MINERAL DEFINITIONS AND ANALYSES: A KEY ASPECT IN MINERAL-BASED PRODUCTS

The Role of Mineral Science in Tactical R&D

SME

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Introduction

Mineral and regulatory terminology, analytical characterizations, conclusions, and presentation of the information will ultimately affect a client's expectations of a research or production project and final products.

Multiple analytical techniques should be used to thoroughly characterize a natural or synthetic mineral or a material.

Today's "plug n' play" instrumental analyses for quick and sometimes thoughtless interpretations of results can lead to erroneous conclusions.

OUTLINE OF TOPICS

- DIALOGUE AMONG ANALYSTS AND BETWEEN CLIENT (S)
- REGULATORY CRITERIA-ISSUES/CONCERNS
- WHAT'S IN A NAME?
- MINERAL/CRYSTAL STRUCTURE DEFINITIONS
- TECHNIQUES FOR MINERAL AND MATERIAL CHARACTERIZATION
- EXAMPLES
- CONCLUSIONS

DIALOGUE

- DOES THE ANALYST/LABORATORY HAVE A GENERAL OR THOROUGH UNDERSTANDING OF MINERALS OR MATERIALS CHARACTERIZATION?
- HOW MUCH SAMPLE IS AVAILABLE FOR CHARACTERIZATION?
- HOW REPRESENTATIVE IS THE SAMPLE (S) SUBMITTED FOR ANALYSIS? IF UNKNOWN, CAN ONE BE GENERATED AND PROVIDED TO THE LABORATORY PRIOR TO DETERMINING A GROUP OF ANALYSES?
- IS A BIASED SAMPLING PREFERRED IN SOME CASES; THEREFORE, HOW WAS THE SAMPLE PREPARED PRIOR TO SUBMISSION?
- HOW WILL THE LABORATORY SUB-SAMPLE THE MATERIAL TO GUARANTEE HOMOGENEITY FOR THE ANALYSES?
- DOES PURITY OR COLOR MATTER TO THE APPLICATION/ PROCESS?

DIALOGUE

- ARE THE CRITERIA FOR THE APPLICATION/PROCESS PHYSICAL OR CHEMICAL/MINERALOGICAL OR A COMBINATION THEREOF?
- WHAT TEMPERATURE (S) OR TEMPERATURE RANGE WILL THE MINERAL (S) OR MATERIAL BE SUBJECTED TO IN THE APPLICATION?

  100 °!   600 °!

  °F OR °C

  100°C (212 °F) ≠ 100 °F (38 °C)

  600°C (1112 °F) ≠ 600 °F (315 °C)

- ARE THE CONDITIONS OXIDIZING OR INERT/REDUCING OR UNDER VACUUM?

  AIR, N_2 or Argon, MIXTURE (N_2,CO_2,O_2)

- IS THE APPLICATION/PROCESS CONDITION WET OR DRY

REGULATORY CRITERIA- ISSUES/ CONCERNS

- ARE ANY REGULATORY CRITERIA TO BE MET IN PRODUCING OR USING THE PRODUCT BY THE COMPANY OR ITS EXTERNAL CLIENT (S) OR BOTH?

    - HEAVY METALS
    - CRYSTALLINE SILICA
        - QUARTZ
            - IS ALL QUARTZ CREATED EQUAL?
        - CRISTOBALITE
            - MISIDENTIFICAITION OF OPALINE PHASES
        - TRIDYMITE

REGULATORY CRITERIA- ISSUES/CONCERNS

- REGULATED ASBESTIFORM MINERALS

SERPENTINE-Chrysotile **AMPHIBOLE-Amosite, Crocidolite, ATA minerals**

Anthophyllite asbestos, Tremolite asbestos, Actinolite asbestos

‘WHILE ALL ASBESTIFORM MINERALS ARE FIBROUS,

NOT ALL FIBROUS MINERALS ARE ASBESTIFORM’

IC 8751 **RI 836T** **ASTM D5755/5756**

Discriminating Amphibole Cleavage Fragments from Asbestos (Wylie)

- IF REGULATORY CRITERIA ARE TO BE MONITORED, HOW OFTEN SHOULD THE SAMPLING/SUB-SAMPLING OCCUR ON A PROCESS AND FINAL PRODUCTS?
- DOES PROCESSING INADVERTANTLY OR UNKNOWINGLY CAUSE A CROSS-CONTAMINATION OR GENERATE A PHASE FORMATION TRANSFORMATION THAT NOW REQUIRES REGULATORY LABELLING?
- DOES THE LABORATORY HAVE THE RELEVANT STANDARDS FOR THE MULTIPLE MATRICES ANALYZED?

WHAT'S IN A NAME?

- BAUXITE
  - MIXTURE OF MINERALS
    - GIBBSITE, BOEHMITE PLUS OTHERS
- FELDSPAR
  - MIXTURE OF MINERALS
    - MICROCLINE, ALBITE, ANORTHITE, QUARTZ
- FULLER'S EARTH
  - USA vs. EUROPEAN
    PALYGORSKITE/MONTMORILLONITE
- LIMESTONE; DOLOMITIC LIMESTONE; DOLOSTONE

LIMESTONE-	>85/90% CALCITE
DOLOSTONE-	>85/90% DOLOMITE
DOLOMITIC LIMESTONE- CALCITIC DOLOMITE	VARIABLE MIXTURE OF CALCITE/ DOLOMITE

WHAT'S IN A NAME?

