# Nanomateriale pentru restaurarea si consolidarea monumentelor istorice


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# Bisericutele de creta Basarabi-Murfatlar

## Istoric

•Ansamblu de bisericute din sec. IX - XI

•Descoperite in1957

•Localizate in sud-estul tarii, in apropiere de Canalul Dunare-Marea Neagra

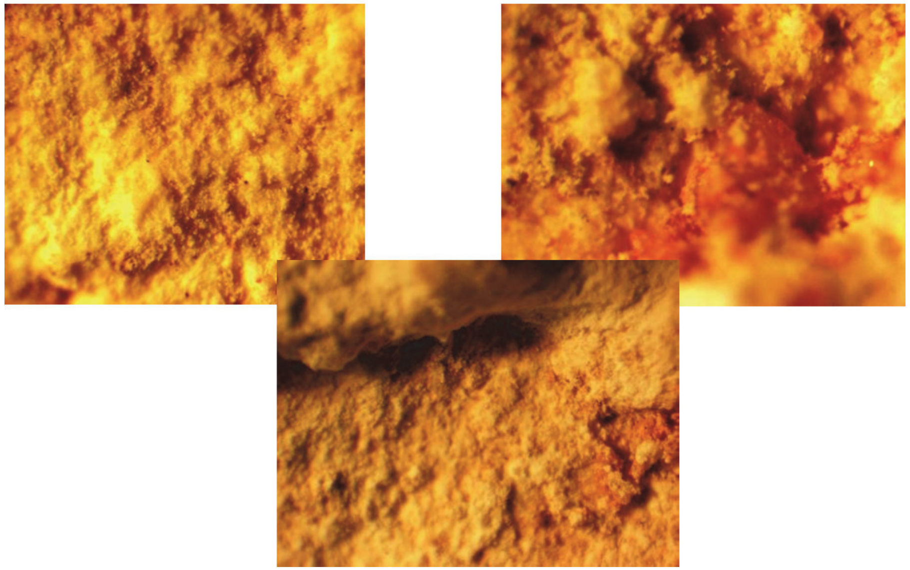
# Istoric

- Origine Vikinga in Dobrogea.
- Monument cu simboluri/texte Chirilice si texte scrise in Ruha.
- Ornamente, desene, figuri stilizate similare cu cele gasite in Peninsula Scandinava (dragoni, animale fantastice si vase cu vole)

# ANSAMBLUL BASARABI - MURFATLAR

- A suferit multe proceduri improprii de restaurare-conservare, precum:
  - Aplicarea  de rasini organice pentru acoperirea găurilor / crapaturilor;
  - Anveloparea cu polipropilena ce a condus la nivel ridicat al umiditatii.

# Stare monument



# Scopul lucrarii

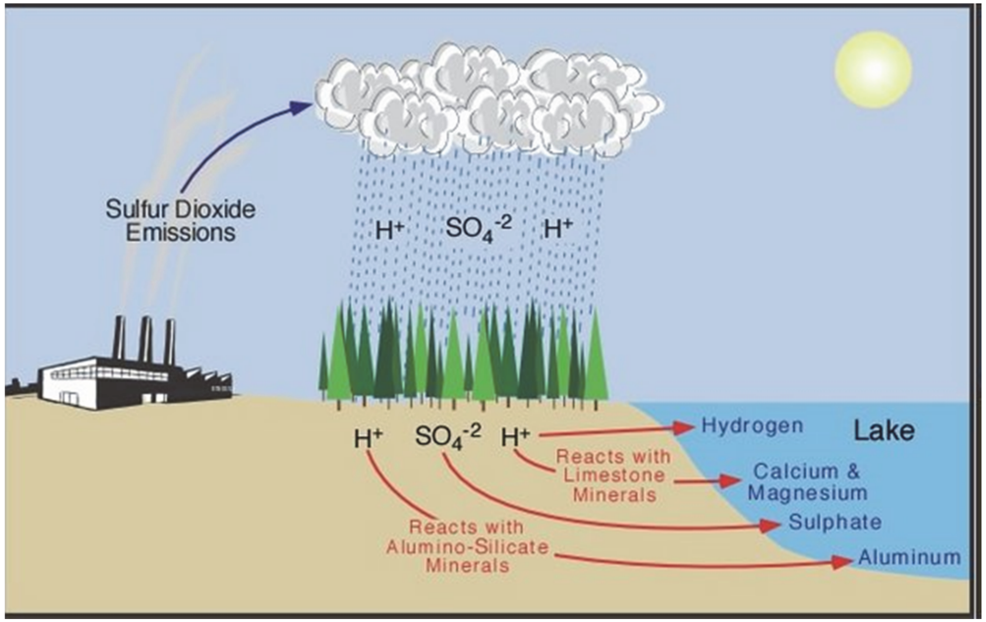
1. Starea actuala a monumentului;
2. Evaluarea efectelor mediului asupra acestui monument (prin diferite investigații analitice);
3. Identificarea  surselor distrugerilor  piatrei;
4. Metode de restaurare preliminara și de pre-tratament cu nanomaterialele

# Creta

Material amorf si compact

# Factori degradativi

1. Conditii climatice:
   Cicluri repetate inghet-dezghet, vanturi puternice , apa de ploaie - usor acida, deoarece dioxidul de carbon din aer se dizolvă în ea. Minerale din roci pot reactiona cu apa de ploaie, determinând eroziunea rocii;
2. Poluarea atmosferica si din sol
   (gaze de ardere eliberate in atmosfera, deversari de deseuri lichide in zona).




http://www.eoearth.org/article/Acid_rain?topic=49506


Alex Dima

# SĂRURILE POT INTRA ÎN MORTARE SAU IN SOLIDE POROASE

$NaCl$, $KCl$, $K_2SO_4$

- foarte solubile în apă
- pot penetra cu usurintă în mortar.

$CaSO_4.2H_2O$, $MgSO_4.7H_2O$, $Na_2SO_4.2H_2O$

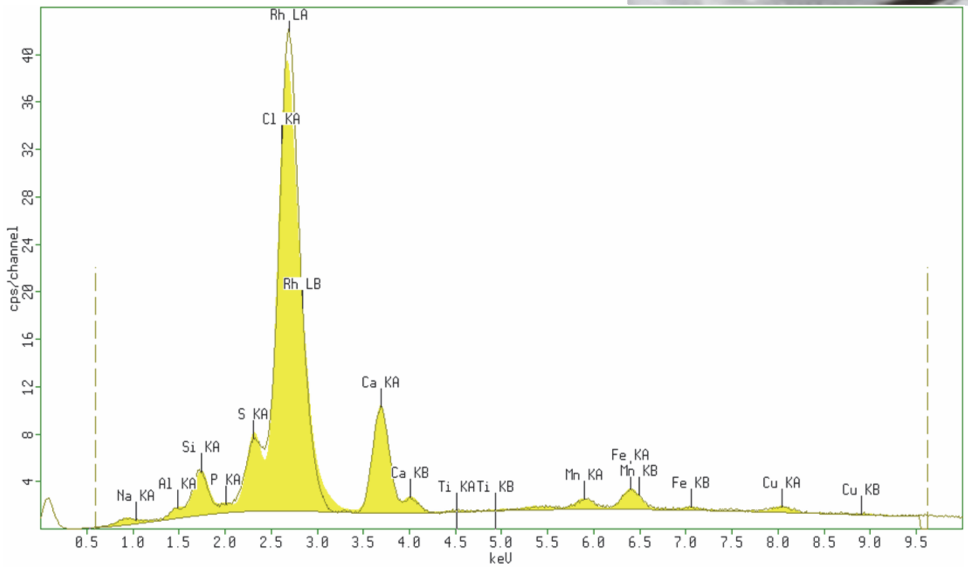
- pot pierde apa de cristalizare la o umiditate scazuta din aer, revenind la forma anhidrita
- prin cresterea umiditatii, reapare recristalizarea.

