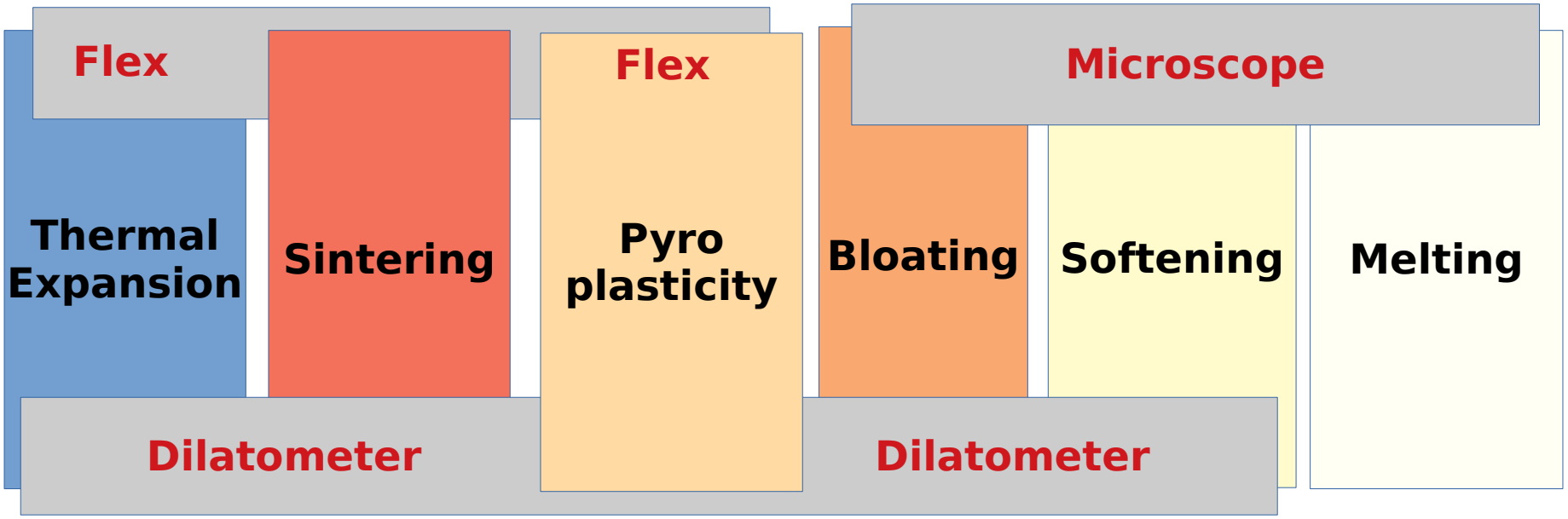
Standards can be to vague to be useful, or of little applicability for your material. We always prioritize materials over standards.

From ISO 540 on ash fusibility, 1995:
3.1 **deformation temperature** (abbreviation DT):
The temperature at which the *first signs of rounding*, due to melting, of the tip or edges of the test piece occur.

From ASTM E381-19 on CTE with thermomechanical analysis:
6.1.3 Sensing element… **+- 50nm** resulting from changes in length of the specimen.
6.3 Micrometer… with a range up to 10mm to determine specimen dimensions within **+- 25000nm**.

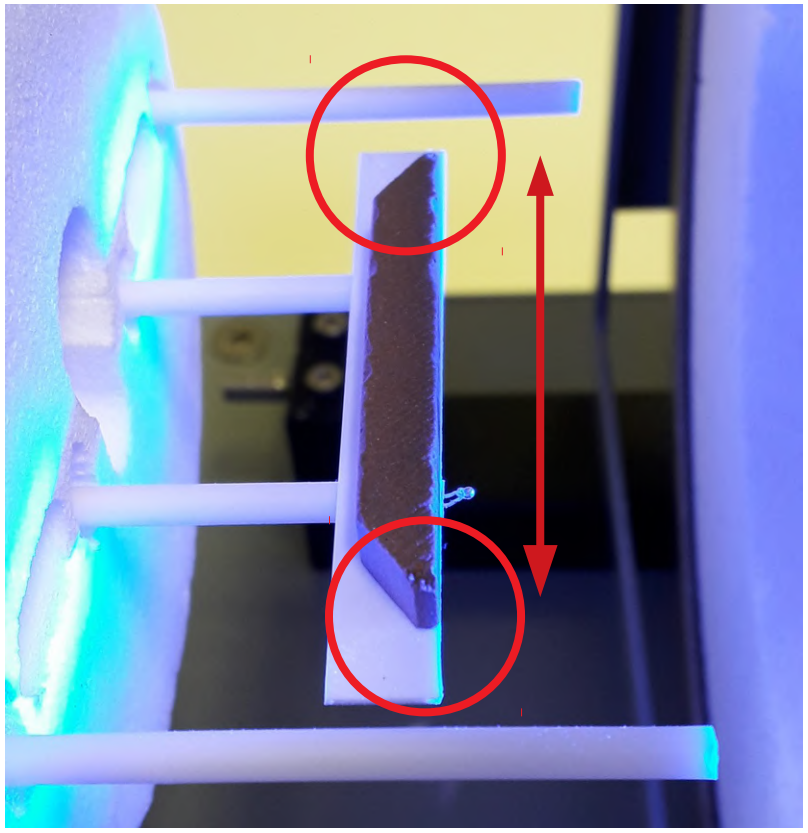
Optical Thermal Analysis for Ceramics

- We measure the deformation that heat and temperature causes in a material, across these behaviours:



Two Points Measurement: Dilatometer

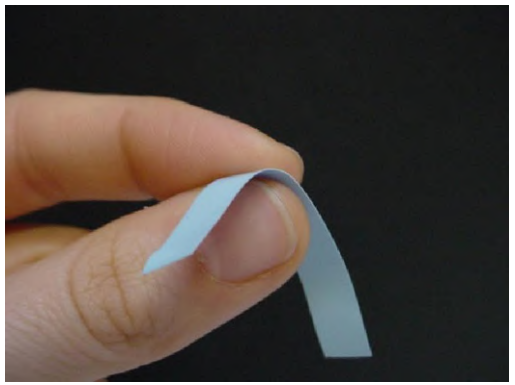
- Measures the difference between the single-point displacements of the **two opposite sample edges**
- Cameras are motorized to follow big displacements (eg: sintering)
- **Absolute** measurement. No need for heating cycle calibration. The measurement system does not heat up.
- Sample dimension: **50x5x5mm. Range: 46-51mm**

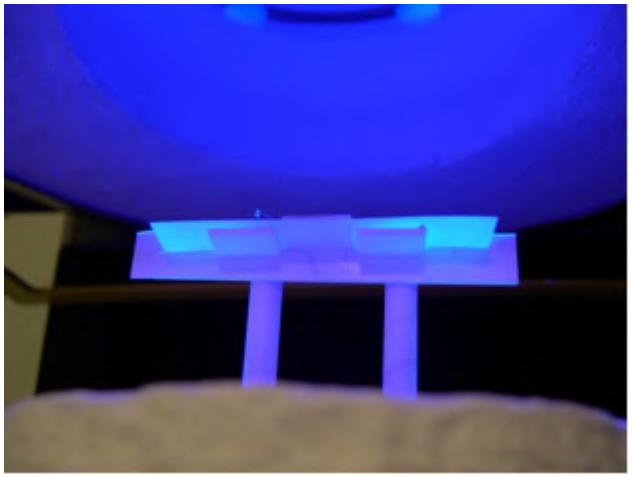


The Optical Dilatometer

The optical dilatomerer is able to measure solid samples up to their softening point, extremely thin sample, soft matter, incoherent samples (like sand).

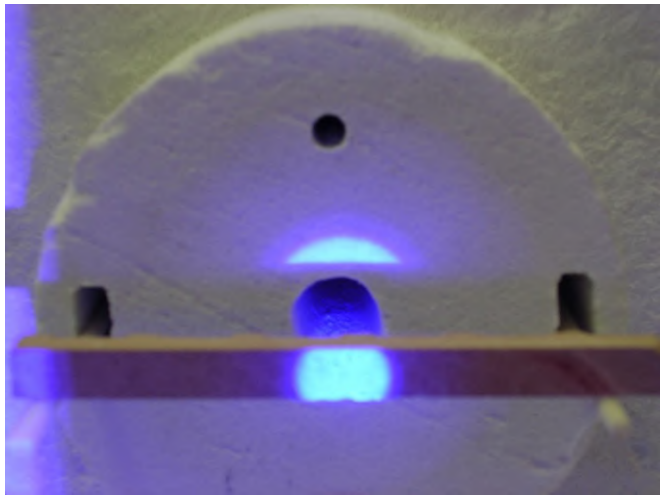
The calibration is performed against NIST SRM738 standard steel (up to 480°C) or Alumina plates (up to 1000°C).

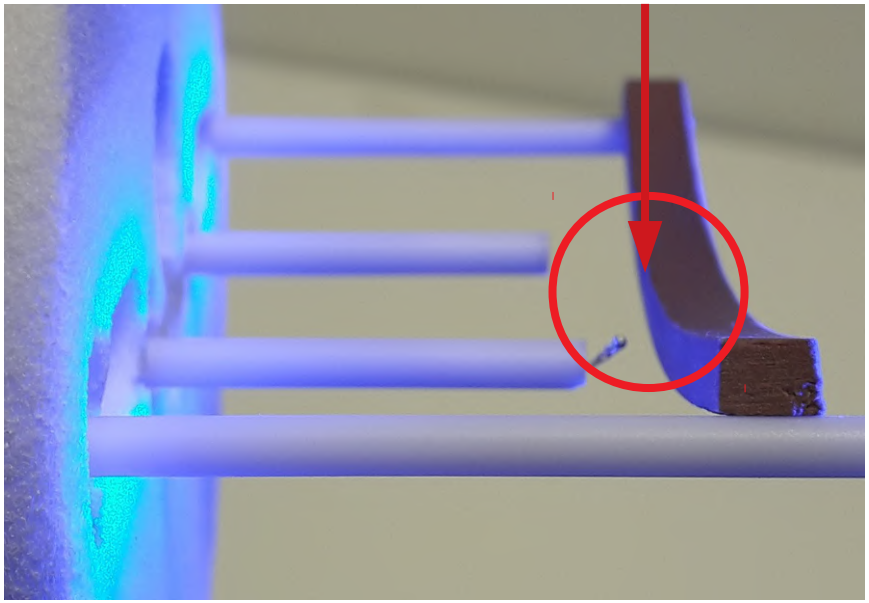




Single Point Measurment: Fleximeter

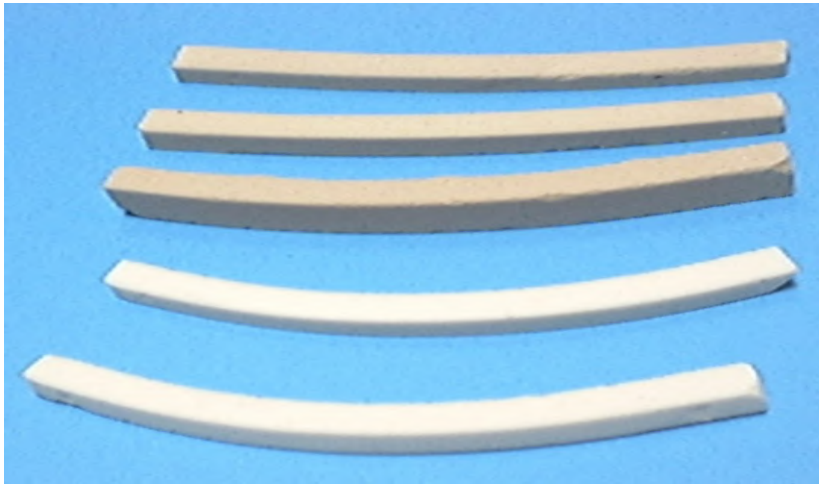
- Measure the downward or upward displacement of the **middle point of a sample suspended** between two holding rods.
- Sample: 80x5x5mm. Range: +3/-6mm





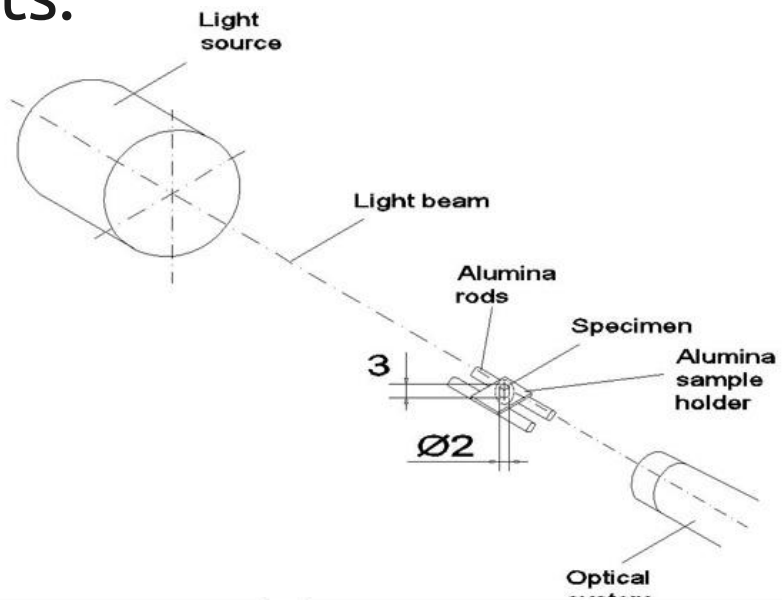
The Optical Fleximeter

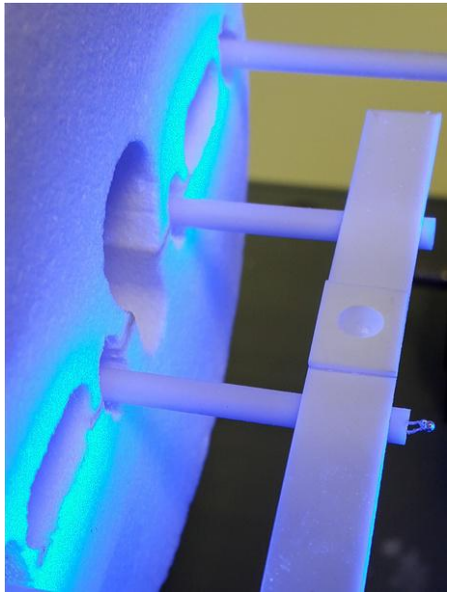
- Visco-elastic deformation.
  - Elastic: expansion coefficient differences in multi-layer materials
  - Viscous: when sample flows and is permanently deformed under its own weight
- Detect the coupling temperature of multi-layer materials, assess their tensions with temperature

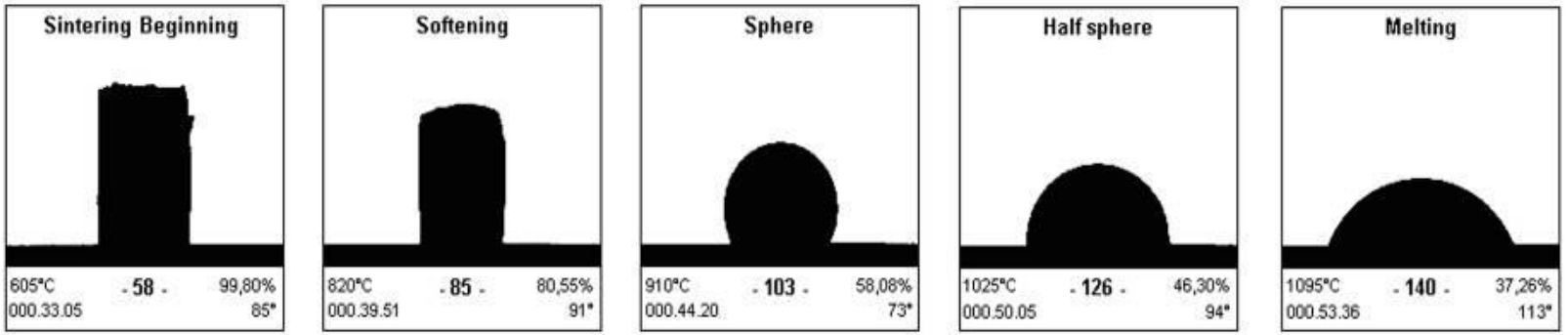


Full shape: Heating Microscope

Follows the change of the entire silhouette of the sample, as it melts.







The Heating Microscope

Computer vision calculates morphometric parameters as **height, width, volume, contact angle, sphericity, and much more**.

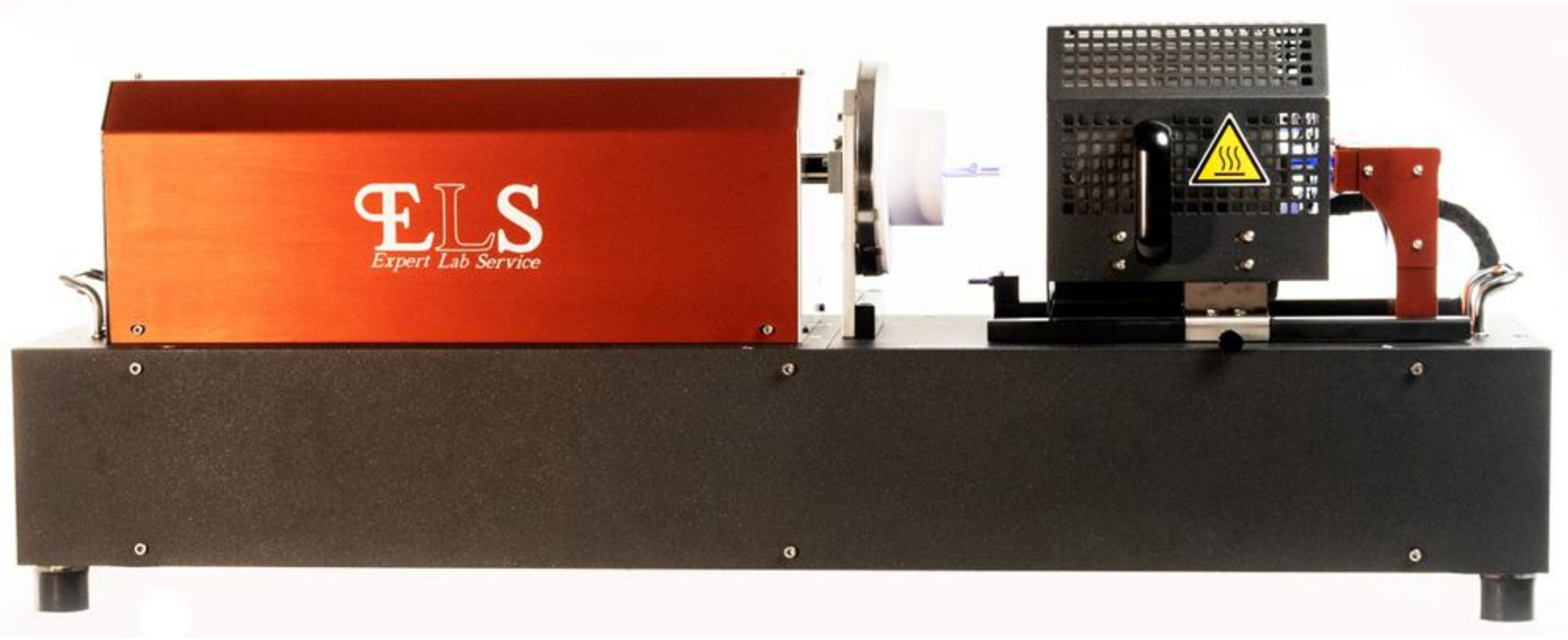
Allows to identify characteristic temperatures: **Sintering, Softening, Sphere, Half-Sphere, Melting**

The viscosity curve of glasses and cerami frits can be calculated.