- CLAY

  < 2 MICRON PARTICLES

  KAOLINITE

- CALCINED CLAY

  META-KAOLIN

  PSEUDO-MULLITE

  MULLITE, PARTIAL MELT/MULLITE

- TRICALCIUM PHOSPHATE (TCP) [Fisher, C-127]

  $Ca_3(PO_4)_2$ Beta & Alpha forms

  HYDROXYAPATITE, $Ca_{10}(PO_4)_6(OH)_2$

- BRUSHITE

  $CaHPO_4 \cdot 2H_2O$

  $CaPO_3OH \cdot 2H_2O$

WHAT'S IN A NAME?

- MAGNESIUM CARBONATE [FISHER, M-27]

  $MgCO_3$

  HYDROMAGNESITE WITH BRUCITE

  $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$, $Mg(OH)_2$

- PLASTER

  PARTIAL DEHYDRATION OF GYPSUM

  LOSS OF 1.5 MOLE H_2O

  BASSANITE, $CaSO_4 \cdot 0.5H_2O$

- ALUMINUM TRIHYDRATE (ATH)

  $Al_2O_3 \cdot 3H_2O$

  $Al(OH)_3$

  GIBBSITE, BAYERITE, NORDSTRANDITE

MINERAL/CRYSTAL STRUCTURE DEFINITIONS

- NATURAL versus SYNTHETIC
- CRYSTAL STRUCTURE/LATTICE
  - HABIT ≠ CRYSTAL STRUCTURE/LATTICE
- POLYMORPHS
  - DISPLACIVE
  - RECONSTRUCTIVE
- MINERAL PHASE DIAGRAMS
  - TEMPERATURE AND PRESSURE
- CRYSTALLINITY/CRYSTALLITE SIZE
- PARTICLE SIZE
  - PARTICLE SIZE ≠ CRYSTALLITE SIZE

MINERAL/CRYSTAL STRUCTURE DEFINITIONS

- PARTICLE
  - PLATY
  - EQUANT
  - PRISMATIC
  - ACICULAR
  - LATH/ROD LIKE
  - FIBROUS
  - ASBESTIFORM
- NANOPARTICLES
  - 10 to 100 NANOMETERS (FOR ALL DIMENSIONS!)

MINERAL/CRYSTAL STRUCTURE DEFINITIONS

- ANHYDROUS
  - FELDSPAR, PYROXENE MINERALS
  - SULFIDES
- HYDROUS
  - HYDRATE
    - GYPSUM
  - HYDROXIDE
    - TALC, KAOLINITE, MONTMORILLONITE, AMPHIBOLES
  - OXYHYDROXIDE
    - GOETHITE, BOEHMITE
- INTERSTITIAL
    - PCC, PRIMARY SEDIMENTARY PHASES

MINERAL/CRYSTAL STRUCTURE DEFINITIONS

- CARBONATES

  LIMESTONE/MARBLE — CALCITE, $CaCO_3$

  MAGNESITE — $MgCO_3$

  DOLOSTONE — DOLOMITE, $CaMg(CO_3)_2$

- SULFUR CONTAINING PHASES

  SULFIDES

  PYRITE, FeS_2 — PYRRHOTITE, $Fe_{1-X}S$

  SULFATE

  GYPSUM, $CaSO_4 \cdot 2H_2O$

  SULFITE

  HANNABECHITE, $CaSO_3 \cdot 0.5H_2O$

TECHNIQUES FOR MINERAL AND MATERIAL CHARACTERIZATIONS

- XRD — X-RAY DIFFRACTION
  - QUALITATIVE/QUANTITATIVE
  - CRYSTALLINE versus AMORPHOUS
  - DEGREES OF CRYSTALLINITY
- TGA-DTA — THERMOGRAVIMETRIC/ DIFFERENTIAL THERMAL
- TGA-DSC — THERMOGRAVIMETRIC/DIFFERENTIAL SCANNING CALORIMETRY
- XRF — X-RAY FLUORESCENCE
- SEM-EDS — SCANNING ELECTRON MICROSCOPY/ ENERGY DISPERSIVE SPECTROSCOPY
- TEM-EDS/SAED — TRANSMISSION ELECTRON MICROSCOPY/ ENERGY DISPERSIVE SPECTROSCOPY/ SELECTIVE AREA ELECTRON DIFFRACTION

TECHNIQUES FOR MINERAL AND MATERIAL CHARACTERIZATIONS

• SELECTIVE DISSOLUTIONS	ACETIC ACID, HCL w/ HEAT or AMBIENT TEMPERATURES
• PLM	POLARIZED LIGHT MICROSCOPY
• FT-IR	FOURIER TRANSFORM/INFRARED
• ICP, ICP-MS	INDUCTIVELY COUPLED PLASMA/ INDUCTIVELY COUPLED PLASMA-MASS SPECTROSCOPY

TECHNIQUES FOR MINERAL AND MATERIAL CHARACTERIZATIONS

- Additional:
  - THERMAL-XRD
  - TGA-DTA/DSC with pressure
  - Karl Fischer Water w/ Vaporizer
  - Total or specific Carbon or Sulfur
  - SSA and PSD
  - SCREEN FRACTIONATION
  - DENSITY
  - HEAVY LIQUID SEPARATION
  - NMR
  - GC-MS
  - AFM

EXAMPLES

- NANO-PARTICLES
- High purity CaO stated to be at > 98%

  Combination of analytical techniques-

  Amorphous $Ca(OH)_2$ and Amorphous $CaCO_3$ @40%
- High purity TiO_2 state to be at >98%

  Combination of analytical techniques-
  not anhydrous; low temperature water losses
  plus intermediate temperature losses of up to
  4% Cl^- (HCl)
- SYNTHETIC TALC
- Stated to be high purity and unique morphology!