# Investigatii analitice ale peretilor bisericii

| Proprietate | Tehnica analitica |
|---|---|
| Continut de metal | ICP-AES, EDXRF |
| Stabilitatea termica | TGA/SDTA |
| Morfologie/topologie/petrografie | SEM/AFM/stereozoom microscopy |
| Dimensiuni de particula | DLS, AFM |
| Produsi de degradare | FTIR |

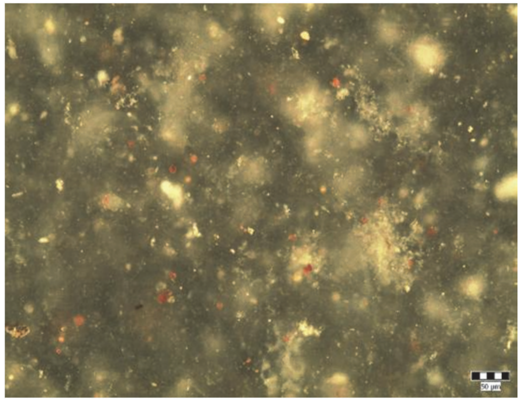
# Aparatura analitica

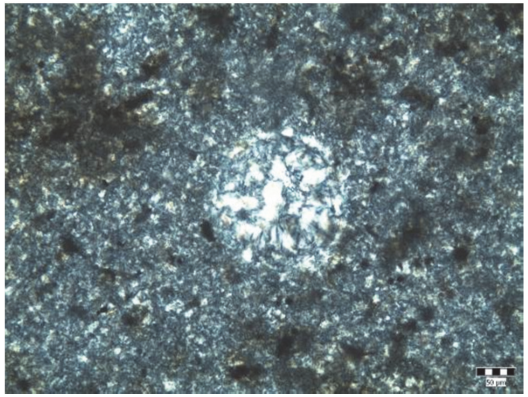

# ICP-AES/EDXRF



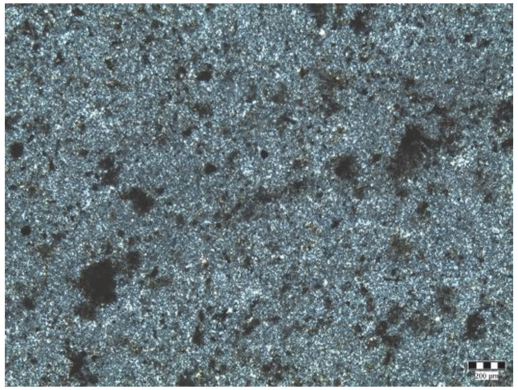

| Metal | Concentration (ppm) |
|---|---|
| Ti | 75.19 |
| Sr | 857.69 |
| Ba | 136.92 |
| Mn | 272.115 |
| Bi | 191.69 |
| Sn | 152.115 |
| Cu | 42.69 |
| K | 2600 |
| Al | 8100 |
| Fe | 4800 |
| Mg | 2300 |
| Na | 8600 |
| Si | 14400 |
| Ca | 241200 |
| Li | 34.61 |
| Zr | 10.77 |

