LAB TECHNIQUES

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Contents

Mineral Analysis

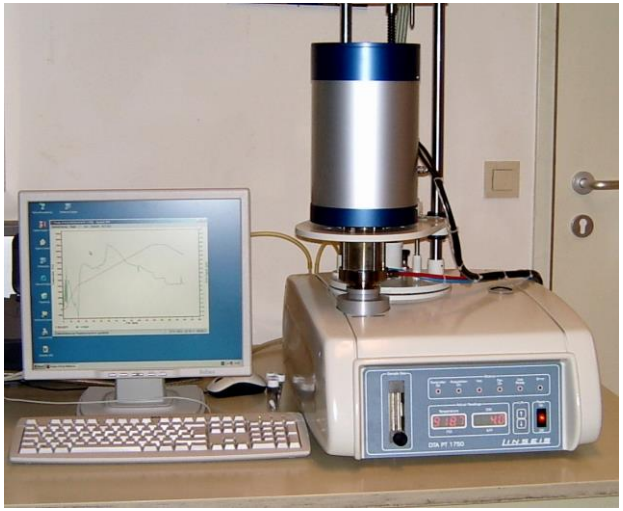
3. **Thermal analyses.**
   - Differential thermal analysis (DTA).
   - Differential scanning calorimetry (DSC).
   - Thermogravimetric analysis (TGA).

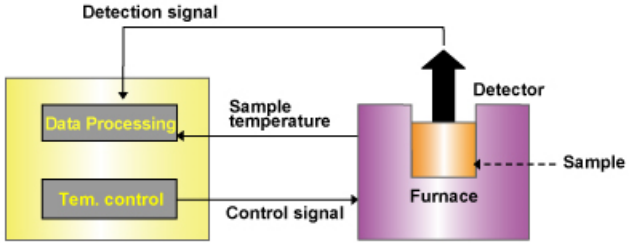
Thermal Analysis

5. Thermal analyses

It is a method where the **properties of minerals** are studied as they **change with temperature**. Several methods are commonly used – these are distinguished from one another by the property which is measured:

1. **Differential thermal analysis (DTA): temperature difference between (sample)** and (**muffle/standard) temperature or time**.
2. **Thermogravimetric analysis (TGA): mass change** versus **muffle temperature or time**.
3. **Differential scanning calorimetry (DSC): heat flow changes between (sample and standard)** versus **muffle temperature or time**.
4. **Dielectric thermal analysis (DEA):** dielectric permittivity and loss factor.
5. **Dilatometry (DIL):** volume changes with temperature change.
6. **Dynamic mechanical analysis (DMA or DMTA):** measures storage modulus (stiffness) and loss modulus (damping) versus temperature, time and frequency.
7. **Evolved gas analysis (EGA):** analysis of gases evolved during heating of a material, usually decomposition products.
8. **Laser flash analysis (LFA)**: thermal diffusivity and thermal conductivity.
9. **Thermomechanical analysis (TMA):** dimensional changes versus temperature or time.
10. **Thermo-optical analysis (TOA):** optical properties.





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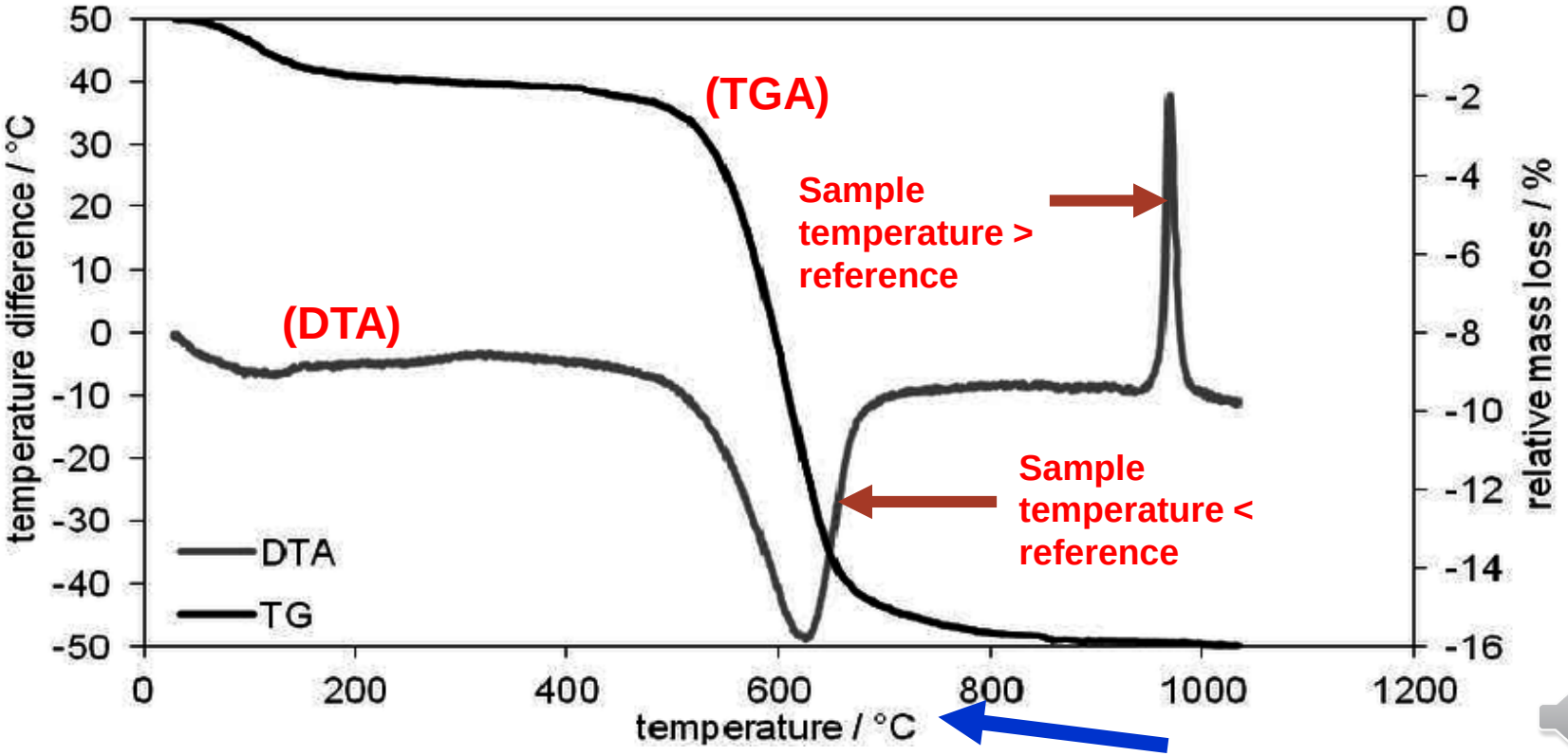
Common Thermal Analysis Methods and the Properties Measured

Method	Abbreviation	Property Measured
Differential thermal analysis	DTA	Temperature difference
Differential scanning calorimetry	DSC	Enthalpy
Thermogravimetric analysis	TGA	Mass
Dynamic mechanical analysis	DMA	Deformation
Dielectric thermal analysis	DEA	Deformation
Evolved gas analysis	EGA	Gaseous decomposition
Thermo-optical analysis	TOA	Optical properties

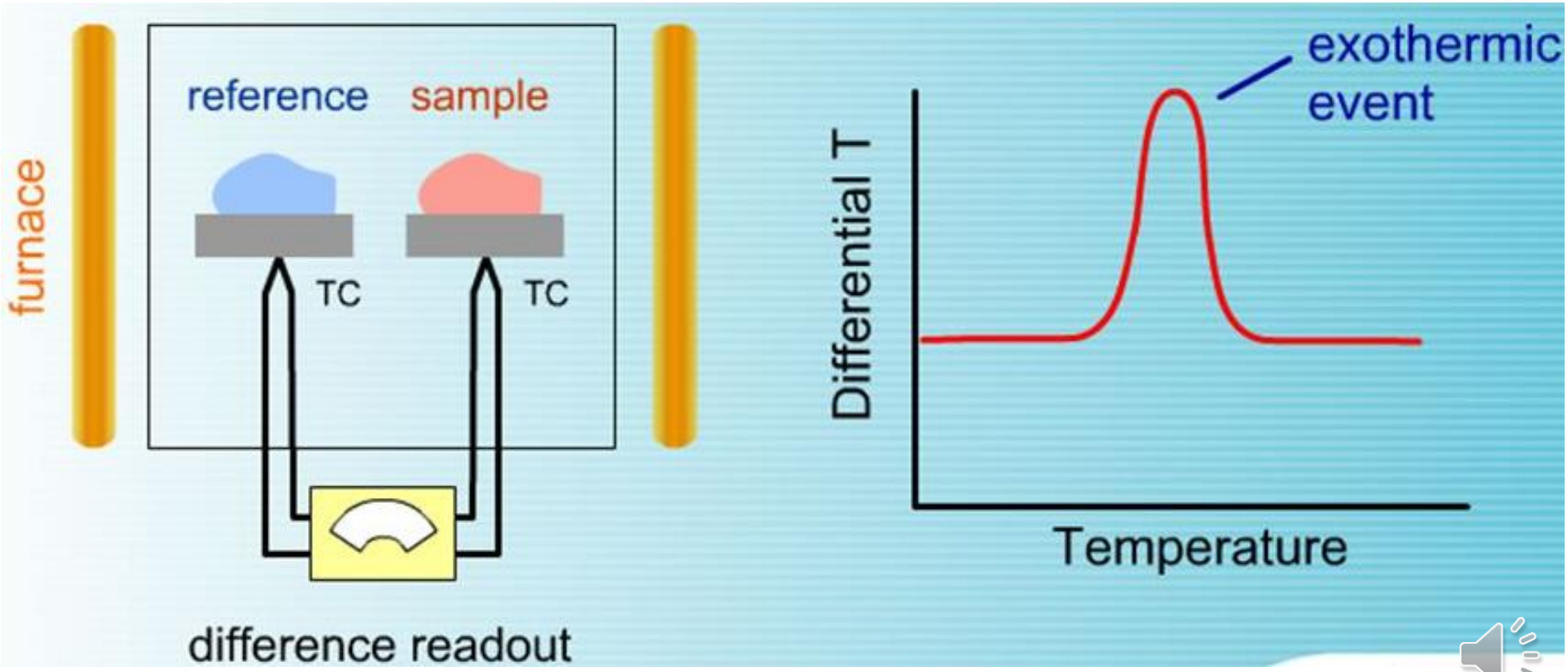
- **Differential thermal analysis (DTA)**

DTA is a technique for **identifying minerals and phases** by observing the thermal behavior of **a sample as it is heated**. **The technique is based on the fact that as a mineral/rock sample is heated, it undergoes reactions and phase changes that involve absorption or emission of heat within the sample. DTA** measures **the temperature necessary to establish a nearly zero-temperature-difference between the sample and the inert reference**

