Effect of the precursor layer on properties of nanoscopic powders formed by thermally induced decomposition of $FeC_2O_4 \cdot 2H_2O$ in air

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Solid State Reactions

Influencing conditions:

1. **Reaction temperature**
2. **Reaction time**
3. **Reaction atmosphere (oxidative, inert, reduction)**

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4. **Precursor particle size**
5. **Participation of conversion gases[1]**
6. **Precursor layer**

… ?

[1] M. Hermanek, R. Zboril, M. Mashlan, L. Machala and O. Schneeweiss, *J. Mater. Chem.*, 2006, 16, 1273

MOTIVATION

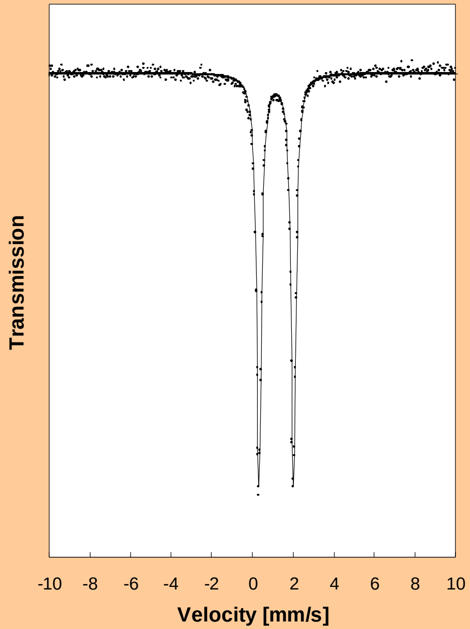
Controversial data on the presence of maghemite during the thermally induced decomposition of ferrous oxalate dihydrate in air.

Precursor characterization

$FeC_2O_4 \cdot 2H_2O$ (Sigma Aldrich)

• homogenization in an agate mortar

RTMS

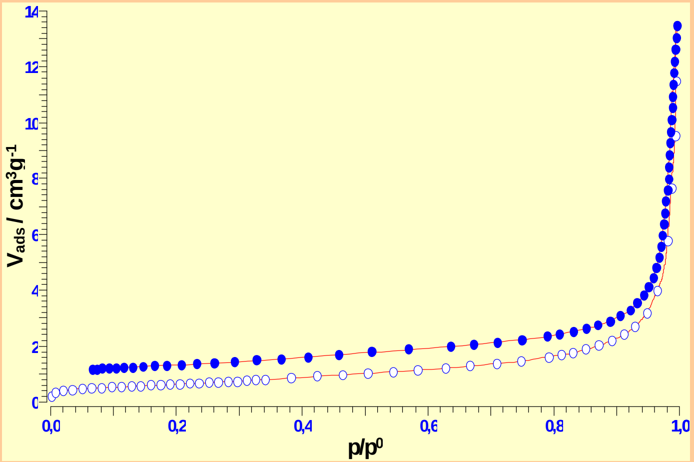


δ = 1.18 mm/s

ΔE_Q = 1.70 mm/s

(values typical for Fe^{2+})

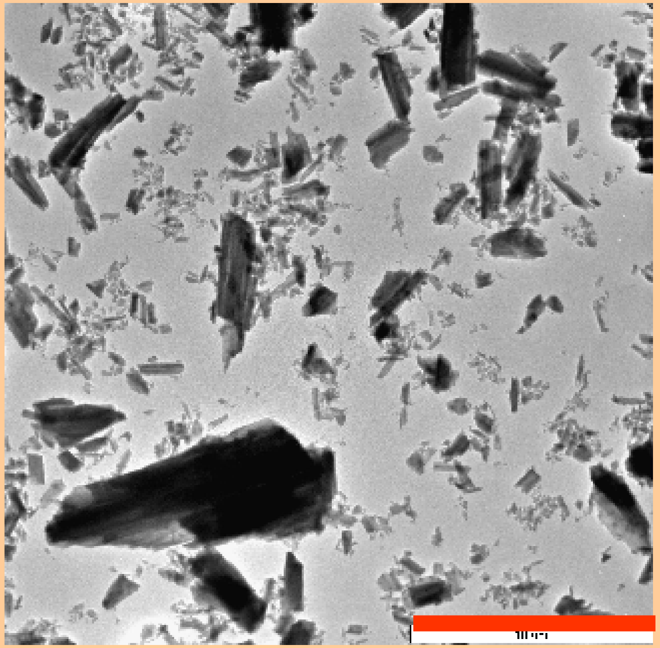
Specific Surface Area (BET)



non-porous particles

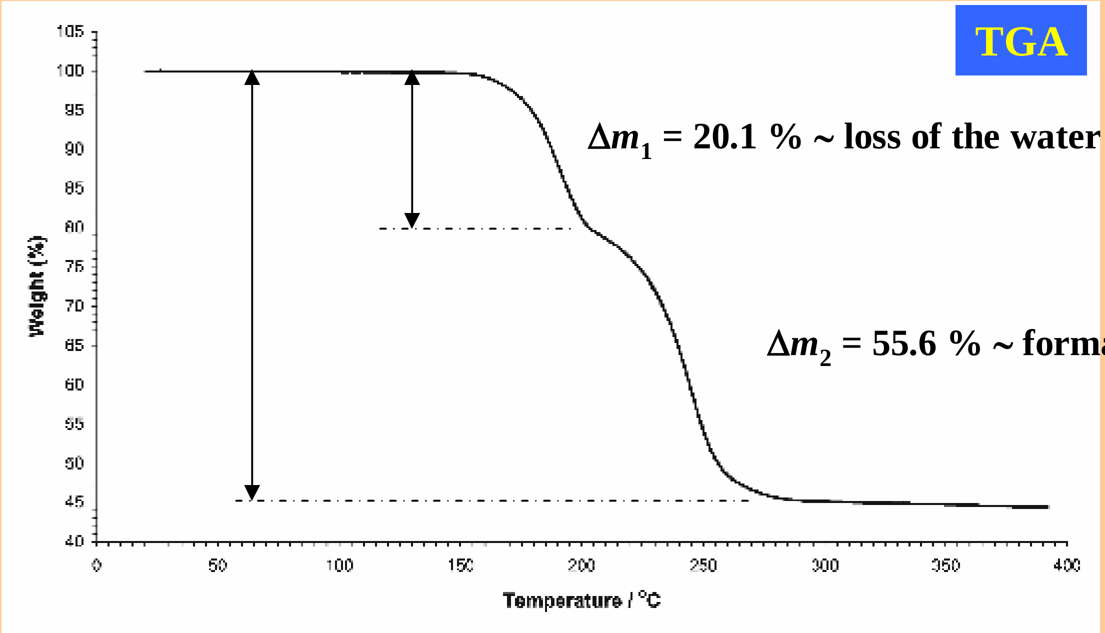
$SA \cong 2.4\ m^2/g$

TEM



10 µm

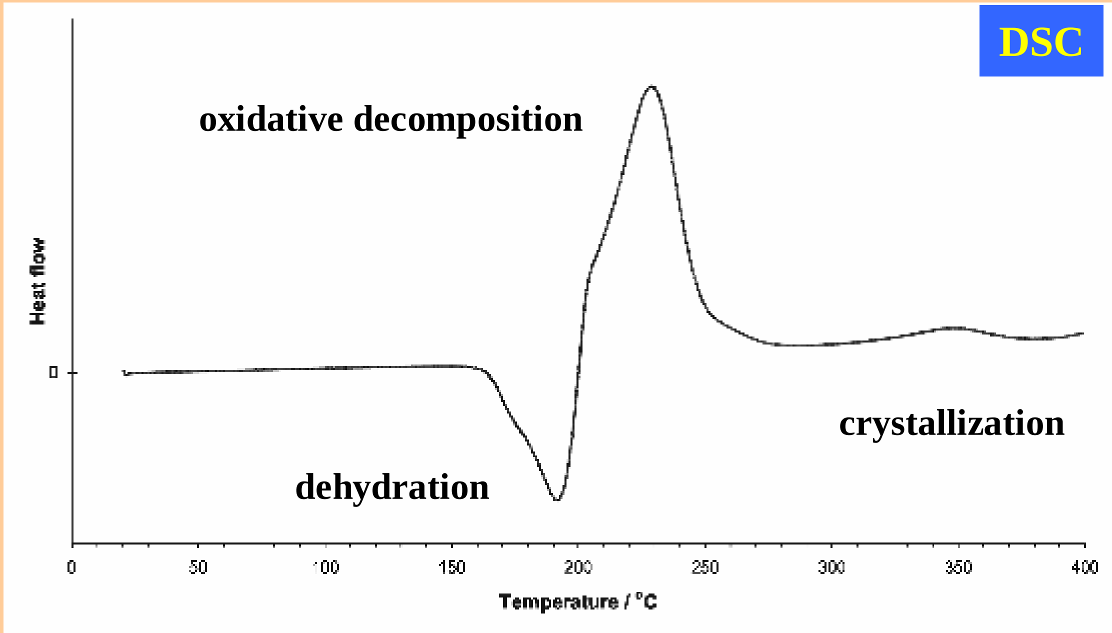
Thermal Decomposition in Air: Thermal Analyses