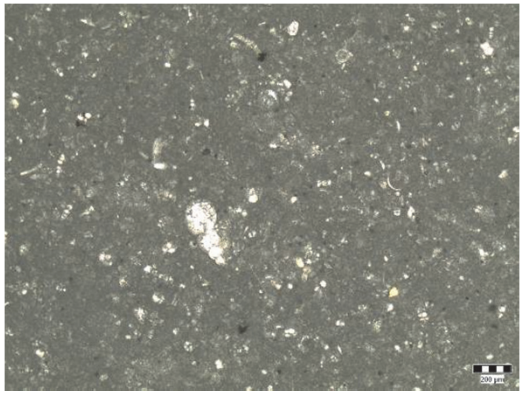
# Analiza petrografica

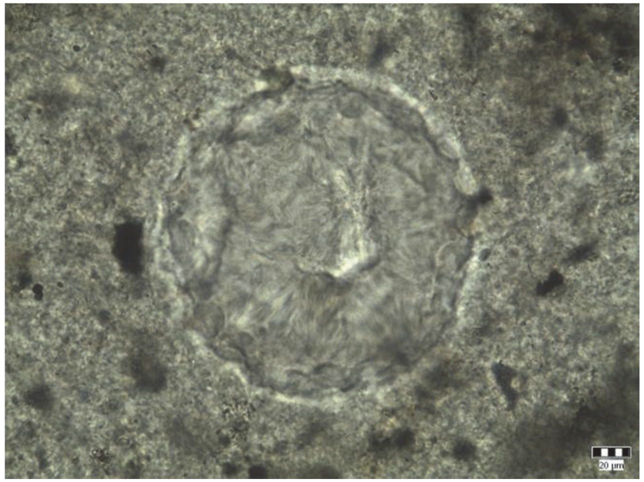




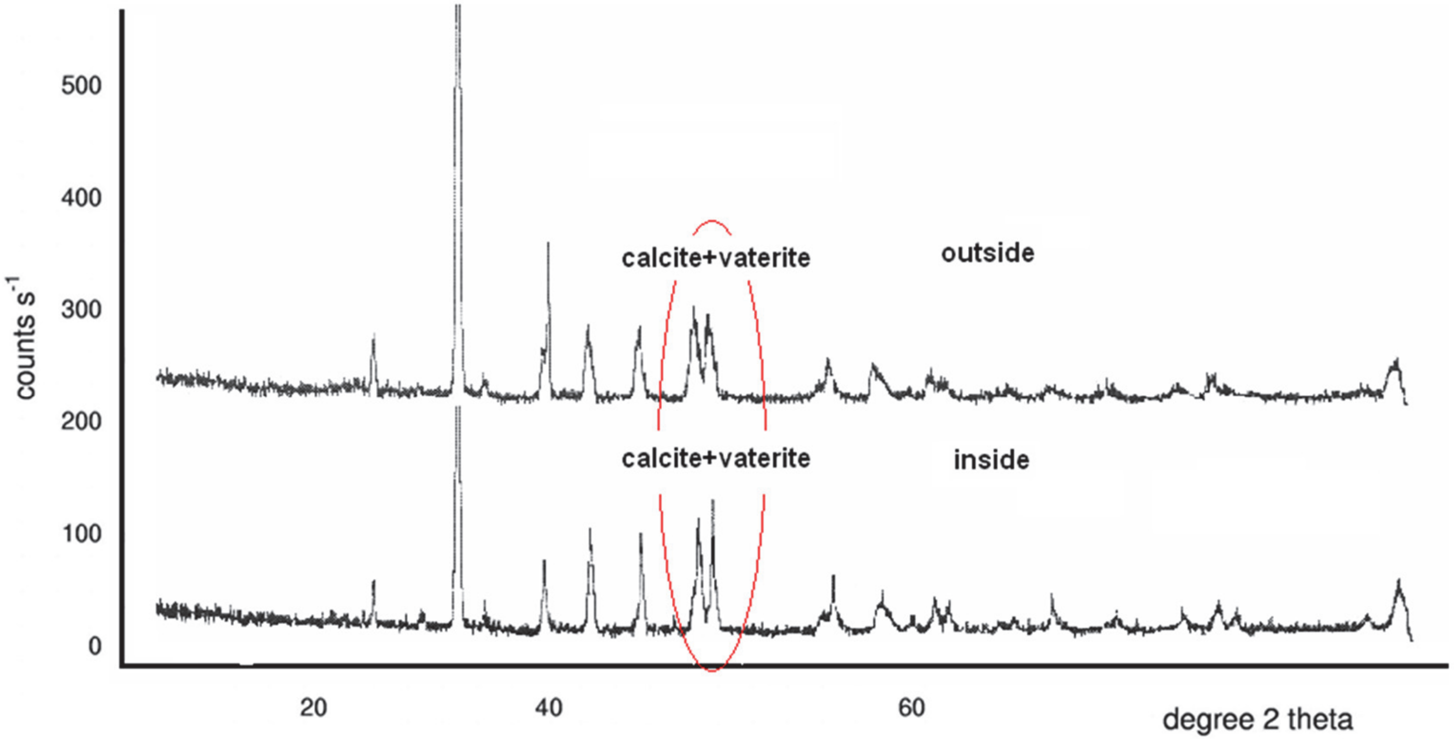
$CaCO_3$ = 91.4 % cu urme de cuartz
Structura poroasa
Structura chimica organogena de tip calcit (si/sau vaterite)
Urme de oxizi de fier si hidroxizi
Foraminifera bioclastica
Recristalizari locale de calcit