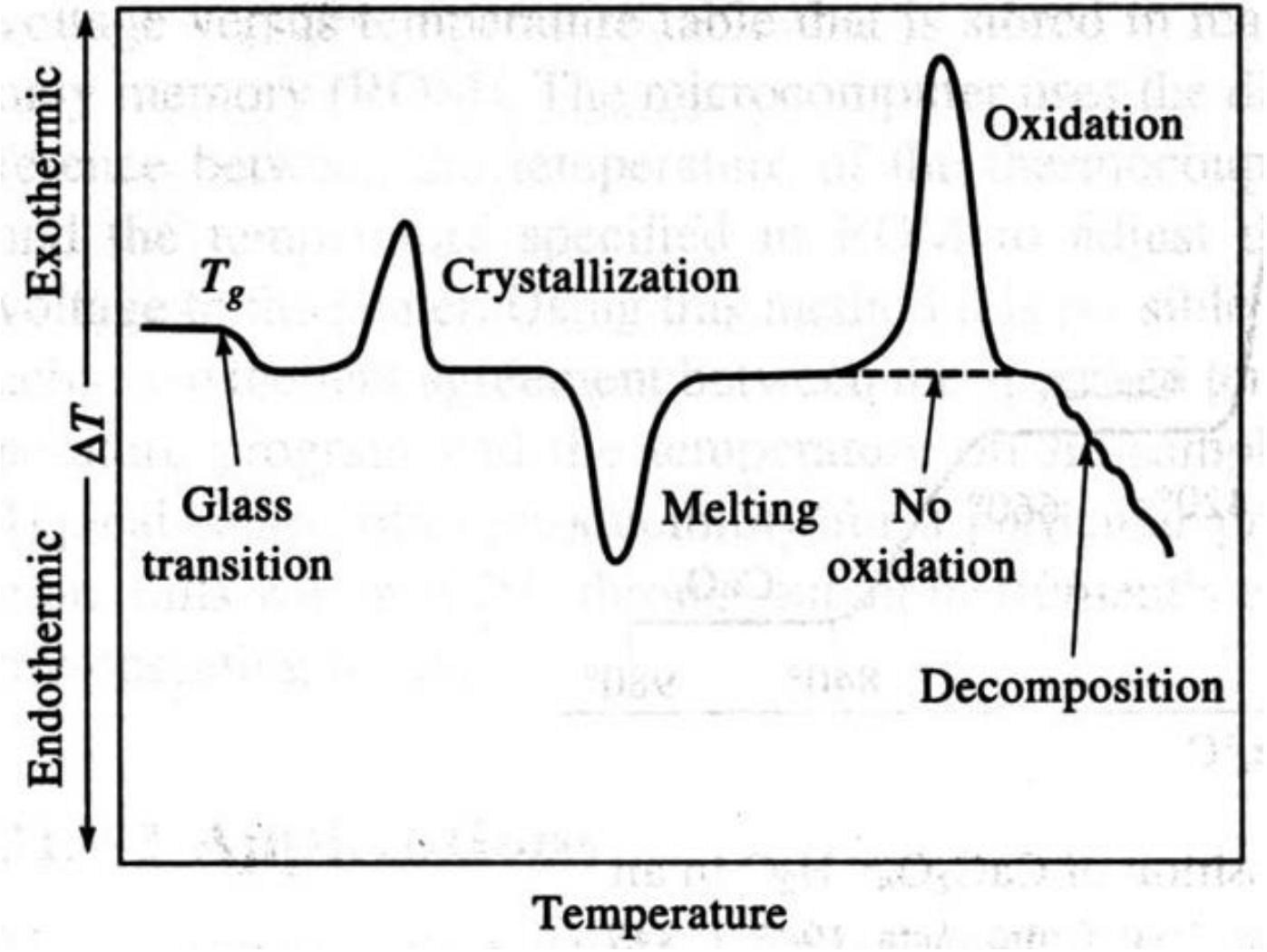


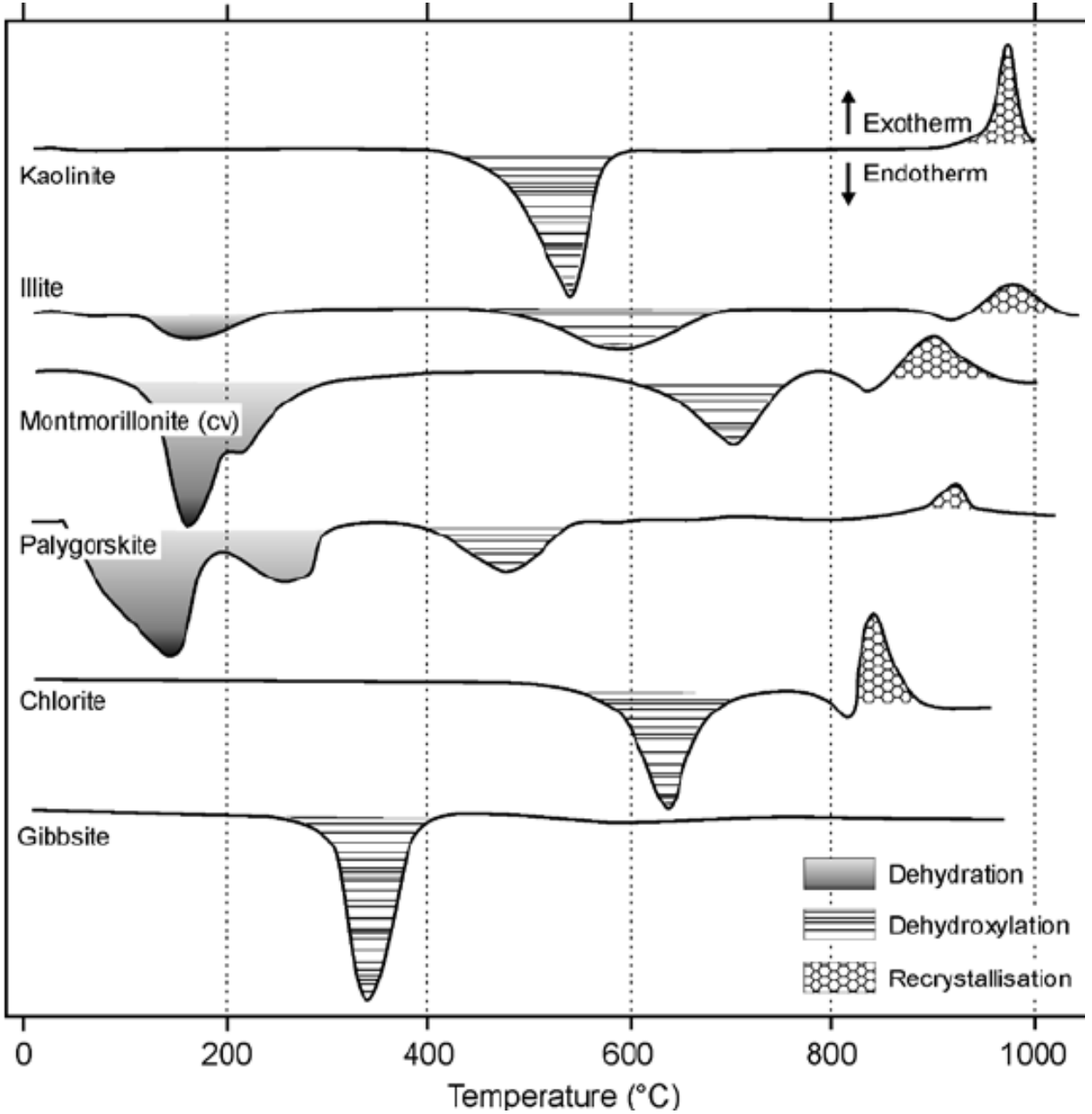
(Muffle/Reference sample temperature)

In **DTA** **the temperature** of the sample is measured relative to **an inert material**, **i.e., reference/standard (not suffering any phase change during heating)**. One thermocouple is imbedded in the sample (to measure the sample temperature during heating) and another in the inert material (to represent the inert/muffle temperature), then connected so that any **differential temperatures** **(temperature difference between both)** generated during heating **(muffle temperature)** are graphically recorded as a series of peaks.



Changes in the sample are either **exothermic or endothermic**. Thus, a **DTA curve** provides data on **the transformations that have occurred in the sample, such as decomposition, crystallization, melting and sublimation at a definite temperature**. The amount of heat (recorded by DCS) involved and temperature (recorded by DTA) at which these changes take place are characteristic for each mineral.

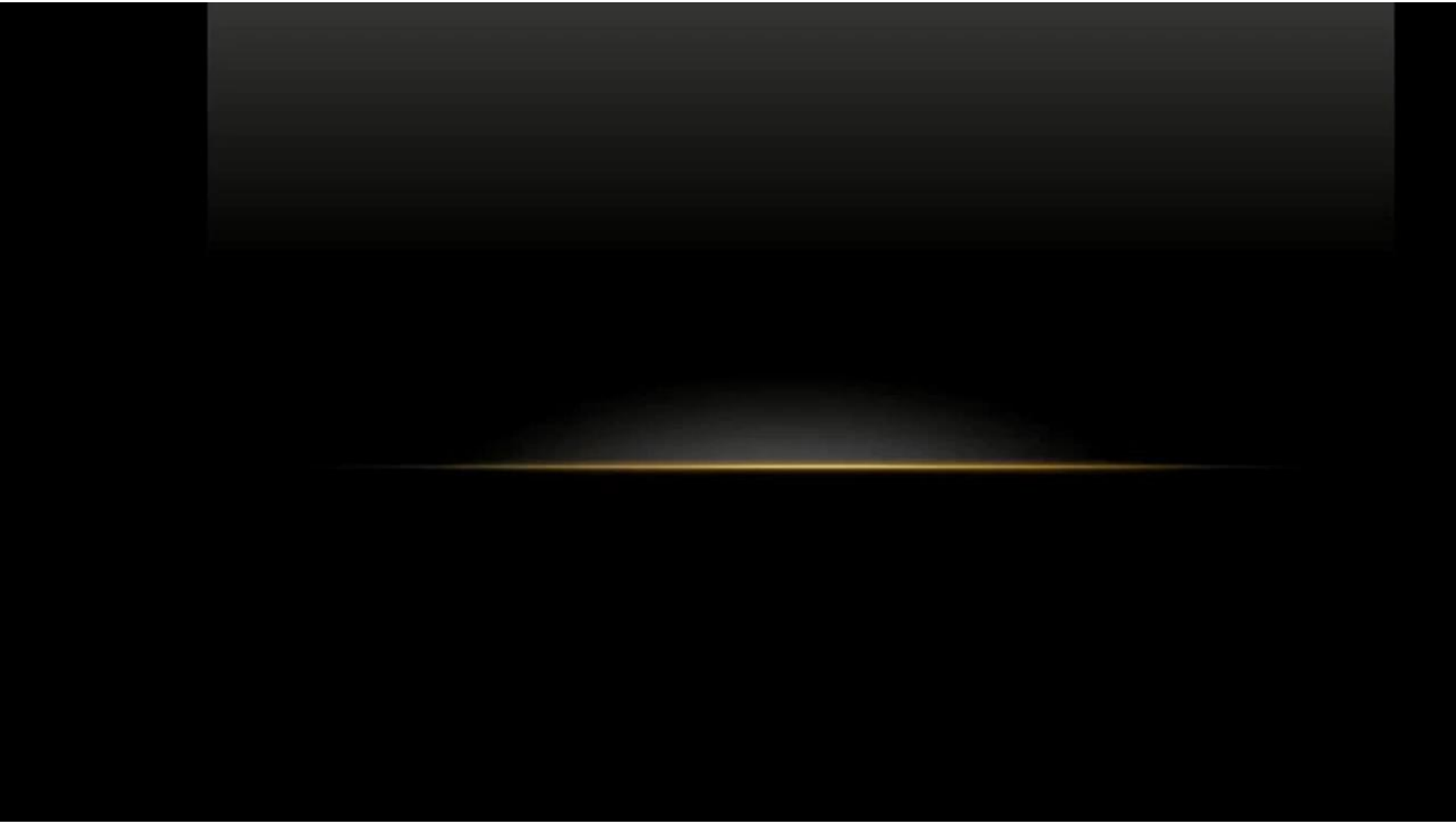




DTA of clay minerals

Analytical Chemistry

Explain the principle or theory of DTA.

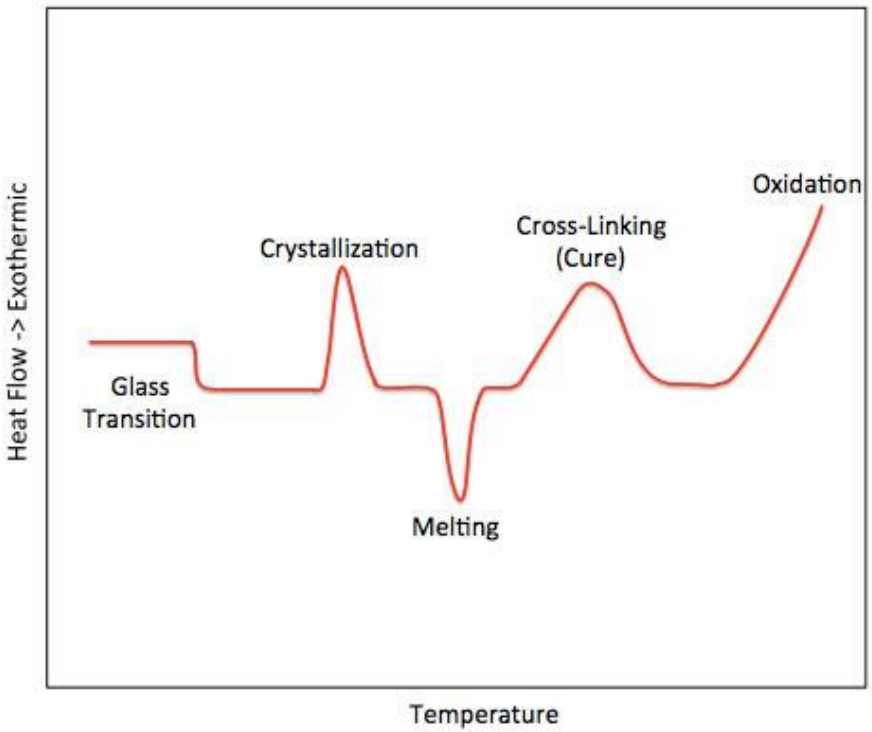


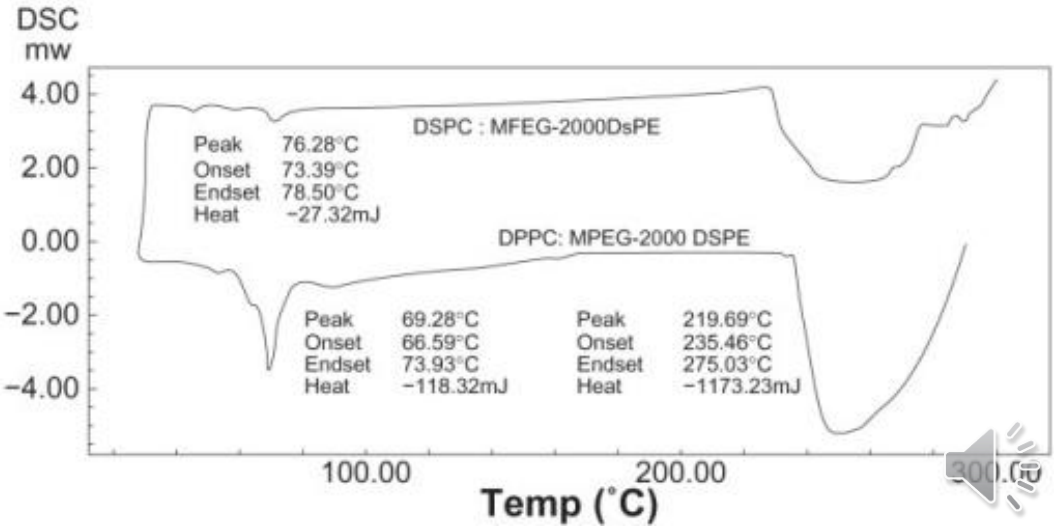
- **Differential scanning calorimetry (DSC)**

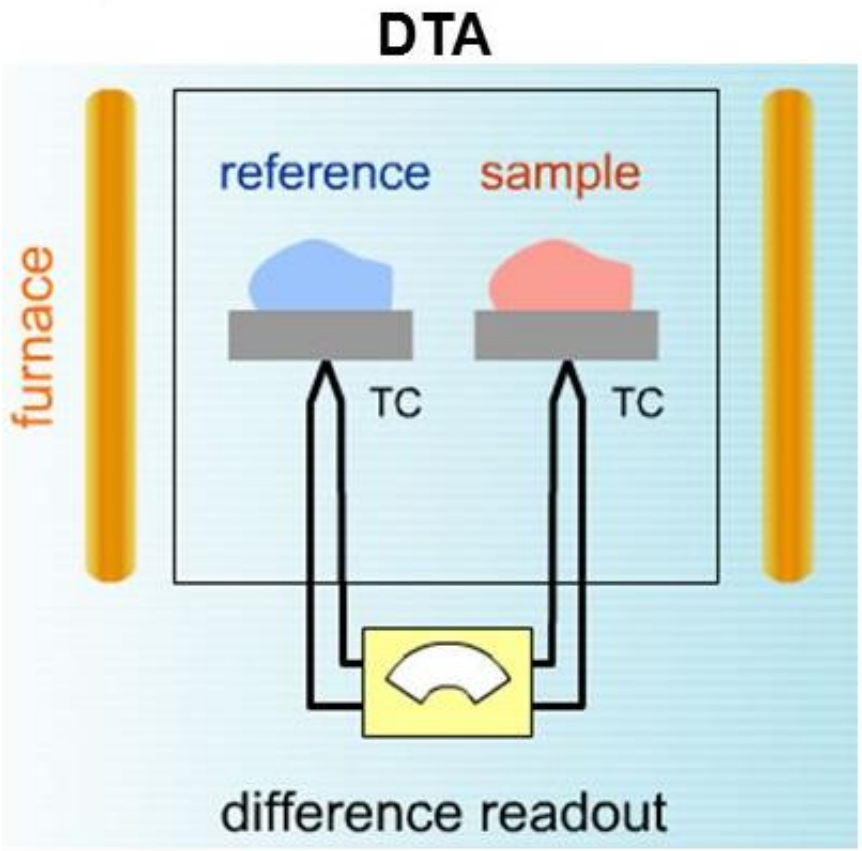
DSC measures **the energy necessary to establish a nearly zero temperature difference between the sample and the inert reference** as the two specimens are subjected to the same temperature at a controlled rate.