  Combination of analytical techniques-
  natural mineral; partial dissolution with
  re-formation of a poorly crystalline Sepiolite
  phase not Talc

EXAMPLES

- ATH
- $2[Al(OH)_3]$ ---> $Al_2O_3 + 3\ H_2O$

  $Al(OH)_3$ ----> 0.5 mole H_2O

  2 moles H_2O, forms $AlO(OH)$
  0.5 mole H_2O, forms γ-Al_2O_3

  @ elevated temperatures, α-Al_2O_3 (Corundum)

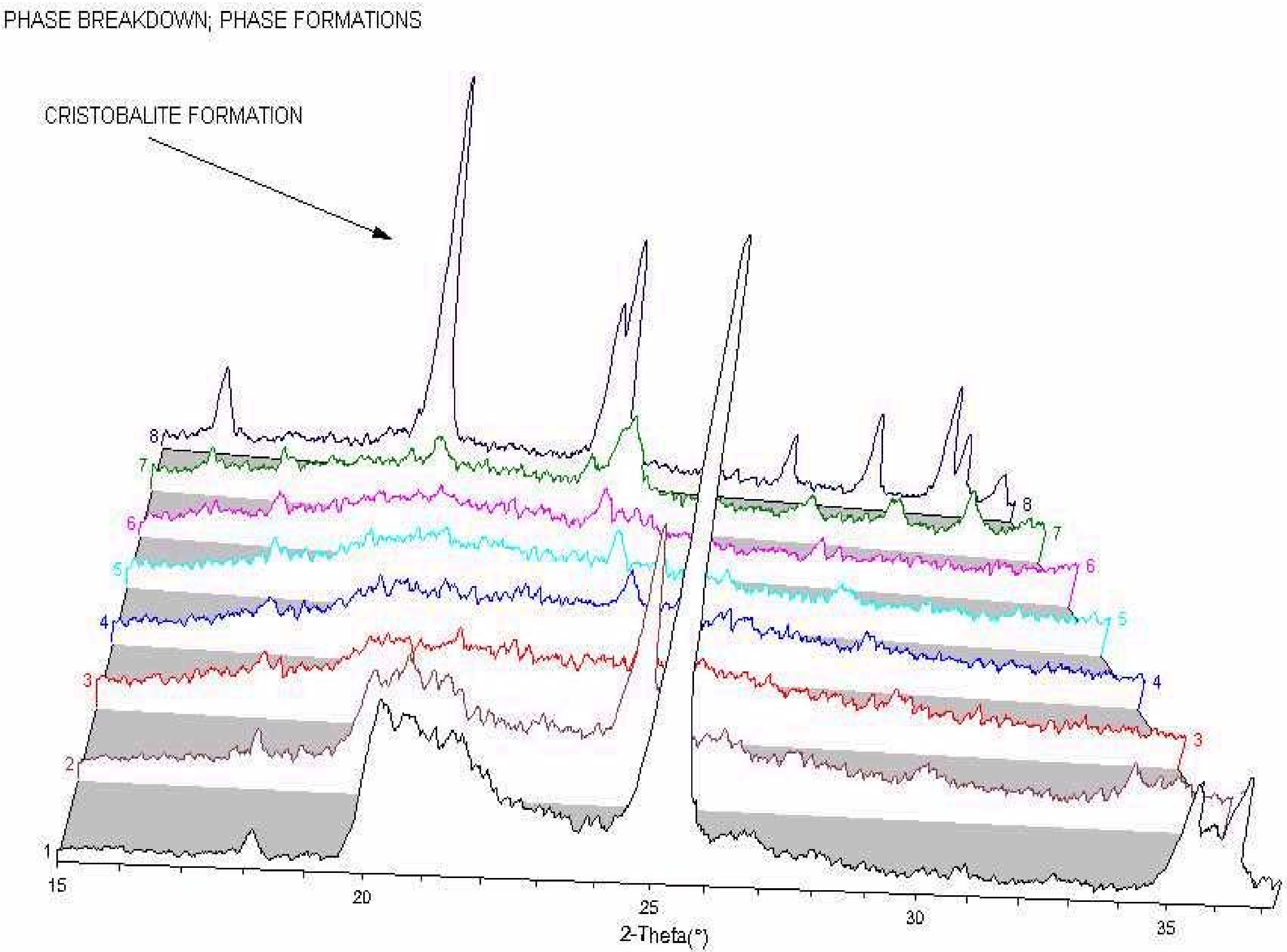
- GYPSUM
- $CaSO_4 \bullet 2H_2O$ ---> $CaSO_4 + 2H_2O$