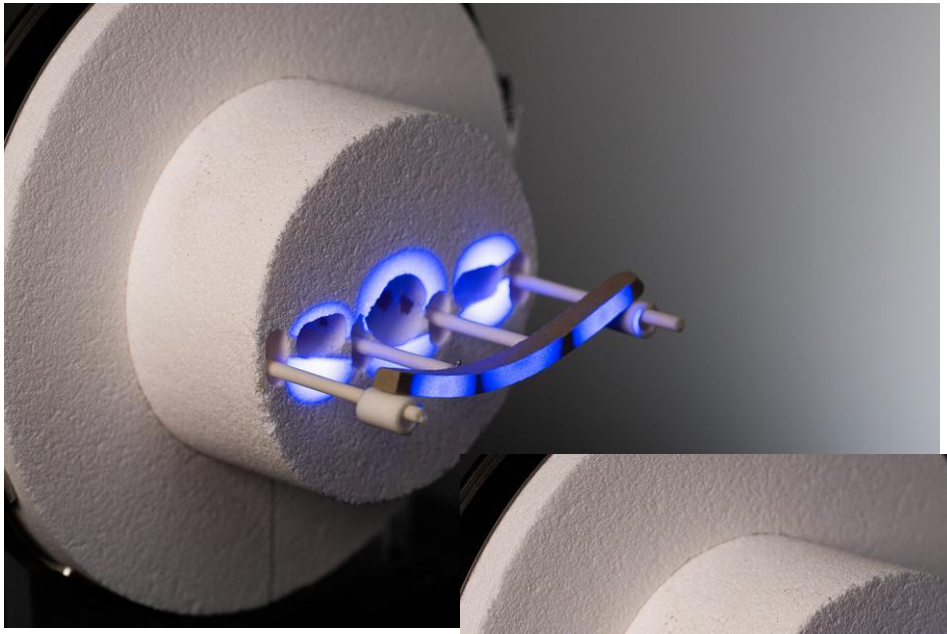
Sample size: 3x2mm cylinder. Up to 4 concurrent samples.

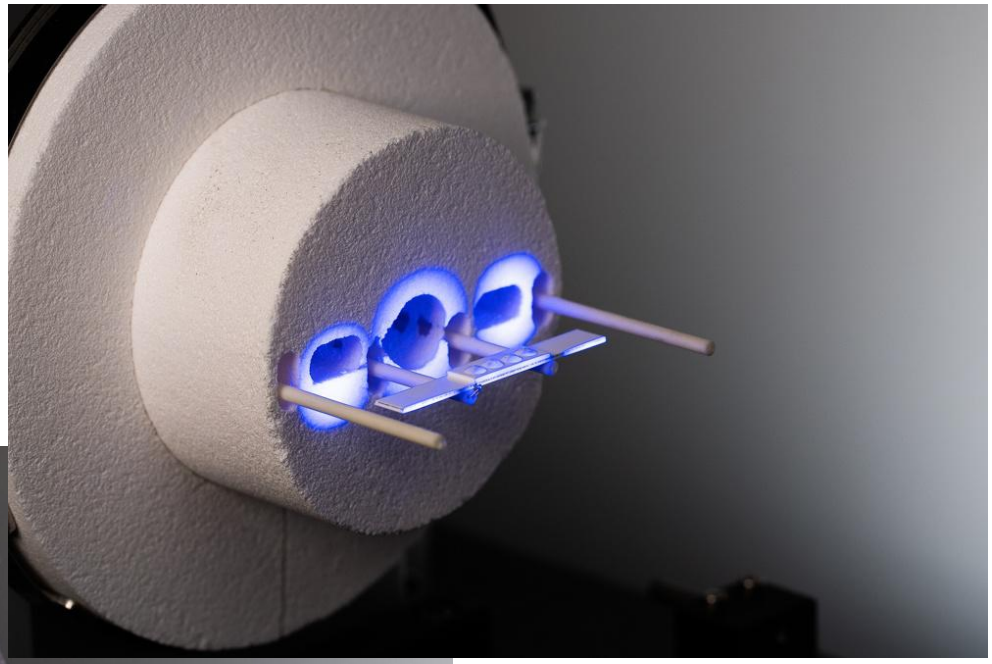
ELS-MDF

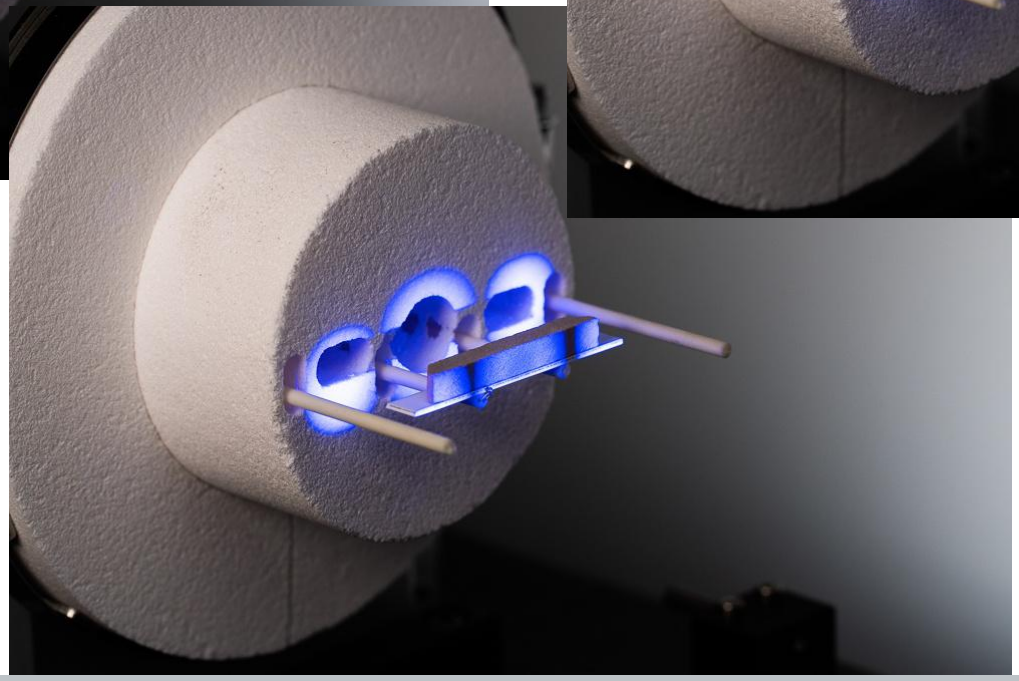
The all-in-one optical thermal analyzer



Microscope, Dilatometer, Fleximeter







Real Quartz+Alumina powders

To validate the method, we prepared pressed samples with **exact proportions of quartz and alumina powders** (10% and 20% in weight).

After drying, we measured their thermal expansion at 10°C/min up to 1000°C. The optical dilatometer is able to accurately measure highly **incoherent samples without exerting any pressure**.

The samples needed at least 2 cycles in order for the powders to adjust and **stabilize**.

After that, the expansion curve is **lower** than the theoretical quartz. A classical explanation is that part of the expansion is absorbed first by filling nearby voids, before causing a macroscopic expansion.

From volume to weight: through density

Without interactions, a dilatometric curve is exclusively related to the fractional volumes of components. To convert a fractional volume to a weight, and thus validate the PTR method, we need the ratio between the quartz density and the total density.

The fractional quartz mass m_Q of a mixture with absolute mass M_Q (quartz) and M_A (Al2O3) and volume Vol_{mix} is obtained from its fractional volume V_Q times the ratio between quartz and total density:

$$V_Q = \frac{Vol_Q}{Vol_{mix}} \quad , \quad Vol_Q = \frac{M_Q}{\rho_Q} \quad , \quad Vol_{mix} = \frac{\left(M_Q + M_A\right)}{\rho_{mix}} = \frac{M_{mix}}{\rho_{mix}}$$

$$V_Q = \frac{M_Q/\rho_Q}{M_{mix}/\rho_{mix}} = \frac{M_Q}{M_{mix}}\frac{\rho_{mix}}{\rho_Q} = m_Q\frac{\rho_{mix}}{\rho_Q}$$

$$m_Q = V_Q\frac{\rho_Q}{\rho_{mix}}$$

From volume to weight: through density

Conversely, the mix density ρ_{mix} is going to be the mean of the quartz ρ_Q and alumina ρ_A densities weighted by their fractional volume V_Q:

$$\rho_{mix} = \frac{M_{mix}}{Vol_{mix}} = \frac{M_Q + M_A}{Vol_{mix}} = \frac{Vol_Q \rho_Q}{Vol_{mix}} + \frac{Vol_A \rho_A}{Vol_{mix}} = V_Q \rho_Q + (1 - V_Q)\rho_A$$

Thus the final equation for converting a fractional volume V_Q into a fractional mass m_Q given separate densities results in:

$$m_Q = V_Q \frac{\rho_Q}{\rho_{mix}} = V_Q \frac{\rho_Q}{(V_Q \rho_Q + (1 - V_Q)\rho_A)}$$

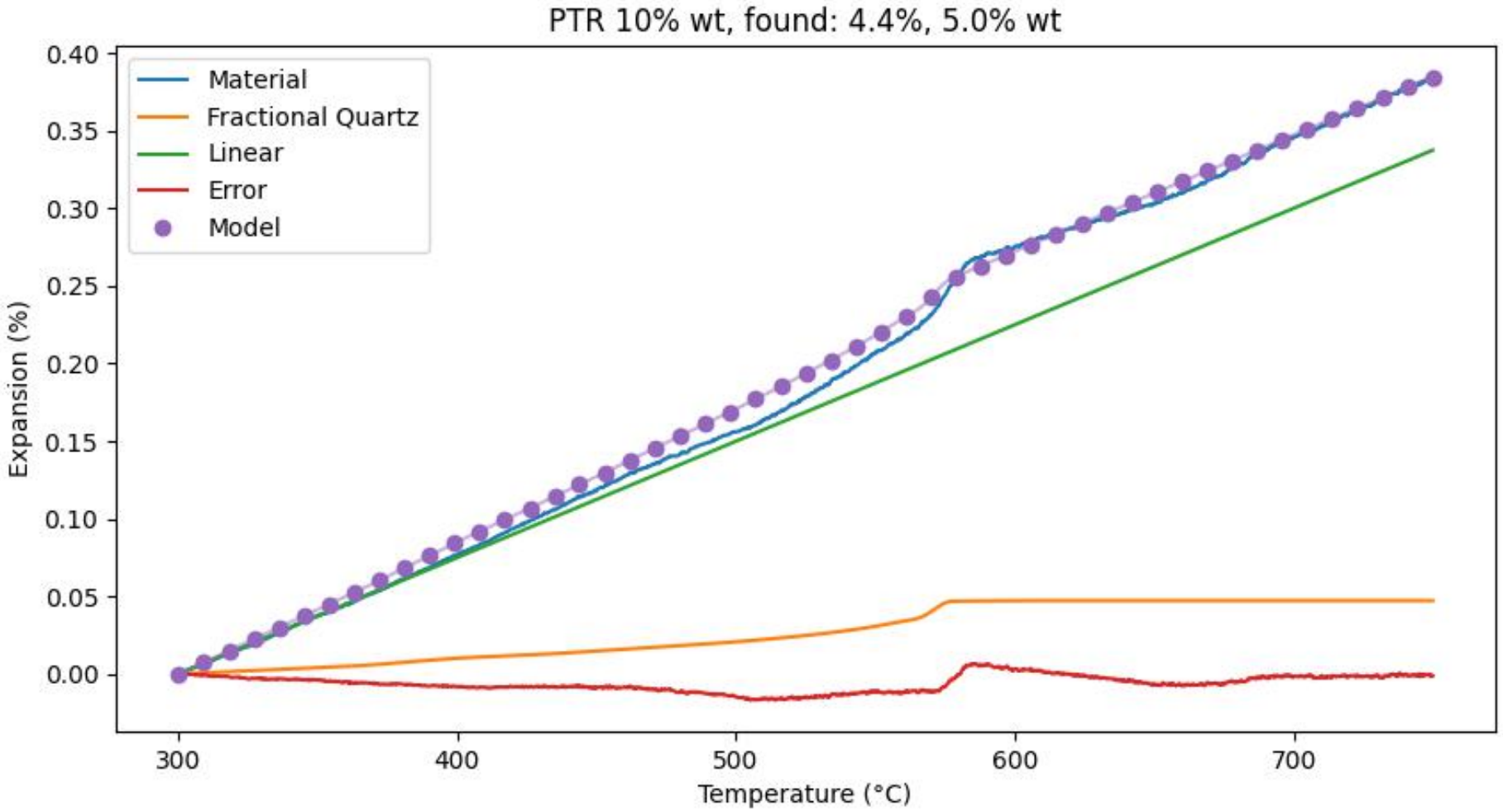
Apparent powder density

Powder densities for quartz and alumina are sensibly different from their solid values. We measure their apparent densities by pressing and drying pure powder samples using the same techniques.

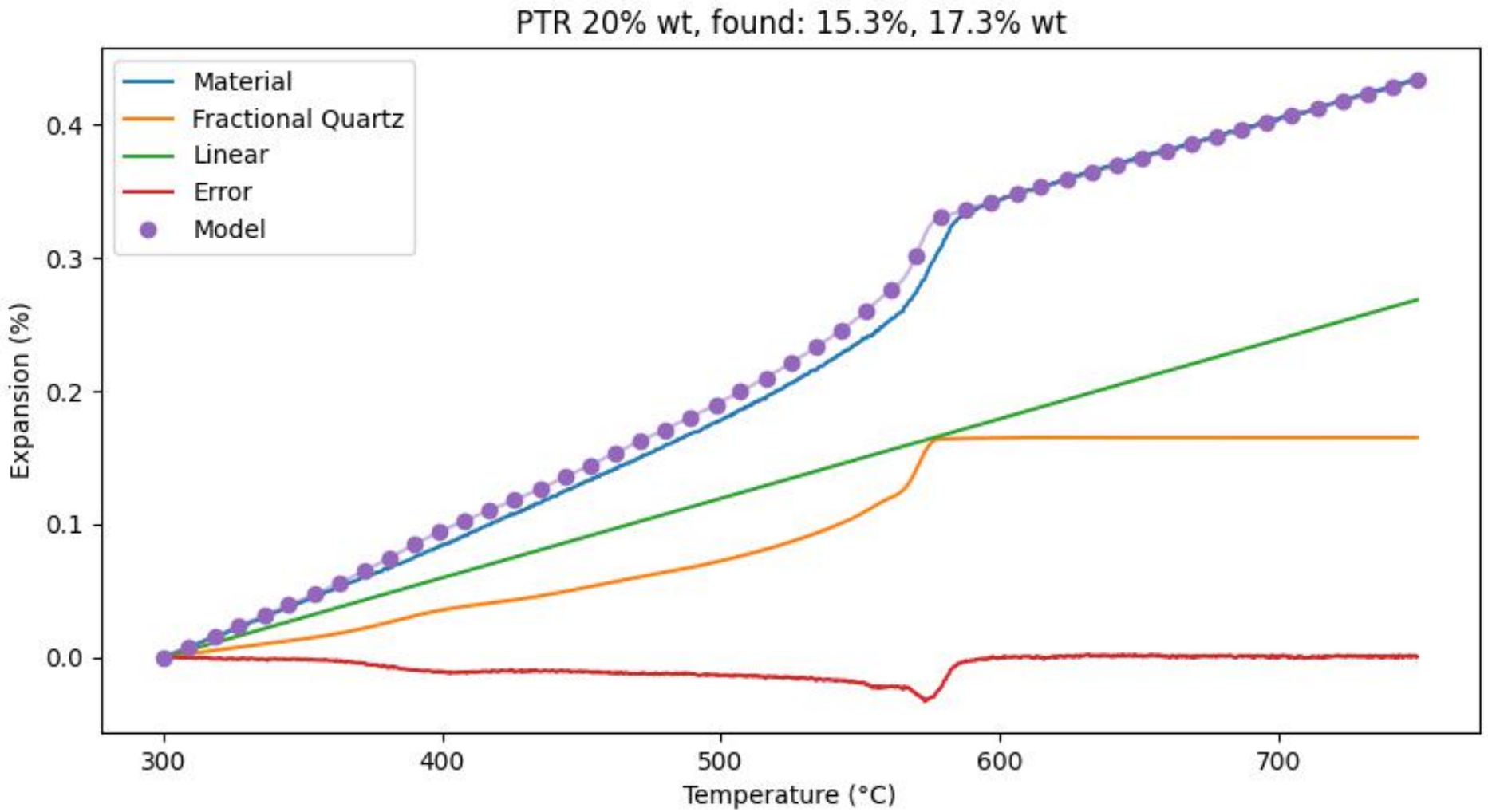
Those will surely vary in the mixture and after the first firing cycle. We hypothesize their ratio remains constant.

Material	Solid density	Pressed+dried powder density
Quartz	2.64 g/cm^3	2.04 g/cm^3
Alumina	3.99 g/cm^3	1.77 g/cm^3

PTR: Quartz 10% Alumina 90% wt



PTR: Quartz 20% Alumina 80% wt



Delayed Smoothing of Quartz (DSQ)

The transition of dispersed powders in a massive sample is delayed and spread over a wider temperature range. This can be modeled by shifting the quartz temperature and smoothing its shape.

Model function with smoothed quartz:

$$\psi(T) = \alpha T + E(N, \tau) * [V_Q Q(T - \delta)]$$

Where α is the linear component; δ is the thermal delay;

* is the convolution operator used for smoothing;

E is the normalized exponential window with length *N* and shape parameter τ:

$$E(n, \tau) = e^{-(n-n_0)\tau^{-1}} \left[\sum_{n_i=0}^{N} e^{-(n_i-n_0)\tau^{-1}} \right]^{-1}$$

The new model has 5 parameters (V_Q, *a, δ, N,* τ), of which N must be integer, and their behavior is inherently non-linear.