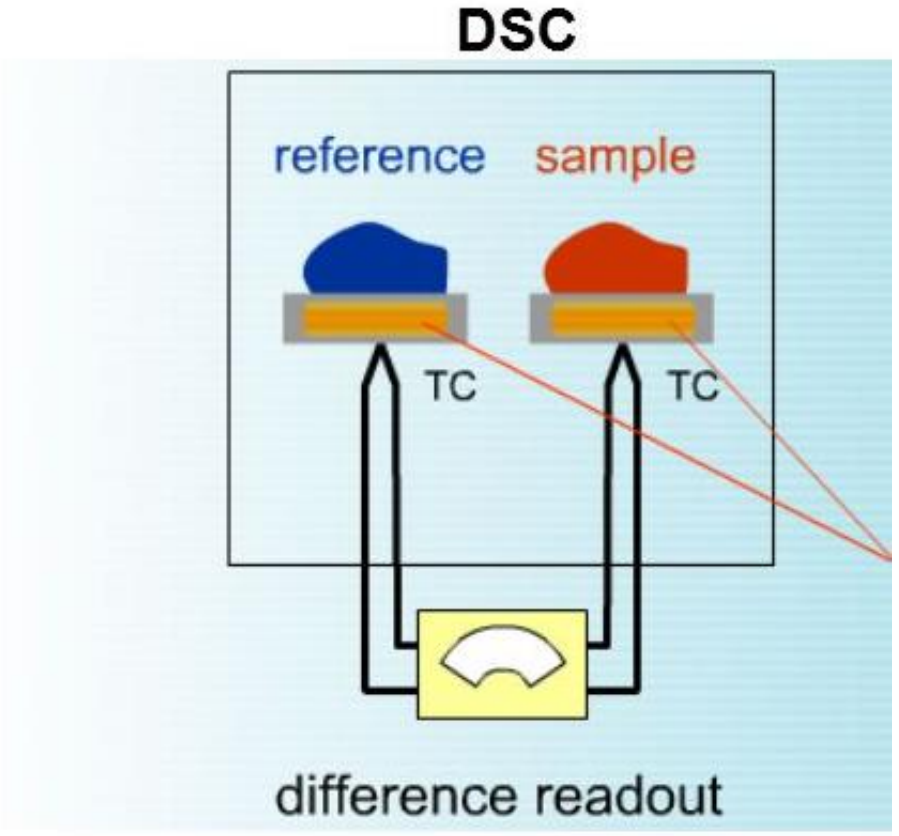
DSC provides quantitative and qualitative information about physical and chemical changes that involve **endothermic or exothermic** processes or **change in heat capacity.**

The area under the peak is directly proportional to the amount of heat energy absorbed or released by the sample.



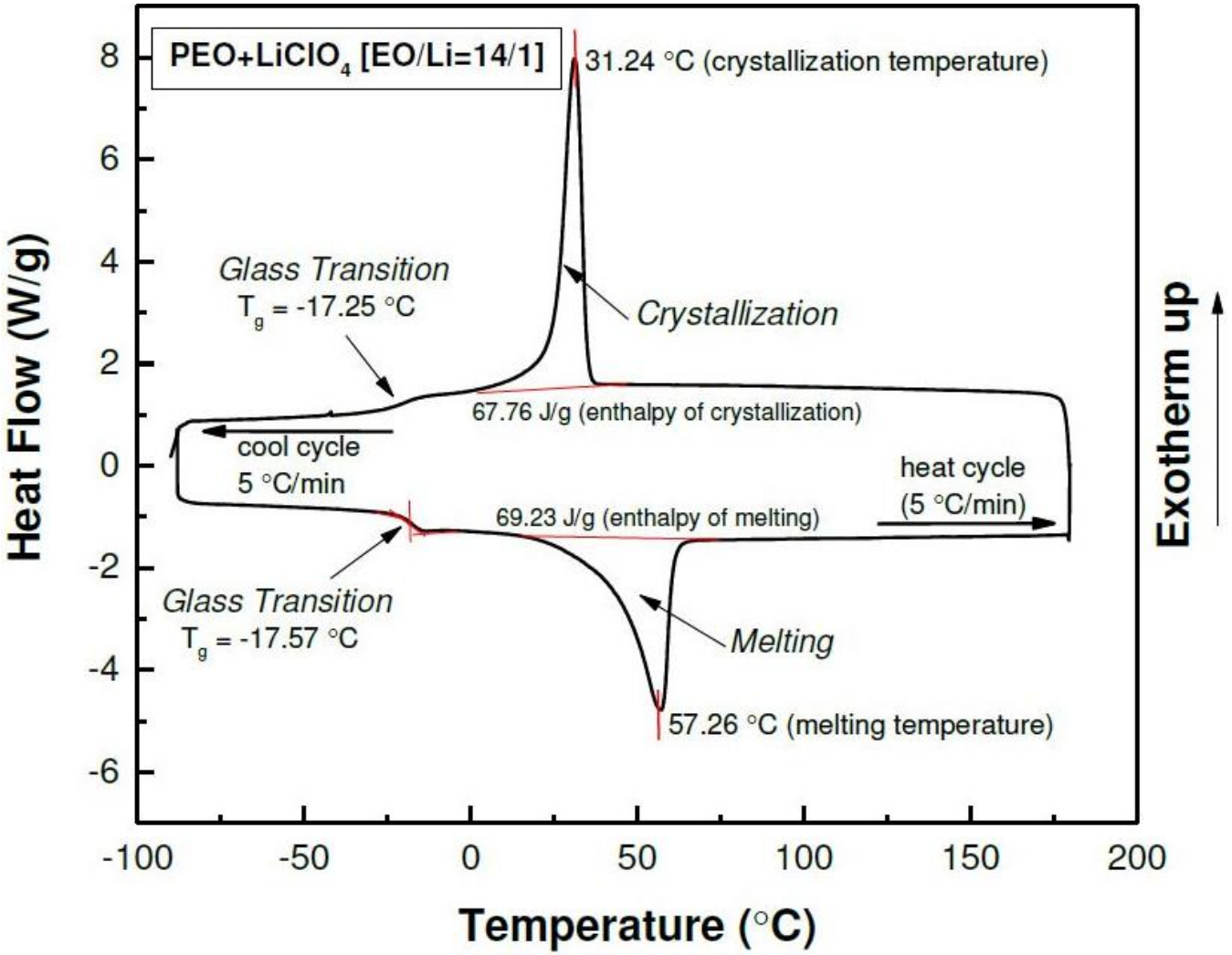






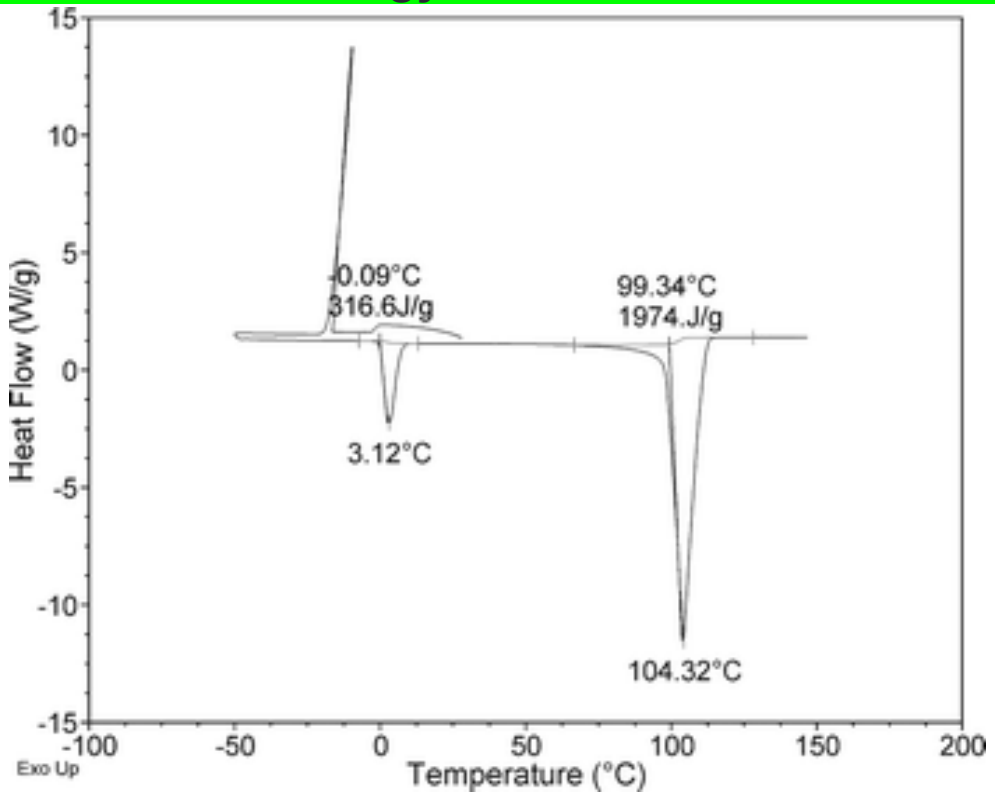
- similar concept as DTA (compare sample & reference)
- measure "heat flow" required to keep both specimens same temperature

The basic principle underlying this technique is that **when the sample undergoes a physical transformation such as phase transitions, more-heat (energy) or less-heat (energy) will need to flow to/from the sample than the reference to maintain both at the same temperature.** Whether less or more **energy** must flow **to/from** the **sample** depends on whether the process is endothermic or exothermic.

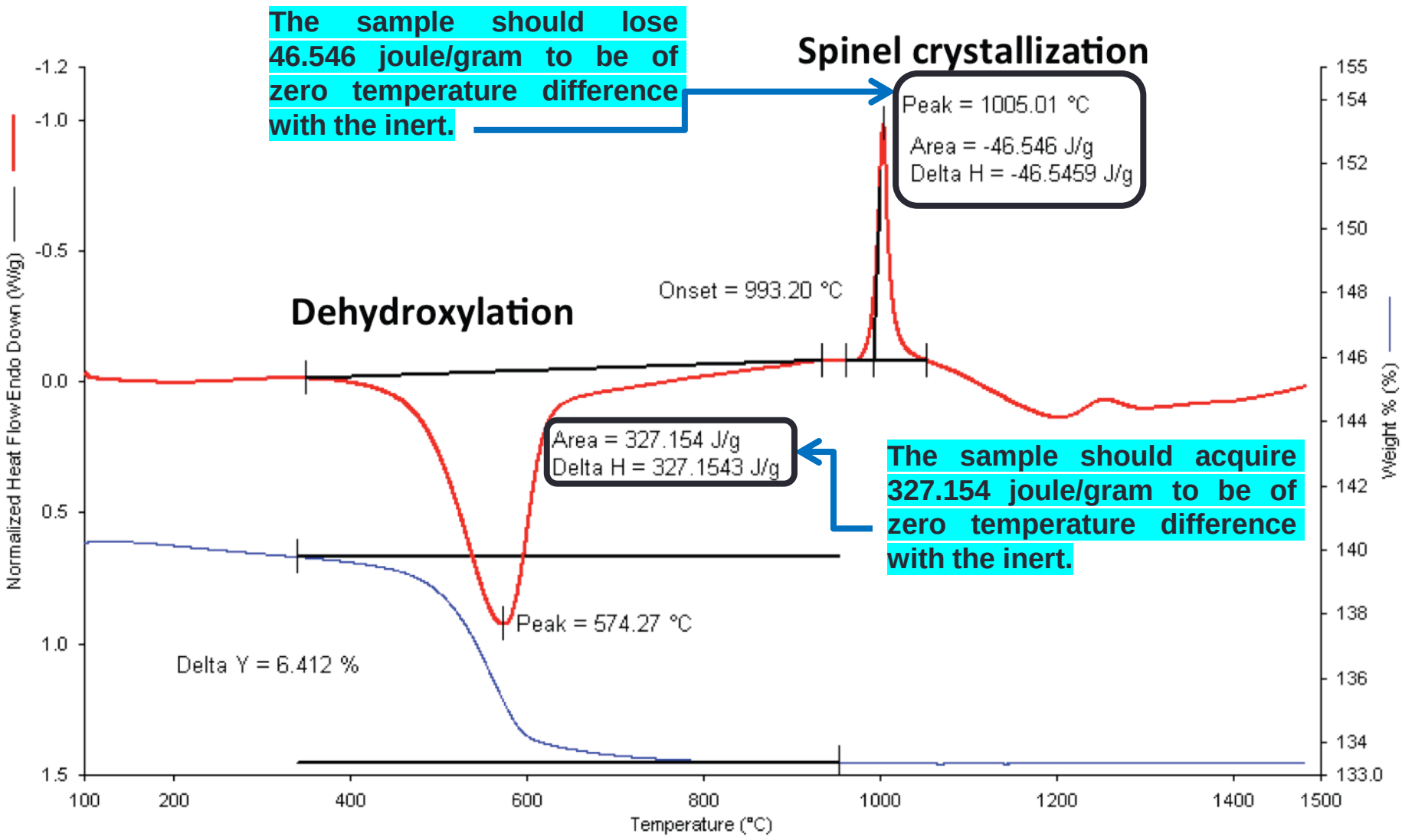


For example, as a **solid sample** melts to **a liquid**, **it will require more energy (heat) flowing to the sample** to increase its temperature at the same rate as the reference. This is due to the **absorption of heat** by the sample as it undergoes the **endothermic phase** transition from solid to liquid (Ice cube is an example).