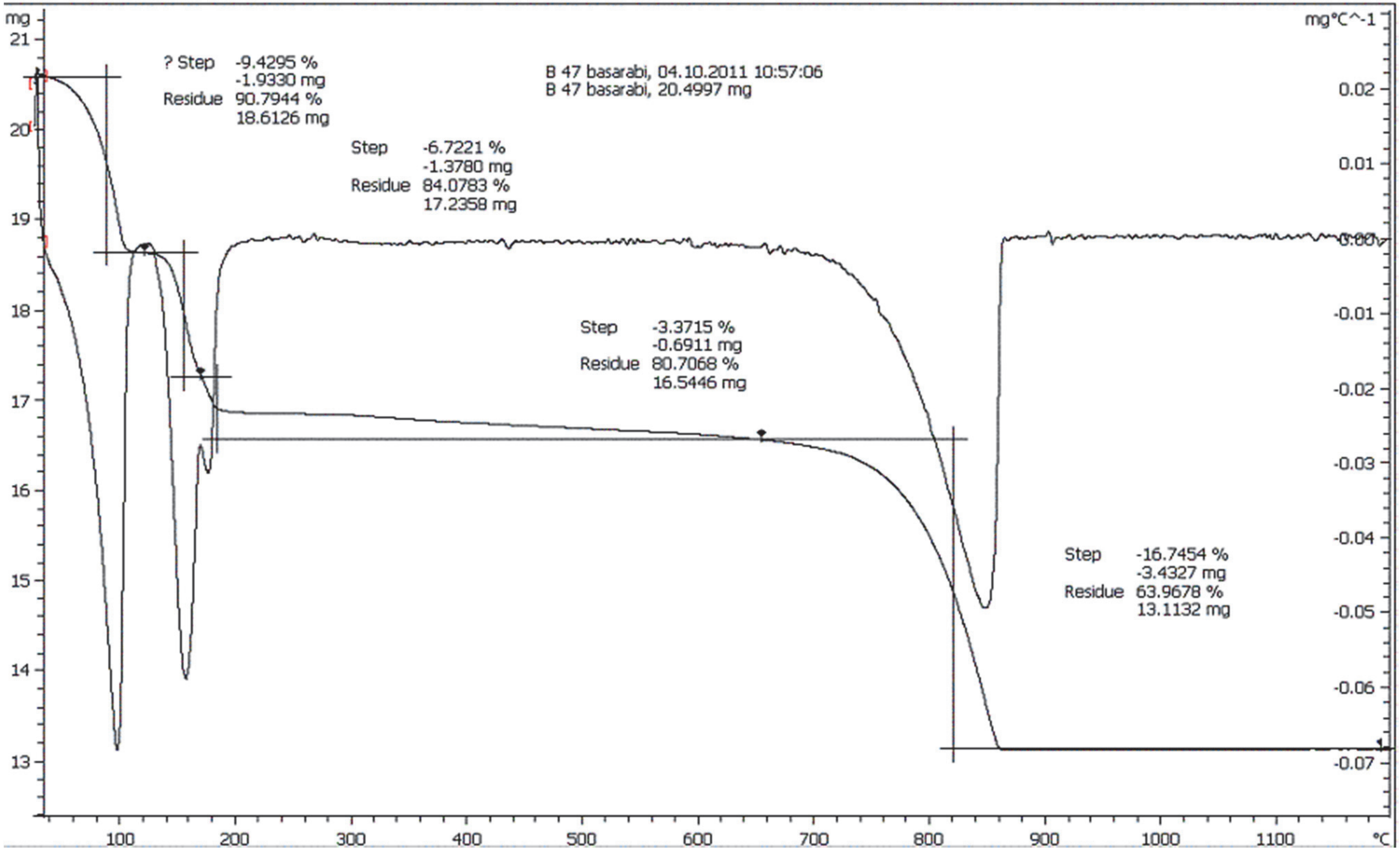


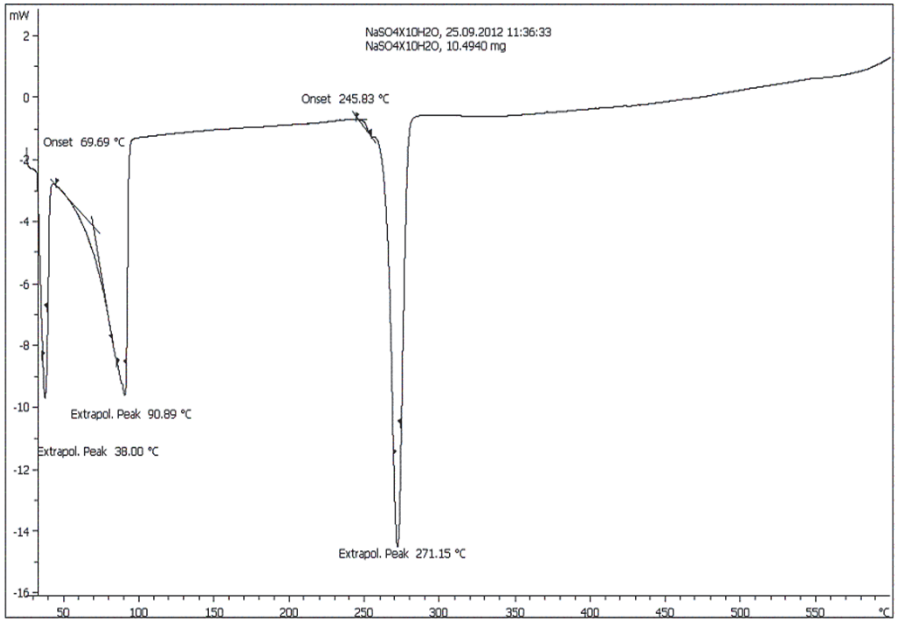
# agregarea vateritului in structuri framboidale

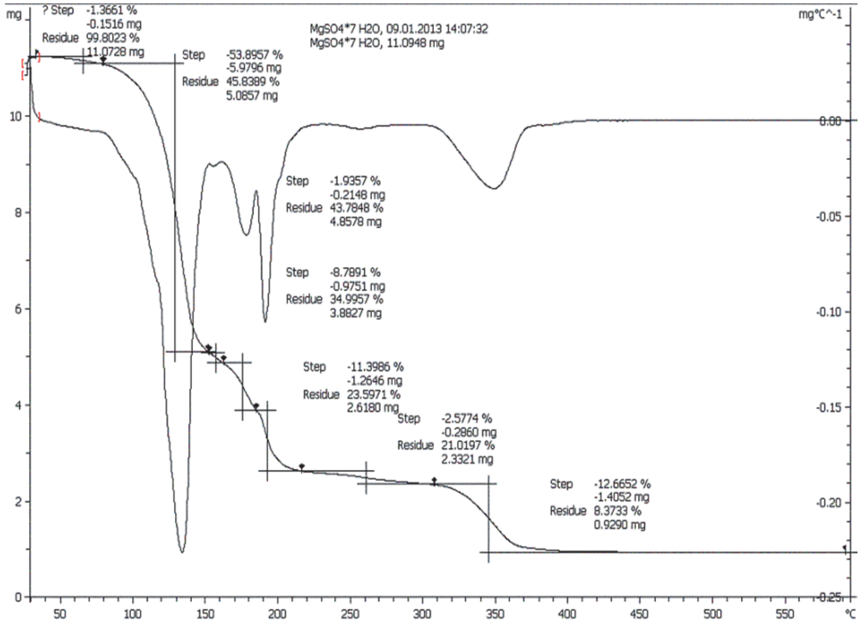


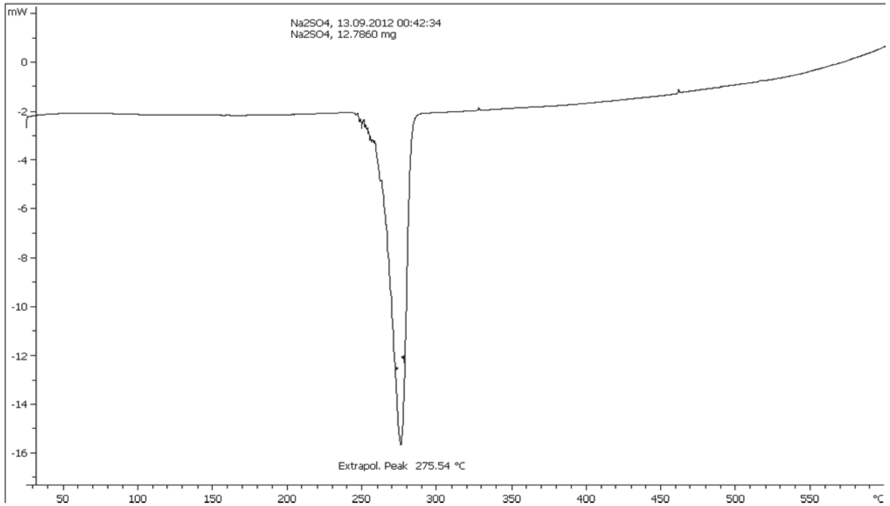

Vateritul este instabil la expunerea la umezeala; poate recristaliza in calcit in 20-25 h la temperatura camerei

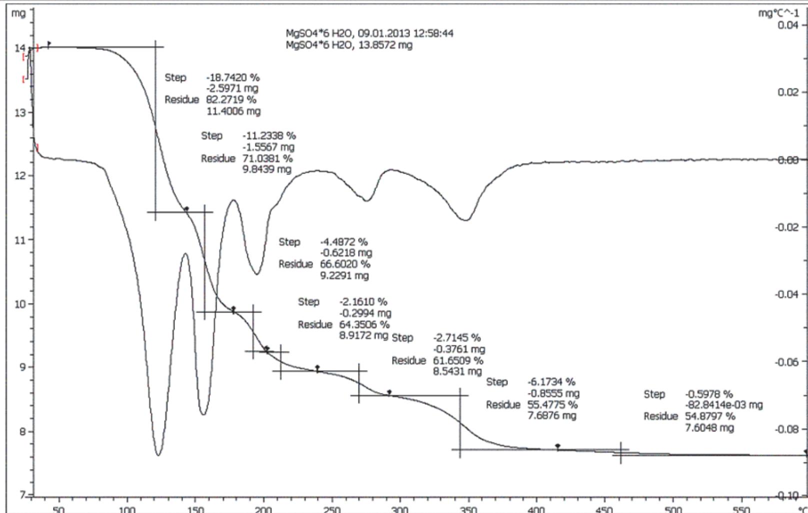
# Thermal analysis




NaSO4X10H2O, 25.09.2012 11:36:33
NaSO4X10H2O, 10.4940 mg
Onset 245.83 °C
Onset 69.69 °C
Extrapol. Peak 90.89 °C
Extrapol. Peak 38.00 °C
Extrapol. Peak 271.15 °C


MgSO4*7 H2O, 09.01.2013 14:07:32
MgSO4*7 H2O, 11.0948 mg
? Step -1.3661 %
-0.1516 mg
Residue 99.8023 %
11.0728 mg
Step -53.8957 %
-5.9796 mg
Residue 45.8389 %
5.0857 mg
Step -1.9357 %
-0.2148 mg
Residue 43.7848 %
4.8578 mg
Step -8.7891 %
-0.9751 mg
Residue 34.9957 %
3.8827 mg
Step -11.3986 %
-1.2646 mg
Residue 23.5971 %
2.6180 mg
Step -2.5774 %
-0.2860 mg
Residue 21.0197 %
2.3321 mg
Step -12.6652 %
-1.4052 mg
Residue 8.3733 %
0.9290 mg