Delayed Smoothing of Quartz (DSQ)

We employ a global search algorithm (Differential Evolution) for the optimal parameters minimizing the error function between model and experimental d(T):

$$min(\varepsilon) = V_Q, \alpha, \delta, N, \tau$$

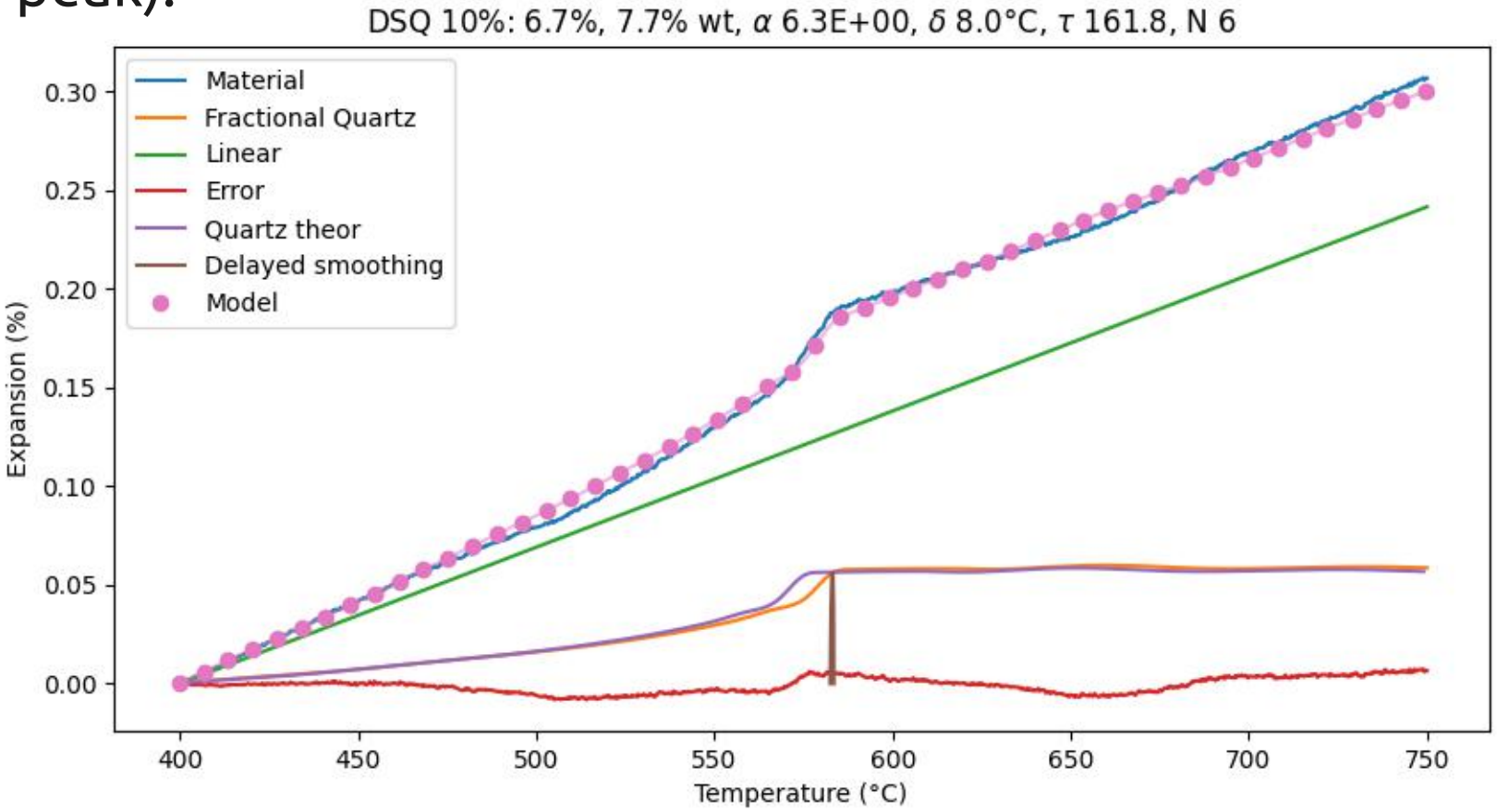
$$\varepsilon = \sum [\psi(T, V_Q, \alpha, \delta, N, \tau) - d(T)]^2$$

Differential evolution is a stochastic population based method: at each pass through the population the algorithm mutates each candidate solution by mixing with other candidate solutions to create the trial candidate.

Note: We choose an exponential smoothing window, assuming an Arrhenius-like physical process. Identical results were obtained with a Gaussian window. Kaiser and Fraser-Suzuki windows were also attempted, with slightly less adherent results and much higher computational cost.

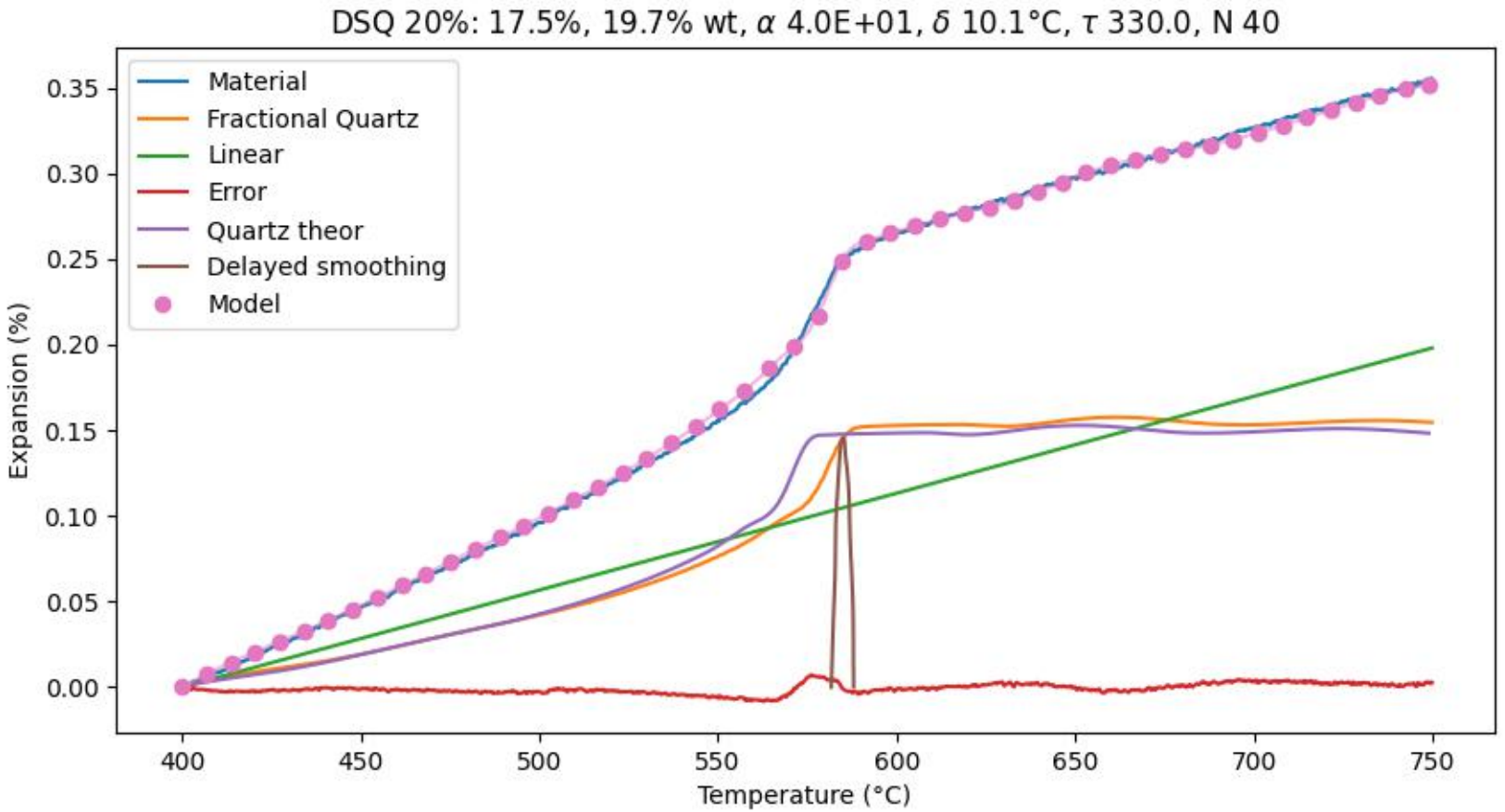
DSQ: Quartz 10% Alumina 90% wt

DSQ finds a better 7.7% of quartz, compared to 5% of PTR. The temperature delay is 8°C. The convolution window is very narrow (brown peak).



DSQ: Quartz 20% Alumina 80% wt

DSQ finds a better 19.7% of quartz, compared to 17.3% of PTR. The temperature delay is 10.1°C. The convolution window is broader.



Green ceramic bodies

Both PTR and DSQ are then applied to real industrial bodies with known mineralogical composition obtained from X-ray.

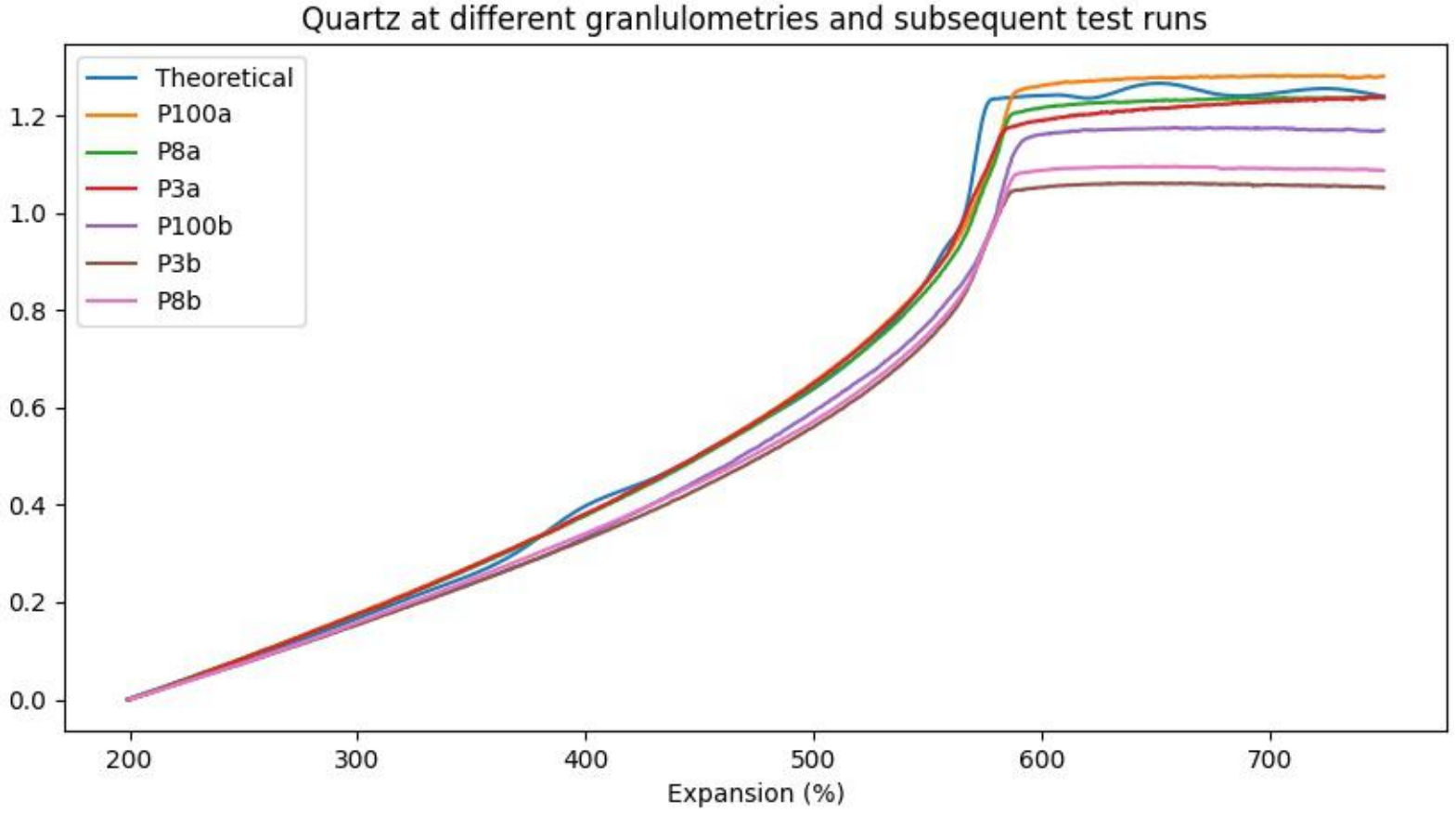
Green samples are pressed, dried and measured with a firing cycle of 10°C/min up to 1000°C then 80°C/min up to 1205°C and -10°C/min down to 200°C.

The apparent density of green slabs is directly calculated from its mass and volume, and plugged into the conversion from volume to mass fractions:

$$m_Q = V_Q \frac{\rho_Q}{\rho_{mix}}$$

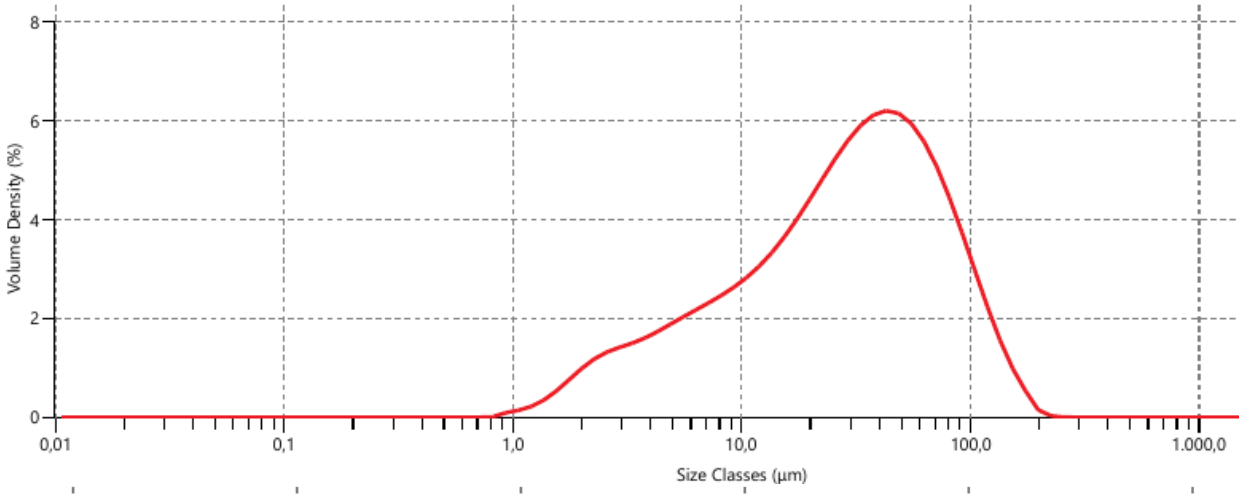
Linear Combination of Granulometries (LCG)

Real ceramics have a much more complex quartz granulometries. To address this fact, we choose two very different quartz powders (Q100 and Q3) and let the model optimize their linear combination.

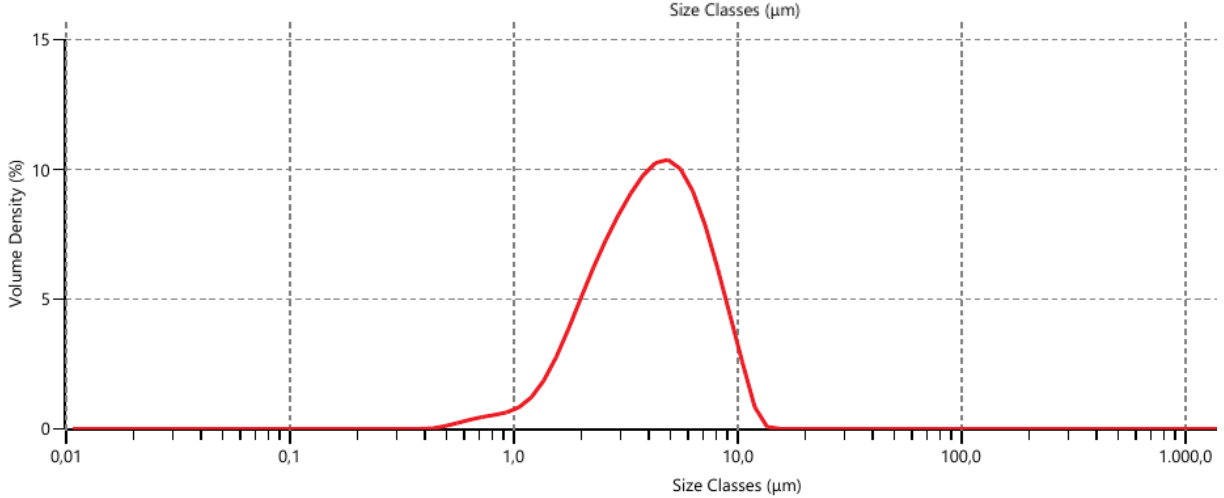


Linear Combination of Granulometries (LCG)

The Mie scattering granulometry for Q100, V_{Q1} and Q3, V_{Q2}



Q100, V_{Q1}
100% < 236um
90% < 86
50% < 30



Q3, V_{Q2}
100% < 13um
90% < 8
50% < 4

Linear Combination of Granulometries (LCG)

The new model replaces the previous fractional volume V_Q with two volumes, one for Q100, V_{Q1} and one for Q3, V_{Q2}

$$\psi(T)=\alpha T+E(N,\tau)*[V_{Q_1}Q_1(T-\delta)+V_{Q_2}Q_2(T-\delta)]$$

The new model thus has 6 parameters:

$$min(\varepsilon)=V_{Q_1},V_{Q_2},\alpha,\delta,N,\tau$$
$$0<V_{Q_1}+V_{Q_2}<1$$
$$\varepsilon=\sum[\psi(T,V_{Q_1},V_{Q_2},\alpha,\delta,N,\tau)-d(T)]^2$$

The DE optimizer allows to impose non linear-constraints, like the above one on volumes.

Real body: A, 22.6% of quartz

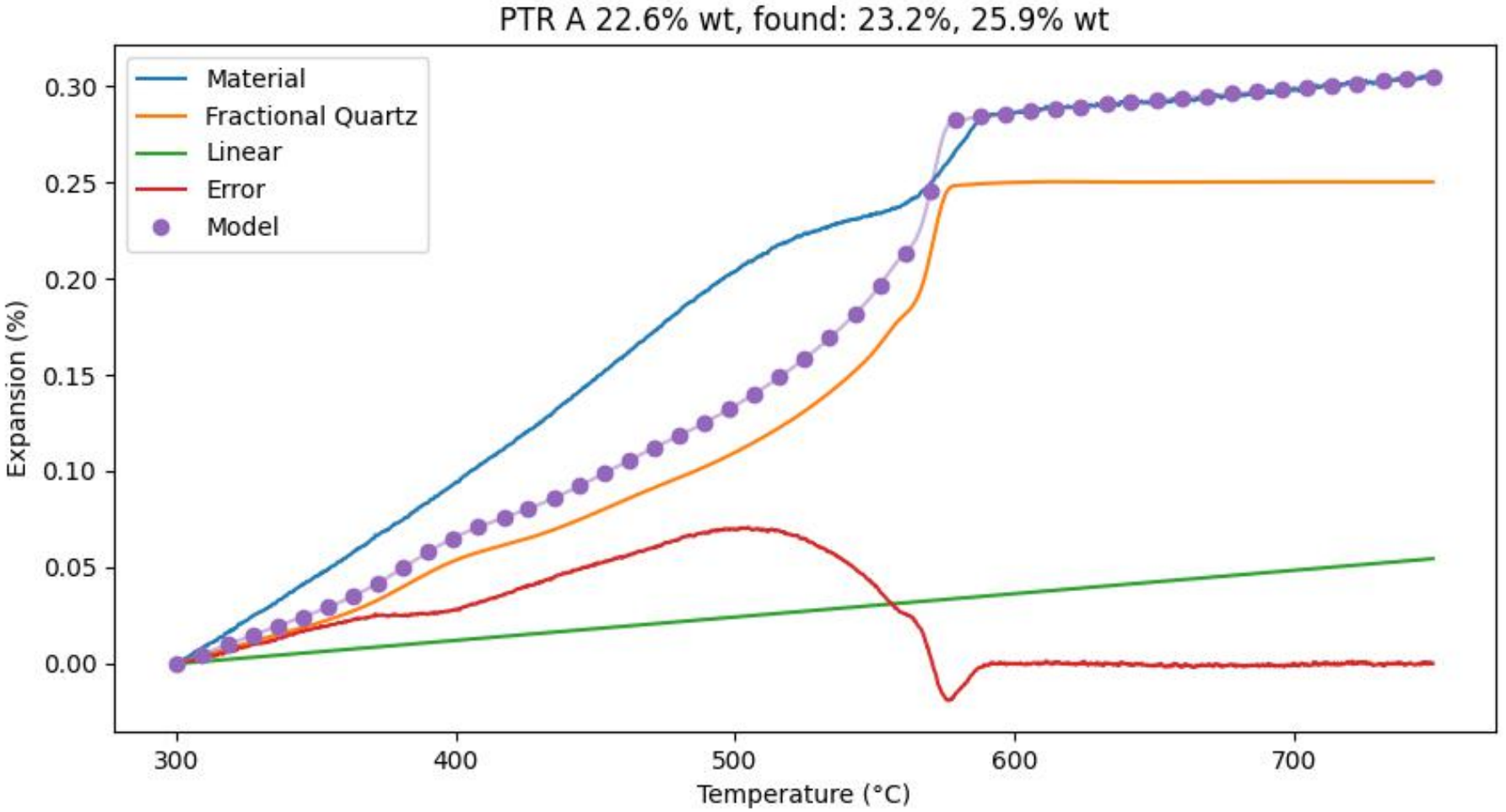
The DSQ method is applied to 3 bodies with different quartz content coming from X-ray analysis. Density: 1.833 g/cm³