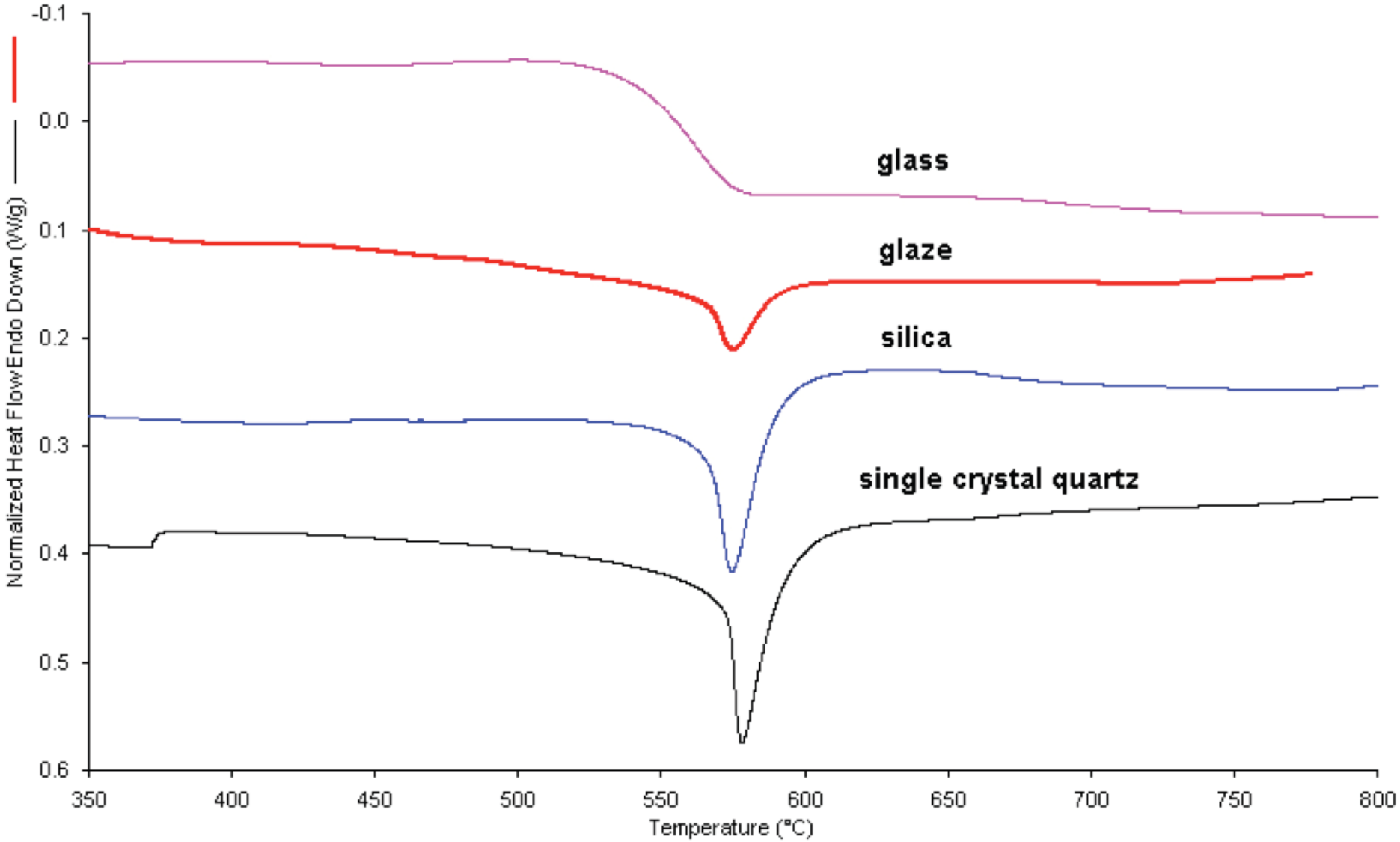
Likewise, as the sample undergoes **exothermic processes (such as crystallization) less heat is required to flow from the sample.** By observing the difference in heat flow between the sample and reference, **differential scanning calorimeters (DSC)** are able to measure **the amount of energy/heat flow absorbed or released during such transitions**.



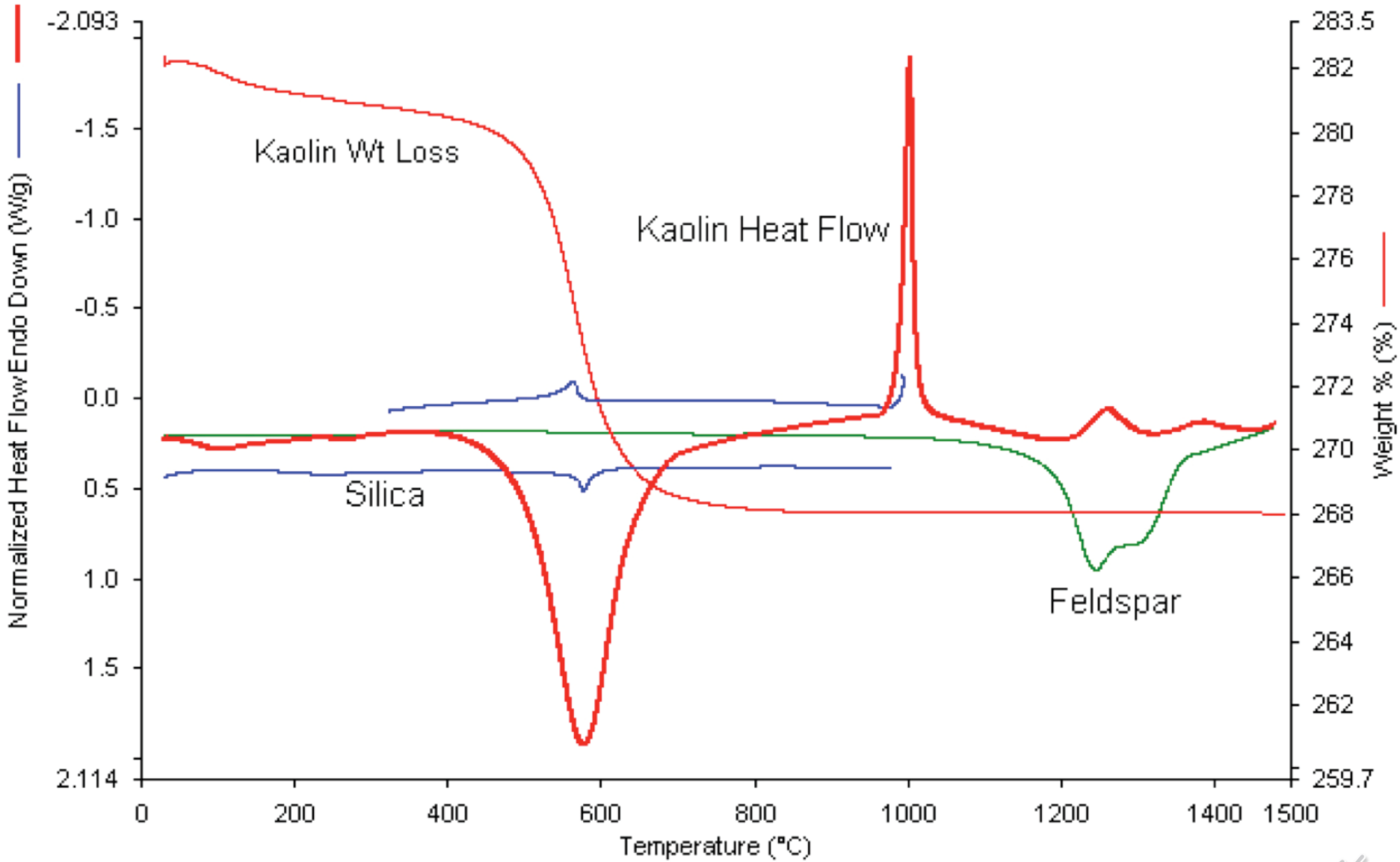
DSC of the ice, showing the ranges of melting and boiling values.



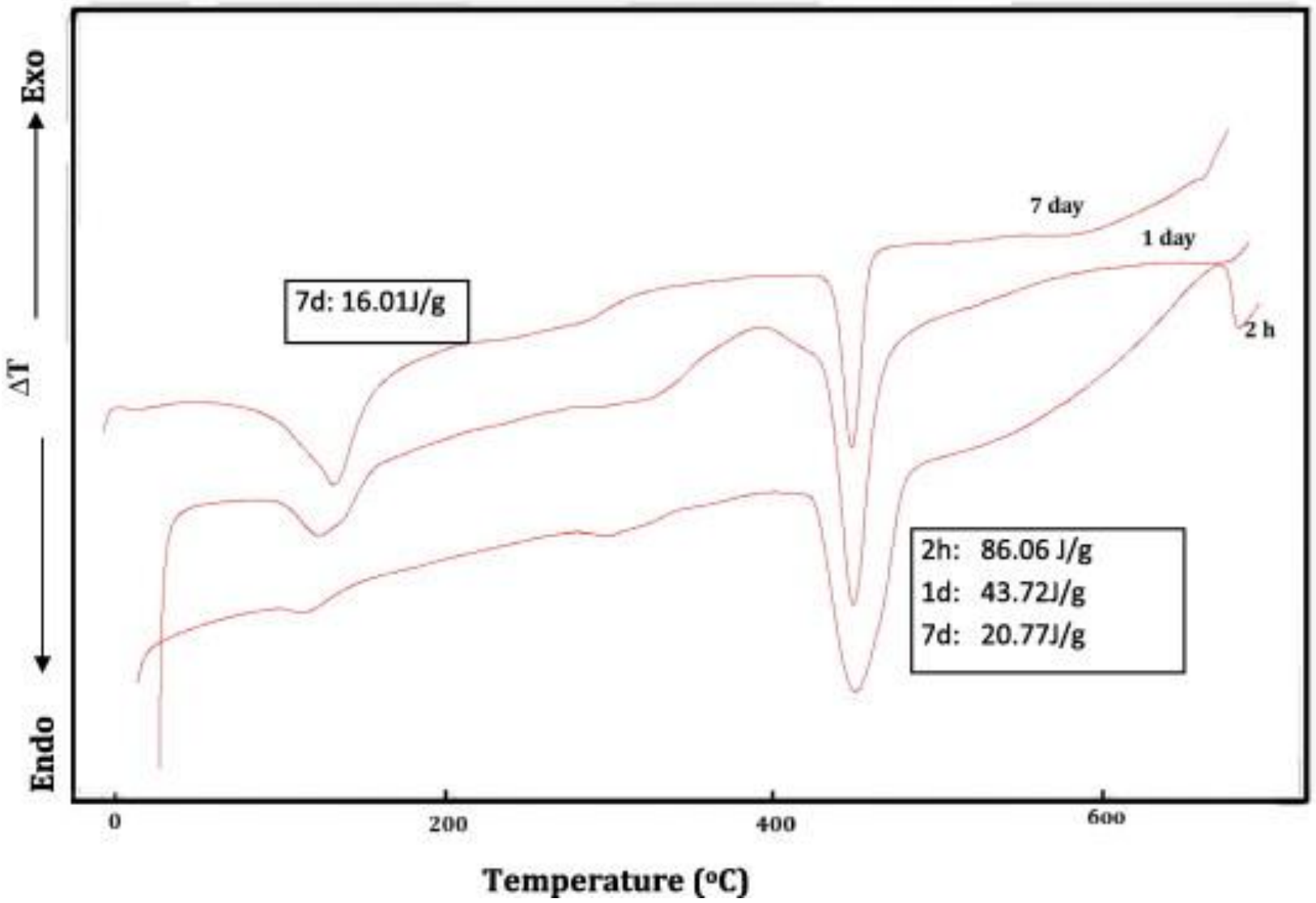
DSC and TGA of kaolinite.



Thermal curves of SiO_2 in window glass, unfired ceramic glaze, commercial silica and single quartz crystal.

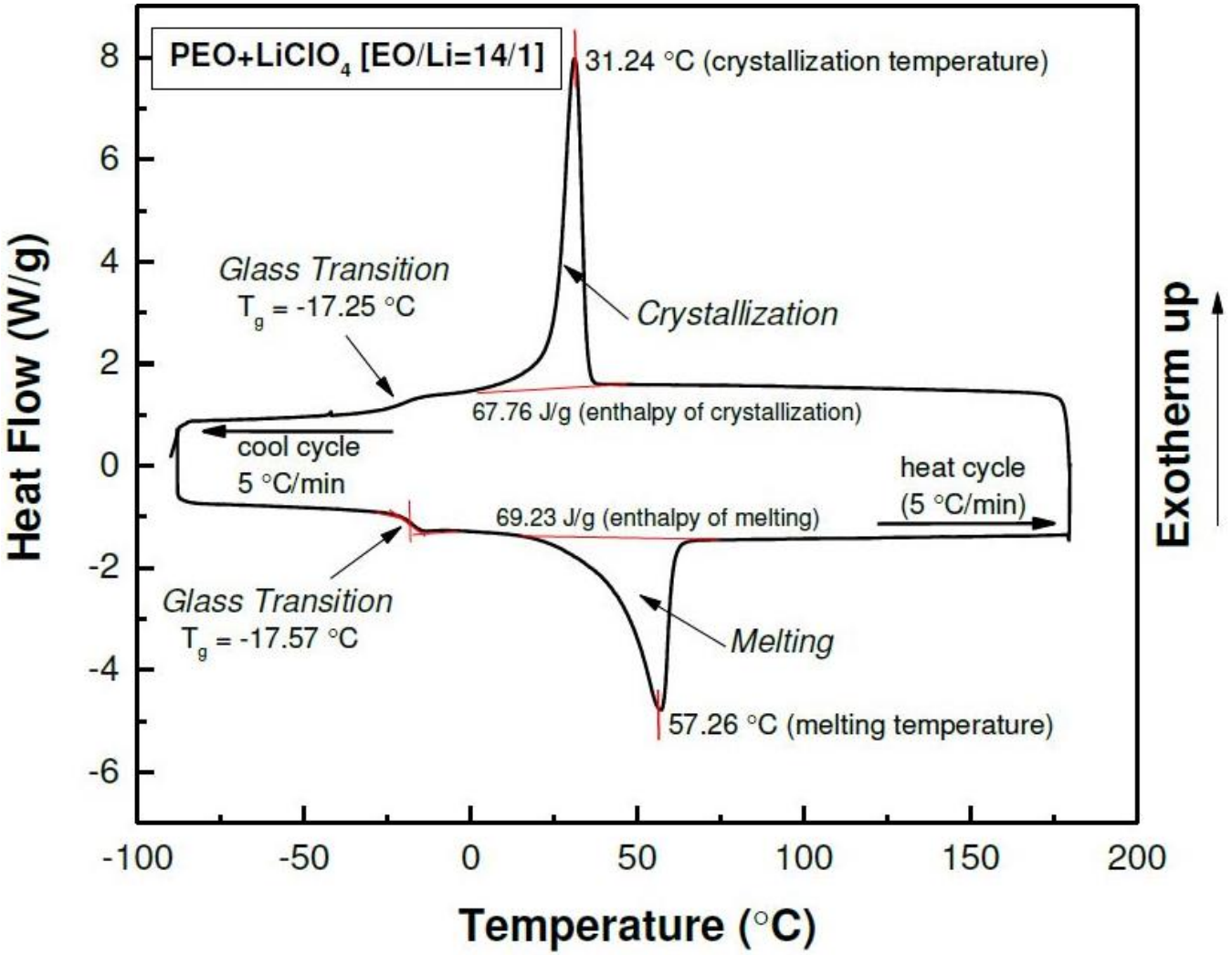


Three main components of porcelain clay run individually (look carefully for the silica).