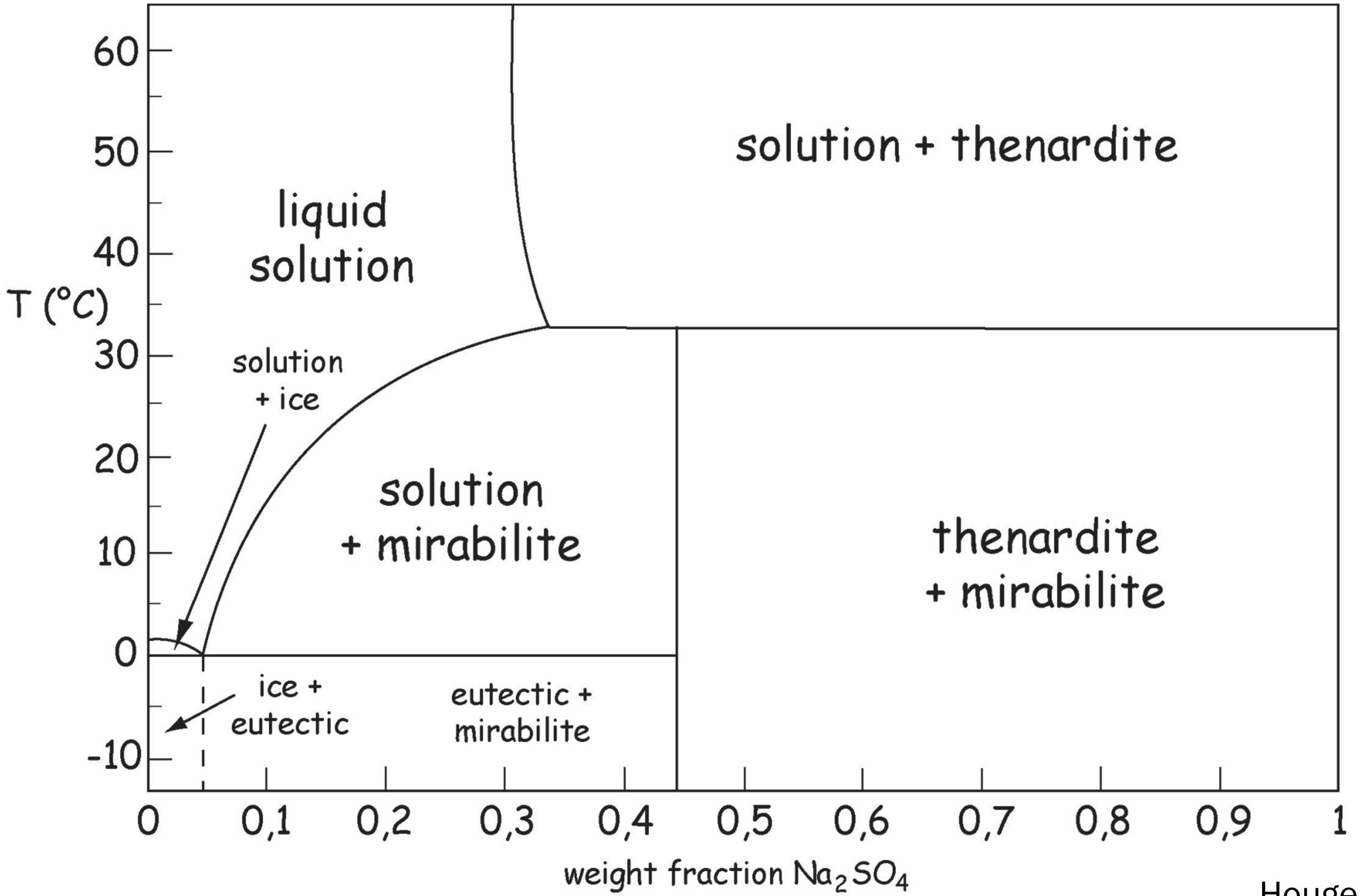

Na2SO4, 13.09.2012 00:42:34
Na2SO4, 12.7860 mg
Extrapol. Peak 275.54 °C


MgSO4*6 H2O, 09.01.2013 12:58:44
MgSO4*6 H2O, 13.8572 mg
Step -18.7420 %
-2.5971 mg
Residue 82.2719 %
11.4006 mg
Step -11.2338 %
-1.5567 mg
Residue 71.0381 %
9.8439 mg
Step -4.4872 %
-0.6218 mg
Residue 66.6020 %
9.2291 mg
Step -2.1610 %
-0.2994 mg
Residue 64.3506 %
8.9172 mg
Step -2.7145 %
-0.3761 mg
Residue 61.6509 %
8.5431 mg
Step -6.1734 %
-0.8555 mg
Residue 55.4775 %
7.6876 mg
Step -0.5978 %
-82.8414e-03 mg
Residue 54.8797 %
7.6048 mg