Chemical Composition		
Oxides	**Green (%)**	**Fired (%)**
SiO_2	65,10	68,70
Al_2O_3	20,10	21,21
Fe_2O_3	1,85	1,95
TiO_2	0,42	0,44
CaO	0,40	0,42
MgO	0,49	0,52
Na_2O	3,08	3,25
K_2O	3,32	3,50
Total without LOI	94,76	100,00
LOI	4,66	
Total	99,42	

Mineralogical Composition	
Minerals	**%**
Quartz	22,6
Kaolinite	13,7
Muscovite	29,7
Plagioclase	26,3
K-Feldspar	3,1
Siderite	2,9
Rutile	0,4
Dolomite	1,3
TOTAL	**100,0**

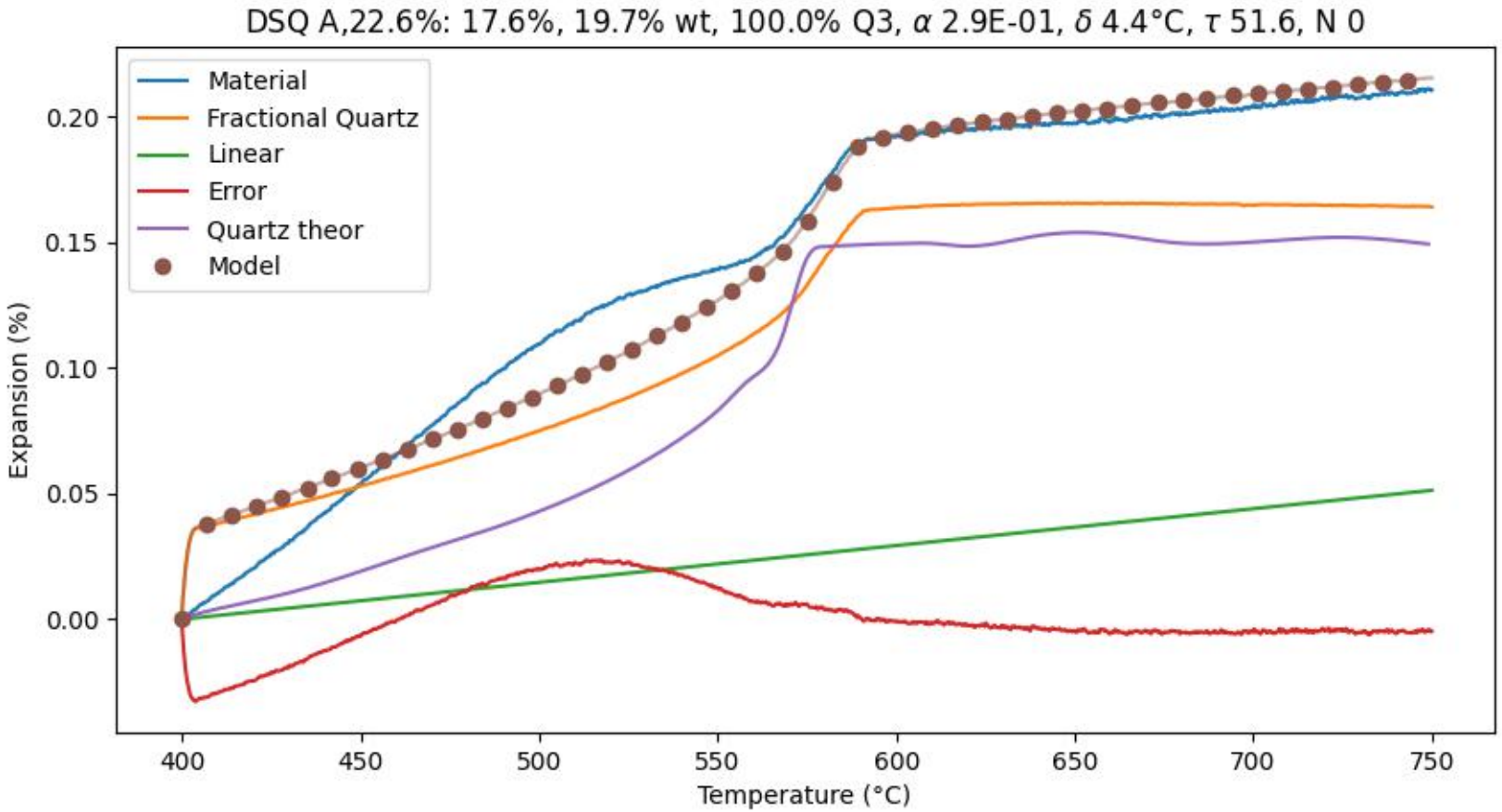
Real body: A, 22.6% of quartz, PTR

Post-Transition Removal finds 25.9% of quartz



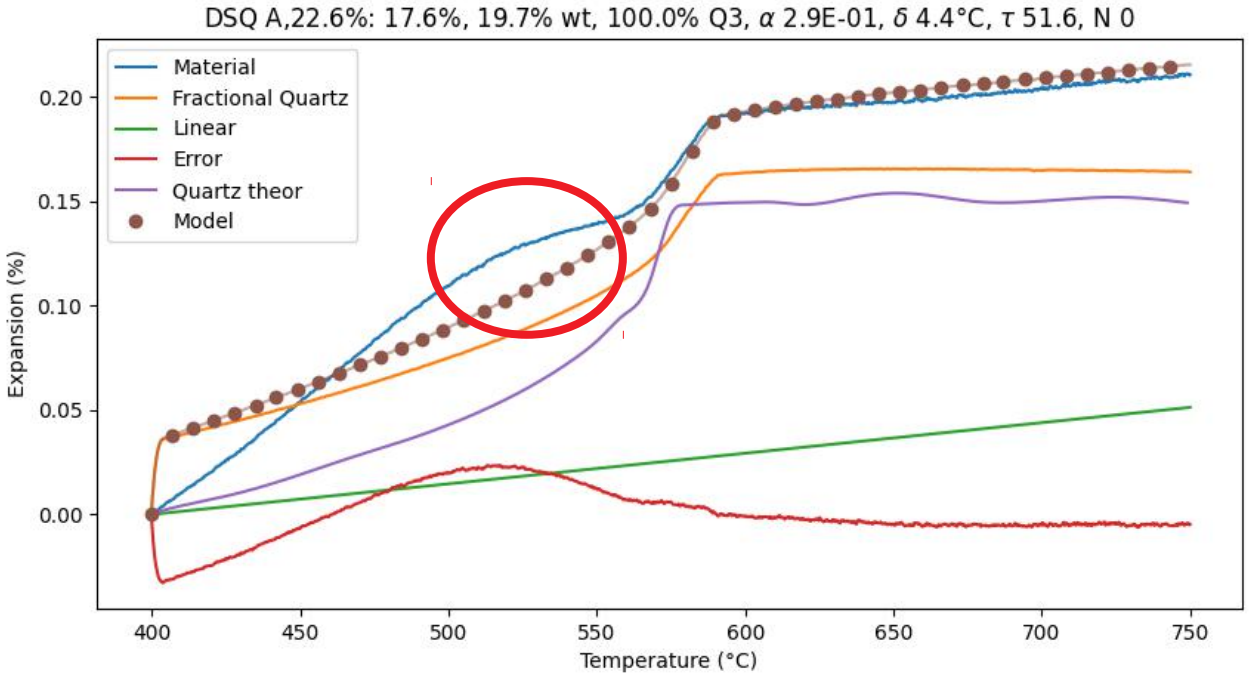
Real body: A, 22.6% of quartz, DSQ+LCG

Delayed Smoothing finds 19.7% of quartz. Only the Q3 fraction was used. The fit is quite poor before the transition.



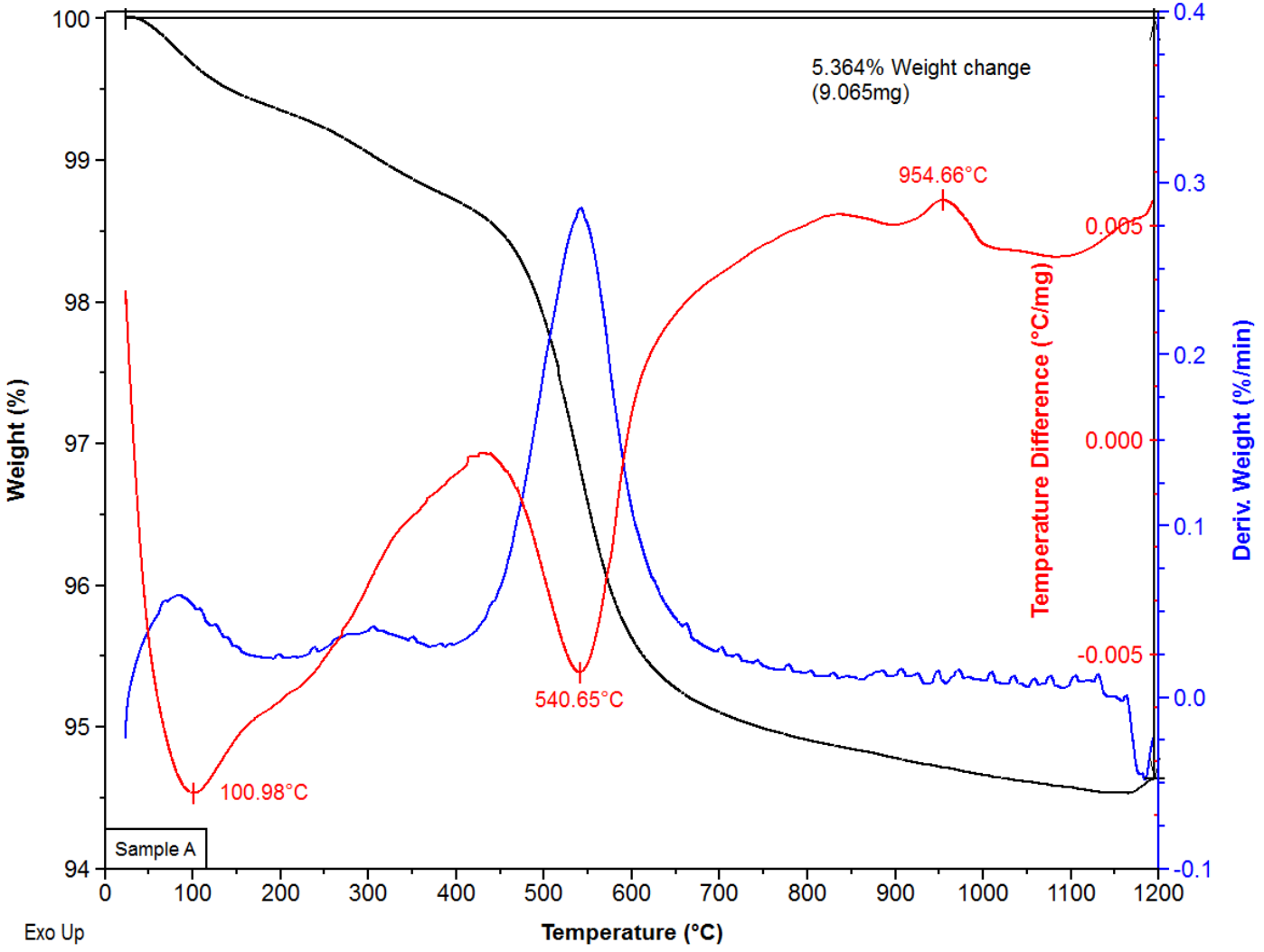
Modeling the anomaly around 500°C

The heating portion presents an anomaly ~500°C which causes a huge discrepancy with the model. This anomaly should be accounted for method validation purpose. In that temperature range we some known phenomena which could possibly overlap to and explain the anomaly: **burning** of organic compounds (binders) or **dehydroxylation** of clay.



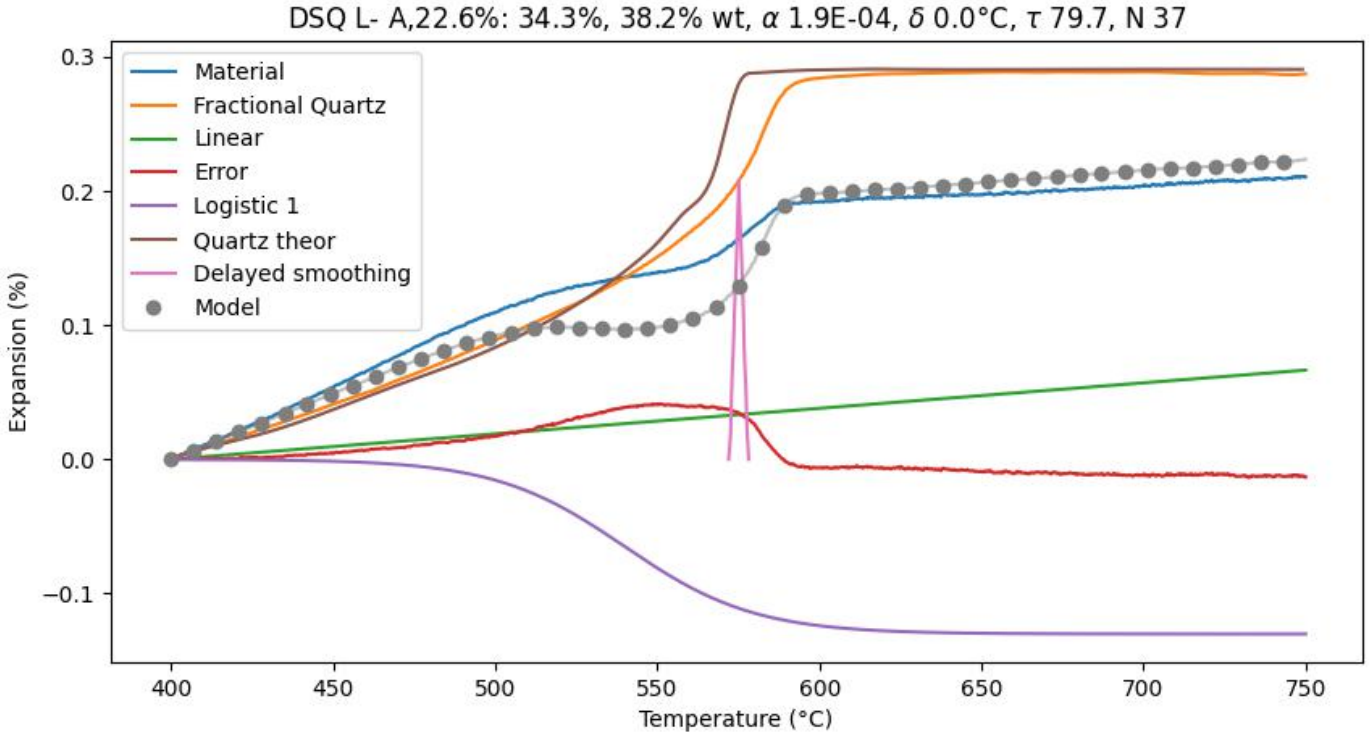
TGA-DTA

The combined TGA-DTA-MS analysis reveals weight losses between 400°C and 700°C. The sample is much smaller than the one used for dilatometry, so the peak at 540 can be significantly shifted.



Direct decomposition → shrinkage?

The total weight loss is ~4%: too small to justify such a huge peak on the expansion curve. Furthermore, to recover from the previous inflection, we would end up requiring too much quartz to be present. The decomposition was modeled with a simple logistic curve added to the model, but then dramatically overestimates the quartz content (38%):



Gas trapping hypothesis (GDSQ+LCG)

This lead to the hypothesis of some sort of process which is first causing then absorbing and expansion. For example, the decomposition/combustion gases could be trapped and slowly released. This process was modeled by adding a Gaussian curve to the model, with 3 more parameters A_G, T_G, σ:

$$\psi(T)=\alpha T+E(N,\tau)[V_{Q_1}Q_1(T-\delta)+V_{Q_2}Q_2(T-\delta)]+A_G e^{\frac{-(T-T_G)^2}{2\sigma^2}}$$

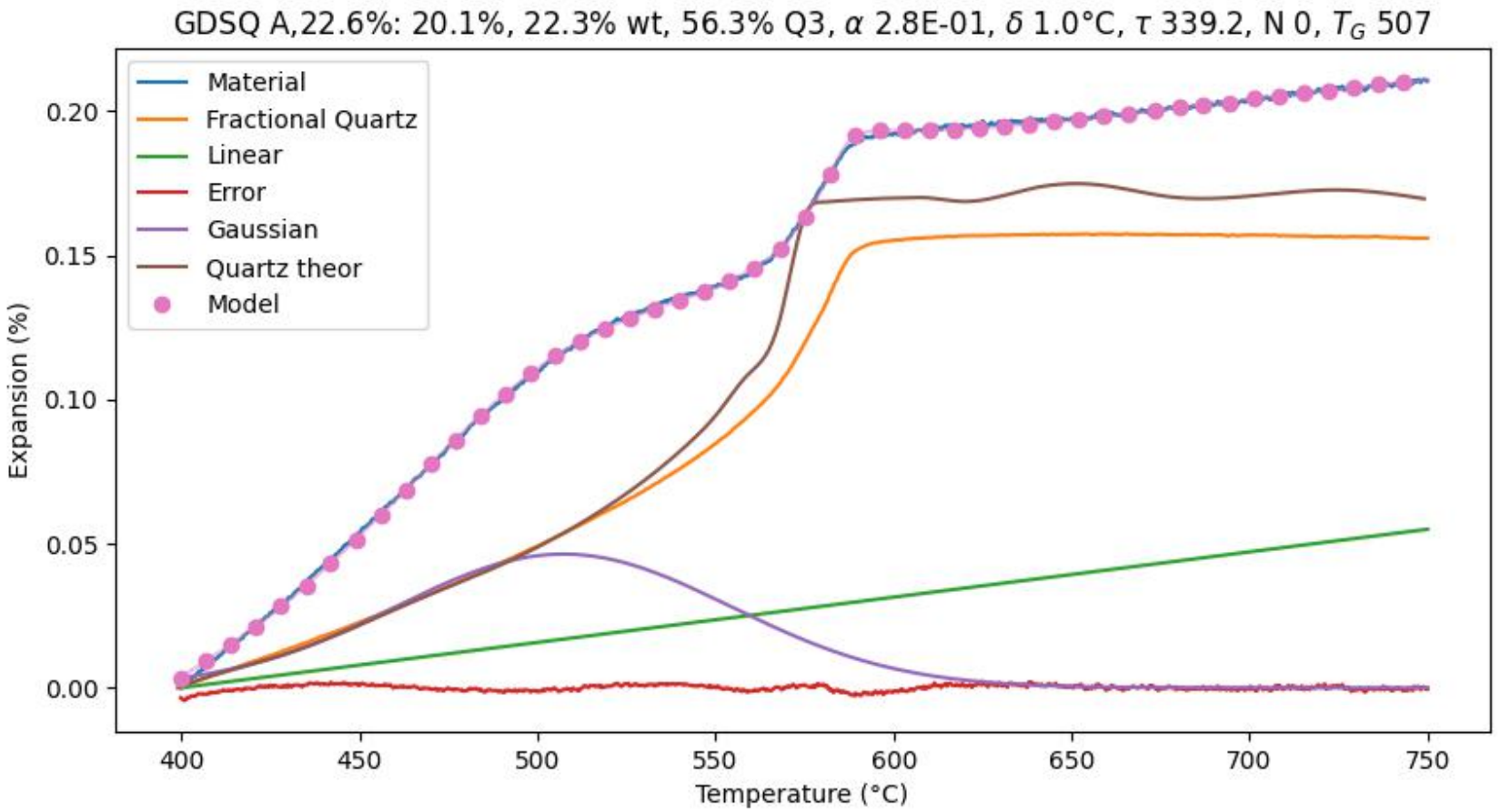
$$min(\varepsilon)=V_{Q_1},V_{Q_2},\alpha,\delta,N,\tau,A_G,T_G,\sigma$$

$$\varepsilon=\sum[\psi(T,V_{Q_1},V_{Q_2},\alpha,\delta,N,\tau,A_G,T_G,\sigma)-d(T)]^2$$