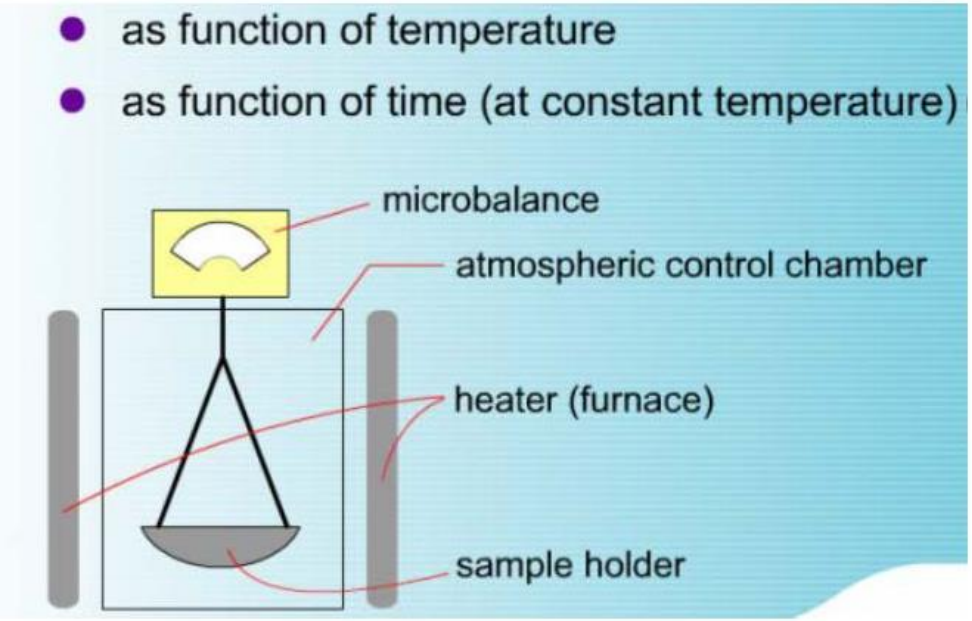
The amount of energy difference could be changed with time for the same material.

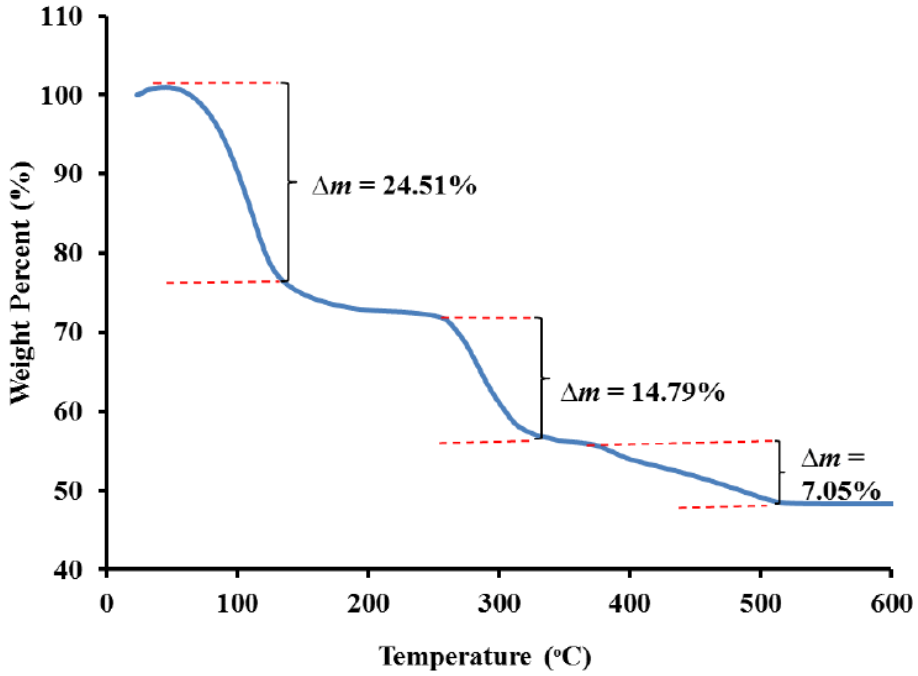
The basic principle underlying this technique is that **when the sample undergoes a physical transformation such as phase transitions, more-heat (energy) or less-heat (energy) will need to flow to/from the sample than the reference to maintain both at the same temperature.** Whether less or more **energy** must flow **to/from** the **sample** depends on whether the process is endothermic or exothermic.

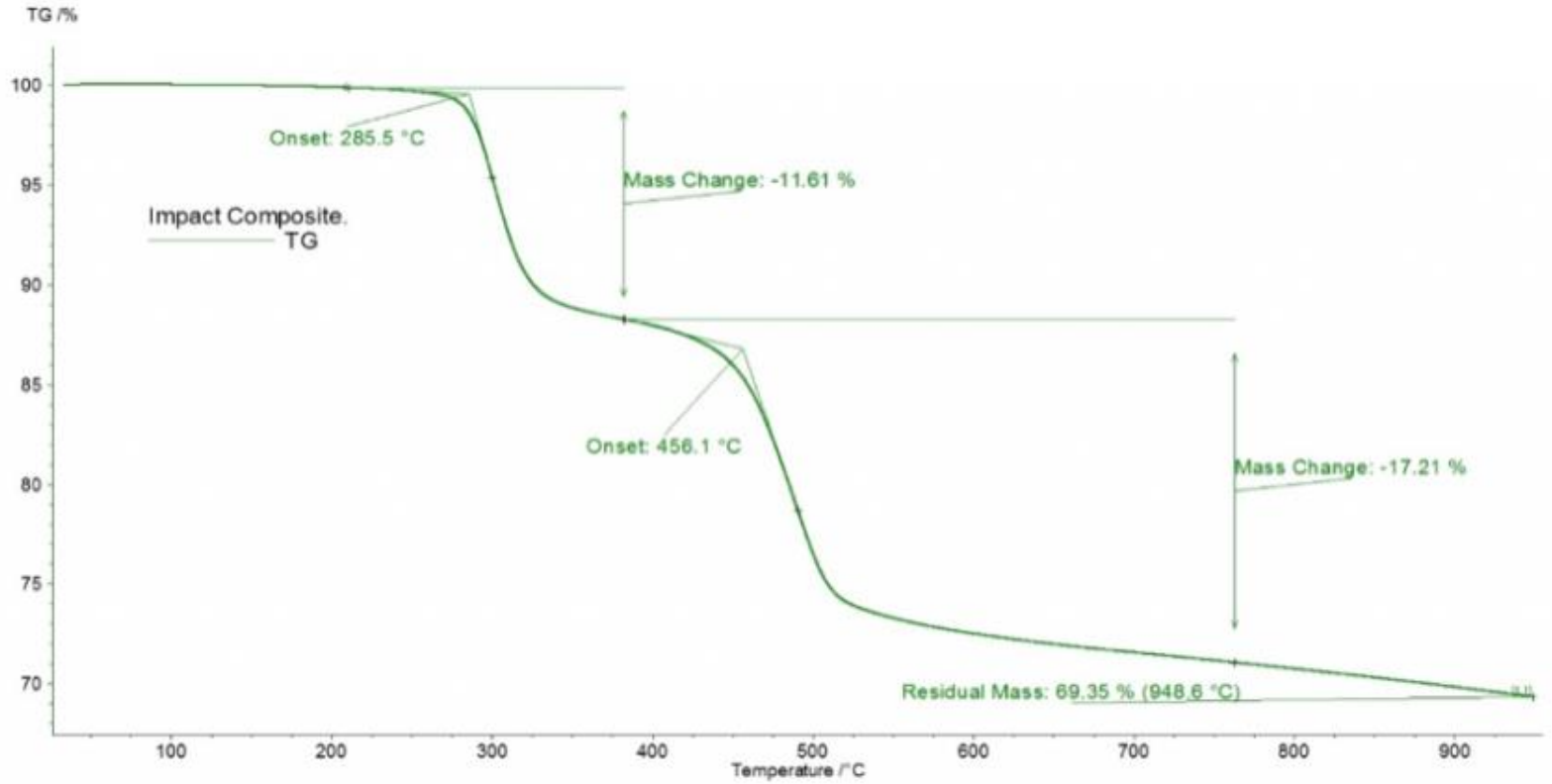


- **Thermogravimetric analysis or thermal gravimetric analysis (TGA)**

TGA is a method of thermal analysis in which the **mass of a sample is measured as the temperature changes over time (no internal reference).** This measurement provides information about physical phenomena, such as **phase transitions**, absorption and desorption; as well as chemical phenomena including chemi-sorptions, thermal decomposition, and solid-gas reactions (e.g., oxidation or reduction).







TGA thermogram of polymer-based composite material. The onsets of decomposition and residual mass are highlighted.

TGA VS DTA VS DSC

TGA	DTA	DSC
TGA is Thermal Gravimetric Analysis	DTA is Differential Thermal Analysis	DSC is Differential Scanning Calorimetry
The change of the mass of a sample with the change of the temperature is observed and analyzed	The temperature difference developed between a sample and a reference compound is measured at identical heat treatments	The heat flow is measured against the temperature change at a particular time
Used to analyze inorganic materials, metals, polymers, plastics, ceramics, glasses and composite materials	Used to analyze thermal properties of minerals, for the characterization of polymers, and biological materials	Used to analyze proteins, antibodies, etc.
Sample can be used as a solid substance	Sample can be used as a solid substance	Sample is always a liquid

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NO	Technique Name	Abbreviation	Instrument Apply	Parameter Measure	Graph
1	Thermogravimetry	TG	Thermobalance	Mass	mass vs temp
2	Derivative Thermogravimetry	DTG	Thermobalance	dm/dt	dm/dt vs temp
3	Diff.Thermal Analysis	DTA	DTA Appts	ΔT	ΔT vs temp
4	Diff.Scanning Calorimetry	DSC	Calorimeter	dH.dt	dH/dt vs temp
5	Thermometric Titrimetry	……..	Calorimeter	Temp.	Temp vs titrant volume
6	Dynamic Reflectance Spectroscopy	DRS	Spectrophotometer	Reflectance	%refle.and temp.

7	Evolved gas detection	EGD	Thermal conductivity cell	T.C.	T.C. vs temp
8	Dialotometry	TMA	Dialatometer	Vol.of Length	Vol or length vs temp
9	Electrical conductivity	EC	Electrometer or Bridget	Current or resistance	I or R vs temp
10	Emanation Thermal Analysis	ETA	ETA appts.	Radioacti vity	E vs temp

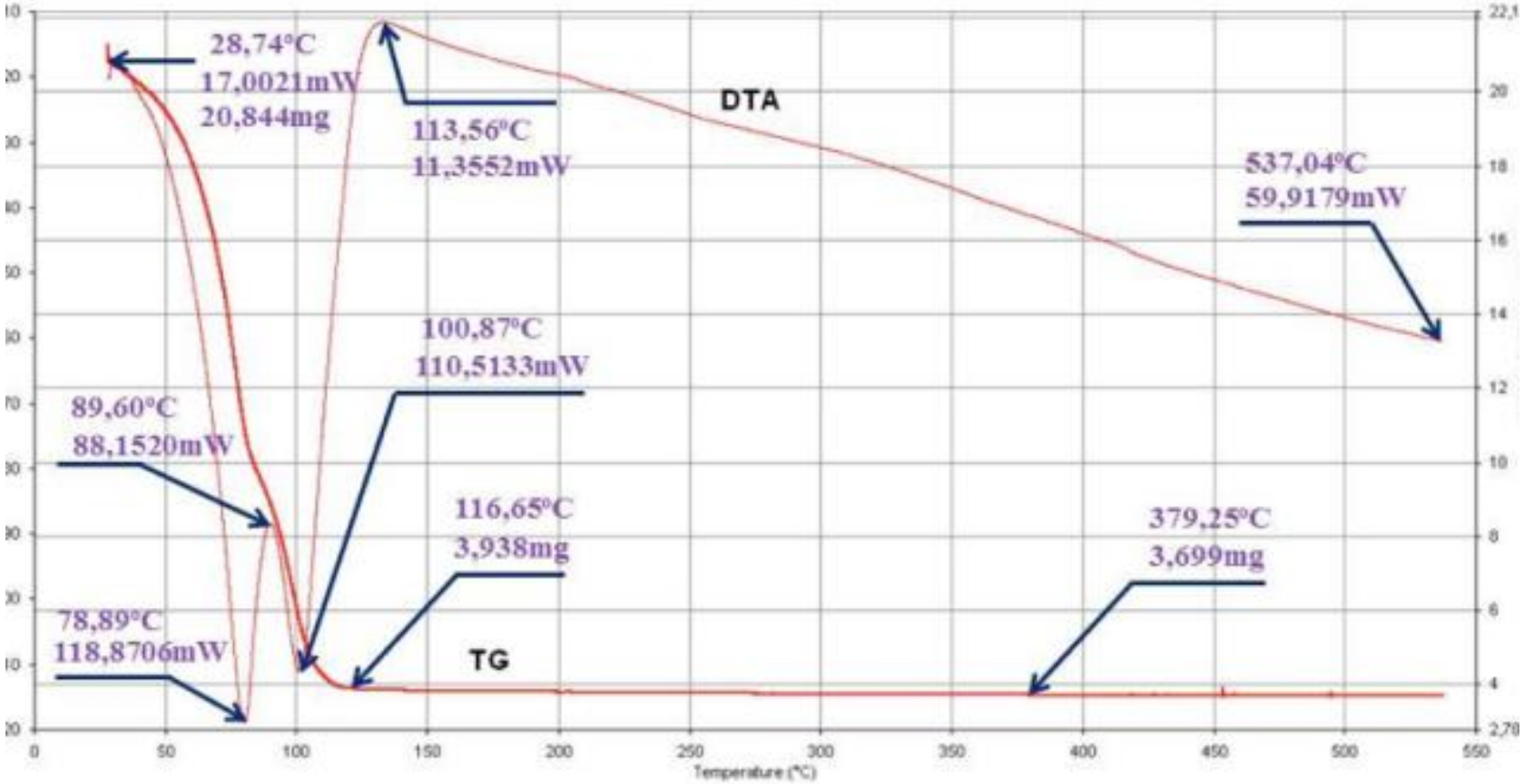
1. **DTA** will provide **the temperature necessary to establish a nearly zero temperature difference between the sample and the inert reference**.