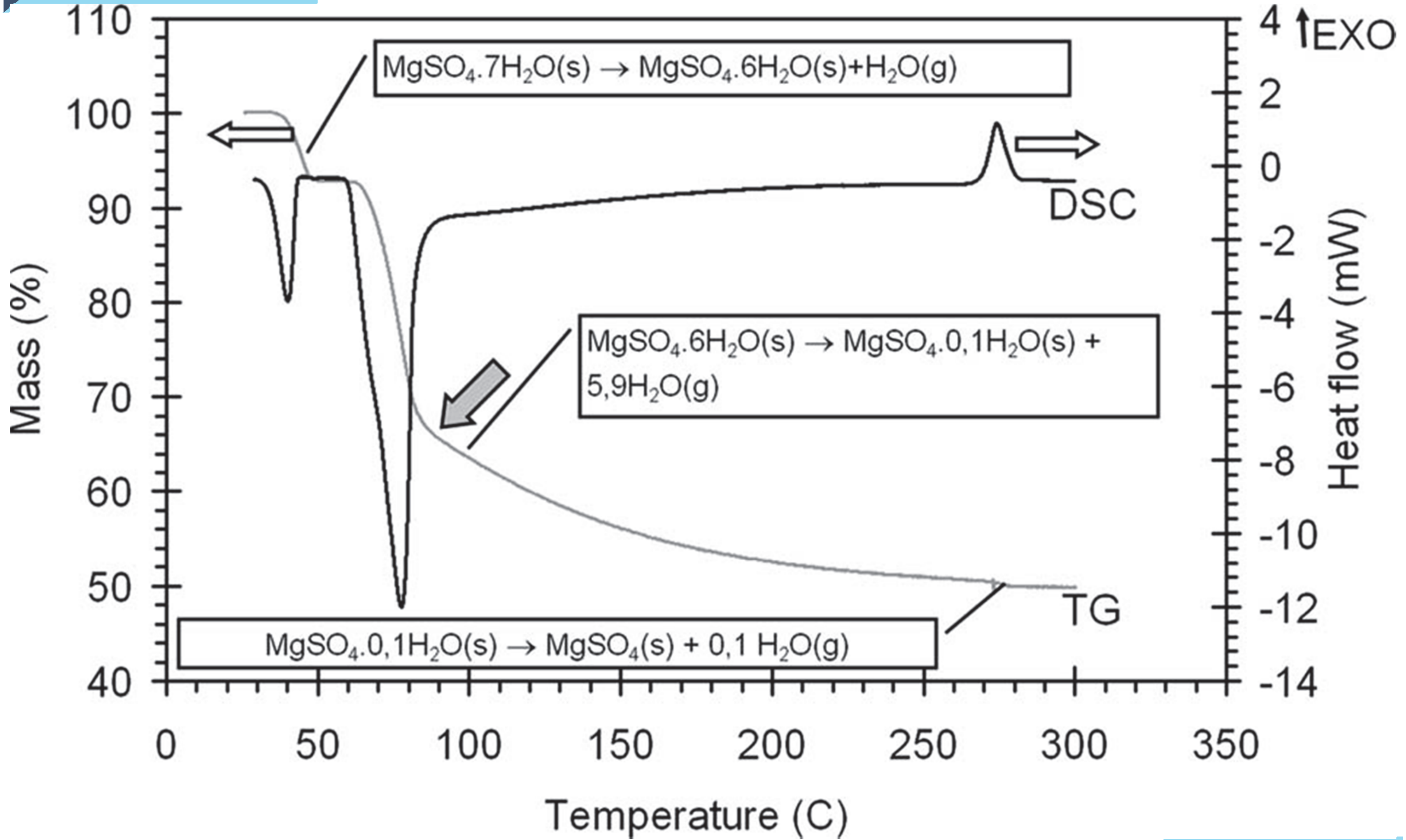
# SULFATUL DE SODIU

- **Foarte agresiv pentru piatra**
- **doua faze stabile la temperatura camerei : thenardit ($Na_2SO_4$) si mirabilit ($Na_2SO_4 \cdot 10H_2O$)**
- **Mirabilitul exista pana la 32°C**
- **In probele analizate, se identifica mirabilit, dar este posibil sa existe thenardit ce se transforma in mirabilit datorita unui numar mare de cicluri inghet-dezghet**

# Diagrama de faza a sulfatului de sodiu




Hougen et al., 1954



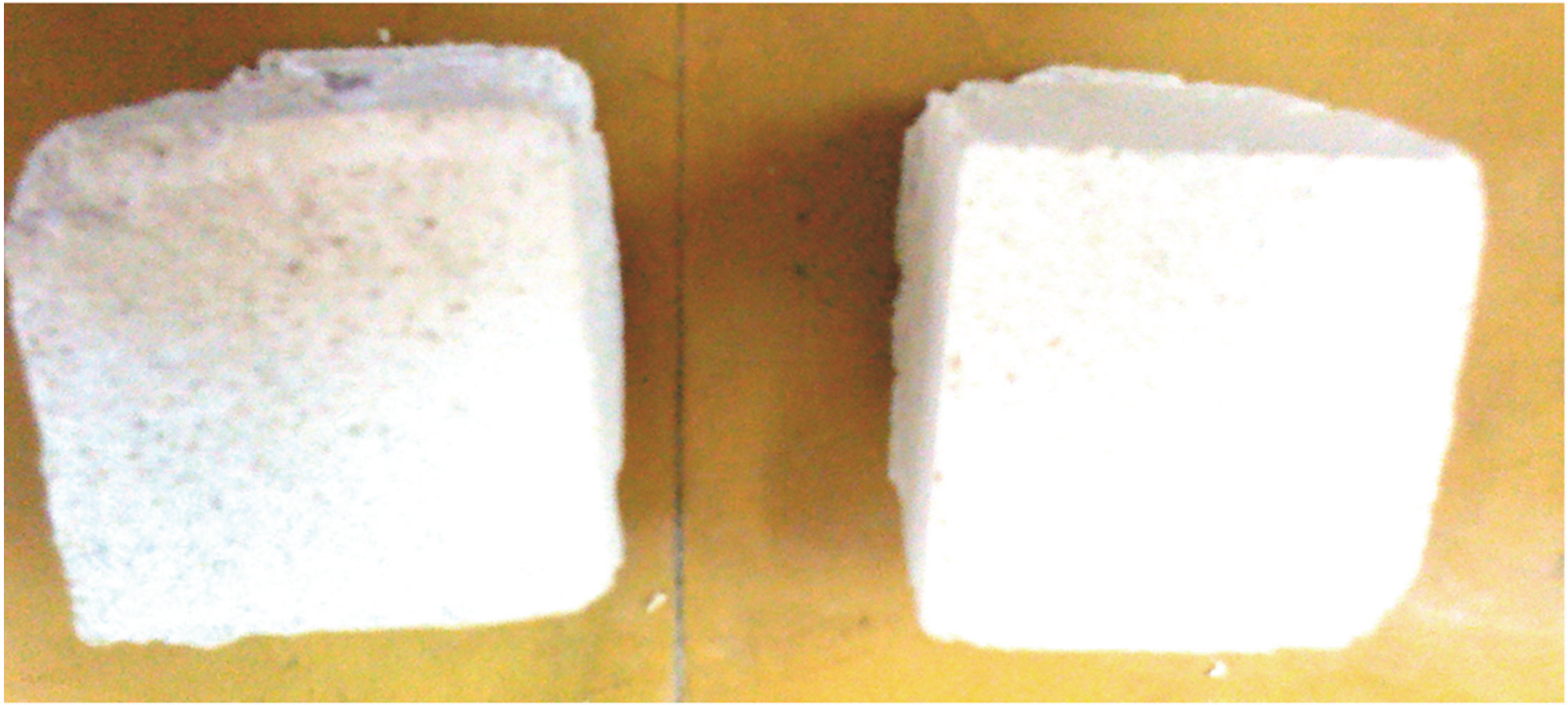
110
100
90
80
70
60
50
40
Mass (%)
4
2
0
-2
-4
-6
-8
-10
-12
-14
EXO
Heat flow (mW)
0
50
100
150
200
250
300
350
Temperature (C)
$MgSO_4.7H_2O(s) \rightarrow MgSO_4.6H_2O(s)+H_2O(g)$
$MgSO_4.6H_2O(s) \rightarrow MgSO_4.0,1H_2O(s) +$
$5,9H_2O(g)$
$MgSO_4.0,1H_2O(s) \rightarrow MgSO_4(s) + 0,1\ H_2O(g)$
DSC
TG

# PREPARAREA PROBELOR

1. Mostre de mortar (4x4x4 $cm^3$) preparate din gips si nisip si apa demineralizata (2:4:1 in volume).
2. Probe prelavate de la Bisericutele Basarabi, detasate din monument si fara valoare de patrimoniu

# Consolidanti

1. Nanosuspensie of $Ca(OH)_2$ in ethanol, sintetizata in lab.
2. CaLoSiL E25 (25g particles per litru isopropanol).
3. Sol $Ca(OH)_2$ : HAp, dispersat in isopropanol (30g/l $Ca(OH)_2$ + 15g/l HAp).