  $CaSO_4 \bullet 2H_2O$ ---> 1.5 moles H_2O, forms Bassanite

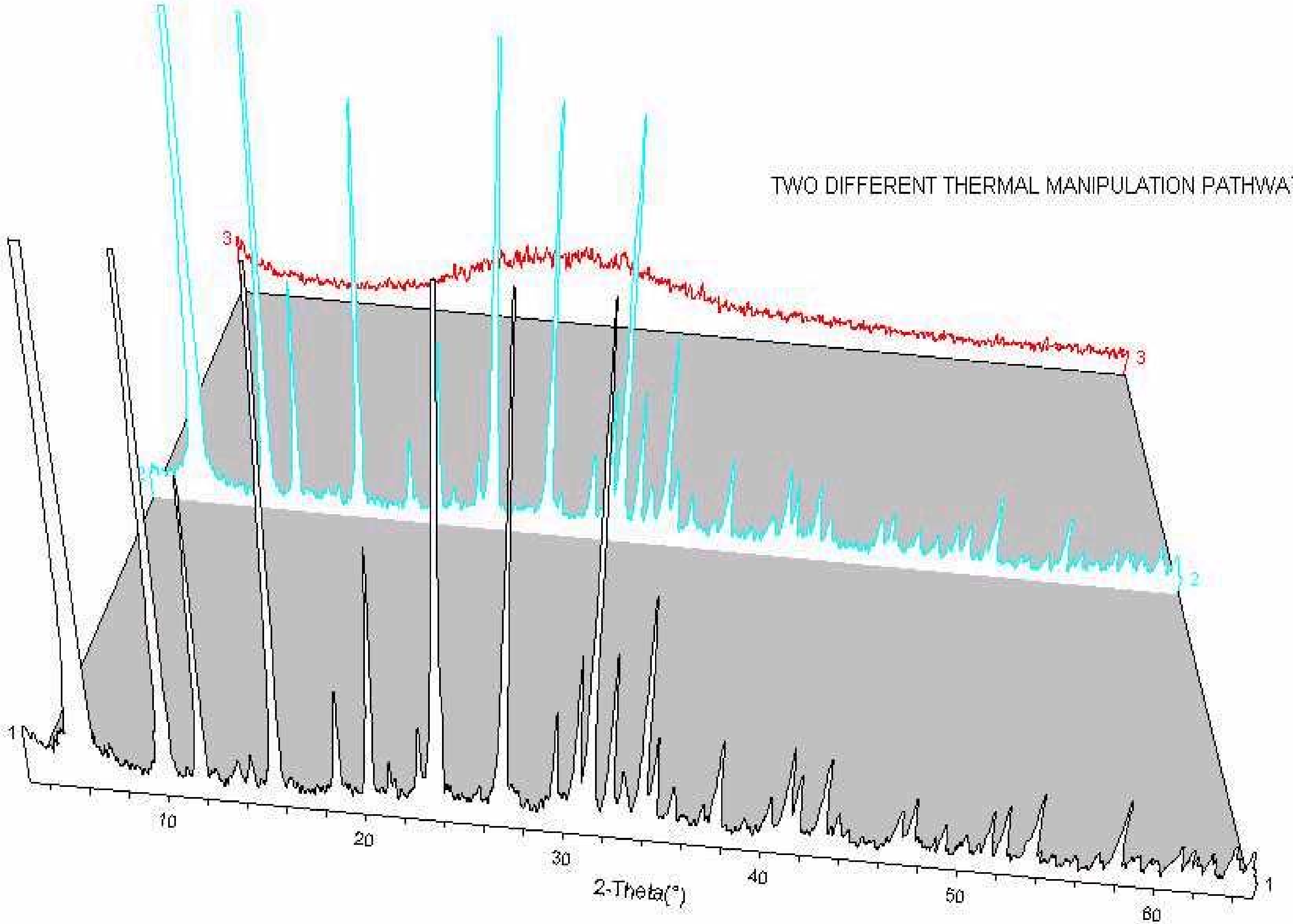
  0.5 mole H_2O, forms γ-$CaSO_4$

  @ intermediate temperatures, $CaSO_4$ (Anhydrite)