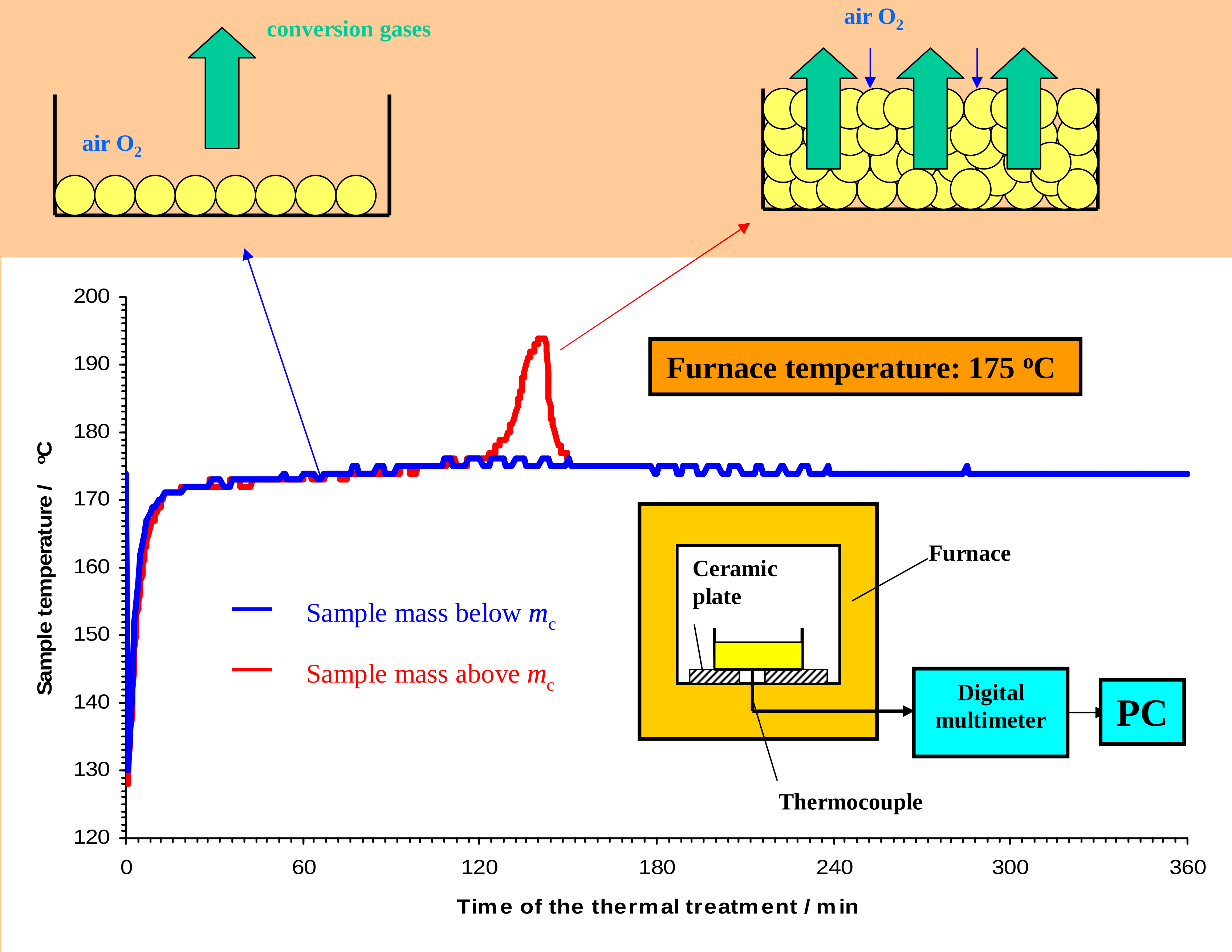
Two-step decomposition process:

$FeC_2O_4{\cdot}2H_2O \rightarrow FeC_2O_4 + 2H_2O$

$2FeC_2O_4 + 3/2\ O_2 \rightarrow Fe_2O_3 + 4CO_2$



Influence of Sample Mass (Sample Layer)!!!

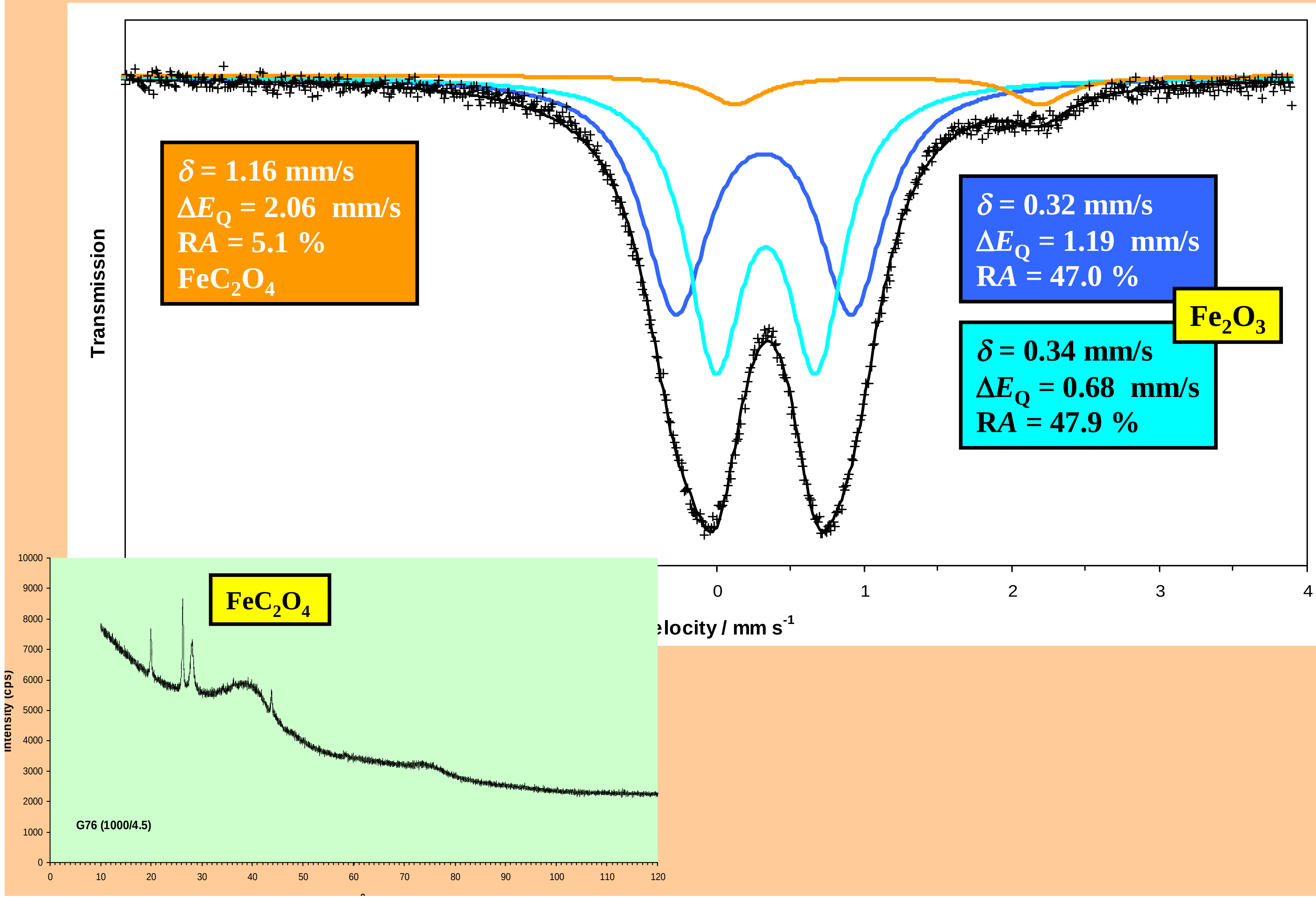


Low-layer samples

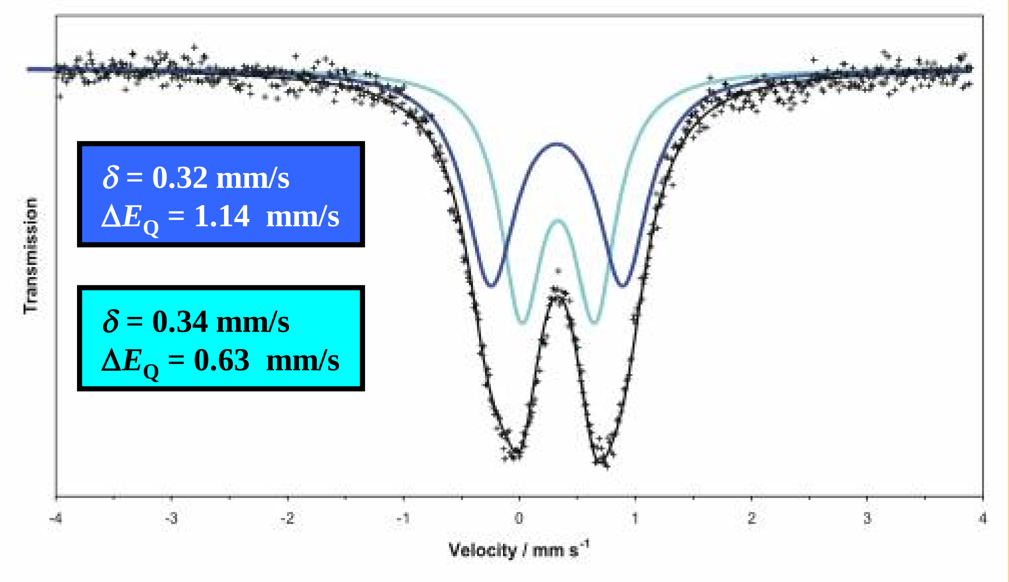
M. Hermanek, R. Zboril, I. Medrik, J. Pechousek and C. Gregor

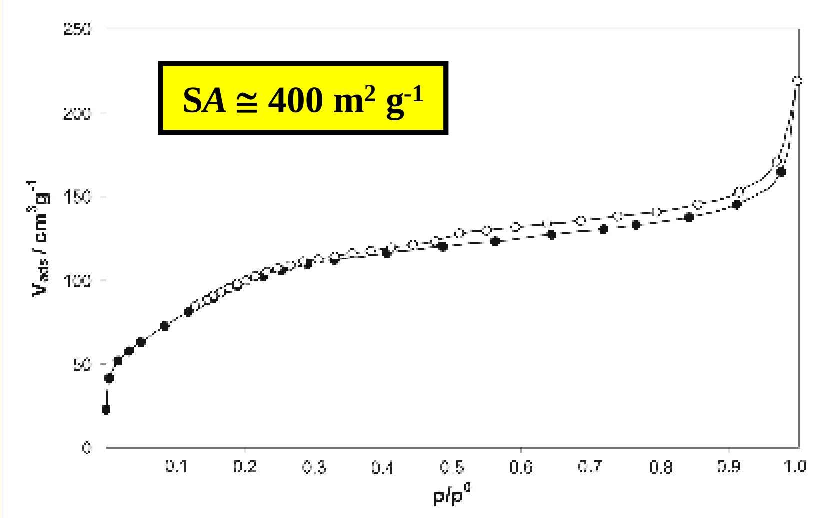
- sample mass 1 g
- isothermal treatment at 175 ^{o}C
- calcination times: 4.5, 6, 8, 10, 12, 15, 17, 30, 64 and 100 hrs
- experimental techniques: (IF)MS, XRD, BET, TEM