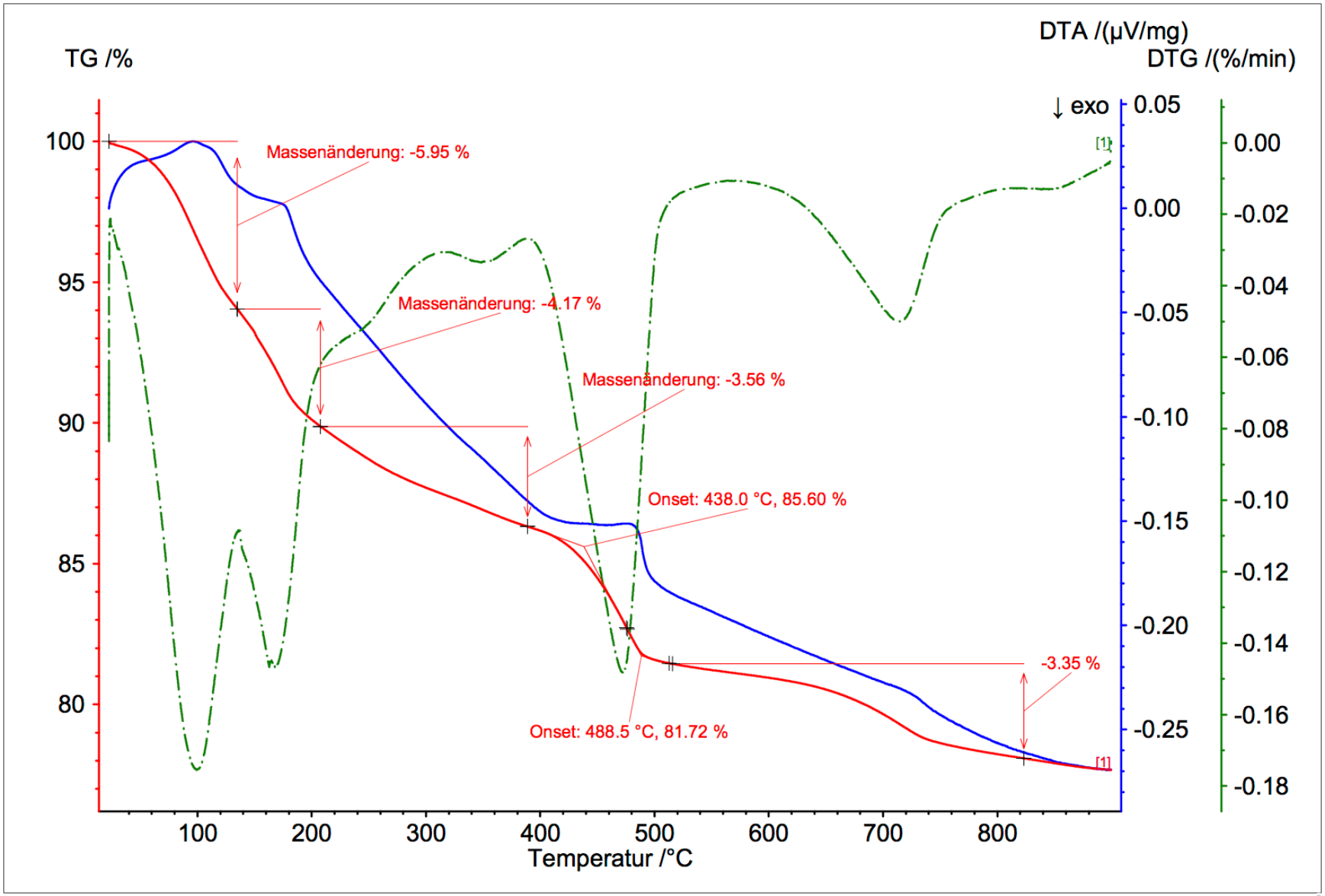
2. **DSC** measures **the energy necessary to establish a nearly zero temperature difference between the sample and the inert reference**

3. **TGA** will give mass change in miligram/microgram as a function of time or temperature subjected to heating.

4. **DTG** will provide the percentage and peak temperature of sample mass change rate with temperature and/or time.

5. **In brief, the DSC/DTA measure the heat flow/temperature and the TGA/DTG measure the weight change of the sample subjected to heating.**


28,74°C
17,0021mW
20,844mg
113,56°C
11,3552mW
DTA
537,04°C
59,9179mW
100,87°C
110,5133mW
89,60°C
88,1520mW
116,65°C
3,938mg
379,25°C
3,699mg
78,89°C
118,8706mW
TG
Temperature (°C)


TG /%
DTA /(µV/mg)
DTG /(%/min)
↓ exo
Massenänderung: -5.95 %
Massenänderung: -4.17 %
Massenänderung: -3.56 %
Onset: 438.0 °C, 85.60 %
Onset: 488.5 °C, 81.72 %
-3.35 %
[1]
[1]
100
95
90
85
80
0.05
0.00
-0.05
-0.10
-0.15
-0.20
-0.25
0.00
-0.02
-0.04
-0.06
-0.08
-0.10
-0.12
-0.14
-0.16
-0.18
100
200
300
400
500
600
700
800
Temperatur /°C

Examples of the DTA analyses of some minerals and rocks

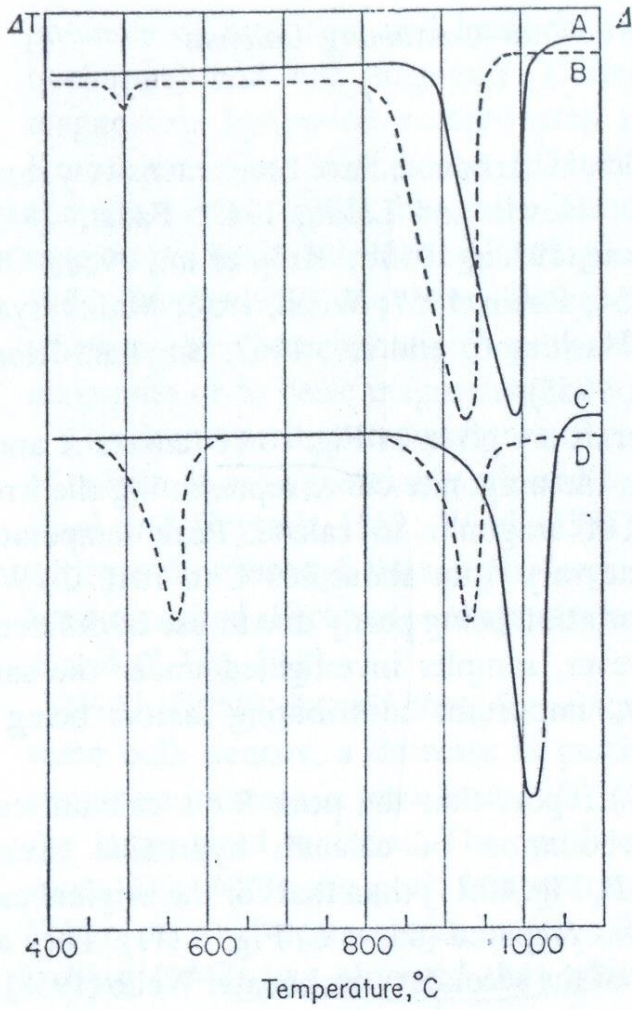


FIG. 10.11. DTA curves for: *A*—typical calcite (Faust, 1950); *B*—aragonite (Faust, 1950); *C*—natural calcite; *D*—sample giving curve *C*, calcined, hydrated and partially recarbonated.

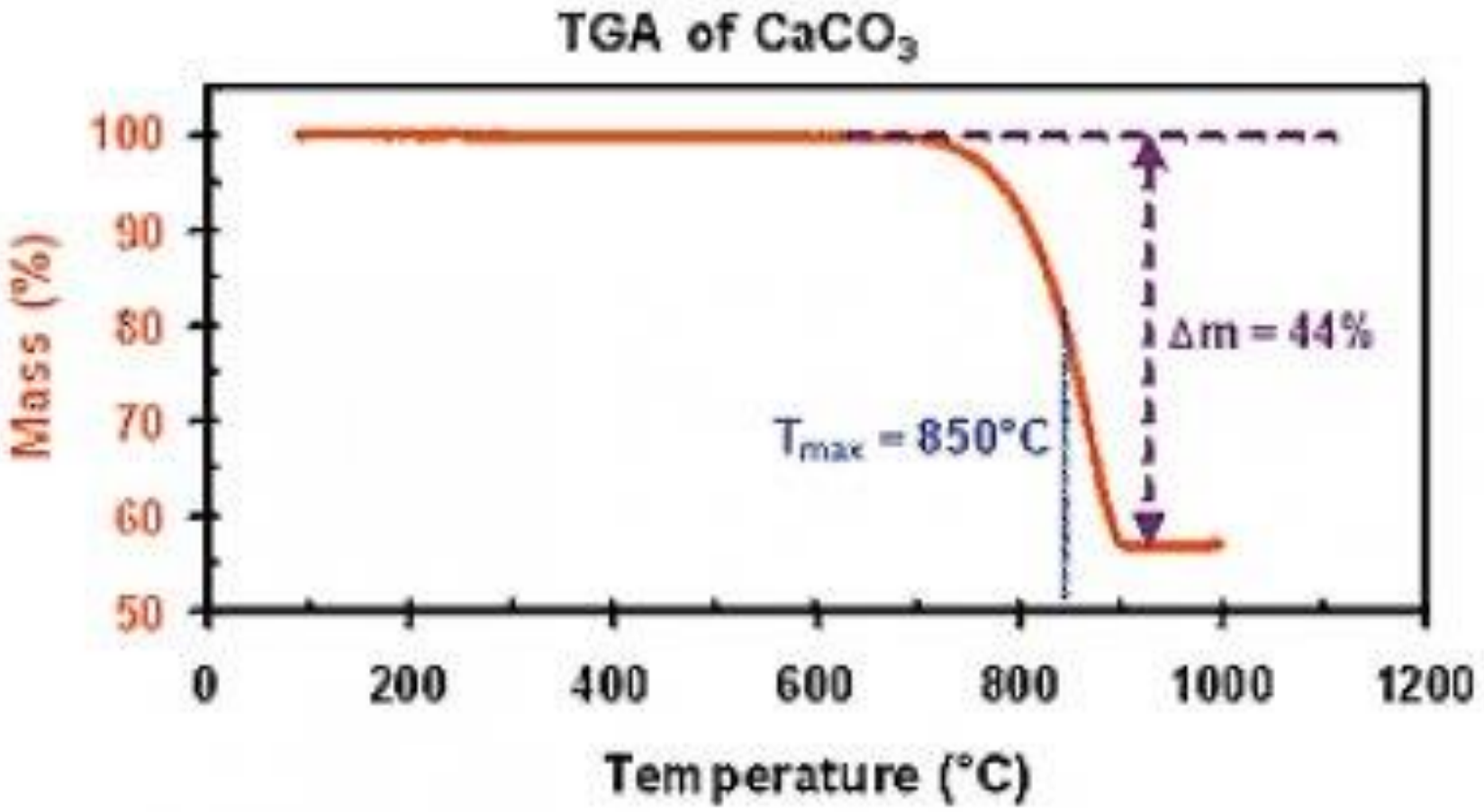
The decomposition of **Calcite** (Fig. A) into lime **"CaO"** starts around 850 and ends at 1020, but maximized at **1000 °C**

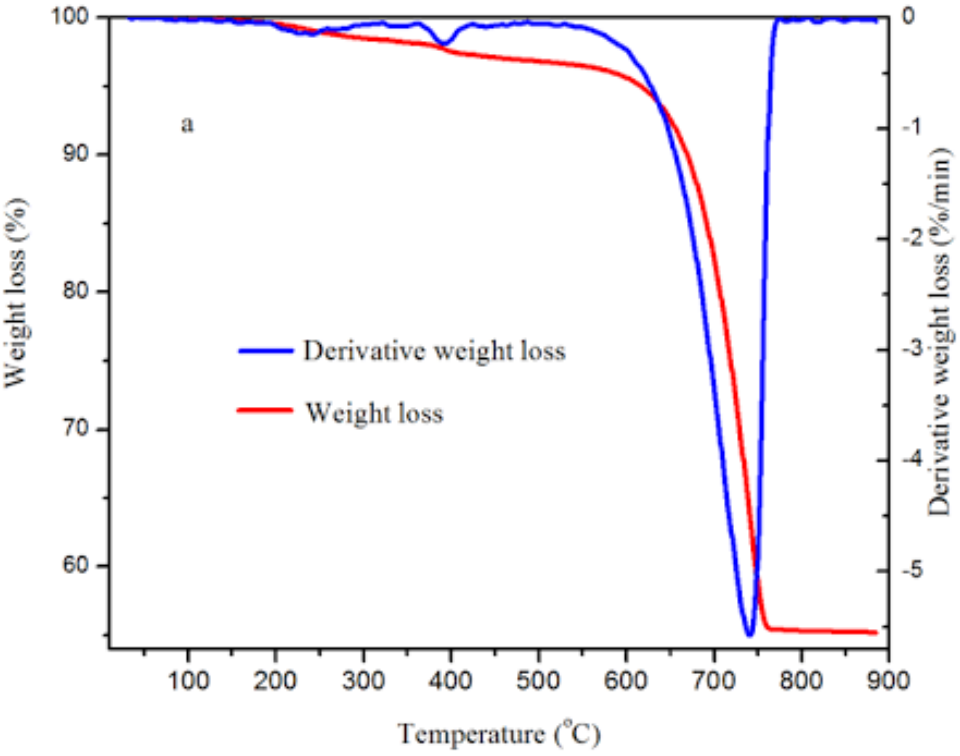
The decomposition of **Aragonite** (Fig. B) occurs at two steps:

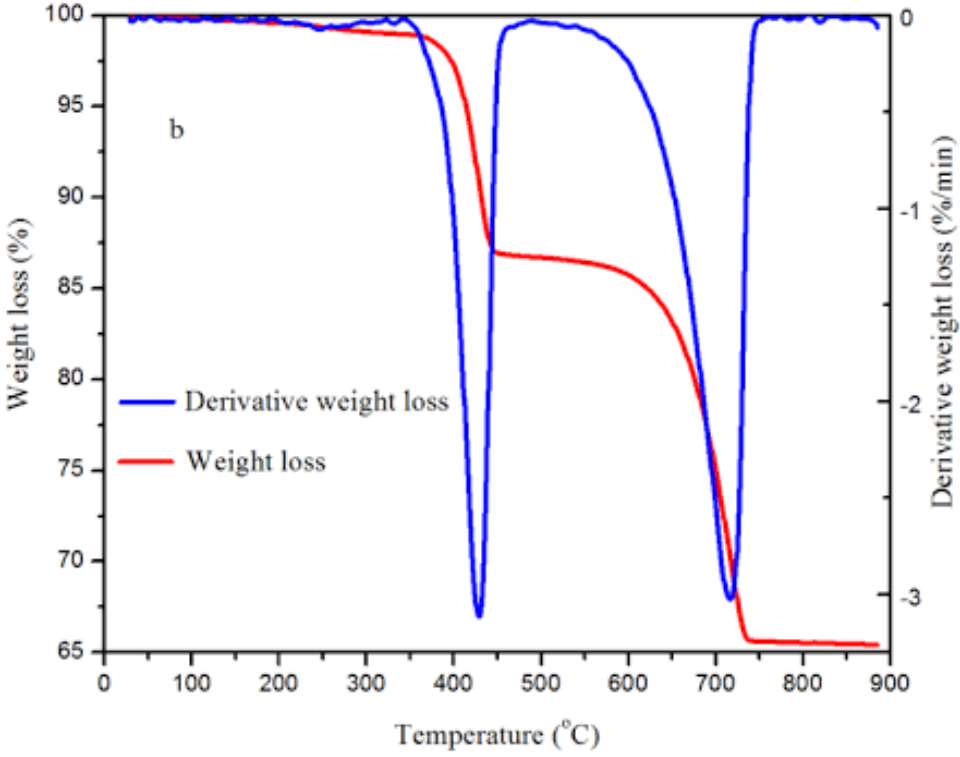
1. The first is the **irreversible conversion of aragonite to calcite.** This begins around 460, ends at 520, but maximized at 500 °C.