Real body: A, 22.6% of quartz, GDSQ+LCG

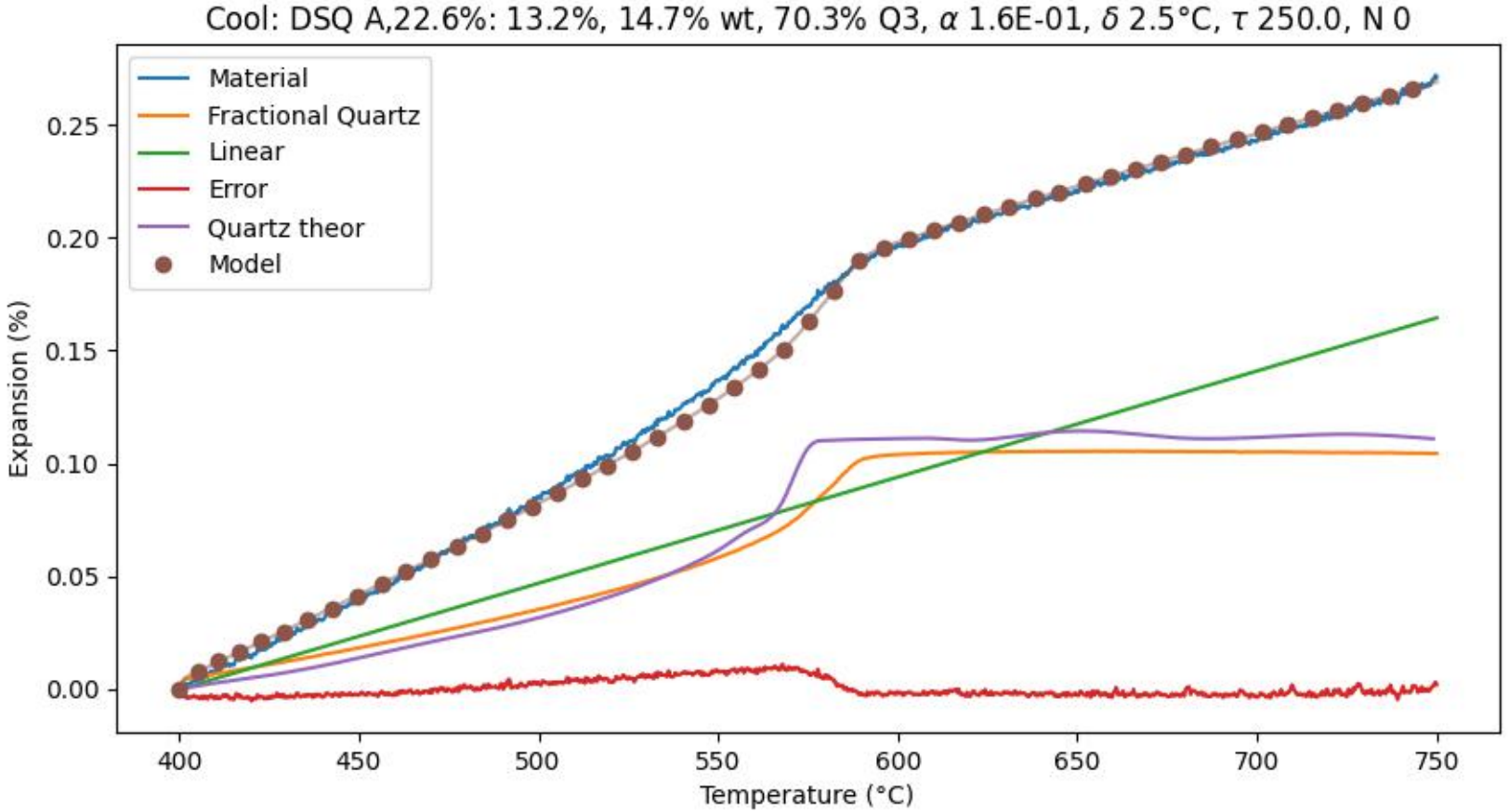
Gaussian+Delayed Smoothing finds 22.3% of quartz, and a much better curve fit. The reaction Gaussian has its peak at 507°C. The Q3 granulometric fraction accounts for 56% of total quartz.

Delay is negligible (δ=1°C) and smoothing is deactivated (N=0), suggesting that LCQ is completely accounting for these effects.



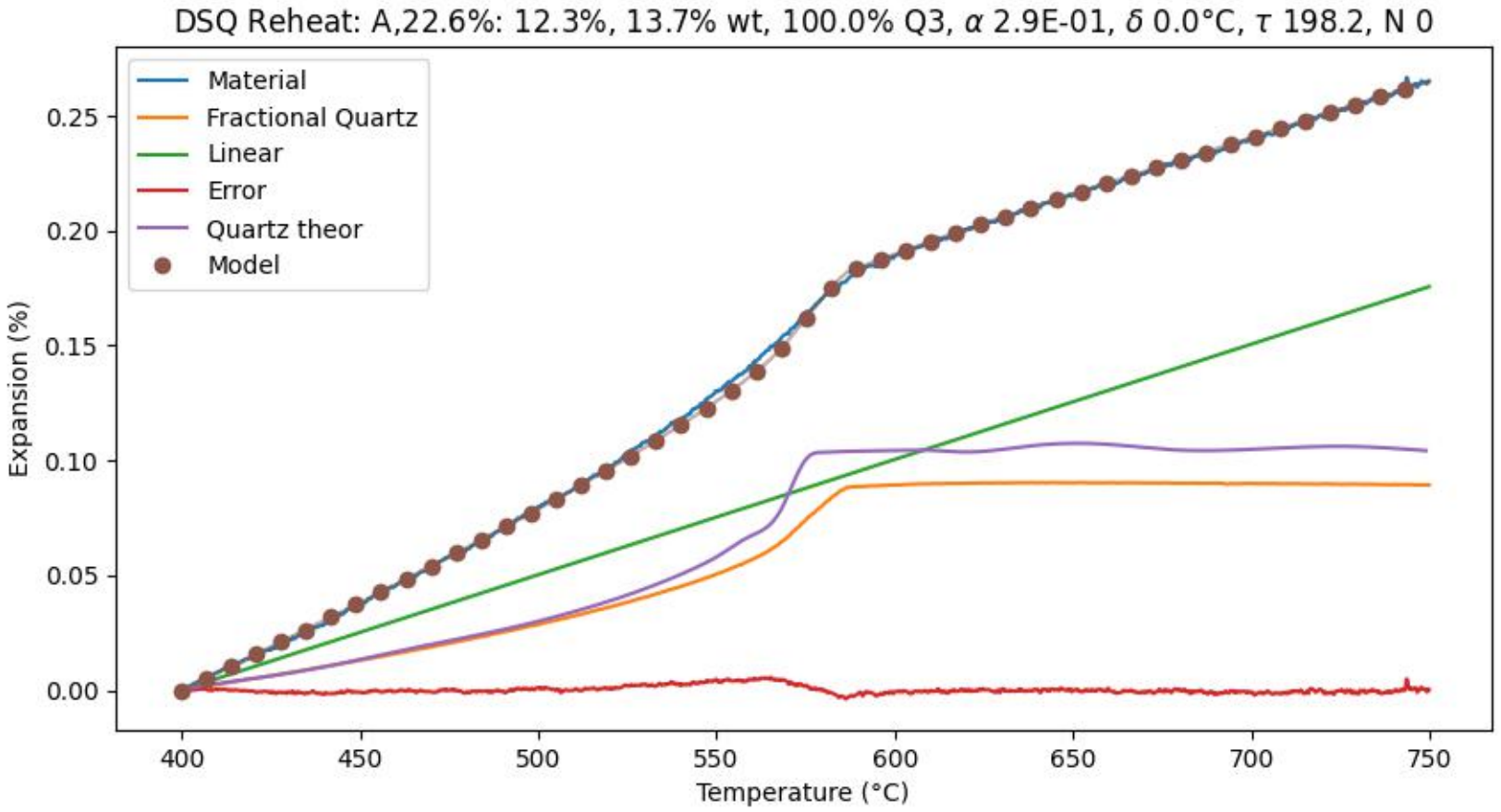
Real body: A, loss of quartz from cooling

The DSQ applied on the reversed cooling portion of the curve reveals a quartz content reduction from 22.3% down to 14.7%. Q3 granulometry rises to 70.3% of quartz.



Real body: A, quartz on reheating

The DSQ applied on reheating the fired sample reveals a similar quartz content: 13.7%.



Real body: B, 42% of quartz

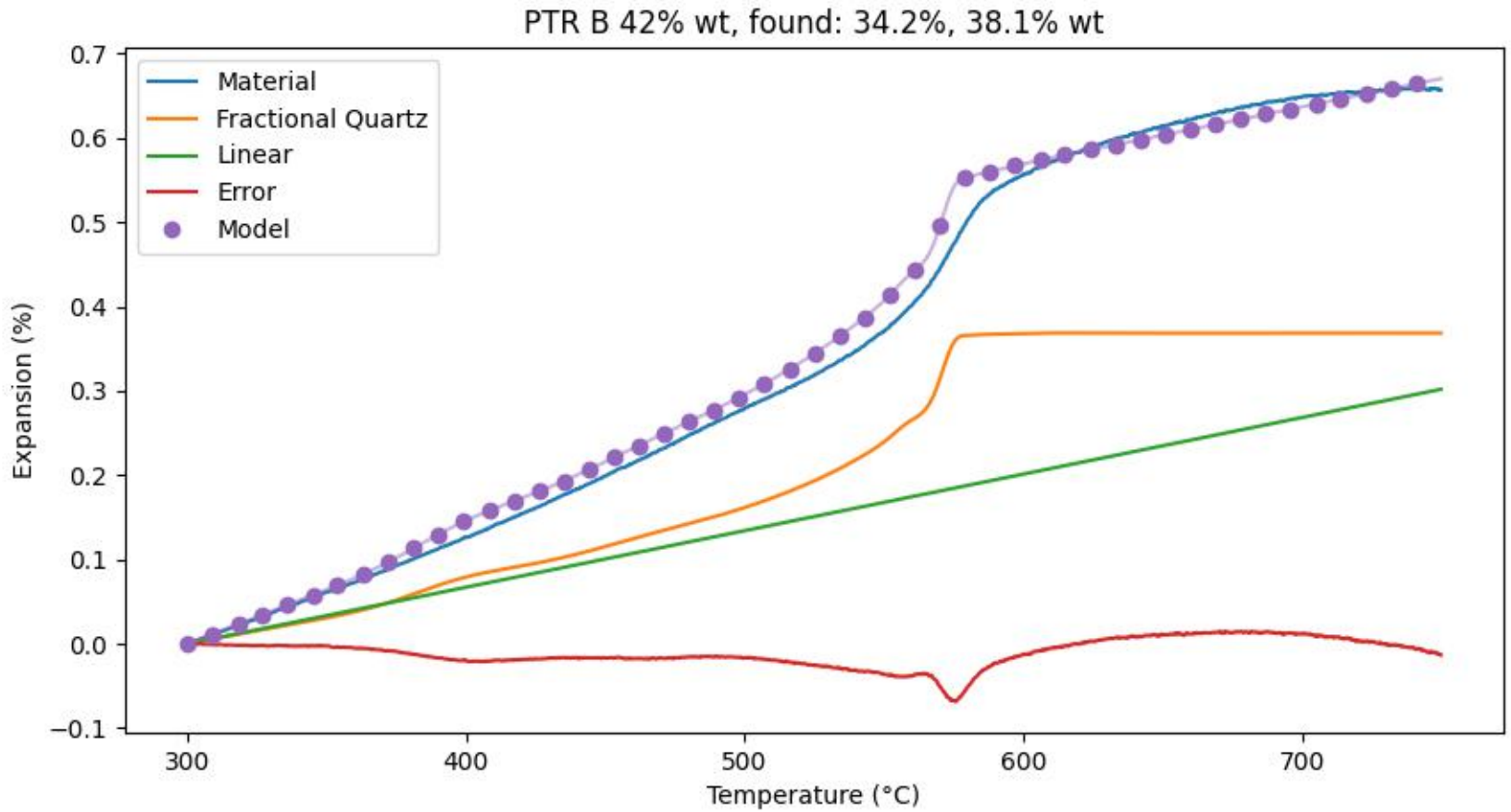
The DSQ method is applied to 3 bodies with different quartz content coming from X-ray analysis. Density: 1.836 g/cm³

Chemical Composition		
Oxides	**Green (%)**	**Fired (%)**
SiO_2	70,90	74,45
Al_2O_3	16,20	17,01
Fe_2O_3	1,12	1,18
TiO_2	0,43	0,45
CaO	1,21	1,27
MgO	1,99	2,09
Na_2O	1,68	1,76
K_2O	1,70	1,79
Total without LOI	95,23	100,00
LOI	4,43	
Total	99,66	

Mineralogical Composition	
Minerals	**%**
Quartz	42,0
Kaolinite	12,2
Muscovite	17,2
Chlorite	6,9
Plagioclase	18,6
K-Feldspar	0,4
Dolomite	1,1
Rutile	0,4
Hematite	1,1
TOTAL	**100,0**

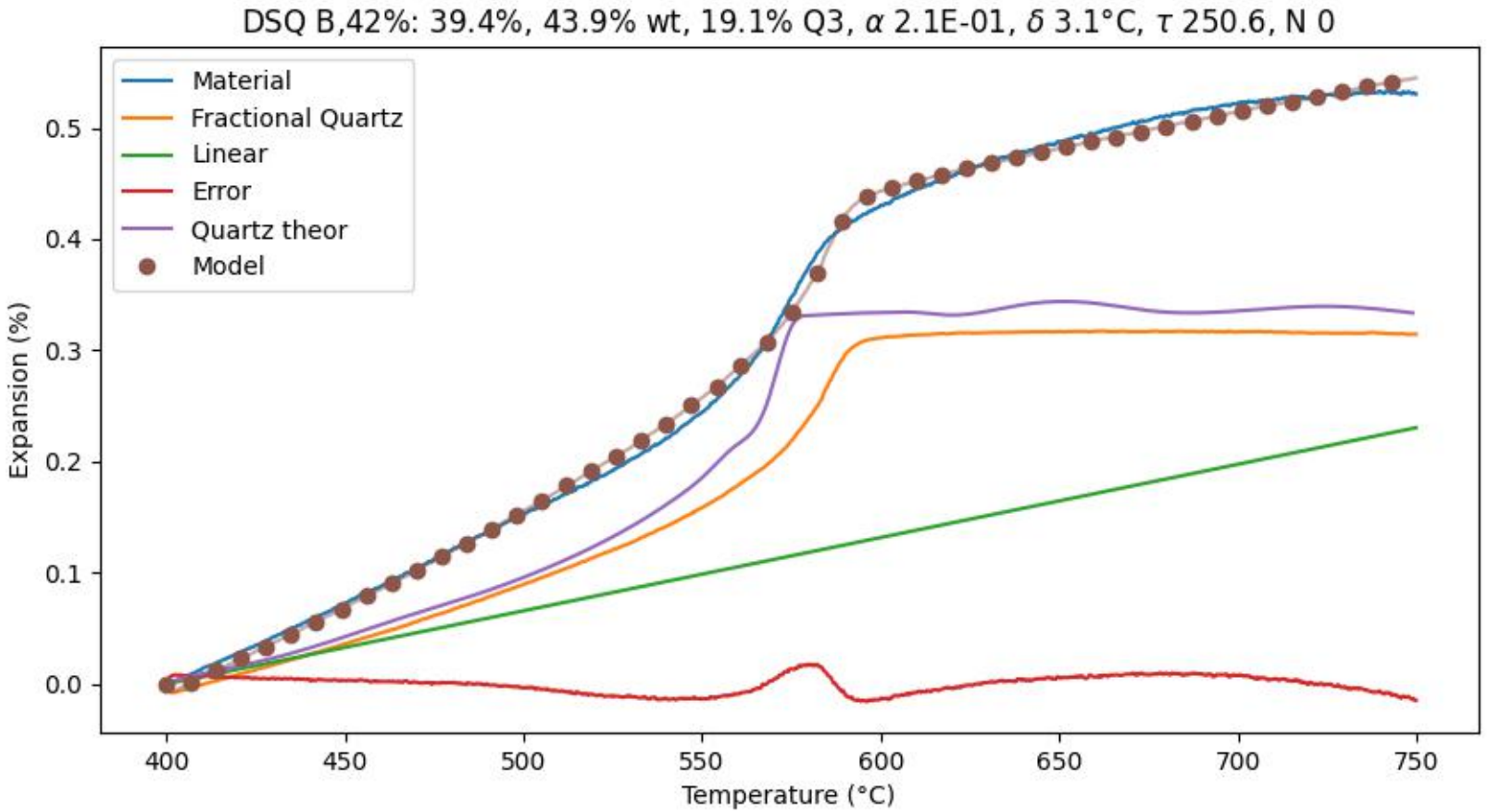
Real body: B, 42% of quartz, PTR

Post-Transition Removal finds 38.1%



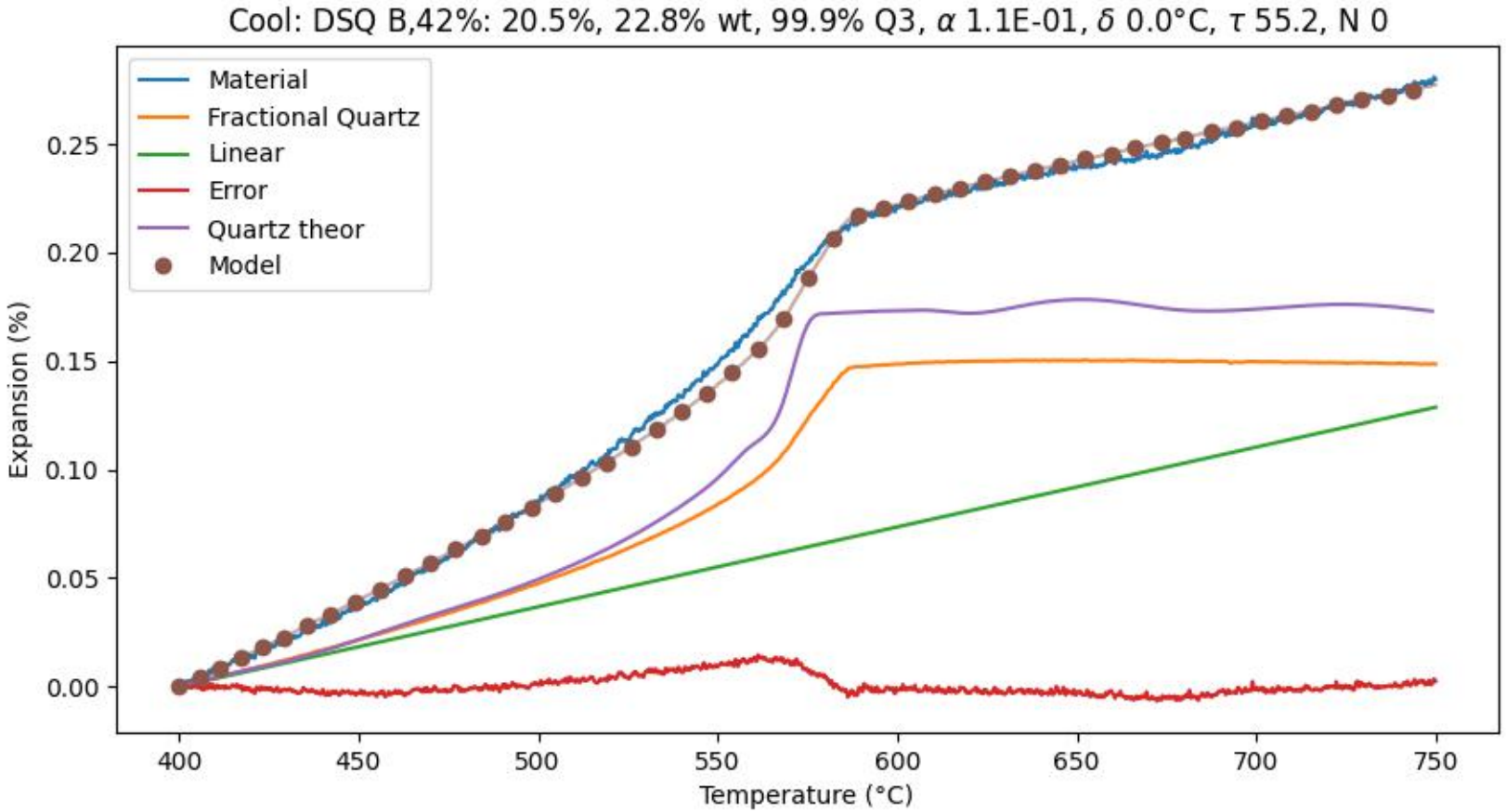
Real body: B, 42% of quartz, DSQ+LCG

DSQ finds 43.5% and no Gaussian component. Q3 accounts for only 19.1% of total quartz.