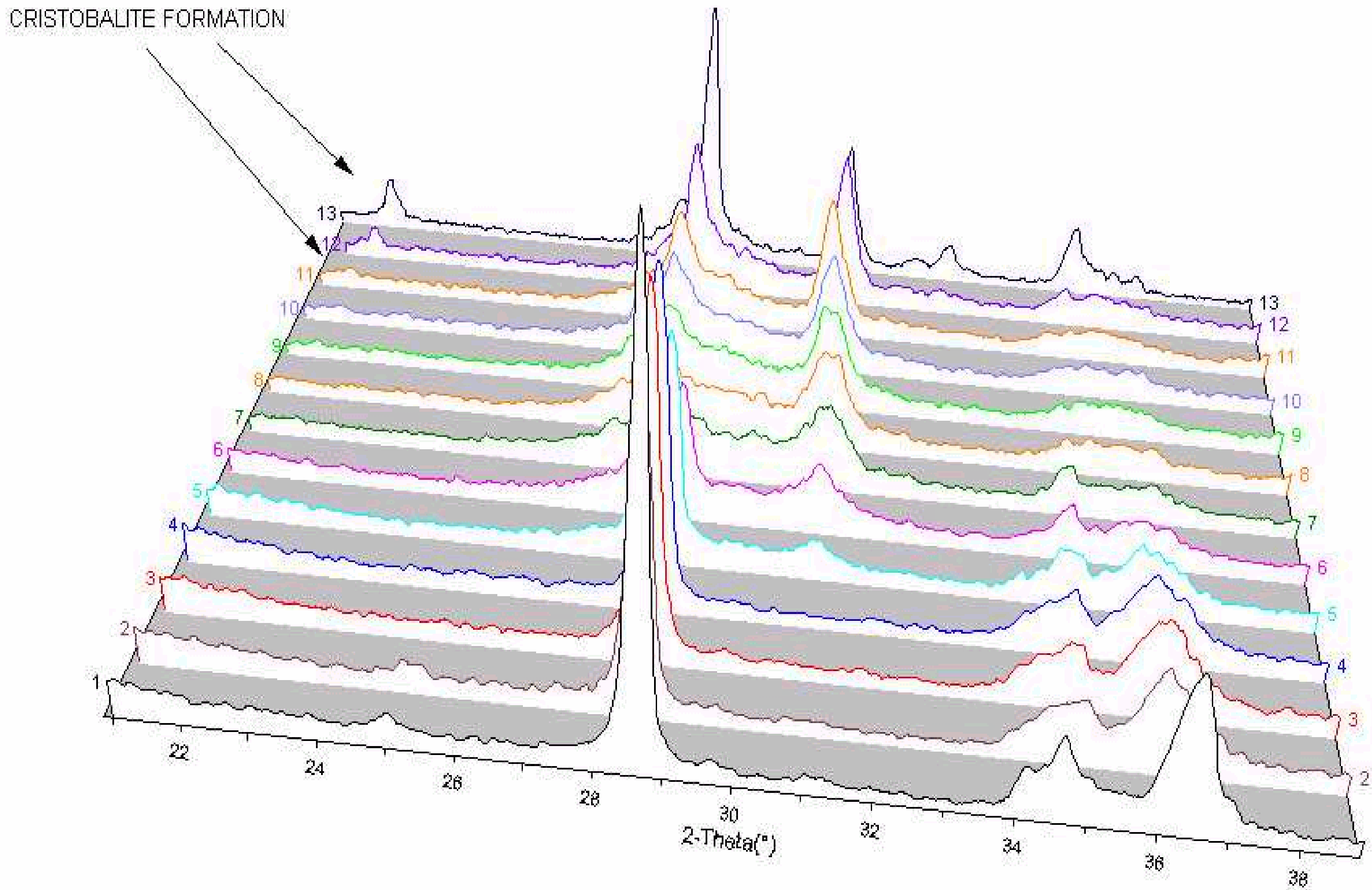
  @ elevated temperatures, forms α-$CaSO_4$



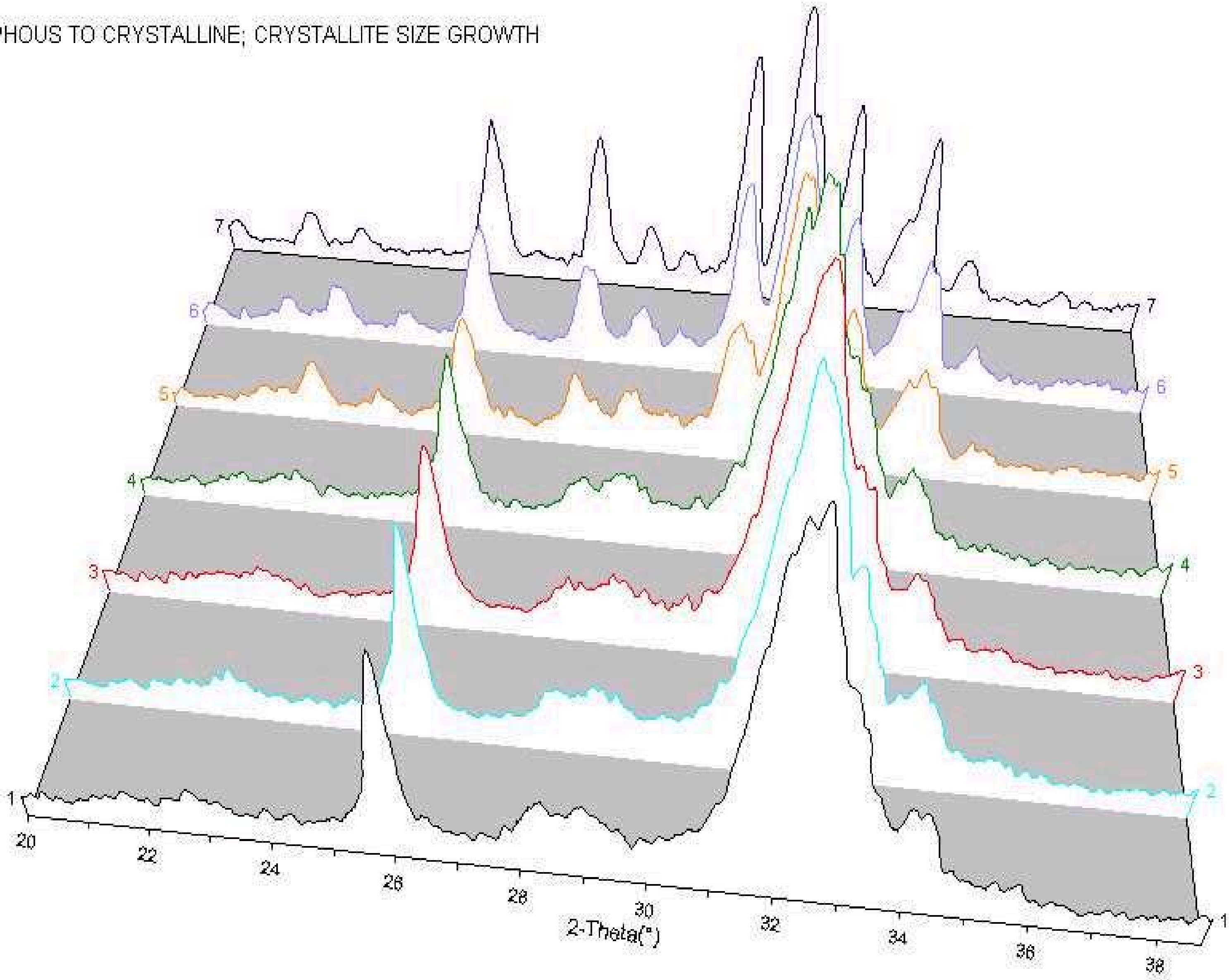
PHASE BREAKDOWN; PHASE FORMATIONS
CRISTOBALITE FORMATION
8
7
6
5
4
3
2
1
15
20
25
30
35
2-Theta(°)