2. The second step is the decomposition of **Calcite** into lime **"CaO"**. This begins around 800, ends at 960 and maximized around 930 °C

Thermal behavior of calcite


TGA of $CaCO_3$
Mass (%)
100
90
80
70
60
50
0
200
400
600
800
1000
1200
Temperature (°C)
T_{max} = 850°C
Δm = 44%


a
Derivative weight loss
Weight loss
Weight loss (%)
Derivative weight loss (%/min)
Temperature (°C)
100
90
80
70
60
0
-1
-2
-3
-4
-5
100
200
300
400
500
600
700
800
900


b
Derivative weight loss
Weight loss
Weight loss (%)
Derivative weight loss (%/min)
Temperature (°C)
100
95
90
85
80
75
70
65
0
-1
-2
-3
0
100
200
300
400
500
600
700
800
900

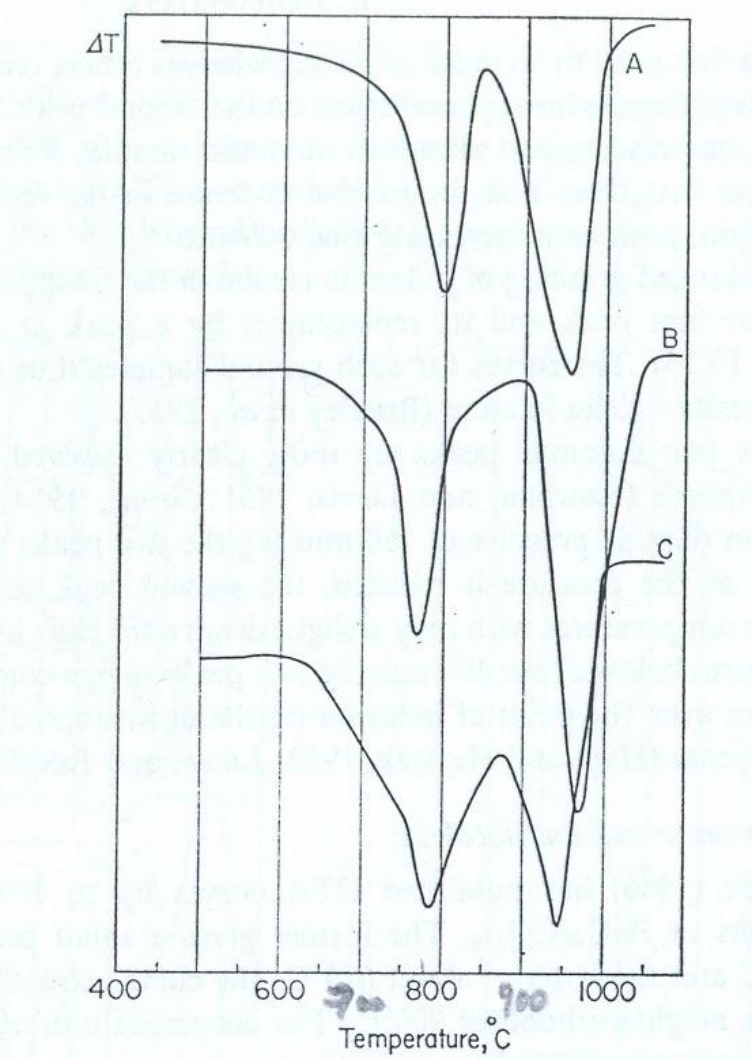


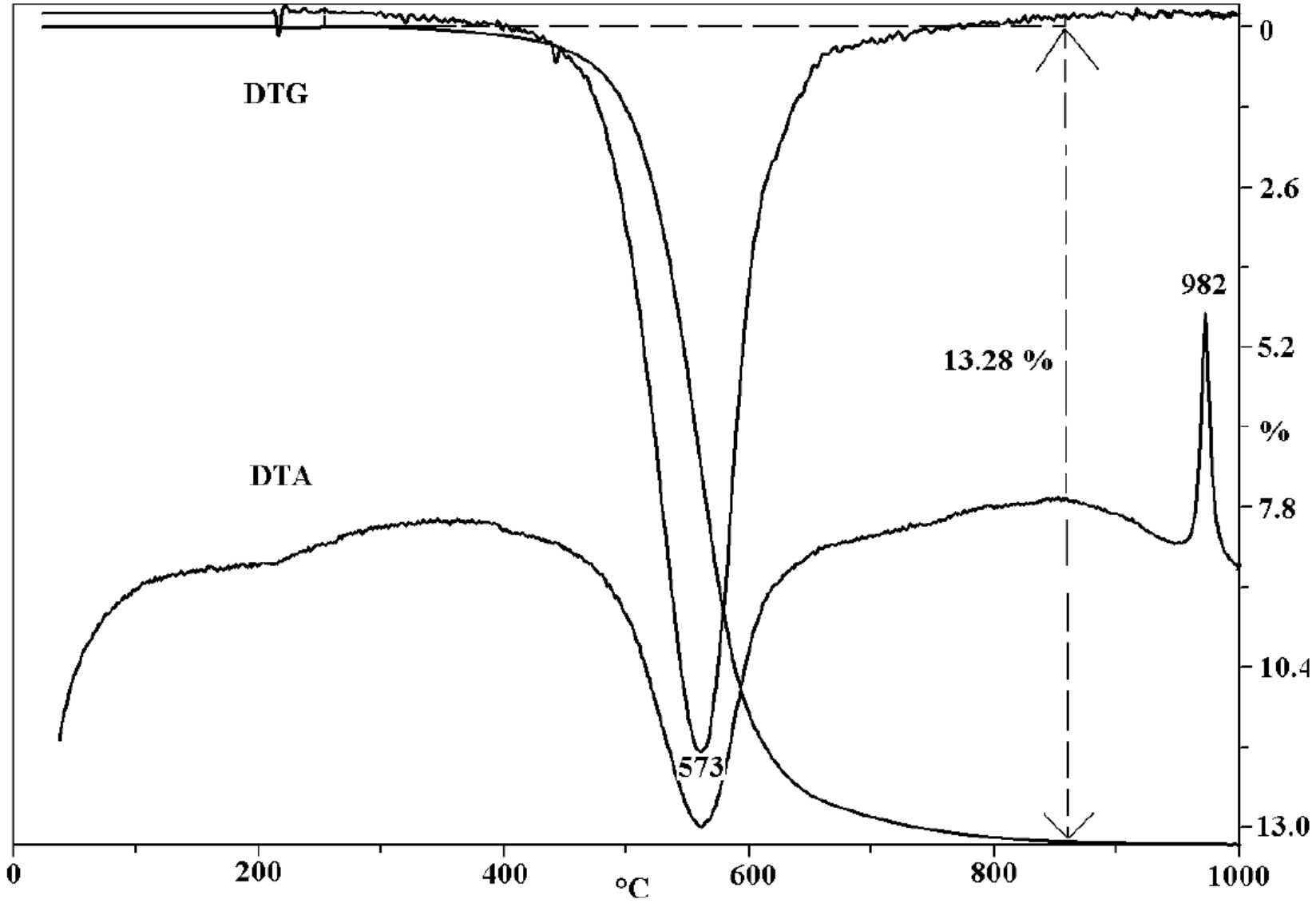
FIG. 10.14. DTA curves for different samples of dolomite.

The decomposition of **Dolomite (Ca Mg $(CO_3)_2$)** occurs on two steps:

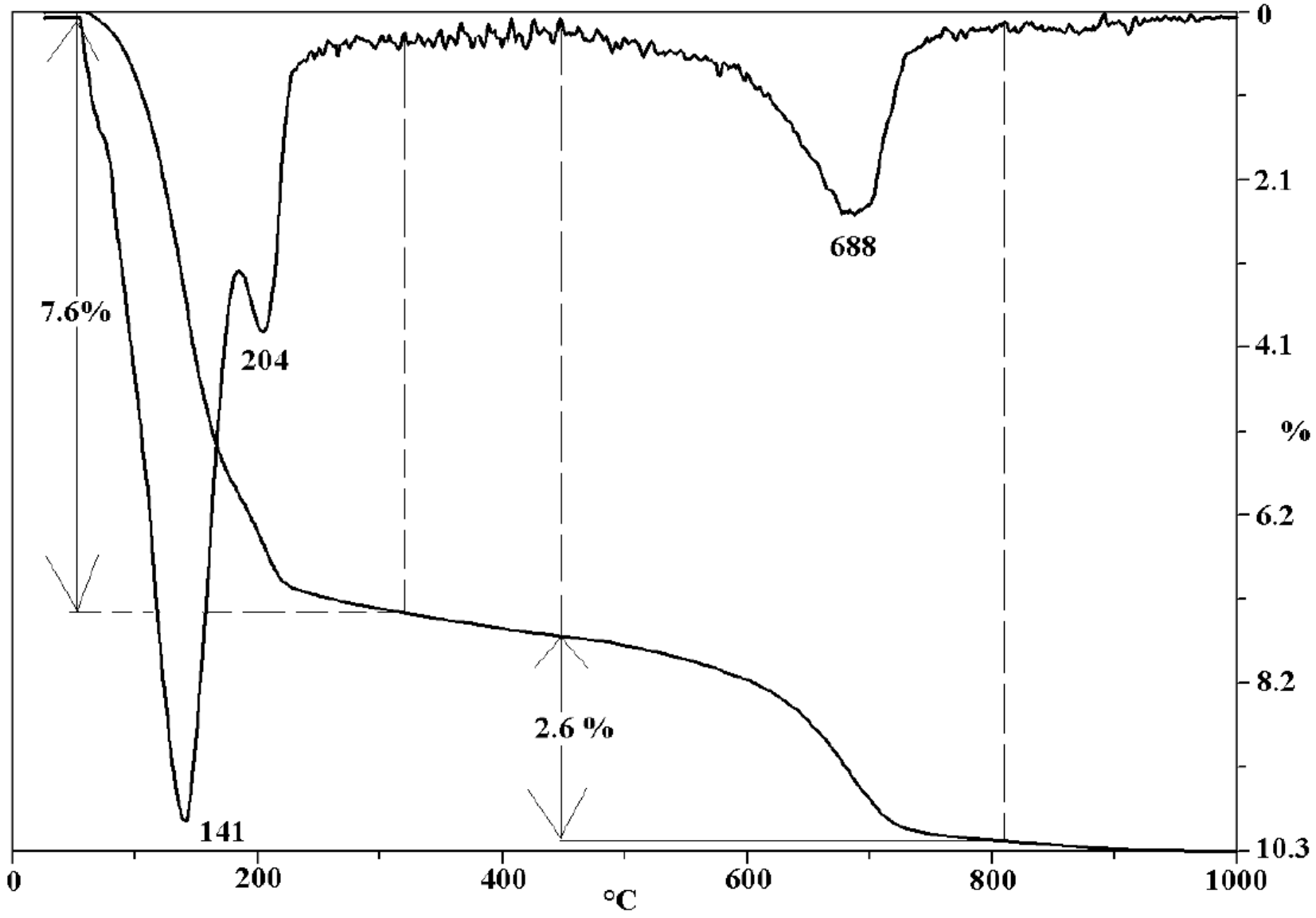
1. The first is to break apart the dolomite structure into $MgCO_3.CaCO_3$ then the decomposition of the **Magnesite** part ($MgCO_3$) into periclase **"MgO"** and **CO_2**. This begins around 690, ends at 850 and maximized at 830 °C.

2. The second step is the decomposition of the **Calcite** ($CaCO_3$) part into lime **"CaO" and CO_2**. This begins around 850, ends at 1020 and maximized around 960 °C.