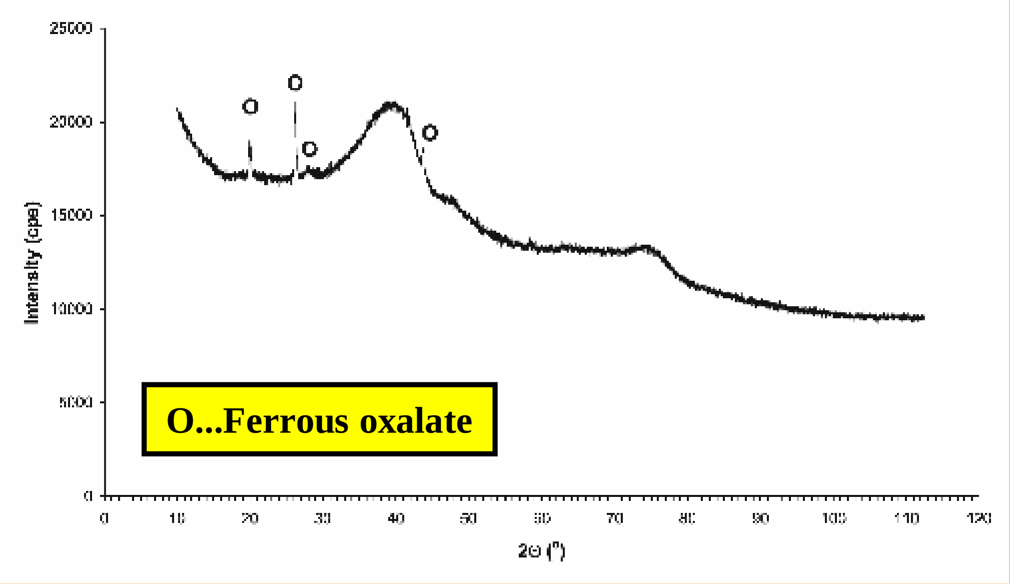
Furnace temperature 175 ºC, 4.5 hrs

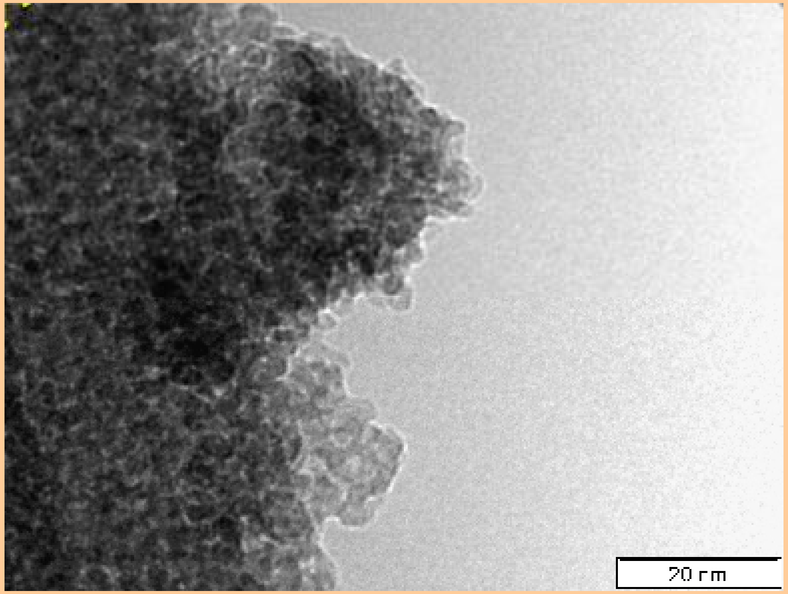


Furnace temperature 175 ºC, 6 hrs

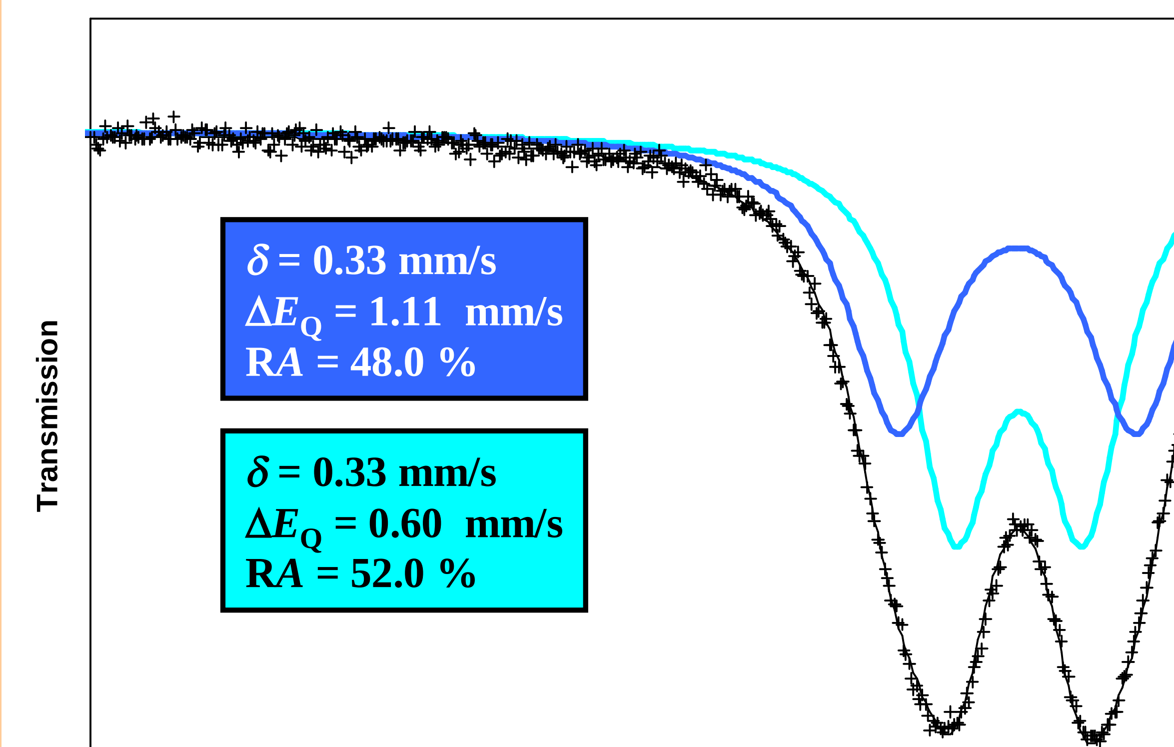


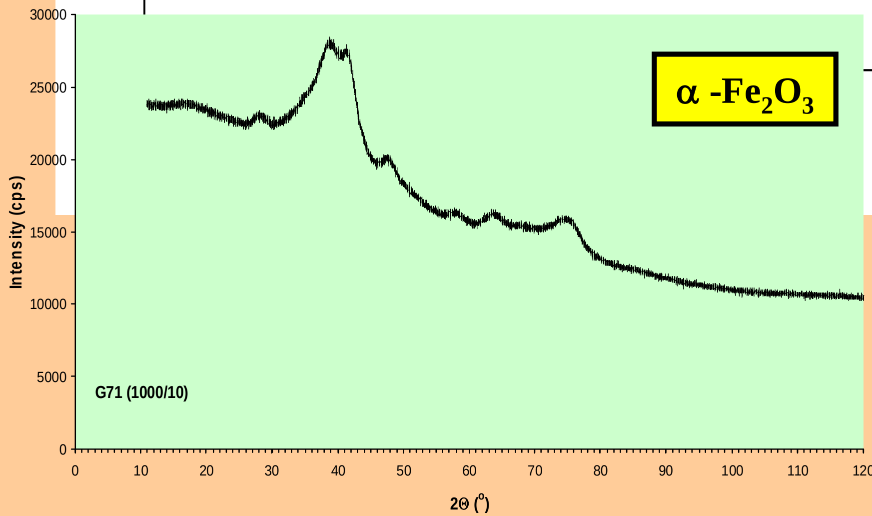


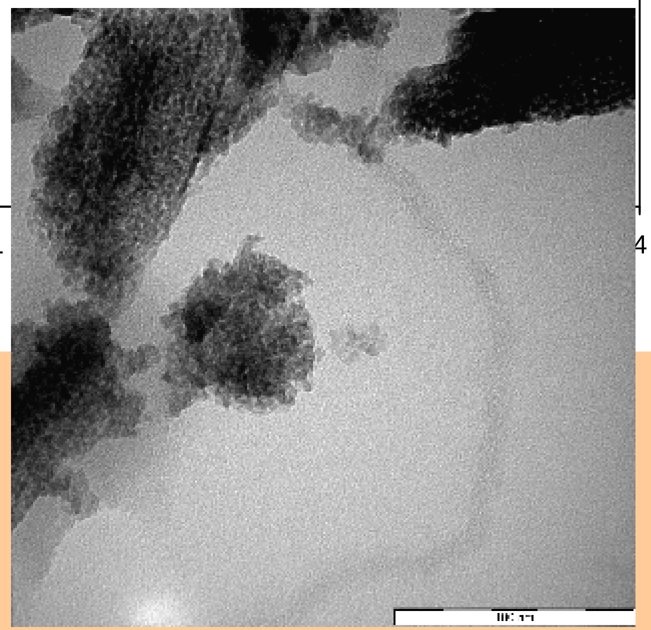




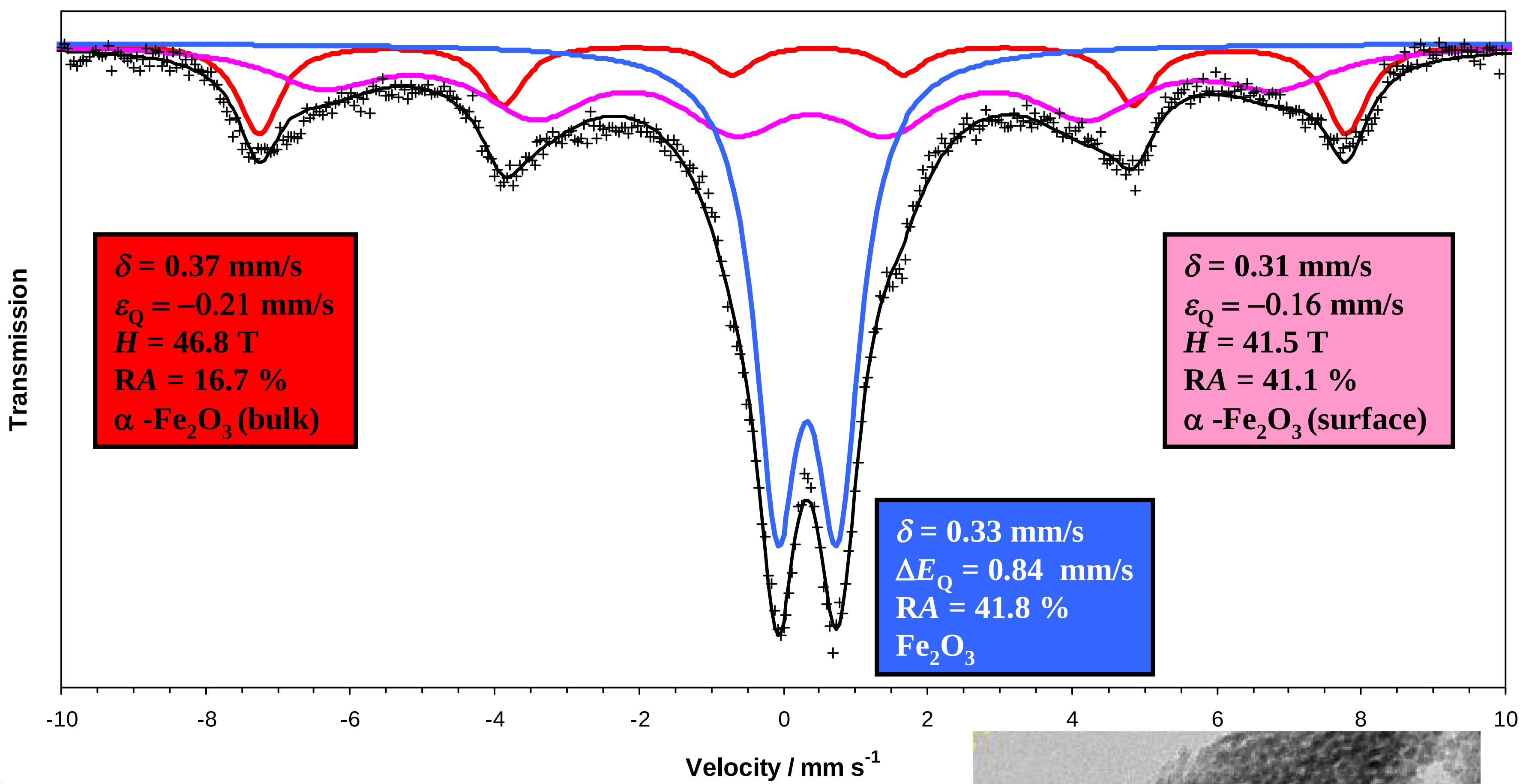
Furnace temperature 175 ºC, 10 hrs

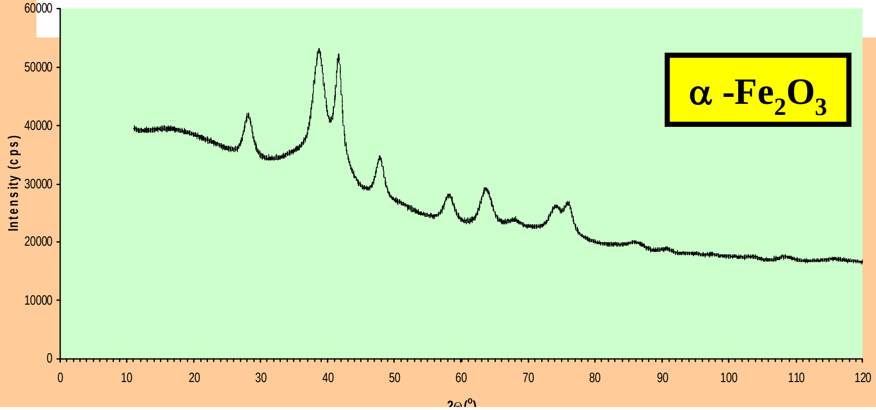