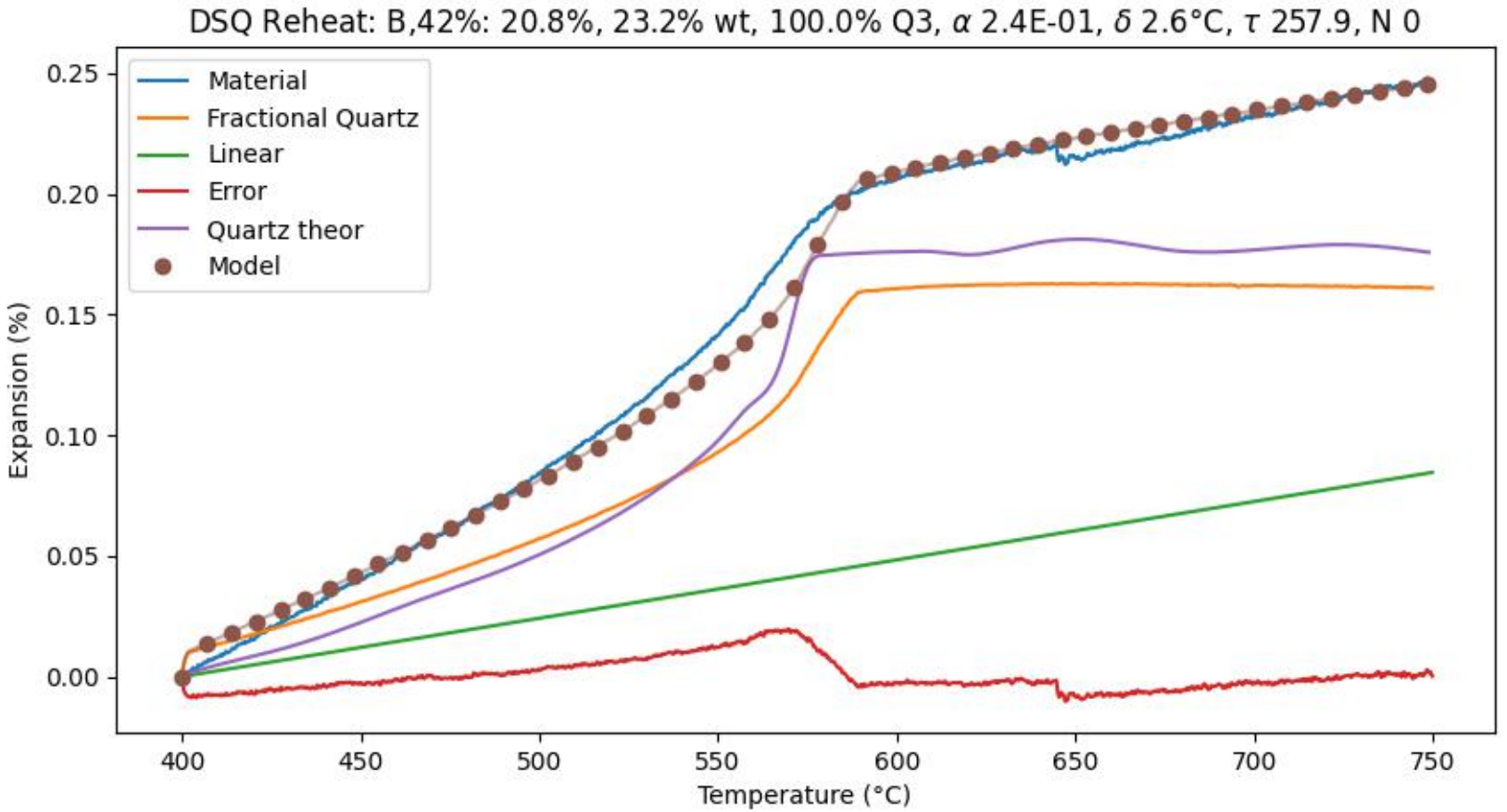
Real body: B, loss of quartz from cooling

The DSQ applied on the cooling portion reveals a quartz content reduction from 43.5% down to 22.8%. The Q3 rises to 100%.



Real body: B, quartz on reheating

The DSQ applied on reheating the fired sample reveals a similar quartz content: 23.2%.



Real body: C, 34.2% of quartz

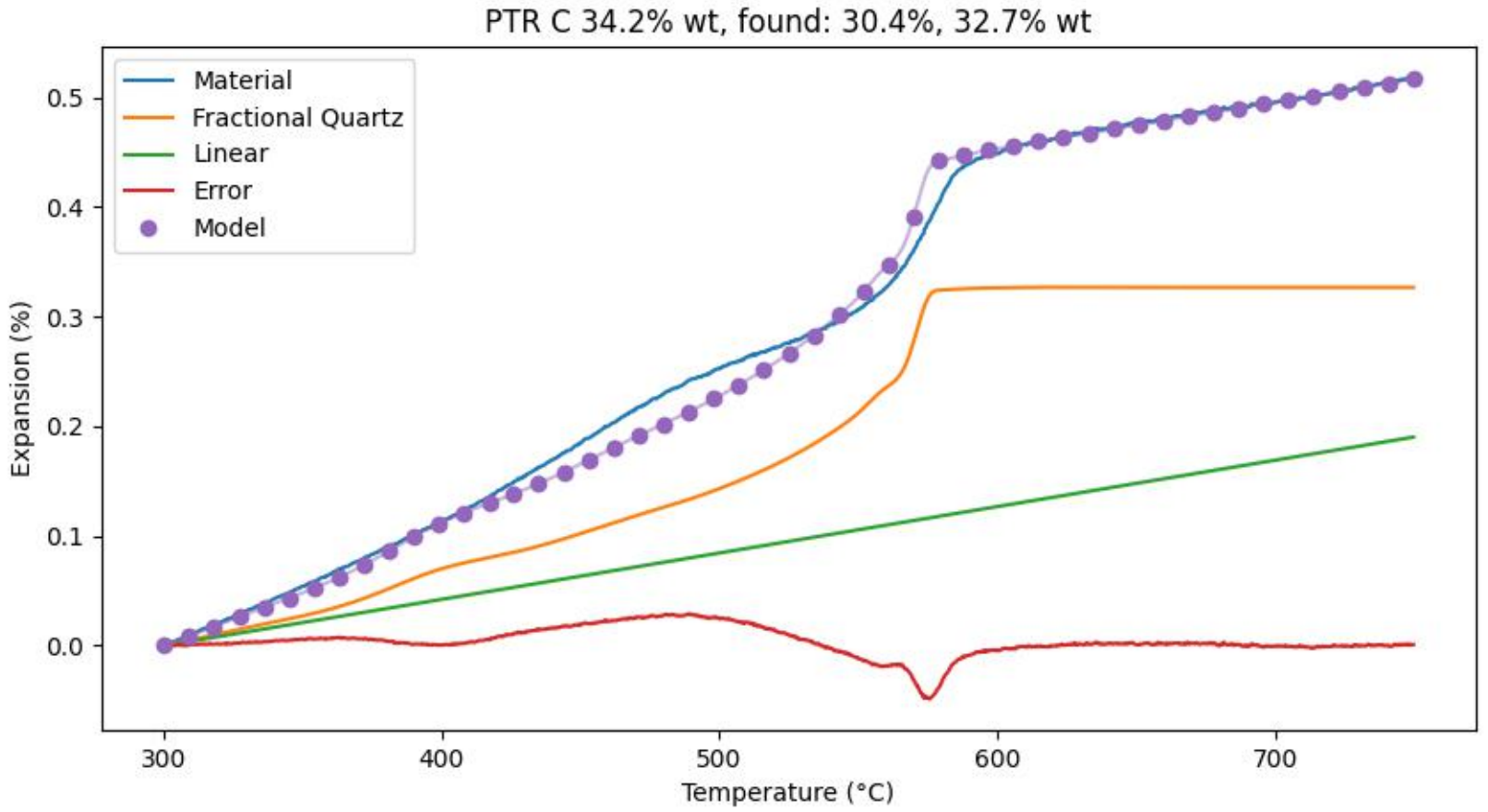
The DSQ method is applied to 3 bodies with different quartz content coming from X-ray analysis. Density: 1.896 g/cm³

Chemical Composition		
Oxides	**Green (%)**	**Fired (%)**
SiO_2	69,40	72,86
Al_2O_3	17,20	18,06
Fe_2O_3	1,00	1,05
TiO_2	0,47	0,49
CaO	1,24	1,30
MgO	0,81	0,85
Na_2O	2,25	2,36
K_2O	2,88	3,02
Total without LOI	95,25	100,00
LOI	4,55	
Total	99,80	

Mineralogical Composition	
Minerals	**%**
Quartz	34,2
Kaolinite	14,0
Muscovite	22,5
Plagioclase	19,6
K-Feldspar	4,4
Dolomite	3,7
Hematite	1,0
Rutile	0,5
TOTAL	**100,0**

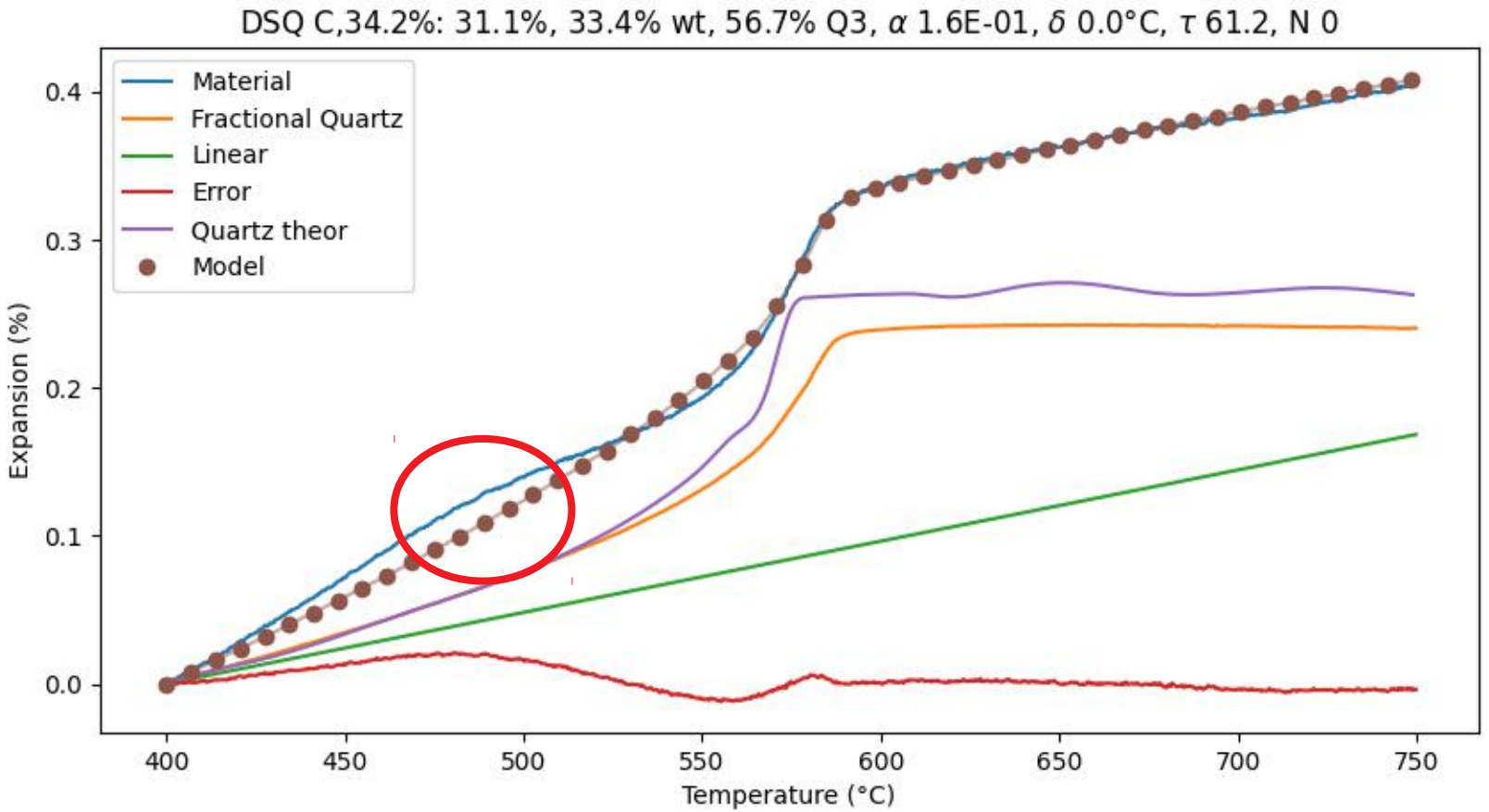
Real body: C, 34.2% of quartz, PTR

Post-Transition Removal finds 32.7%



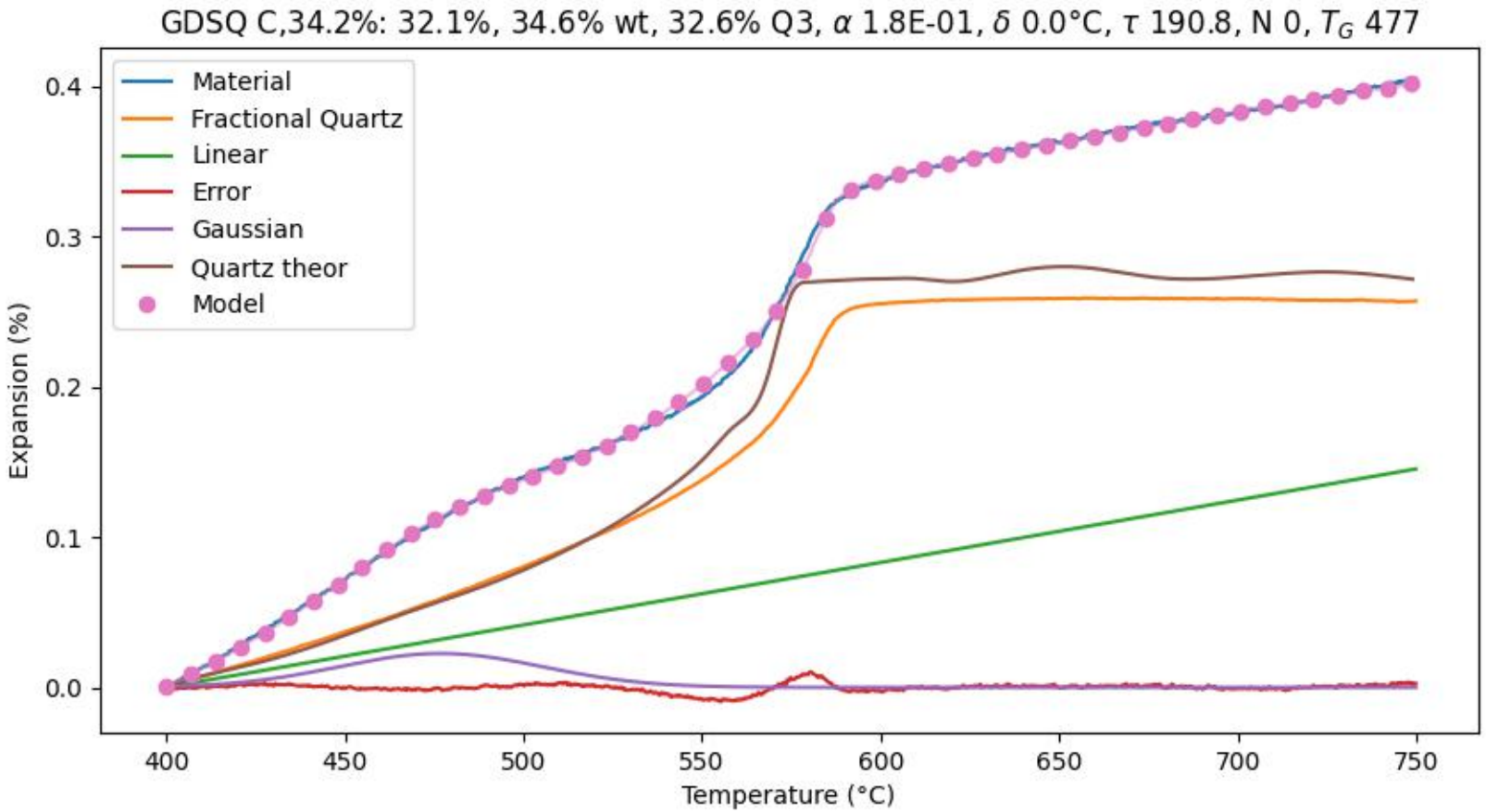
Real body: C, 34.2% of quartz, DSQ+LCG

Delayed Smoothing of Quartzs finds 33.4% and 56.7% of Q3 granulometry.