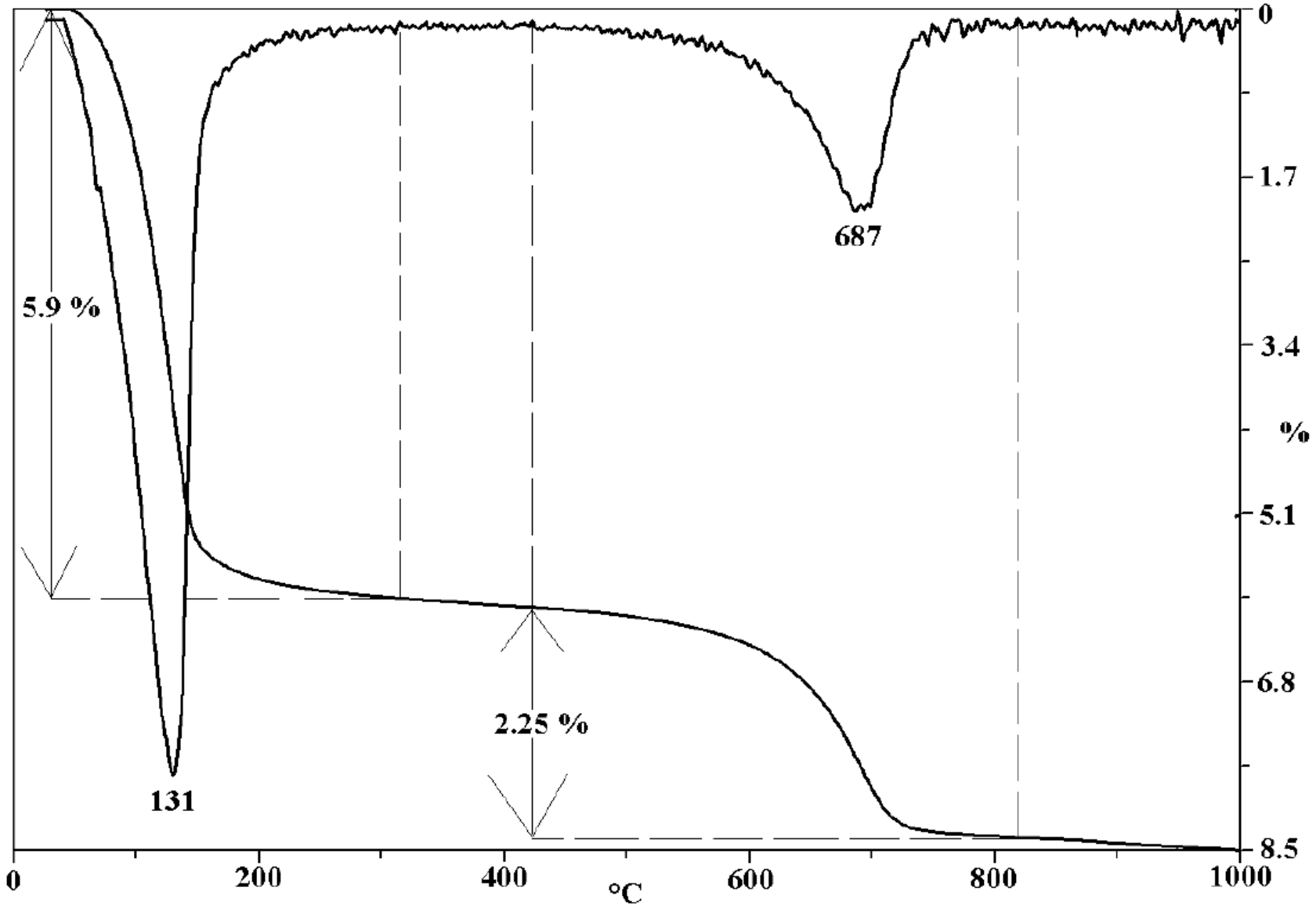
Thermal behavior of dolomite



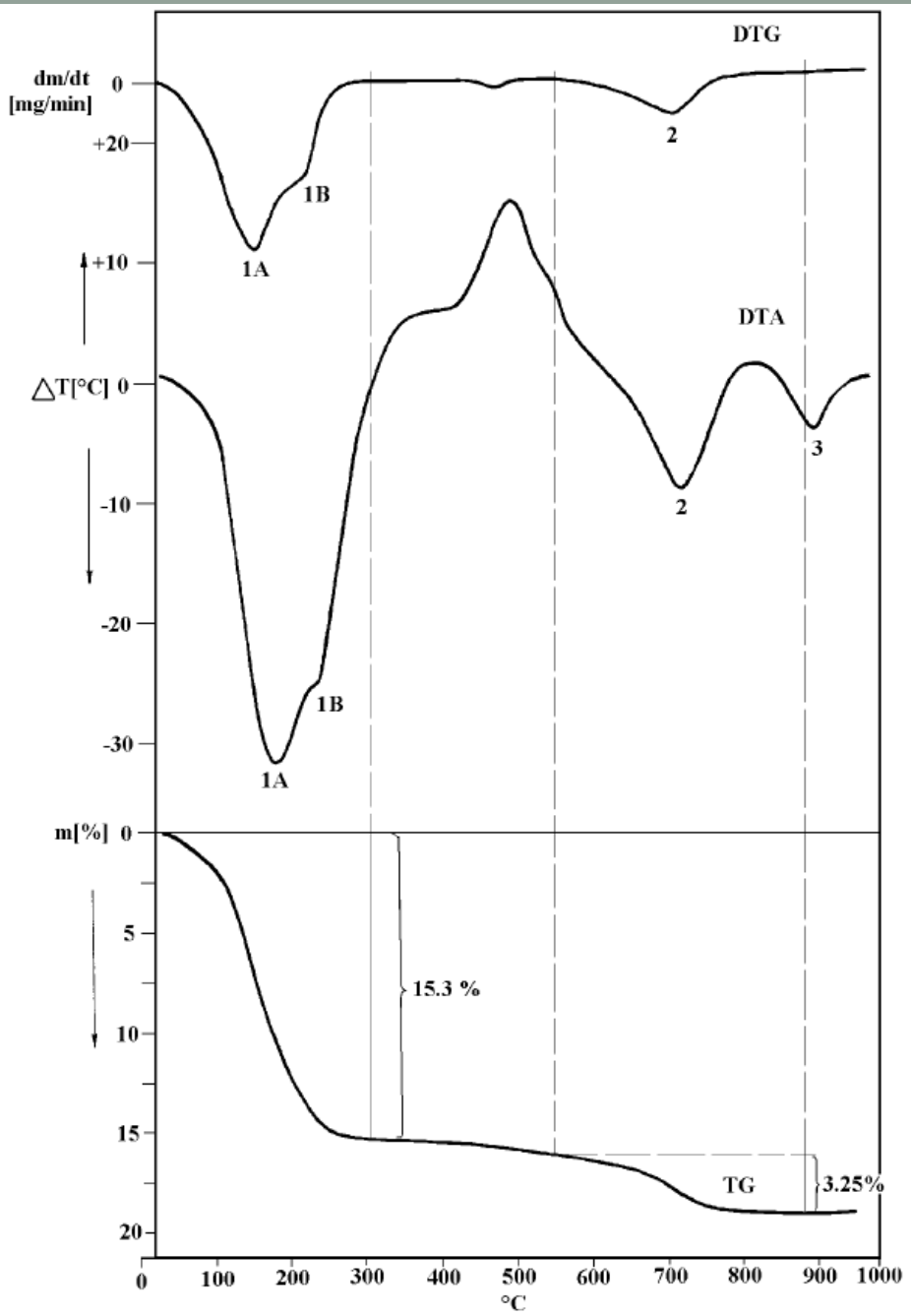
Thermal behavior of kaolinite



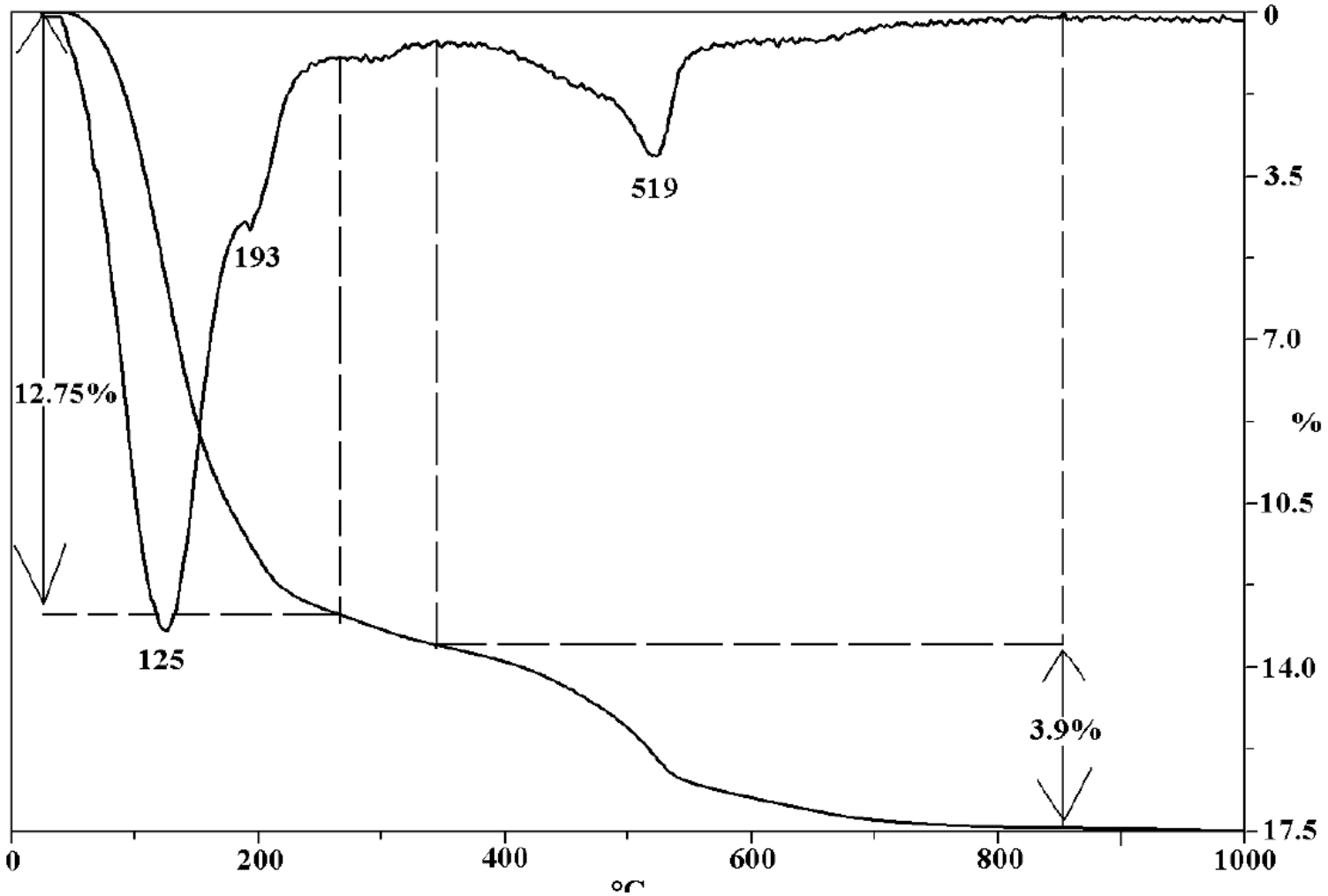
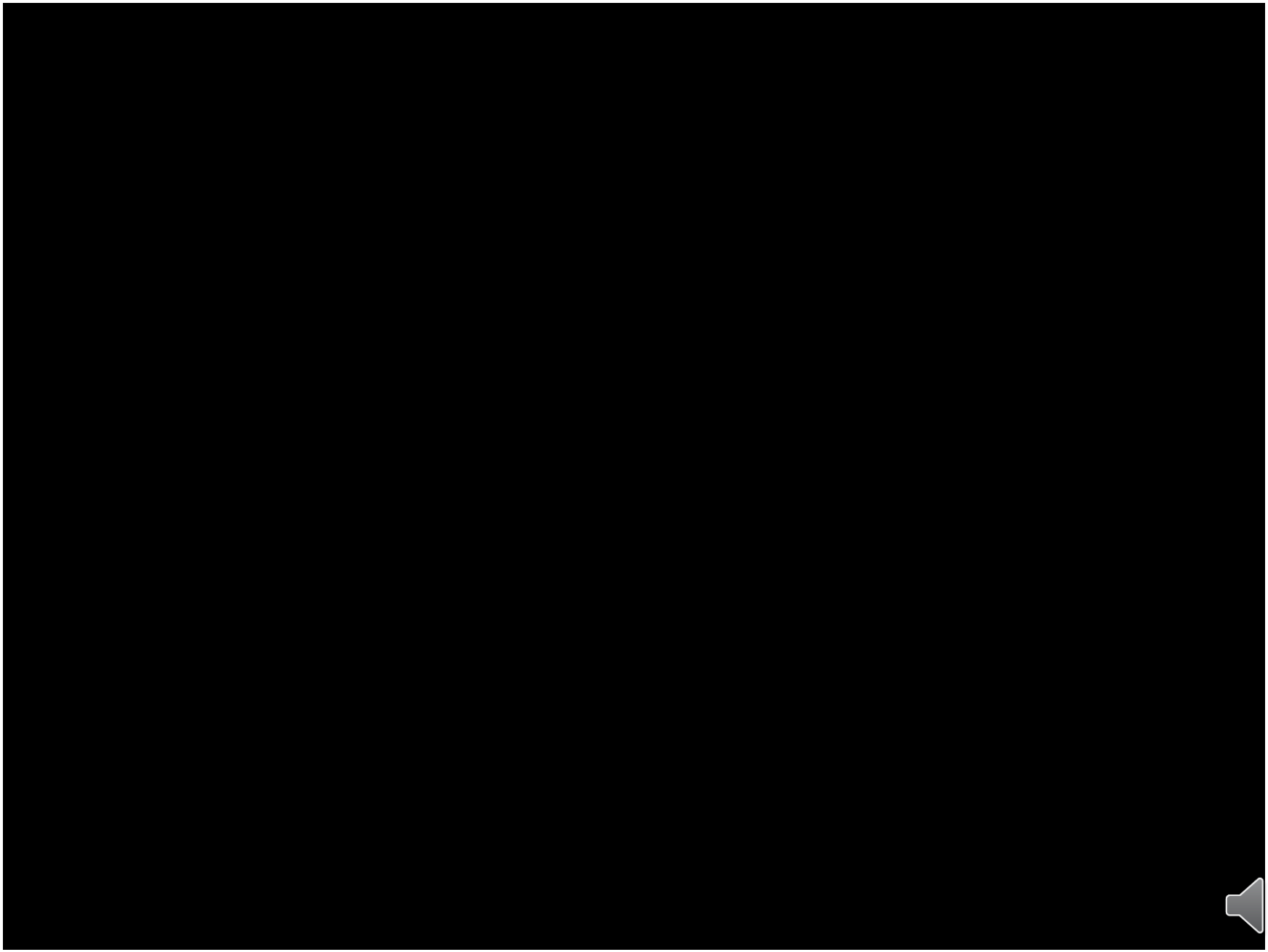
Thermal behavior of Ca-Montmorillonite



Thermal behavior of Na-Montmorillonite



Thermal behavior of Montmorillonite



Thermal behavior of Montmorillonite of low temperature dehydroxylation