TWO DIFFERENT THERMAL MANIPULATION PATHWAYS
1
2
3
10
20
30
40
50
60
2-Theta(°)

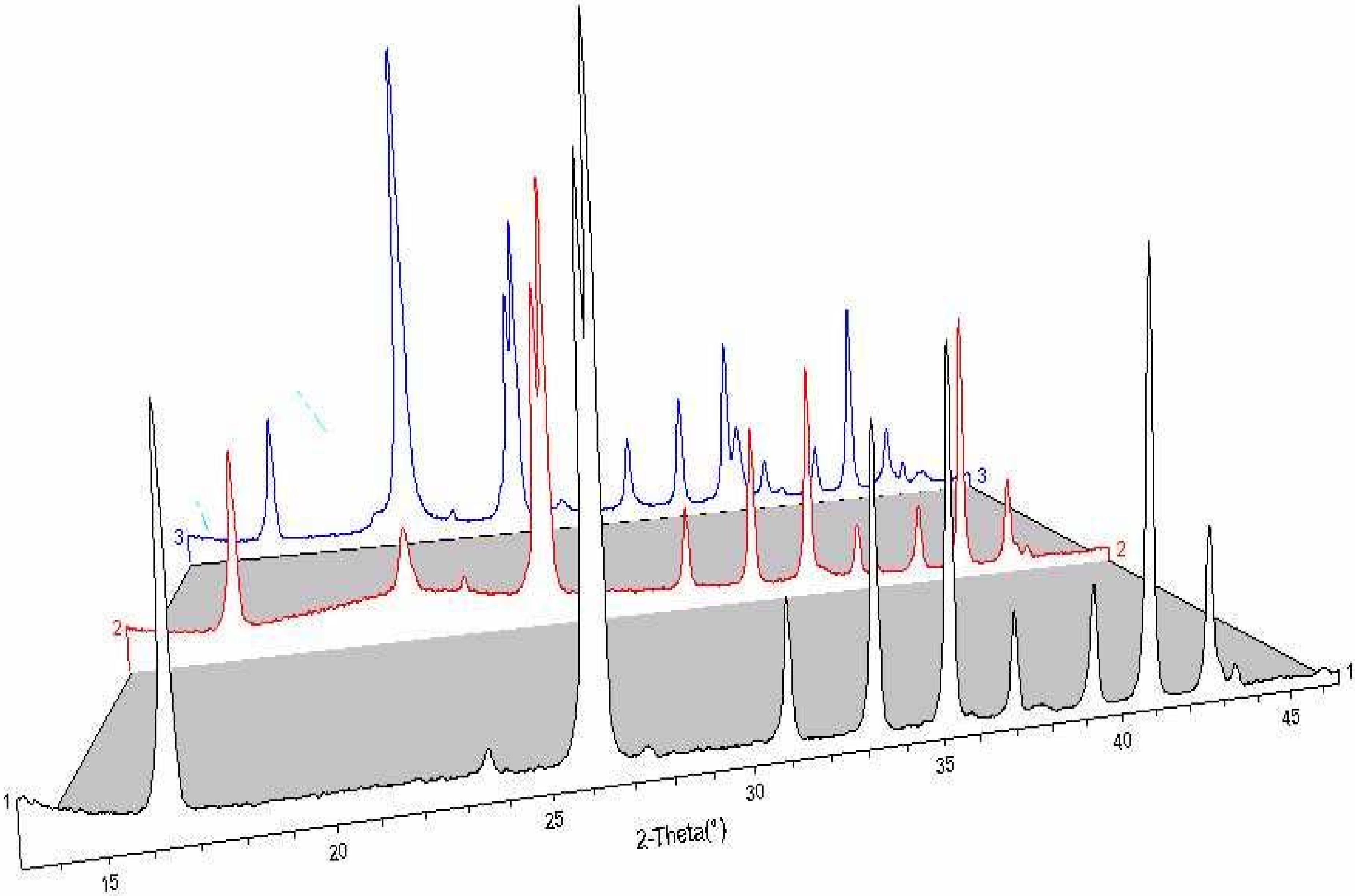
PHASE BREAKDOWN; PHASE FORMATION; POLYMORPH TRANSITIONS; NEW PHASE FORMATION

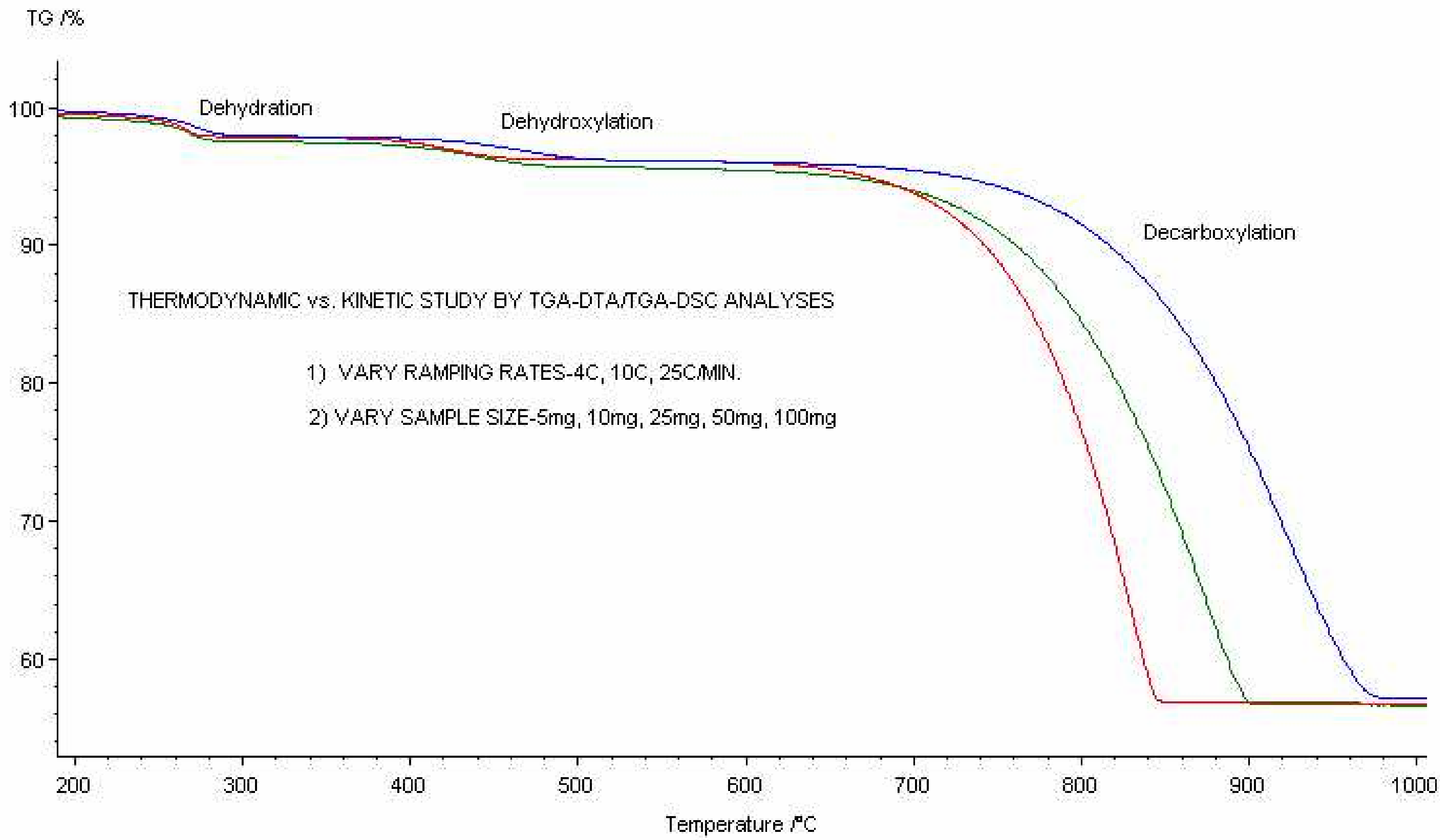


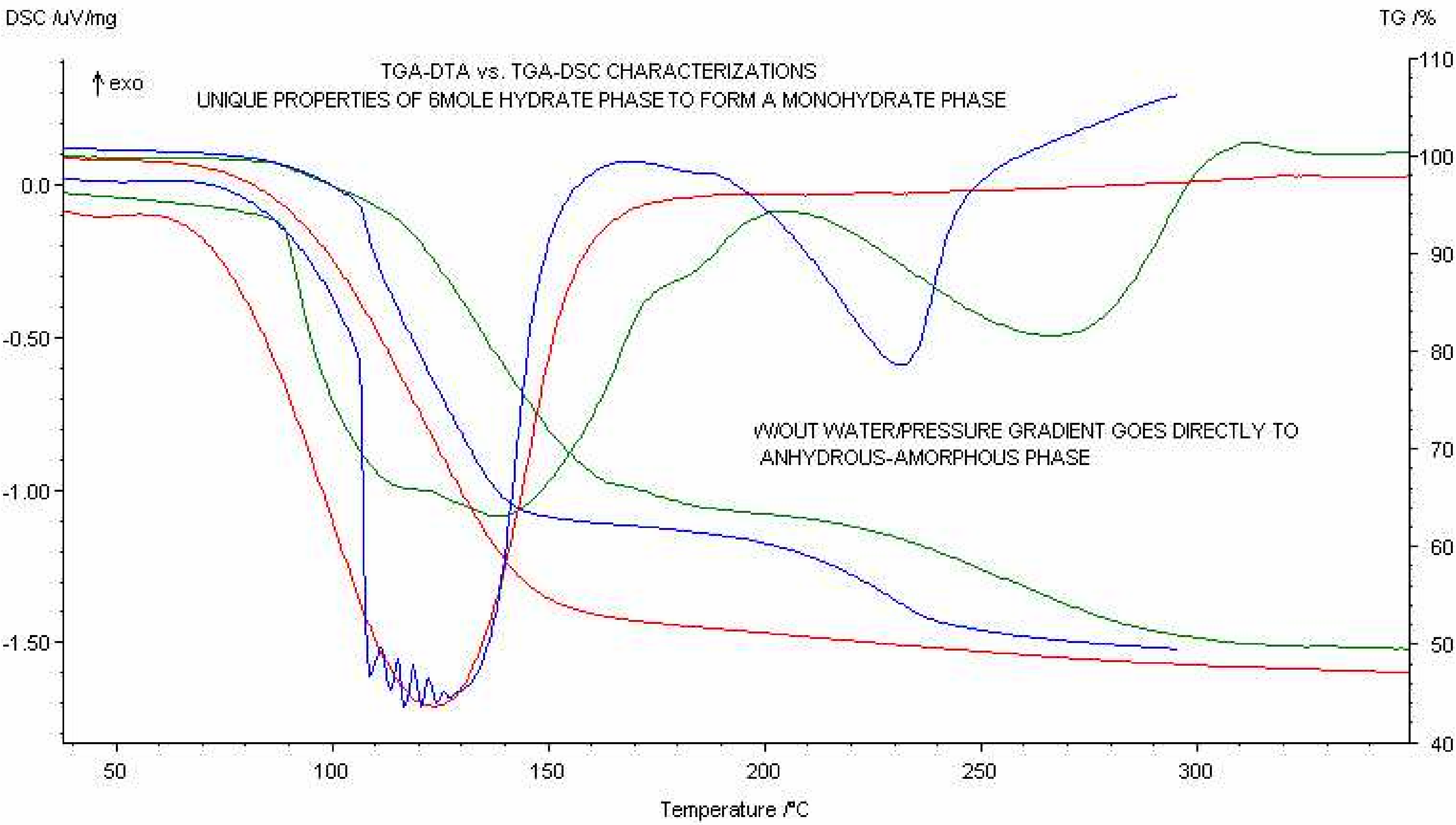
AMORPHOUS TO CRYSTALLINE; CRYSTALLITE SIZE GROWTH



TWO DIFFERENT SOURCES; TWO DIFFERENT THERMAL PROFILES




TG /%
100
90
80
70
60
Dehydration