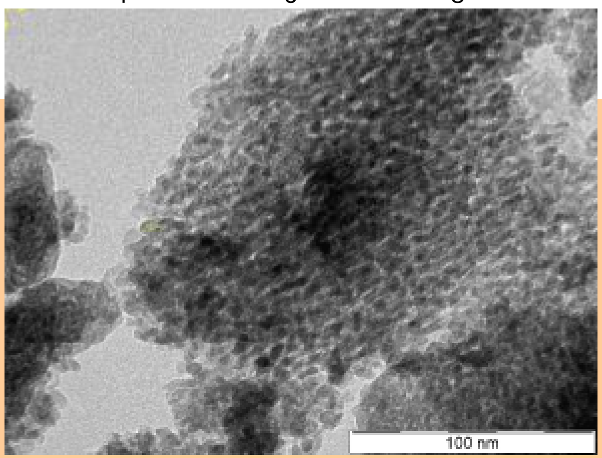




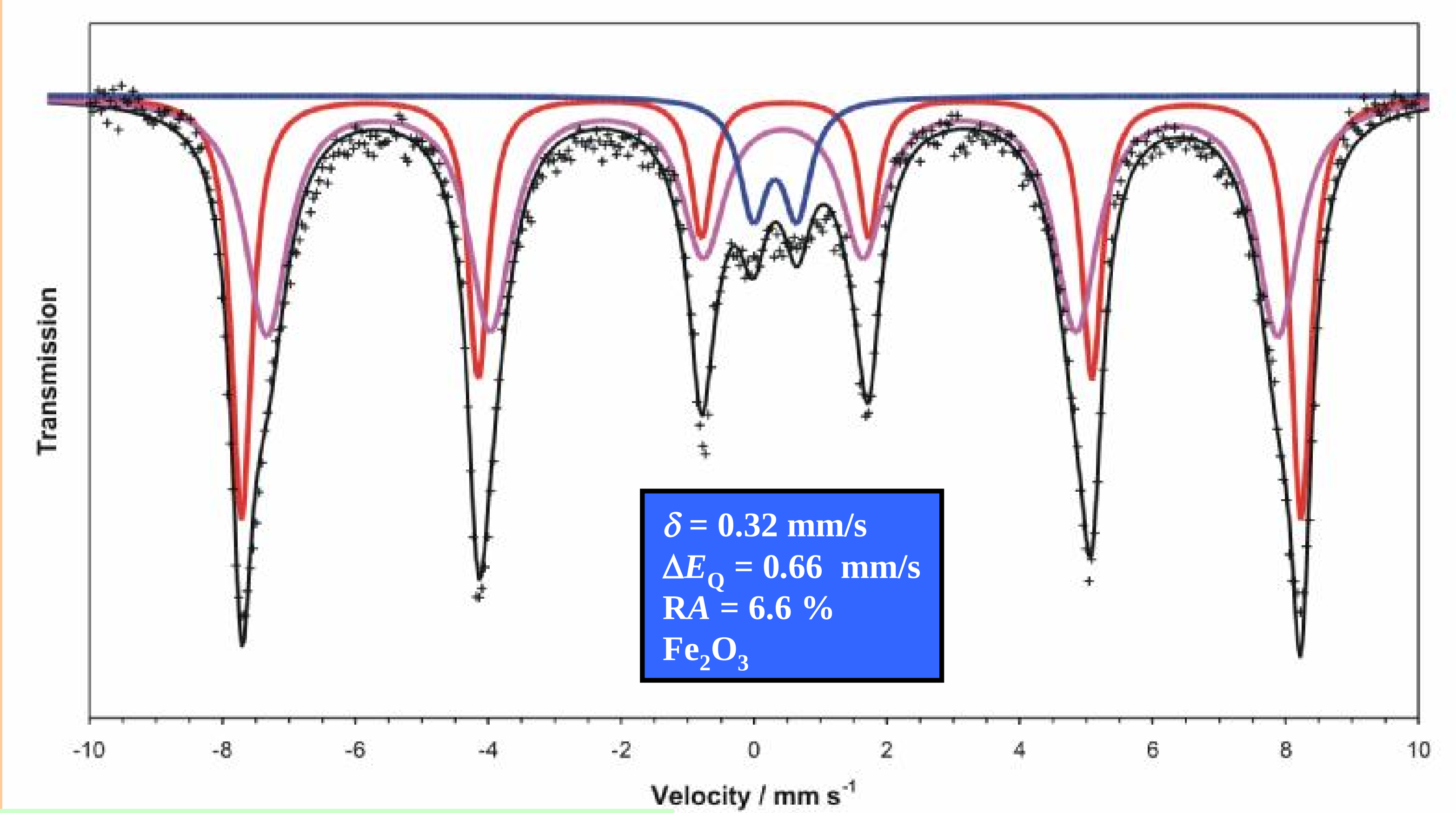
Furnace temperature 175 ºC, 30 hrs

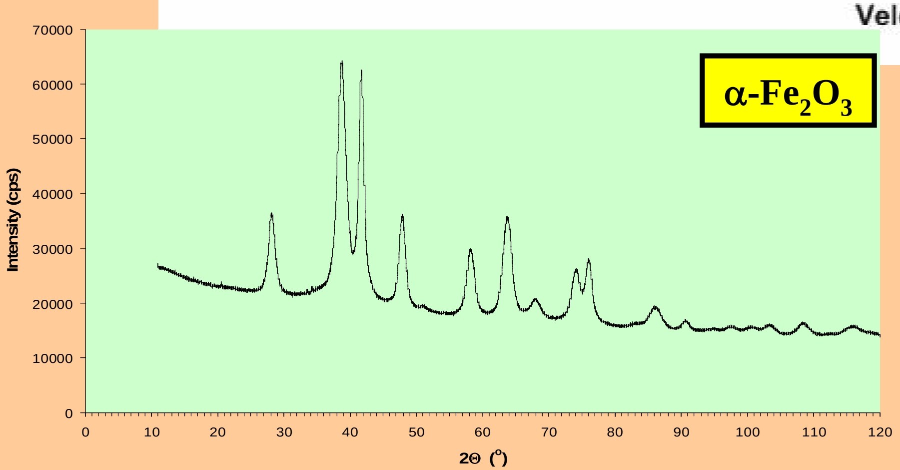






Low-layer samples: furnace temperature 175 ºC, 100 hrs

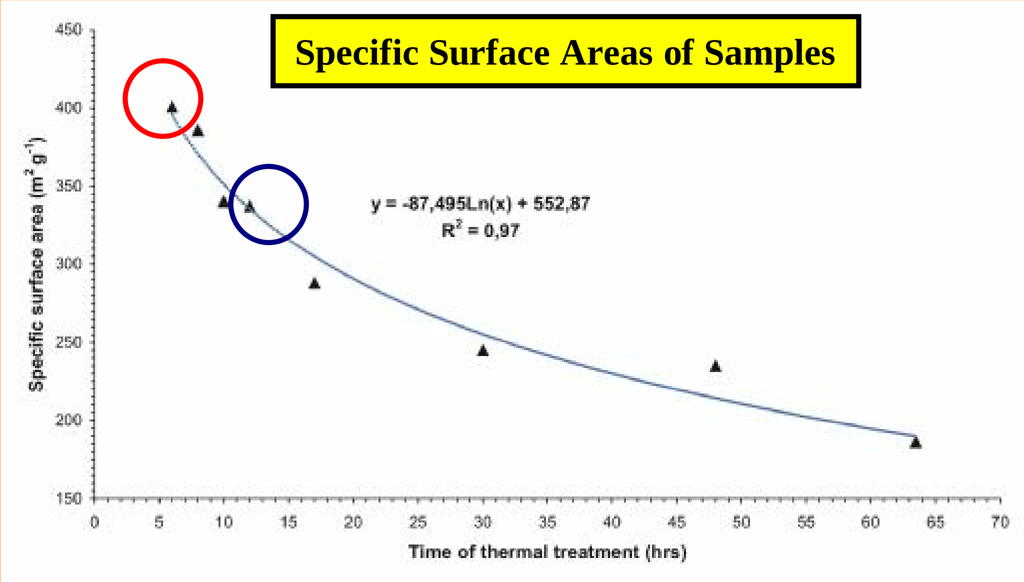




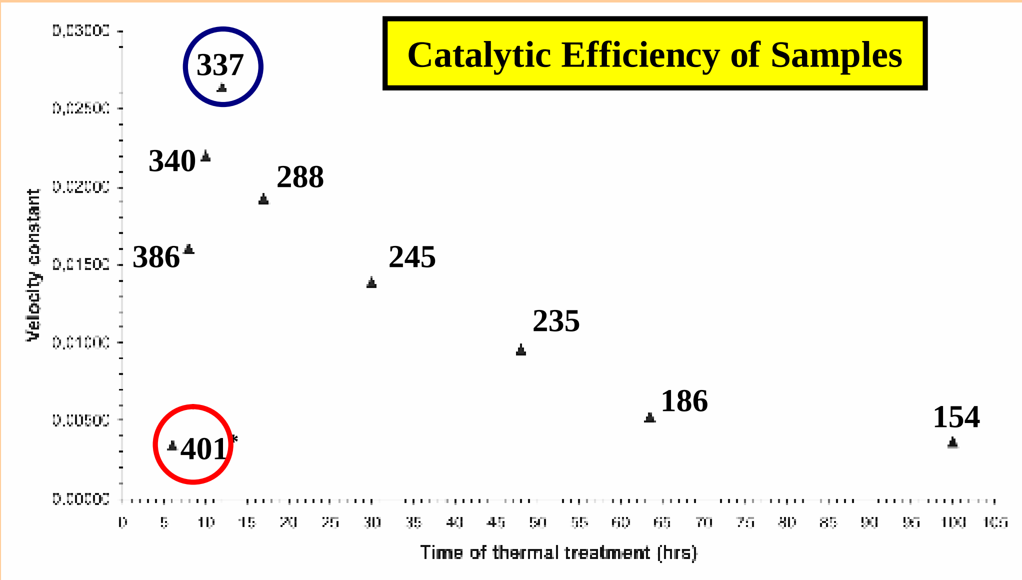
δ = 0.37 mm/s
ε_Q = –0.21 mm/s
H = 49.5 T
RA = 36.9 %
α -Fe_2O_3 (bulk)