# HIDROXIAPATITA si CaLoSil

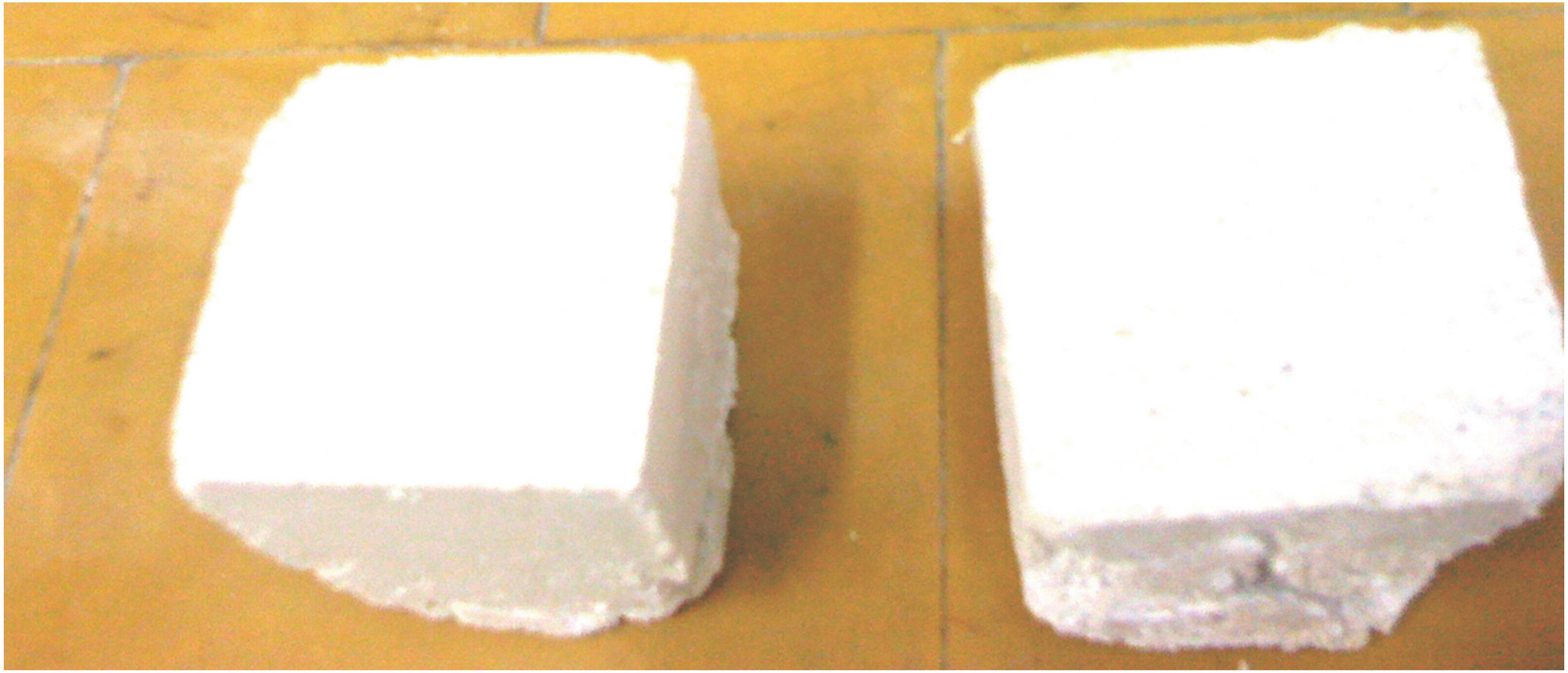
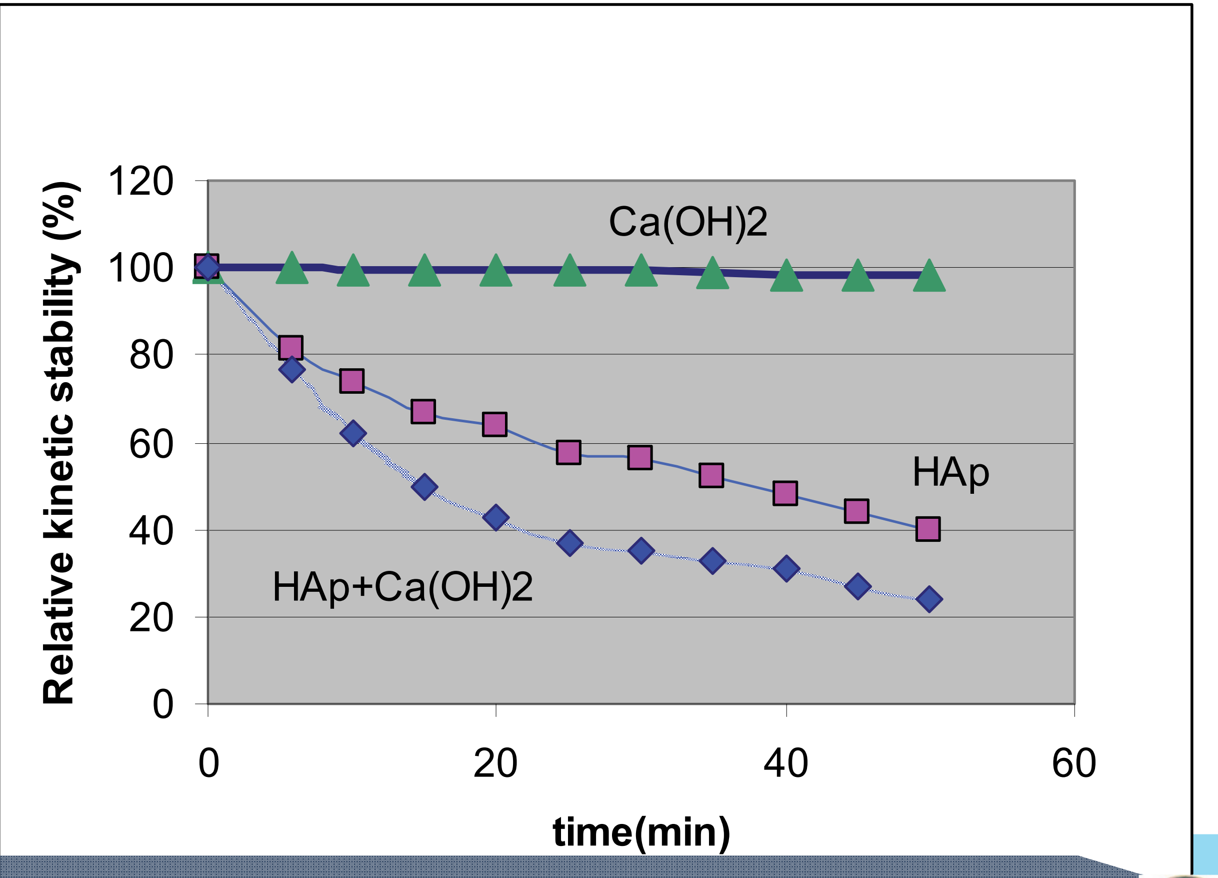
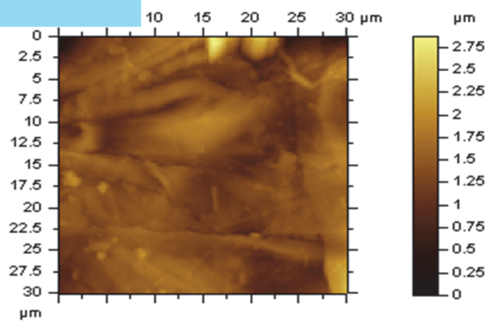
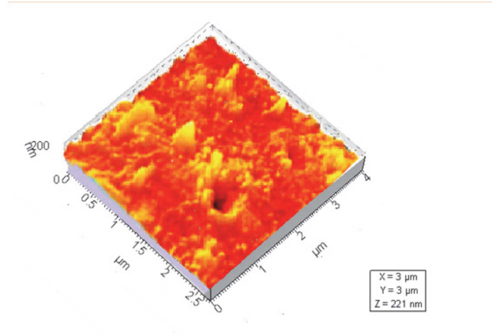