Dehydroxylation
Decarboxylation
THERMODYNAMIC vs. KINETIC STUDY BY TGA-DTA/TGA-DSC ANALYSES
1) VARY RAMPING RATES-4C, 10C, 25C/MIN.
2) VARY SAMPLE SIZE-5mg, 10mg, 25mg, 50mg, 100mg
200
300
400
500
600
700
800
900
1000
Temperature /°C


DSC /uV/mg
TG /%
↑ exo
TGA-DTA vs. TGA-DSC CHARACTERIZATIONS
UNIQUE PROPERTIES OF 6MOLE HYDRATE PHASE TO FORM A MONOHYDRATE PHASE
W/OUT WATER/PRESSURE GRADIENT GOES DIRECTLY TO
ANHYDROUS-AMORPHOUS PHASE
0.0
-0.50
-1.00
-1.50
110
100
90
80
70
60
50
40
50
100
150
200
250
300
Temperature /°C

CONCLUSIONS

- ASK PERTINENT QUESTIONS
- DO NOT APPROACH THE ANALYSIS OF A SAMPLE (S) AS JUST ROUTINE
- TRY TO UNDERSTAND THE MATRIX, THE PROCESSING, SAMPLING PROTOCOL, AND THE APPLICATION
- DEVISE A PLAN TO SYSTEMATICALLY ANALYZE AND EVALUATE A MATRIX; USE NON-DESTRUCTIVE TECHNIQUES-FIRST
- “PLUG N’ PLAY” WILL NOT ALWAYS SAVE THE DAY!