δ = 0.36 mm/s
ε_Q = –0.16 mm/s
H = 41.5 T
RA = 47.3 %
α -Fe_2O_3 (surface)

Applicability – enormous *SA* (400 $m^2\ g^{-1}$) – catalysis?!



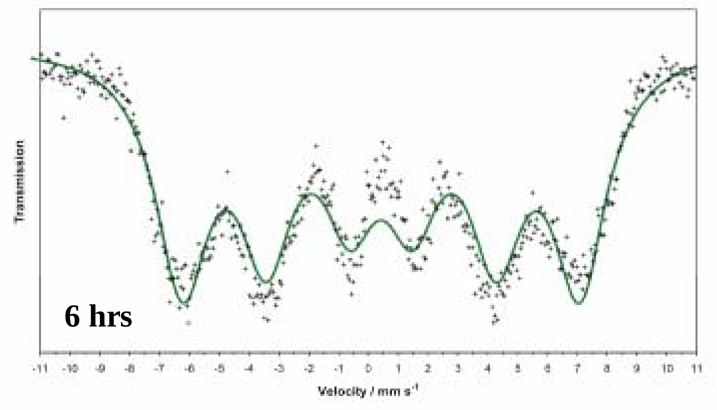
Time of the thermal treatment (hrs)	Specific surface area ($m^2\ g^{-1}$)	Velocity constant
6	401	0.00338
8	386	0.01605
10	340	0.02200
12	337	0.02641
17	288	0.01923
30	245	0.01388
48	235	0.00958
64	186	0.00520
100	154	0.00362



surface area
vs.
degree of crystallinity???

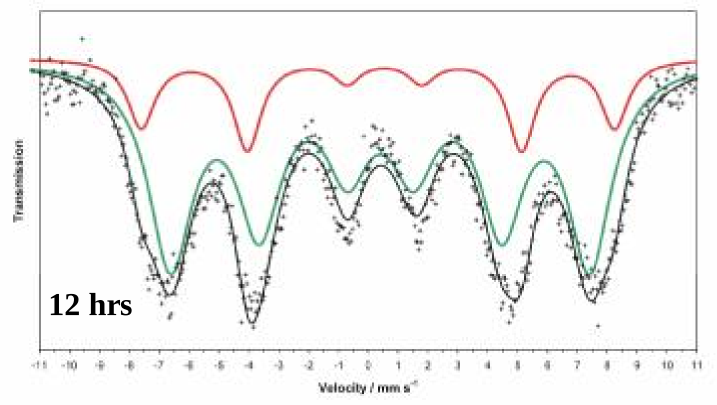
*** surface areas**

LTMS of samples after 6, 12 and 17 hrs of the thermal treatment



maximum surface area (ca. 400 $m^2\ g^{-1}$)
minimum catalytic efficiency

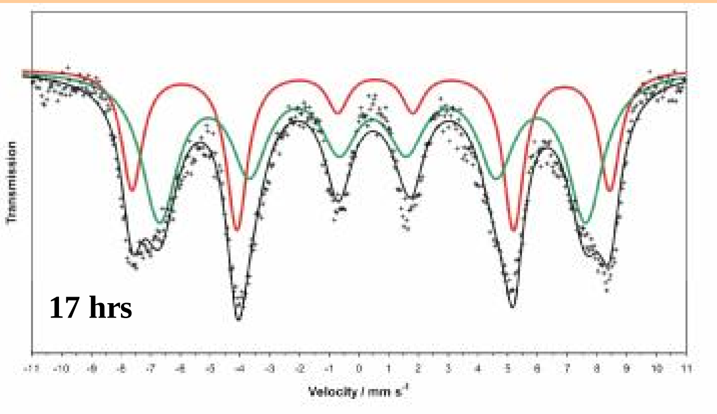
δ = 0.43 mm/s
ε_Q = 0 mm/s
H = 41.4 T
Γ = 2.17 mm/s
am -Fe_2O_3



surface area of 337 $m^2\ g^{-1}$)
maximum catalytic efficiency

δ = 0.41 mm/s
ε_Q = – 0.02 mm/s
H = 43.2 T
Γ = 1.73 mm/s
RA = 73.4 %
am -Fe_2O_3

δ = 0.45 mm/s
ε_Q = – 0.04 mm/s
H = 49.0 T
Γ = 1.21 mm/s
RA = 26.6 %
α-Fe_2O_3



surface area of 288 $m^2\ g^{-1}$)
2nd best catalytic efficiency

δ = 0.47 mm/s
ε_Q = 0 mm/s
H = 44.5 T
Γ = 1.47 mm/s
RA = 62.9 %
am -Fe_2O_3

δ = 0.49 mm/s
ε_Q = – 0.14 mm/s
H = 49.9 T
Γ = 0.85 mm/s
RA = 37.1 %
α-Fe_2O_3

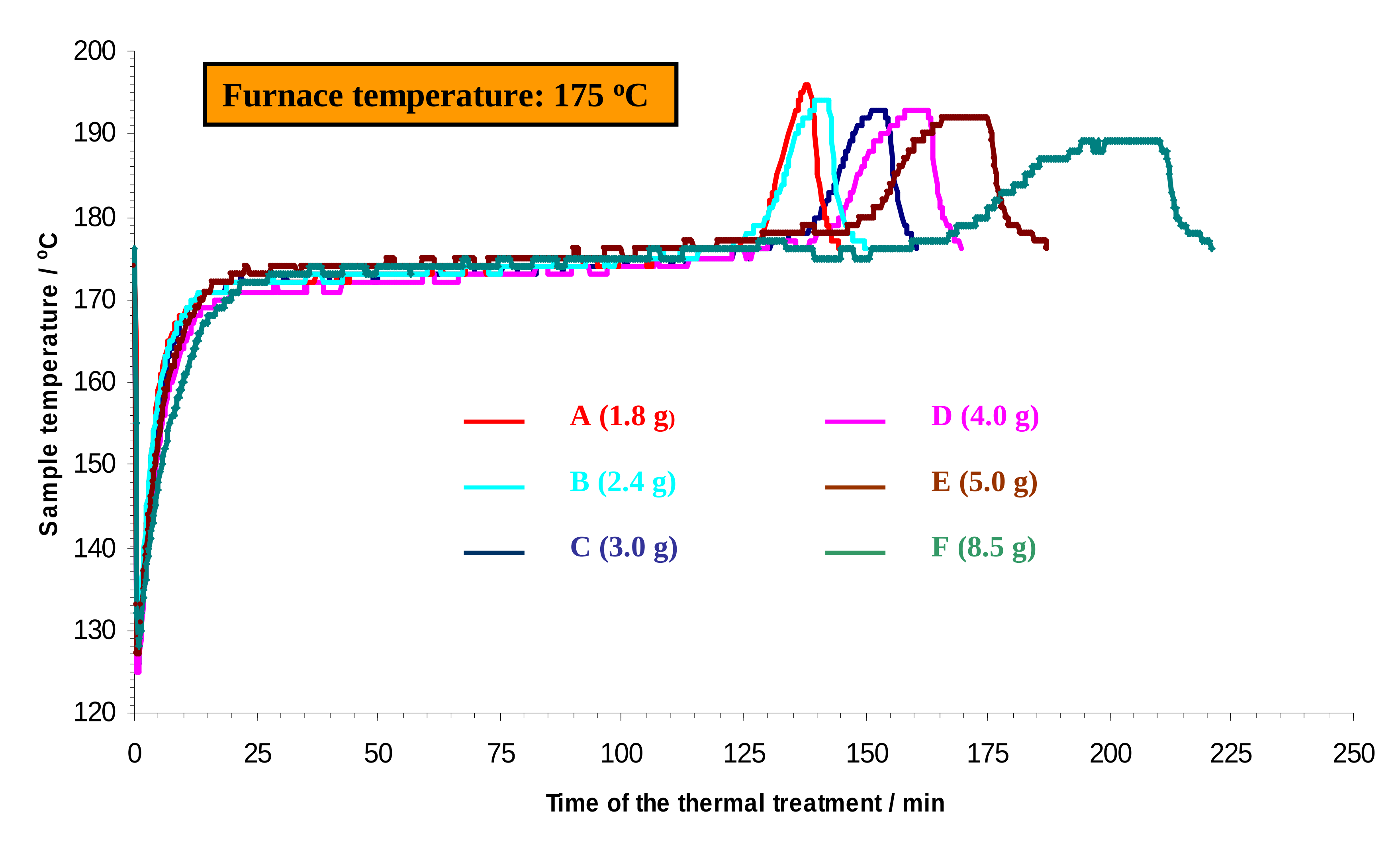
CRYSTALLIZATION

Catalytic activity = surface area *vs.* degree of crystallinity!!!