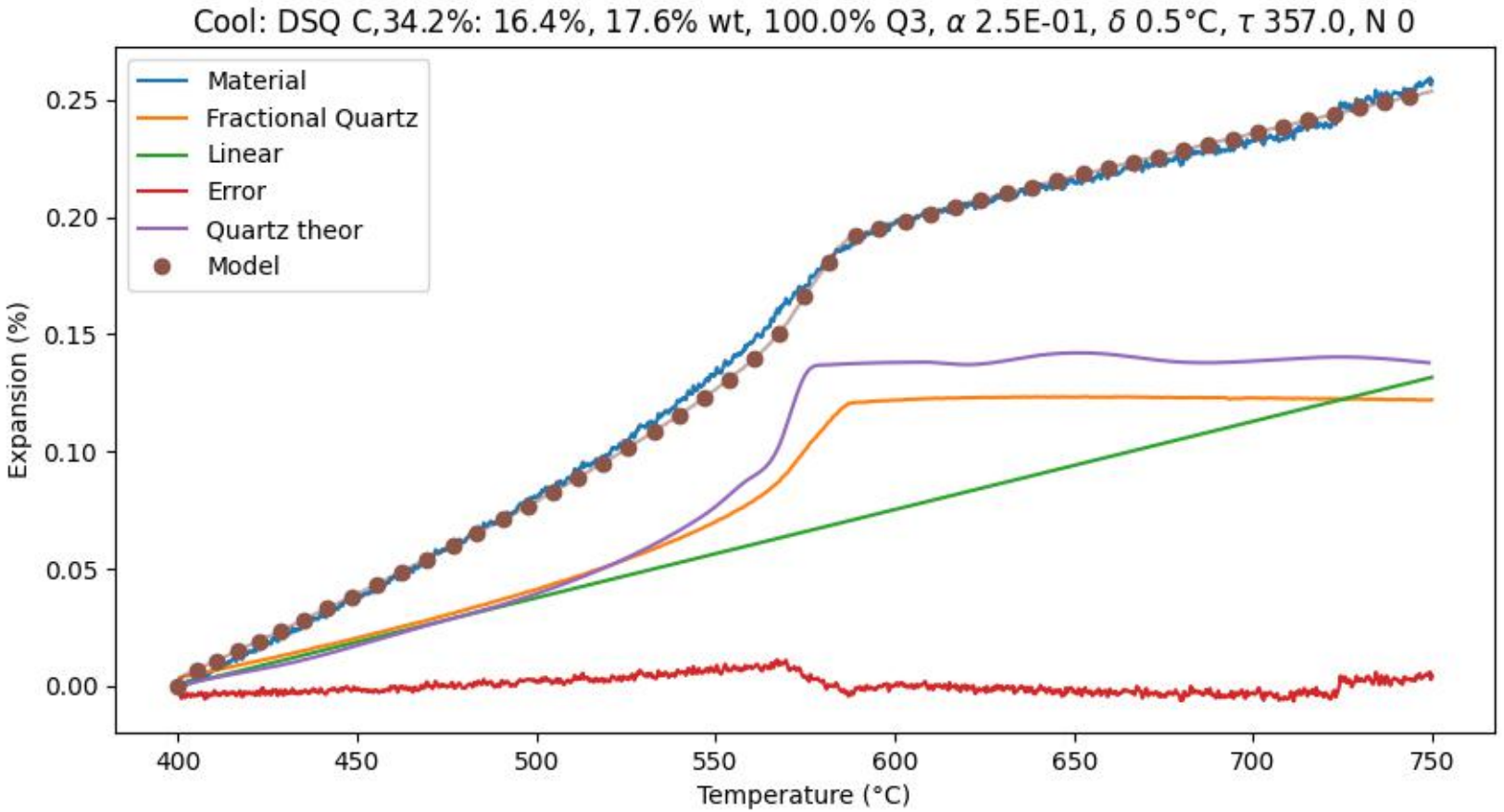
Real body: C, 34.2% of quartz, GDSQ+LCG

Gaussian Delayed Smoothing of Quartz finds a better 34.6%, with the Gaussian peak at 477°C. Q3 accounts for 32.6%.



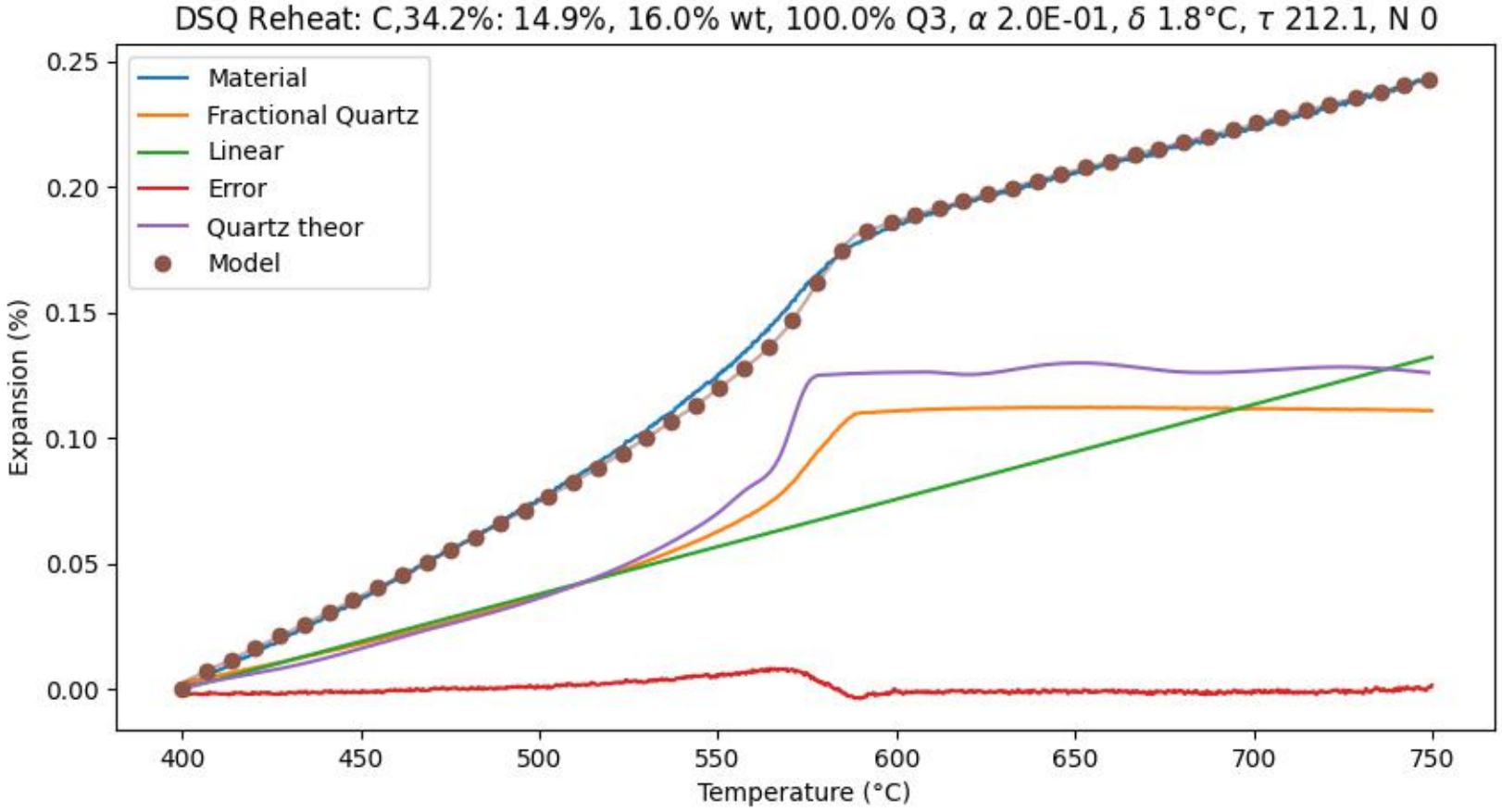
Real body: C, loss of quartz from cooling

The DSQ applied on the cooling portion reveals a quartz content reduction from 34.6% down to 17.6%. Q3 rises to 100%.



Real body: c, quartz on reheating

The DSQ applied on reheating the fired sample reveals a similar quartz content: 16%.

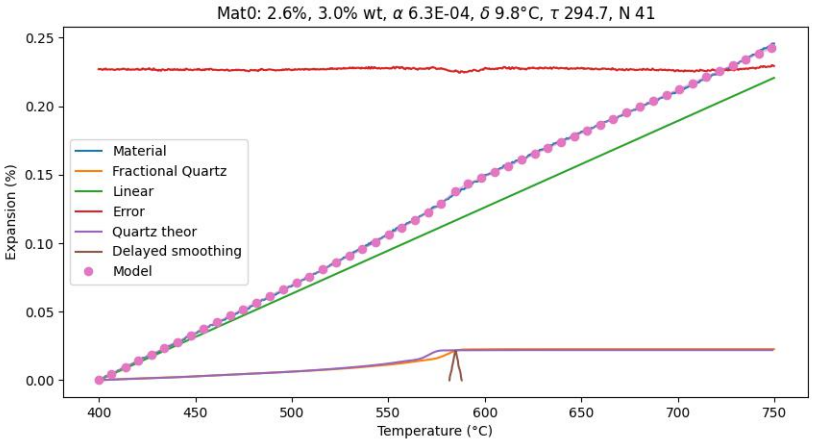


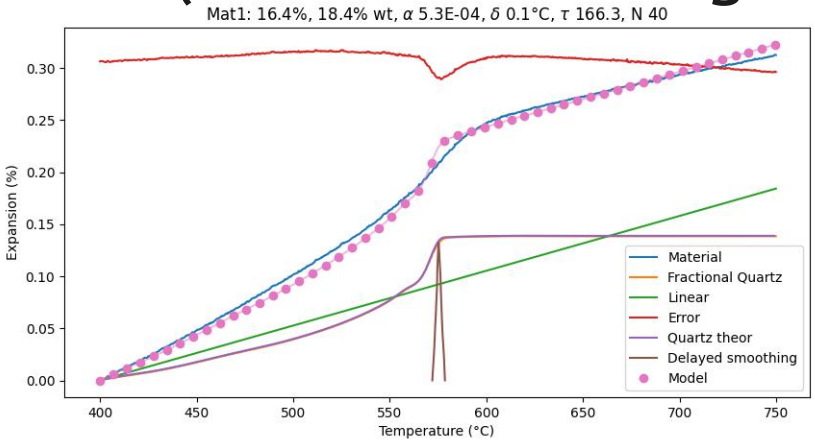
Comparison: Quantification of transient quartz in pressed powders

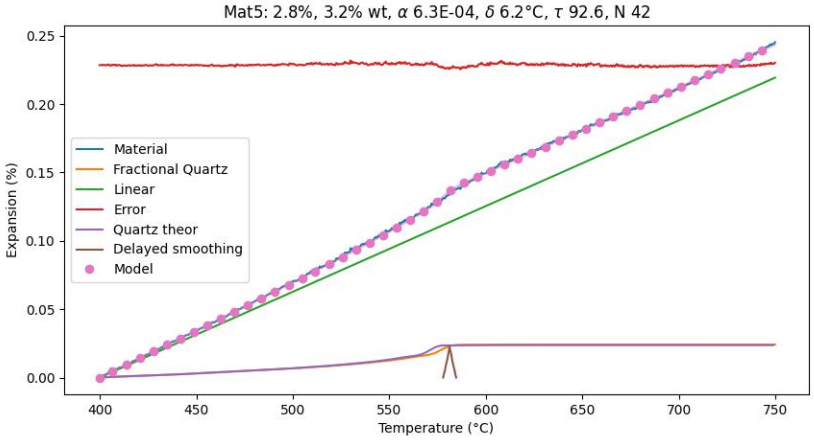
Material	X-Ray	GDSQ	LCG	PTR	Cooling	Reheat
Quartz 10% + Al2O3	10	-	7.7	5	-	-
Quartz 20% + Al2O3	20	-	19.7	17.3	-	-
Body A	22.6	22.3 Q3: 56.3	19.7 Q3: 100	25.9	15.2 Q3: 70	13.6 Q3: 100
Body B	42	-	43.9 Q3: 19.1	38.1	22.8 Q3: 99.9	23.1 Q3: 100
Body C	34.2	34.6 Q3: 56.7	33.4 Q3: 56.7	32.7	17.6 Q3: 100	16 Q3: 100

Screening through undetermined materials: bodies

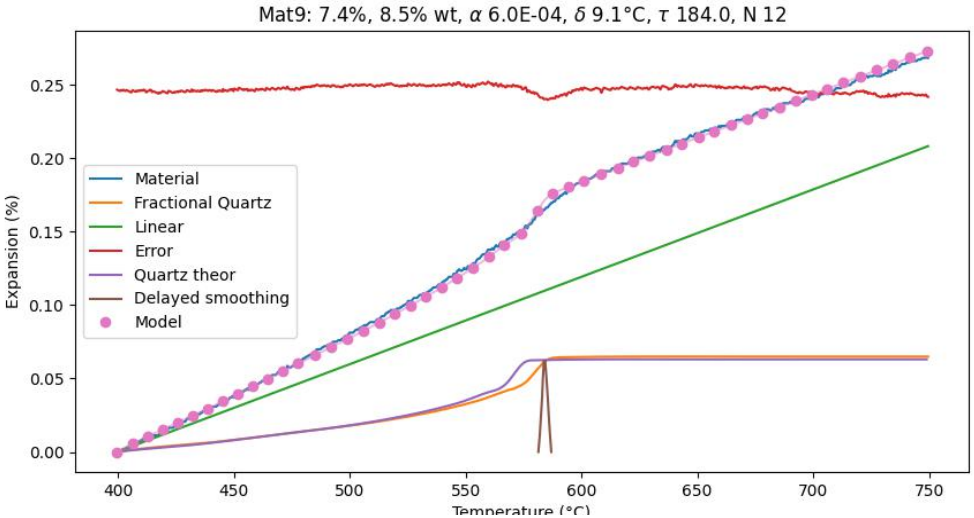
The DSQ was applied to 17 thermal expansion curves related to ceramics but of unknown composition (either bodies or glazes).

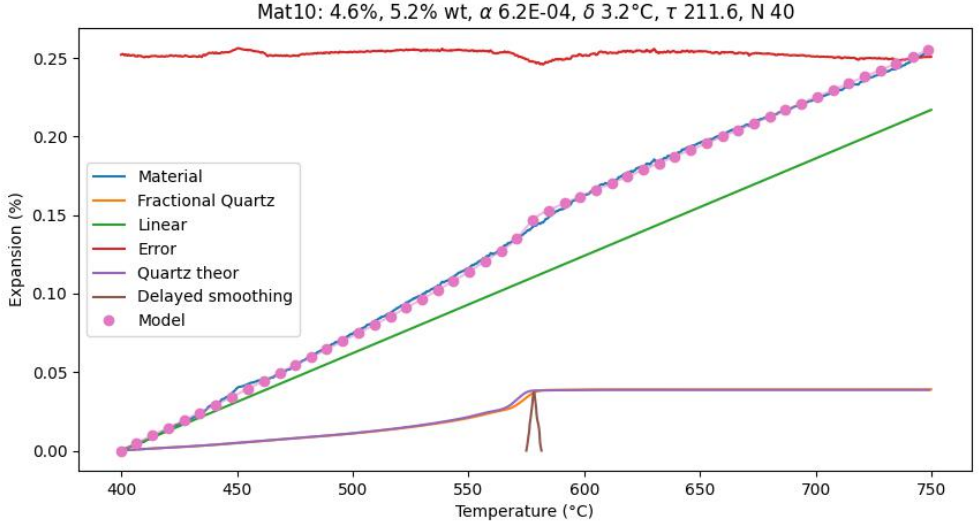


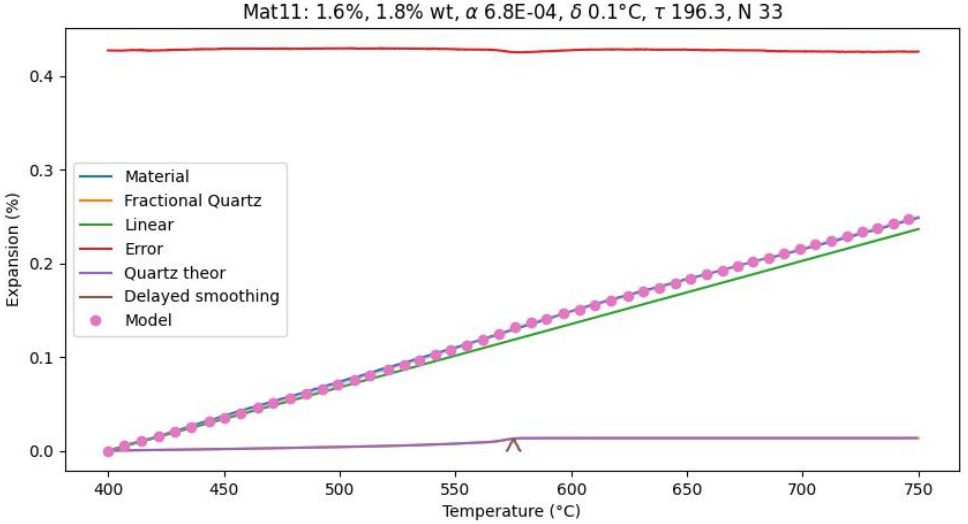




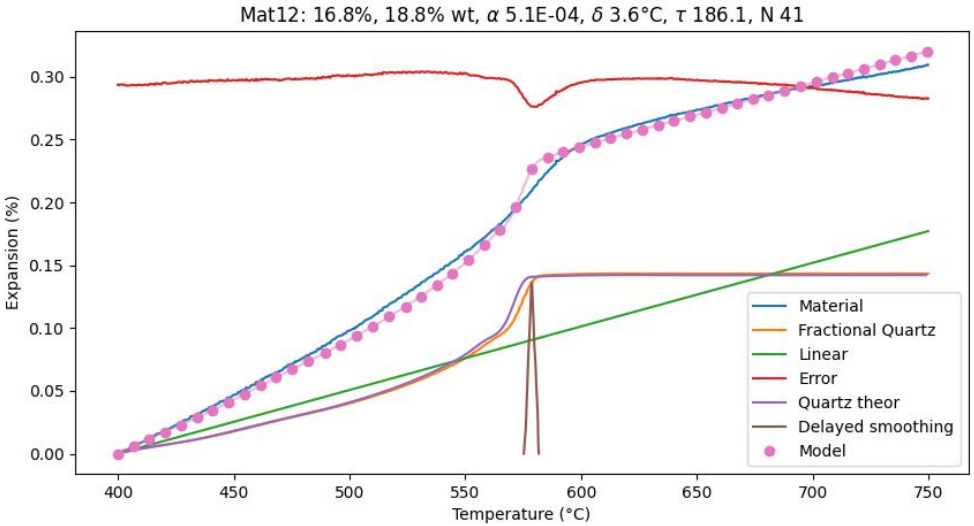
Screening through undetermined materials: bodies 2