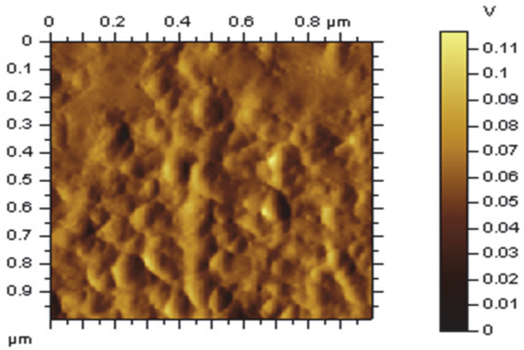
Table 2: Lattice parameters of calcite, HAp and calcium hydroxide

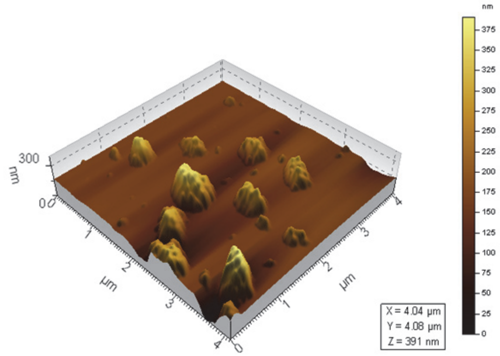
| Mineral | a (Å) | b (Å) | c (Å) |
|---|---|---|---|
| Calcite | 9.98 | 9.98 | 33.82 |
| Hydroxyapatite | 9.45 | 9.44 | 6.90 |
| Calcium hydroxide | 12.59 | 29.27 | 20.34 |

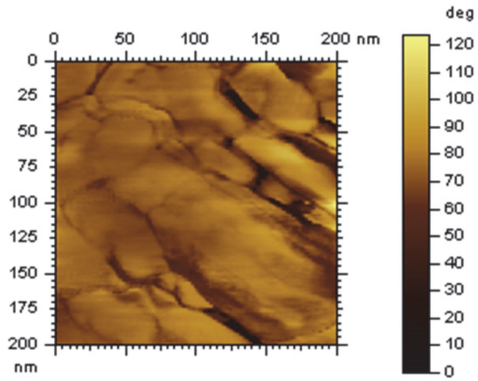


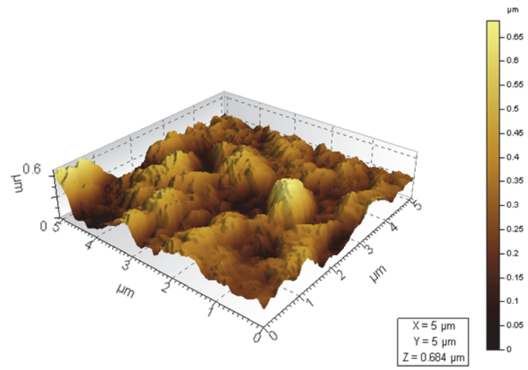

10 15 20 25 30 µm
0 2.5 5 7.5 10 12.5 15 17.5 20 22.5 25 27.5 30
µm
µm
2.75 2.5 2.25 2 1.75 1.5 1.25 1 0.75 0.5 0.25 0


X = 3 µm
Y = 3 µm
Z = 221 nm


0 0.2 0.4 0.6 0.8 µm
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9
µm
V
0.11 0.1 0.09 0.08 0.07 0.06 0.05 0.04 0.03 0.02 0.01 0


300
nm
X = 4.04 µm
Y = 4.08 µm
Z = 391 nm


0 50 100 150 200 nm
0 25 50 75 100 125 150 175 200
nm
deg
120 110 100 90 80 70 60 50 40 30 20 10 0


0.6
µm
X = 5 µm
Y = 5 µm
Z = 0.684 µm

# Eficienta de conservare

| Sample | Treatment | Drilling resistance Mean (N) (10 mm) | Compressive strength (Silver Schmidt) (MPa) (5 mm) |
|---|---|---|---|
| Model-sample | Not treated | 6.2±1.73 | 11±4.0 |
| | $Ca(OH)_2$ | 9.63±2.31 | 13.33±3 |
| | HAp | 12.04±3.29 | 20.33±2.6 |
| | $Ca(OH)_2$ : HAp | 10.73±2.40 | 16.66±4.3 |
| Chalk sample | Not treated | 13.19±1.83 | 20±3.2 |
| | $Ca(OH)_2$ | 6.18±2.52 | 40±2.3 |
| | HAp | 16.87±3.71 | 25±3.5 |
| | $Ca(OH)_2$: HAp | 11.34±6.45 | 33±3.2 |

| Sample | Treatment | Water absorbed ($cc/cm^2s$) |
|---|---|---|
| Sample model | Not treated | 2.87±0.09 |
| | $Ca(OH)_2$ | 2.53±0.08 |
| | HAp | 1.27±0.05 |
| | $Ca(OH)_2$: HAp | 1.80±0.09 |
| Chalk sample | Not treated | 2.22±0.10 |
| | $Ca(OH)_2$ | 2.25±0.22 |
| | HAp | 2.05±0.084 |
| | $Ca(OH)_2$: HAp | 2.01±0.065 |

-prin rezistenta la compresiune (Silver Schmidt Hammer L);

- Prin rezistenta la gaurire cu DRMS (Drilling Ressistance Measurement System) SINC Technology;

# Analiza microbiologica