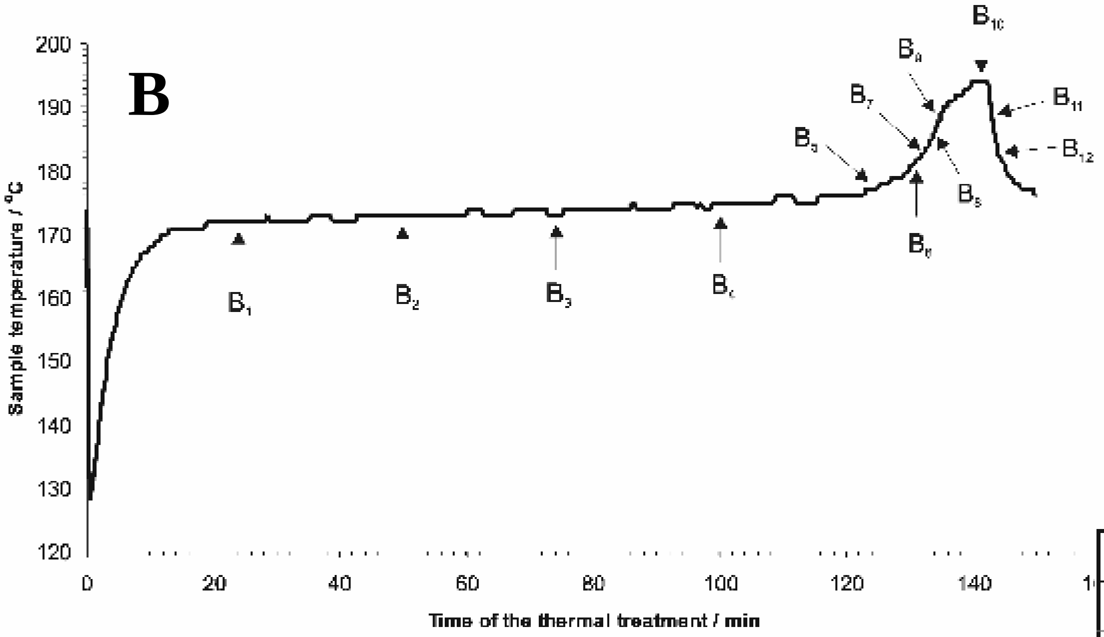
High-layer samples

M. Hermanek, R. Zboril and I. Medrik

High-layer samples: furnace temperature 175 ºC



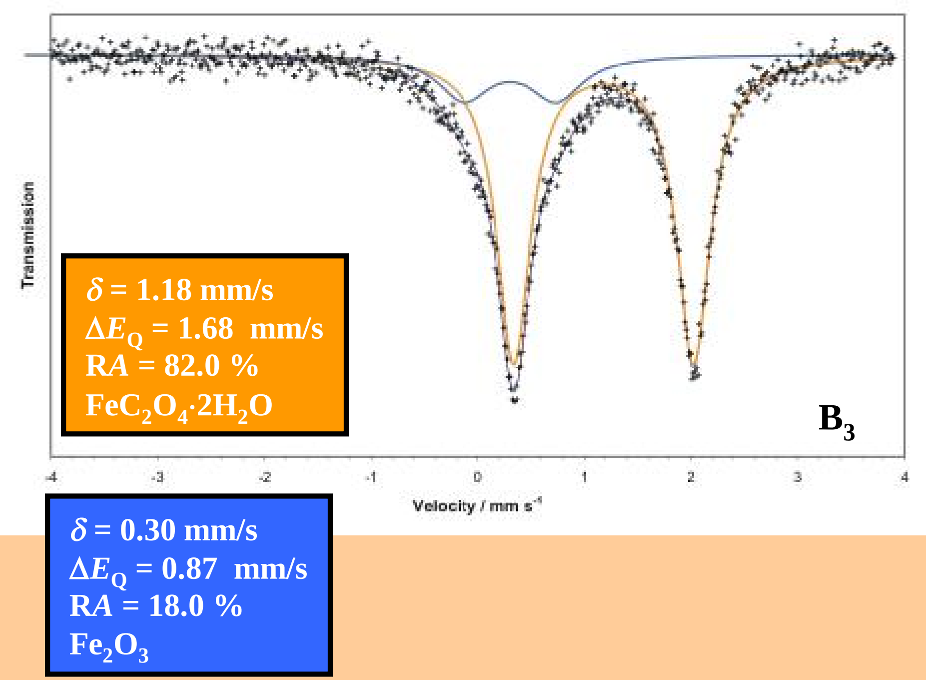
High-layer sample B: furnace temperature 175 ºC

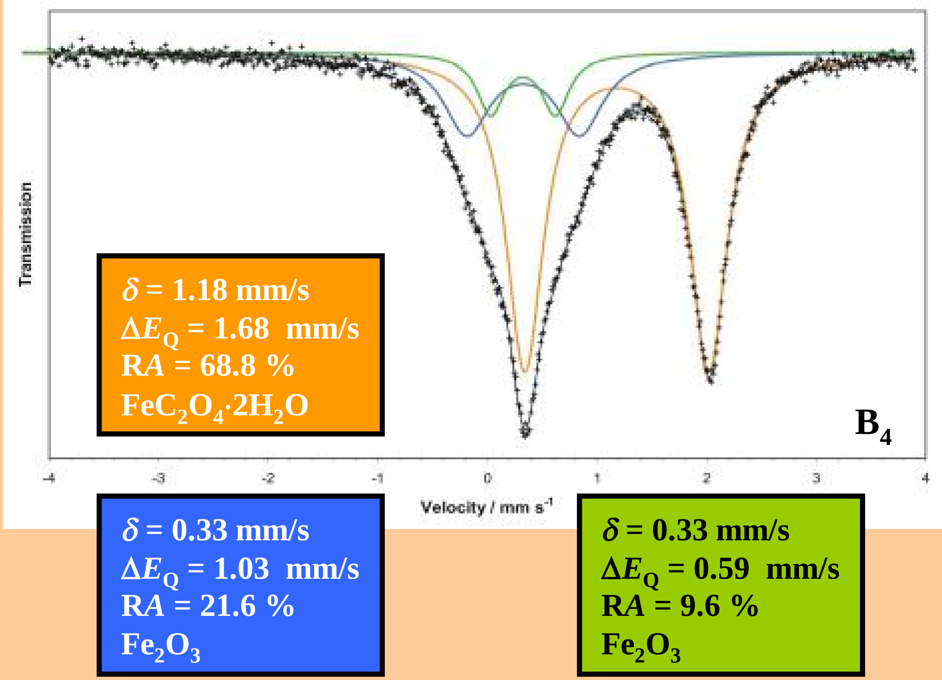


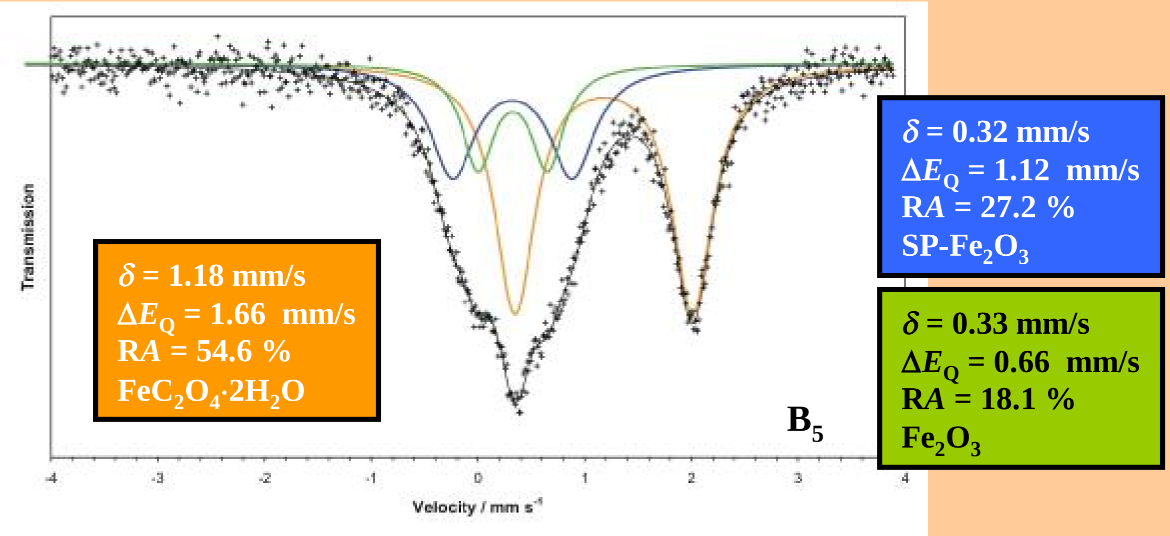
Mossbauer & XRD characterization
of samples B_1-B_{12}

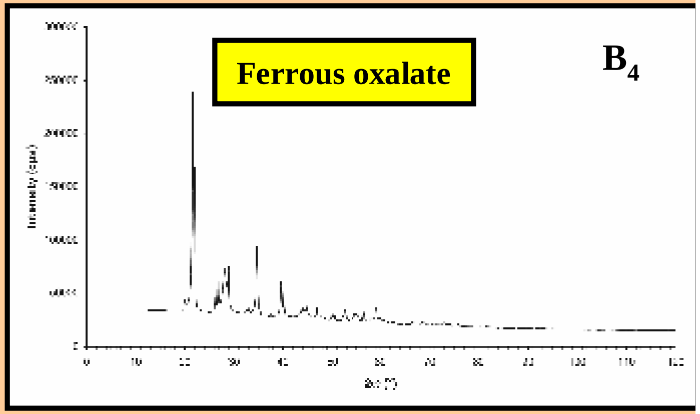
Sample	Conditions of preparation
B_1	25 min of the isothermal treatment
B_2	50 min of the isothermal treatment
B_3	75 min of the isothermal treatment
B_4	100 min of the isothermal treatment
B_5	Sample temperature of 177 °C, temp. effect – upward trend
B_6	Sample temperature of 179 °C, temp. effect upward trend
B_7	Sample temperature of 181 °C, temp. effect upward trend
B_8	Sample temperature of 183 °C, temp. effect upward trend
B_9	Sample temperature of 188 °C, temp. effect upward trend
B_{10}	Sample temperature of 194 °C, maximum of the effect
B_{11}	Sample temperature of 188 °C, temp. effect – downward trend
B_{12}	Sample temperature of 183 °C, temp. effect – downward trend

High-layer samples B_3-B_5 (75 and 100 min, 175 ºC, 177 ºC of *ST*)