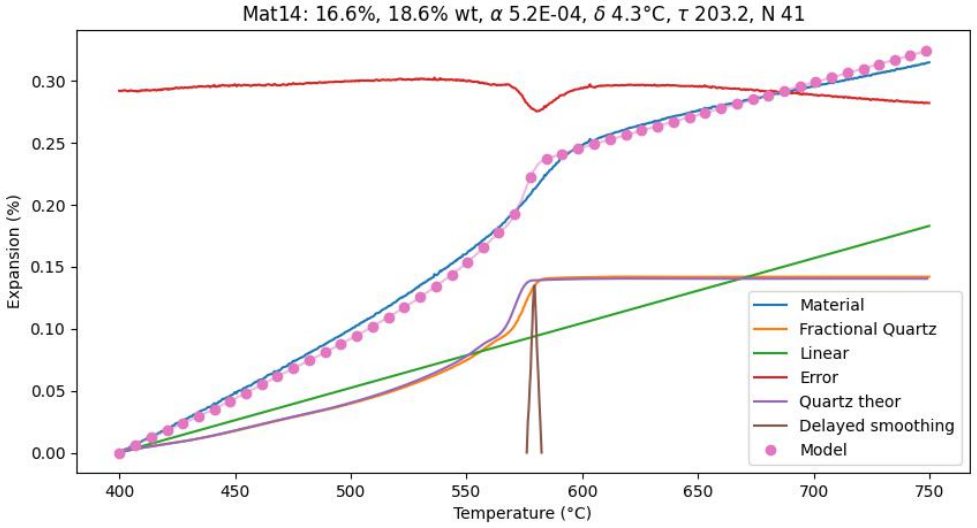


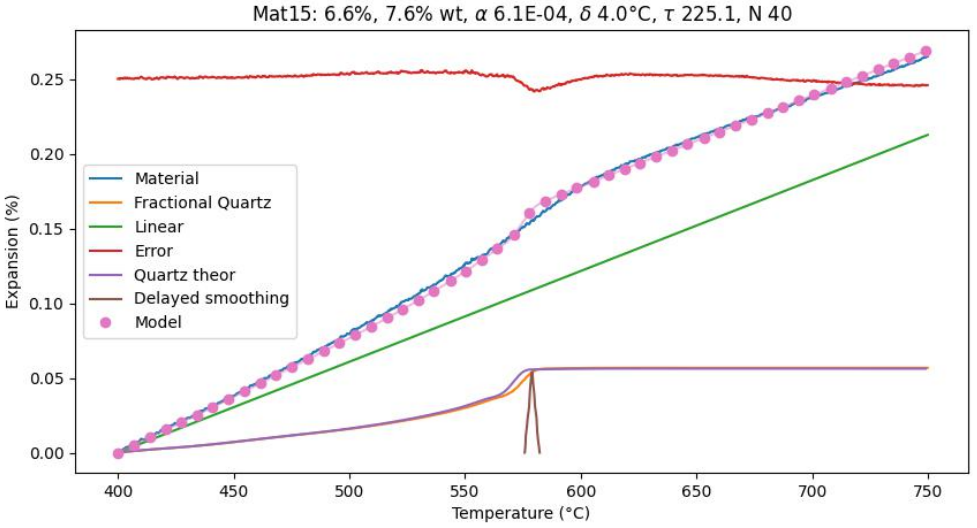




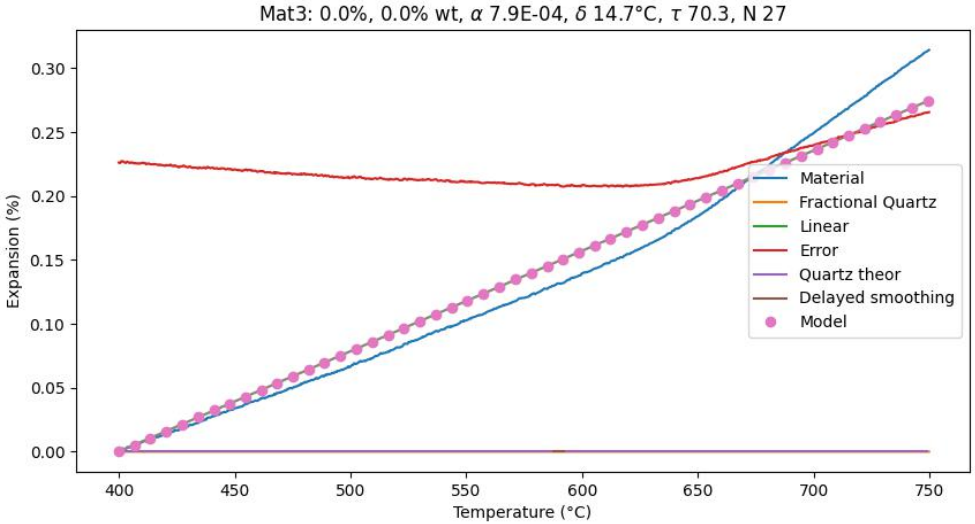
Screening through undetermined materials: bodies 3

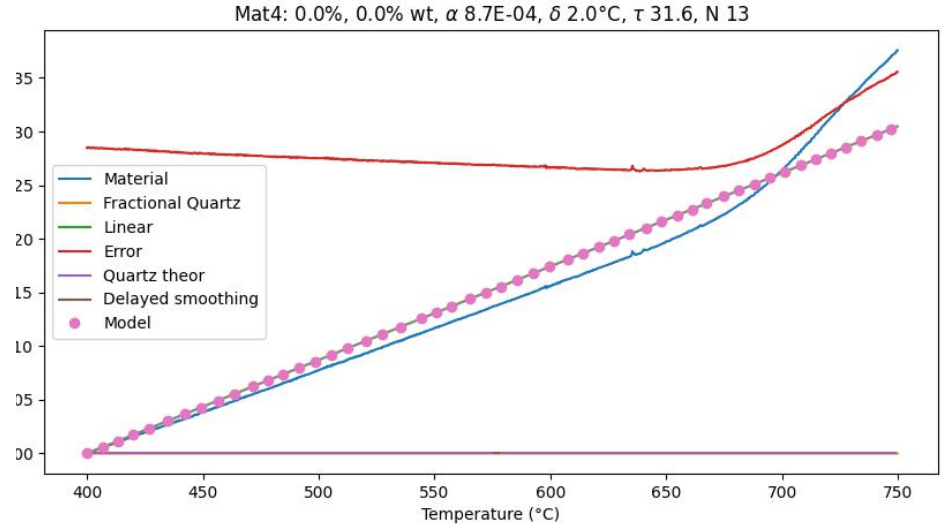


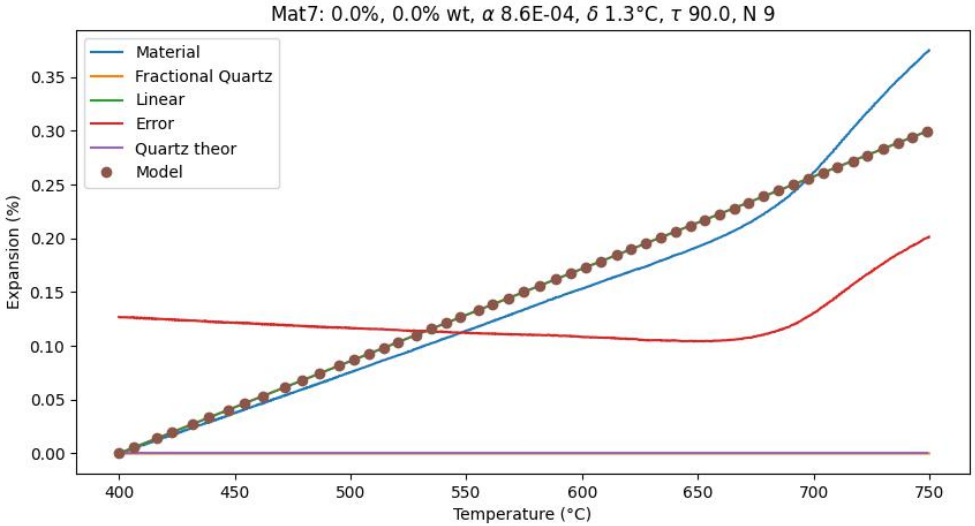


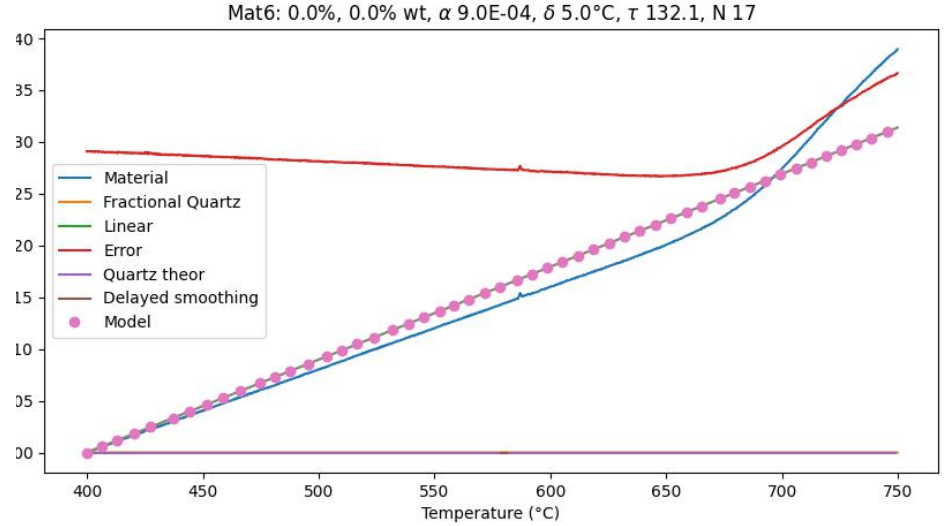


Screening through undetermined materials: glazes

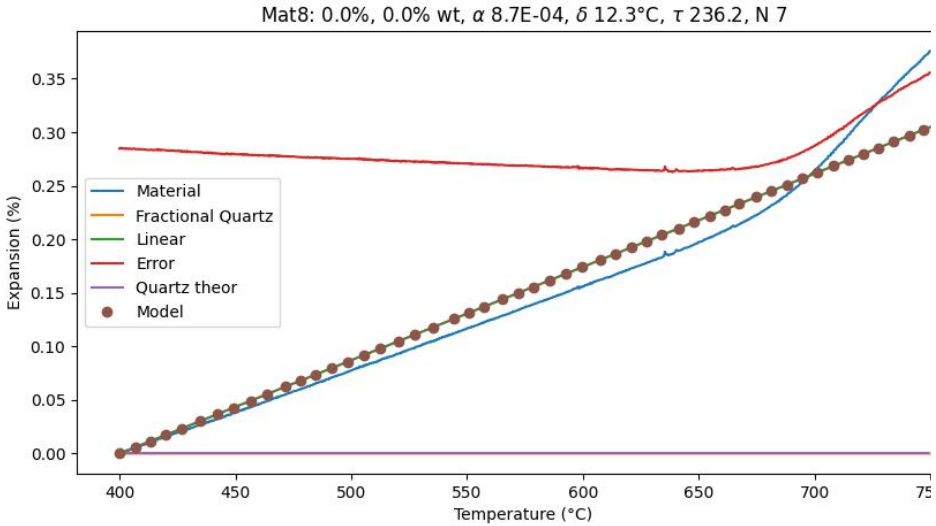


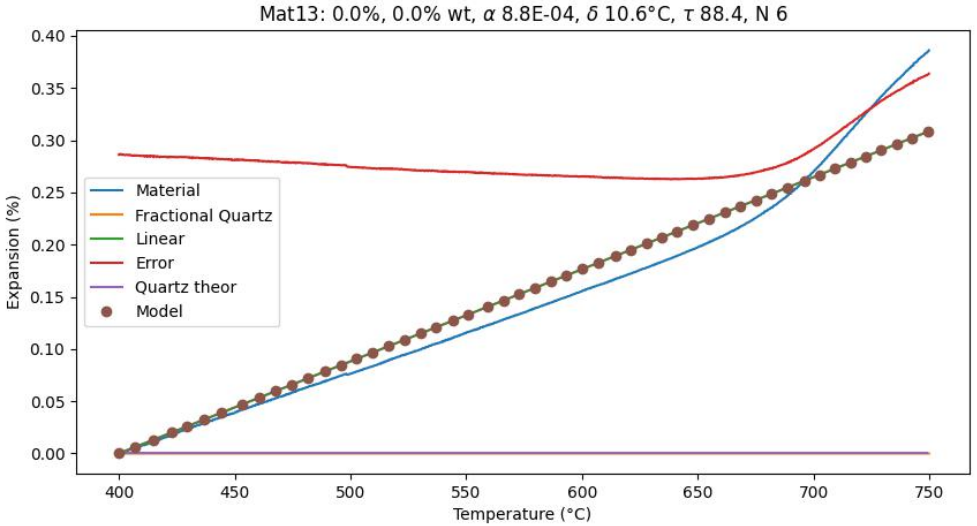


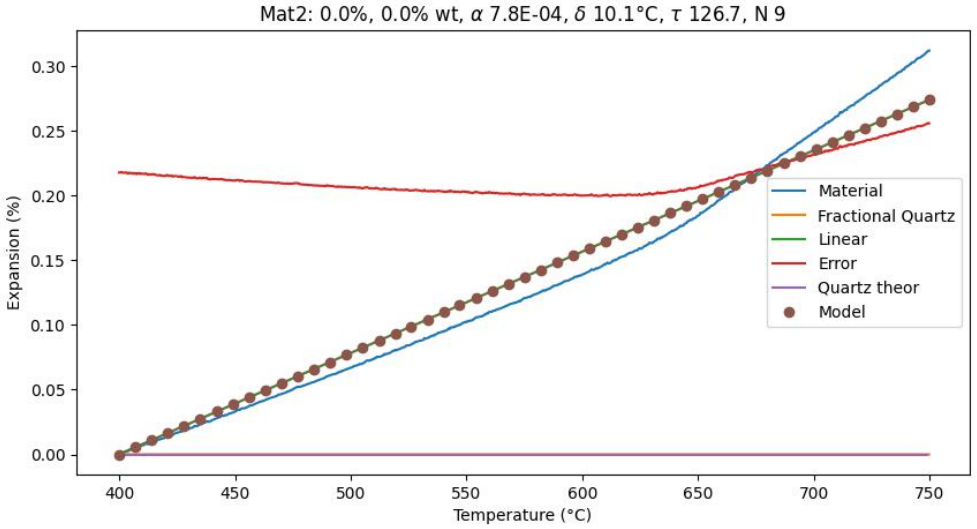


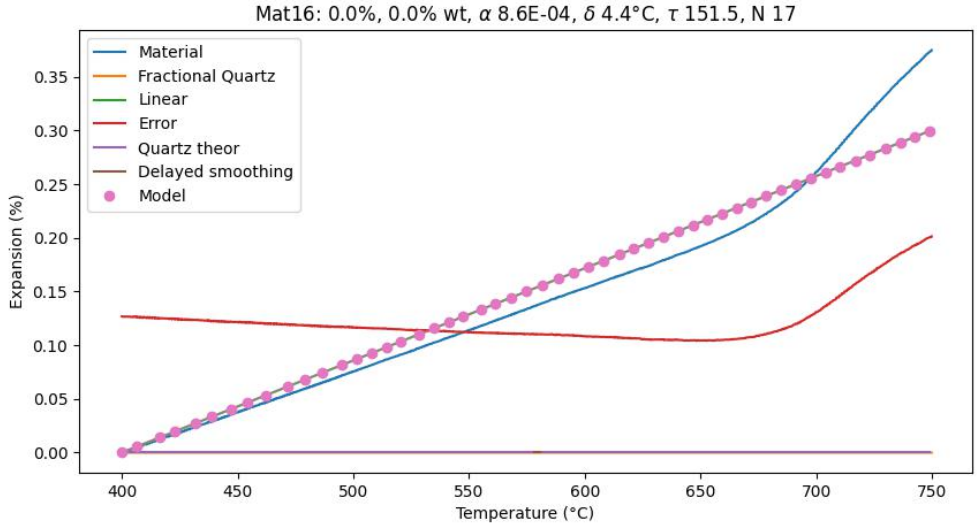


Screening through undetermined materials: glazes,2









Conclusions

This **practical** methods proves valid in giving a **rapid** and **simple** volumetric **quantification** of transient quartz in fired materials. That's what most matters for applications having to deal with **stresses induced during the cooling phase**, like large and/or thin tiles.

It would nevertheless be unreasonable to include this calculation into the average quality control routine, because of its inherent mathematical complexity.

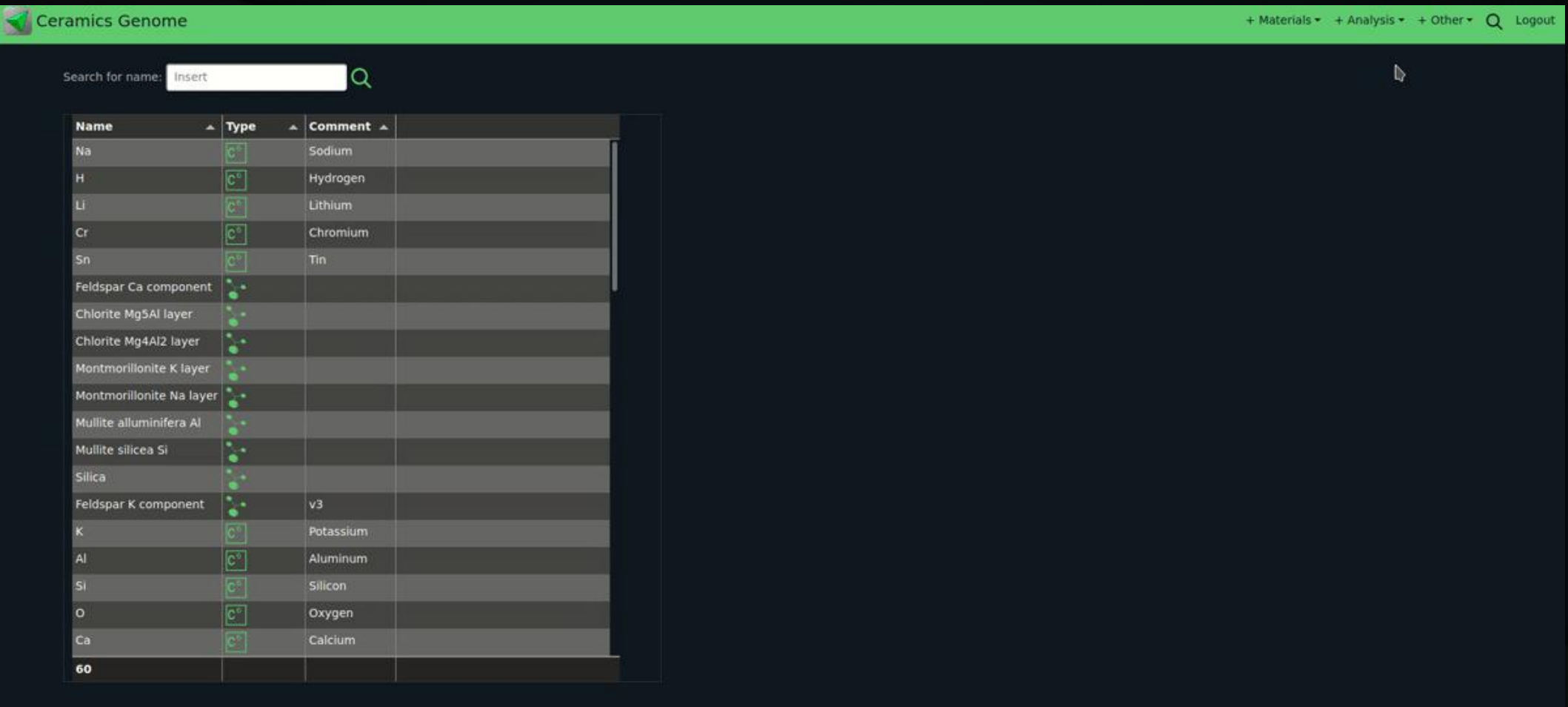
For this reason, this algorithm has been implemented in our new software service, **Ceramics Genome**.

Ceramics Genome

Bring Ceramics Alive

Daniele Paganelli – Expert Lab Service Srls
IceRS – Materie Prime – 24 Feb 2022

Quartz Model



Name	Type	Comment
Na		Sodium
H		Hydrogen
Li		Lithium
Cr		Chromium
Sn		Tin
Feldspar Ca component		
Chlorite Mg5Al layer		
Chlorite Mg4Al2 layer		
Montmorillonite K layer		
Montmorillonite Na layer		
Mullite alluminifera Al		
Mullite silicea Si		
Silica		
Feldspar K component		v3
K		Potassium
Al		Aluminum
Si		Silicon
O		Oxygen
Ca		Calcium
60		

ELS

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Thank you

Expert Lab Service is a boutique of ceramic engineering solutions, materials analysis services and **tailor-made laboratory instruments**.