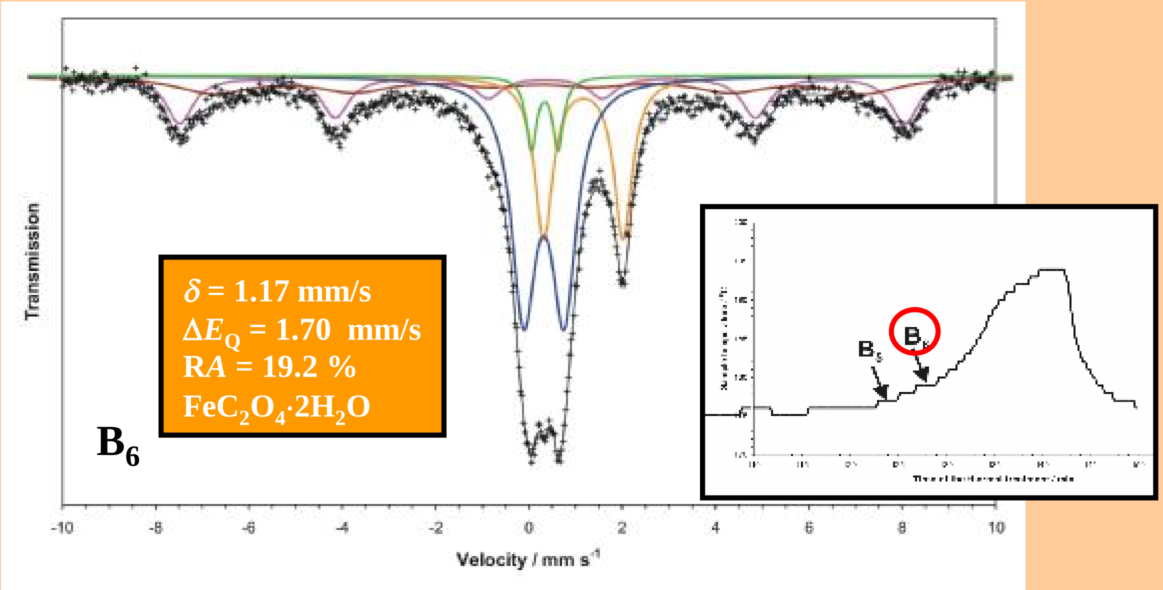








High-layer sample B_6 (179 ^{o}C of ST)



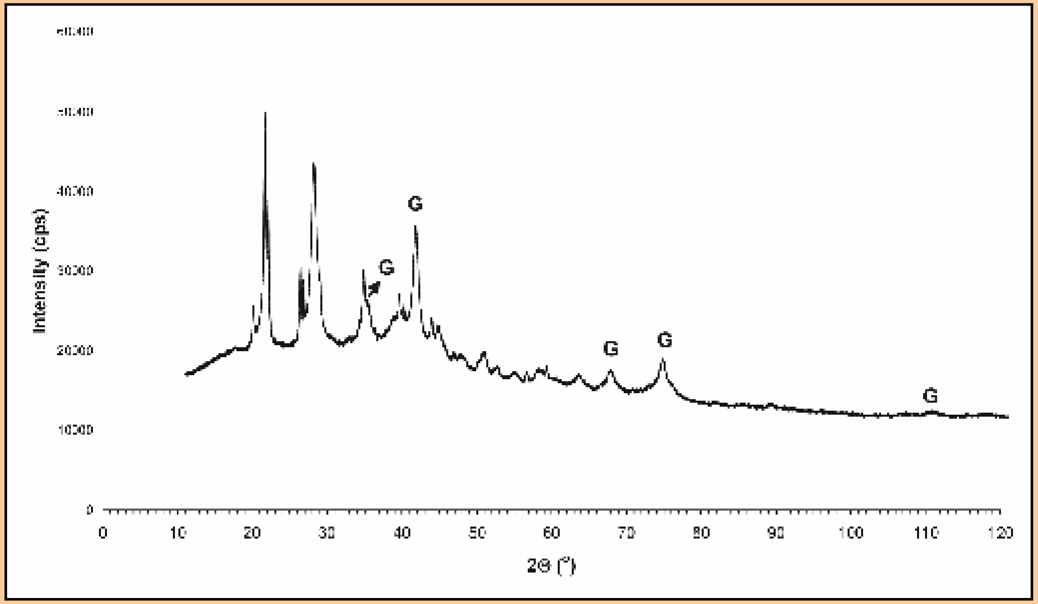
δ = 1.17 mm/s
ΔE_Q = 1.70 mm/s
RA = 19.2 %
$FeC_2O_4{\cdot}2H_2O$

δ = 0.32 mm/s
ε_Q = 0.06 mm/s
H = 48.3 T
RA = 20.2 %
γ -Fe_2O_3 (bulk)

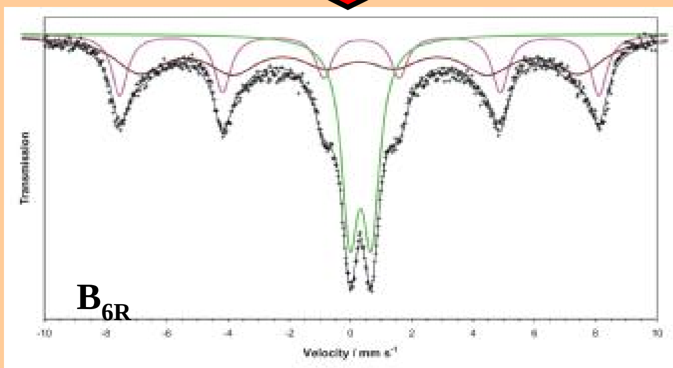
δ = 0.34 mm/s
ΔE_Q = 0.57 mm/s
RA = 4.9 %
Fe_2O_3

δ = 0.26 mm/s
ε_Q = 0.07 mm/s
H = 43.2 T
RA = 19.1 %
γ -Fe_2O_3 (surface)

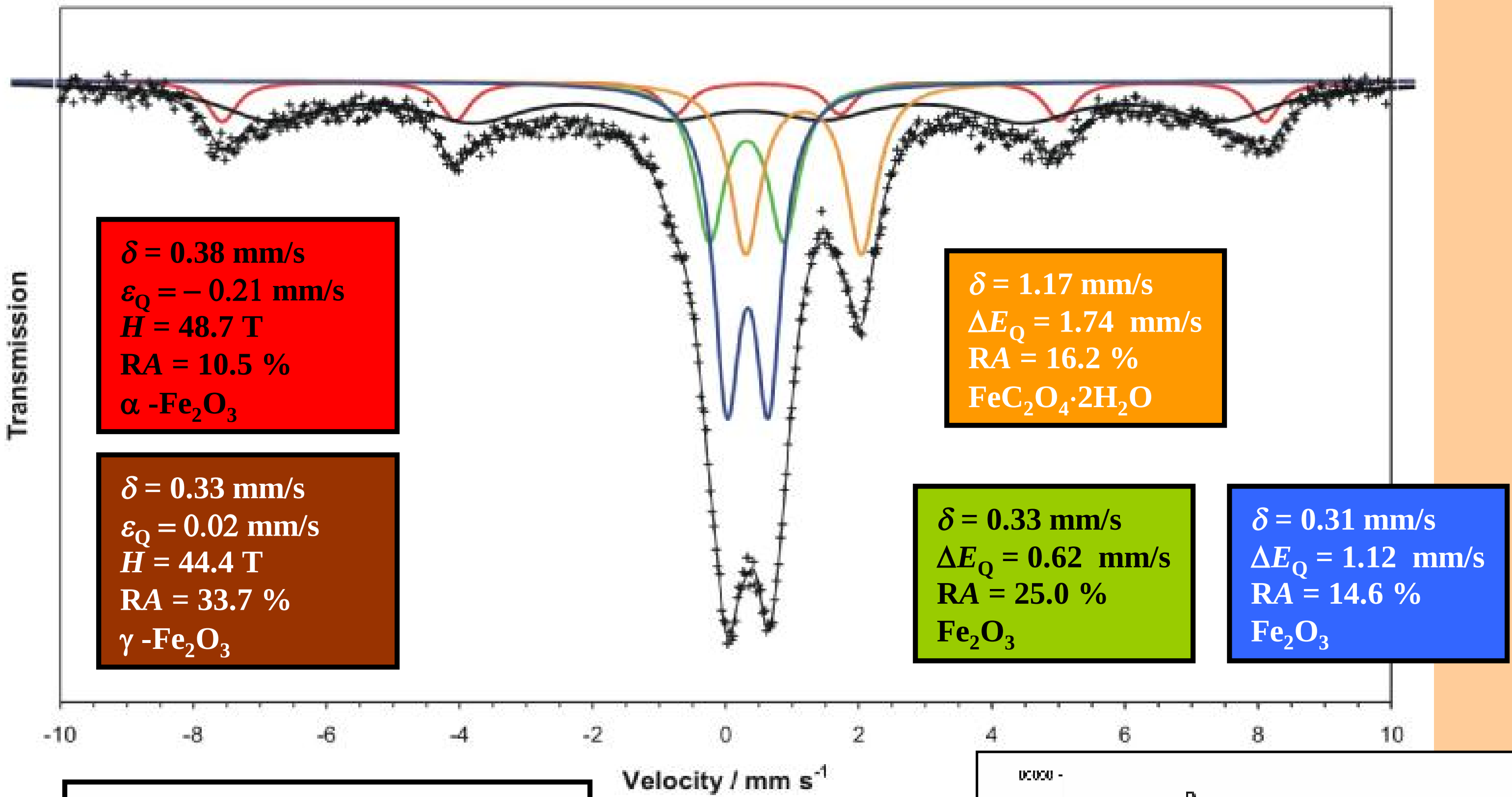
δ = 0.32 mm/s
ΔE_Q = 0.87 mm/s
RA = 36.6 %
Fe_2O_3

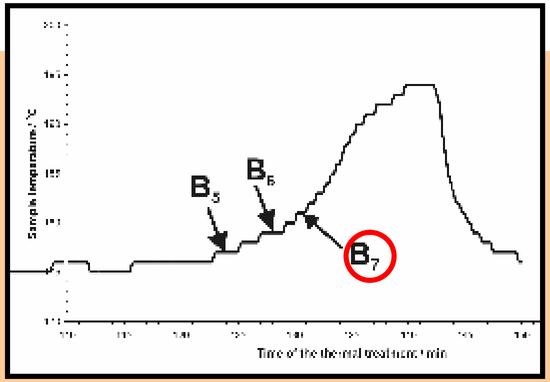


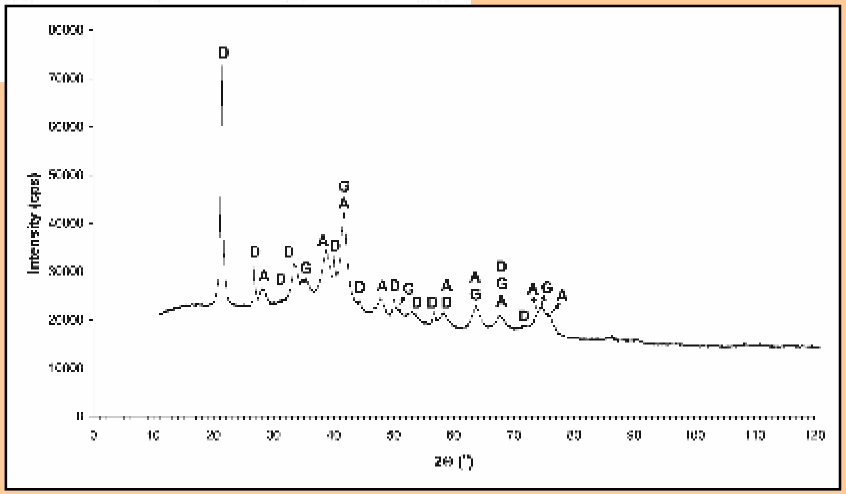
Synthesis of pure MAGHEMITE



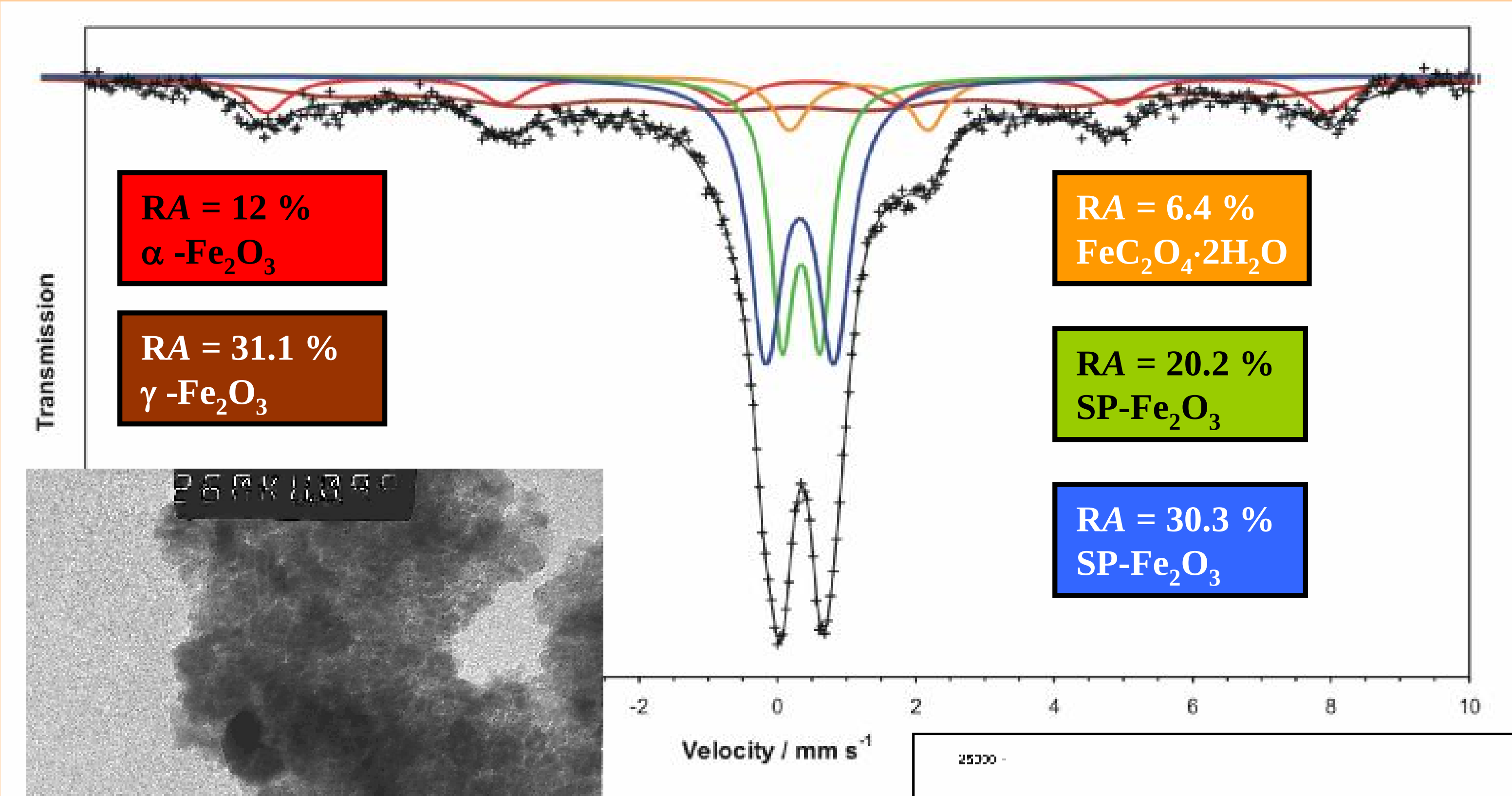
High-layer sample B_7 (181 °C of S*T*)

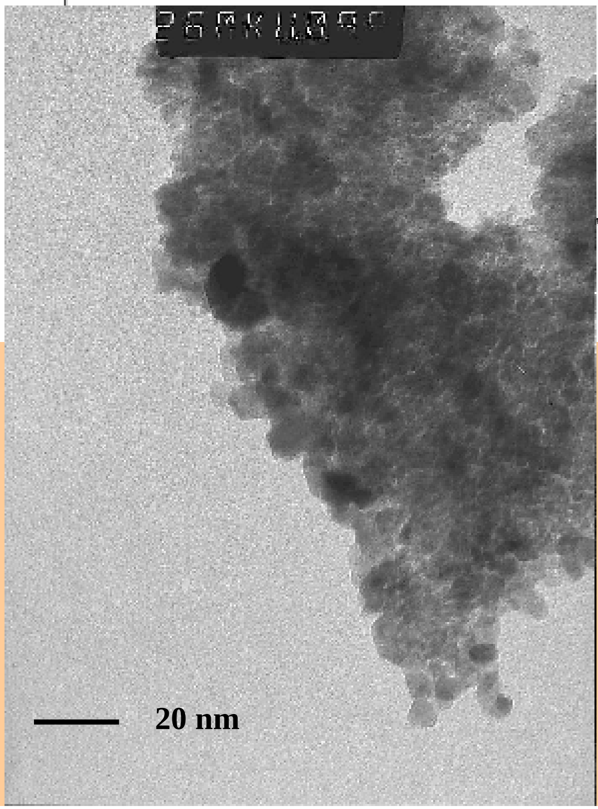


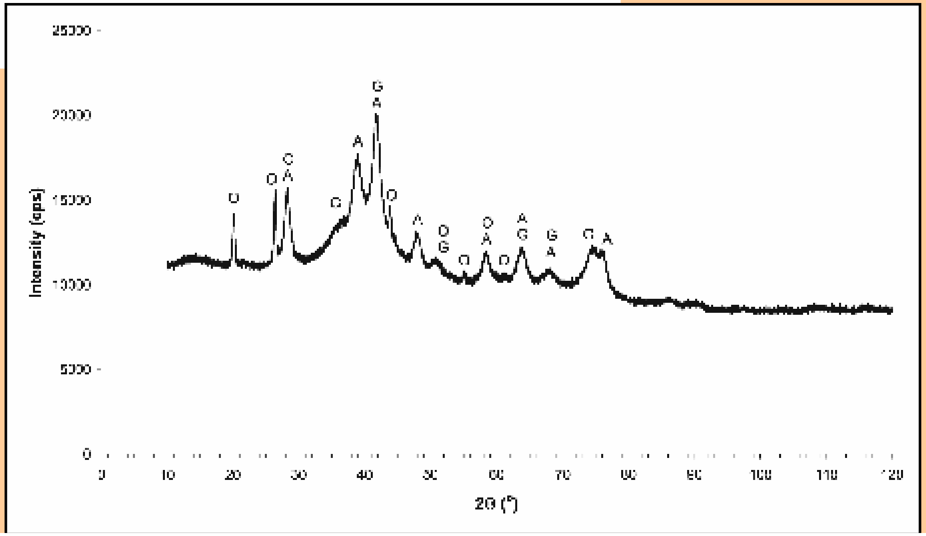




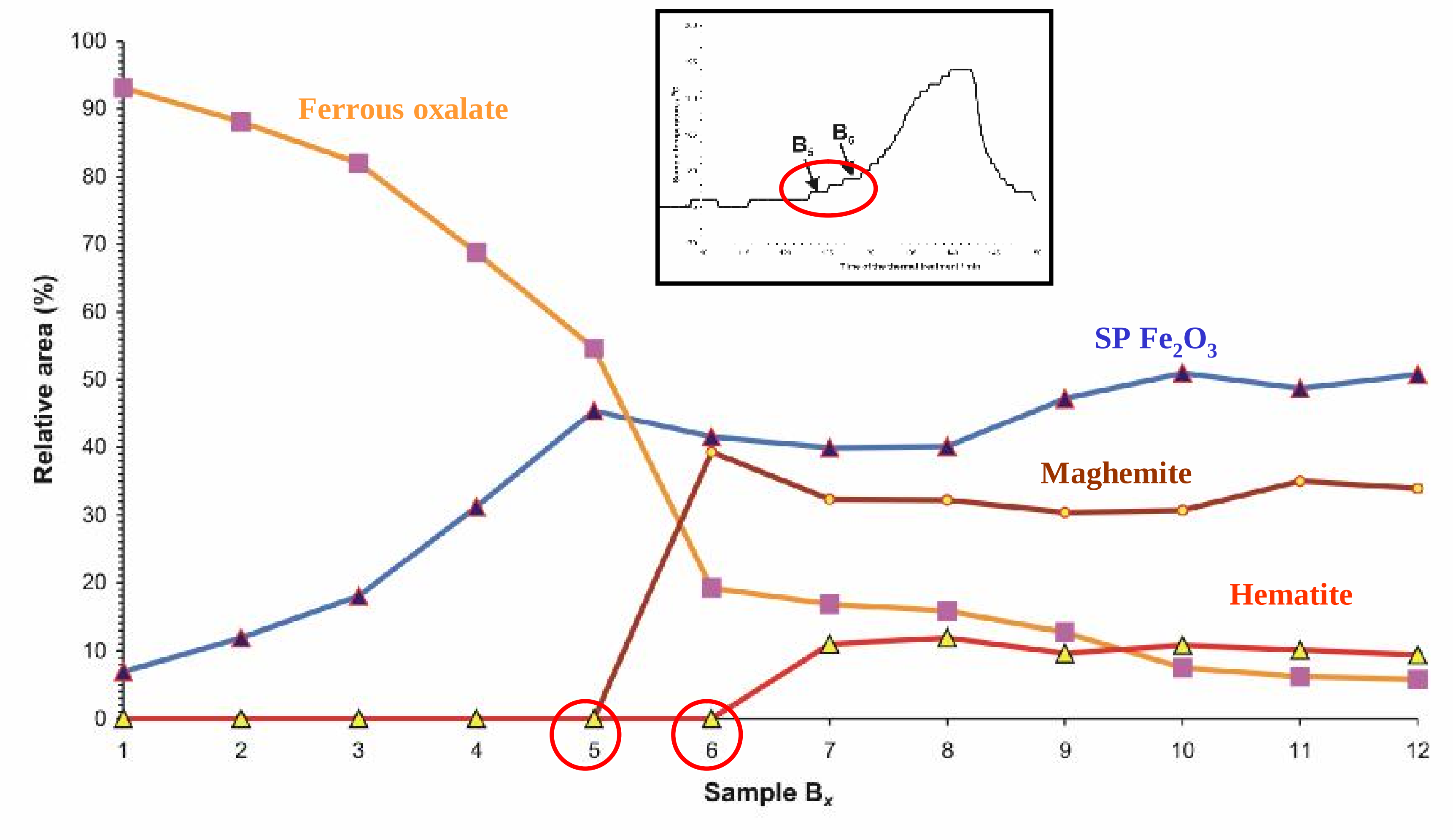
High-layer samples B (end of the temperature effect)







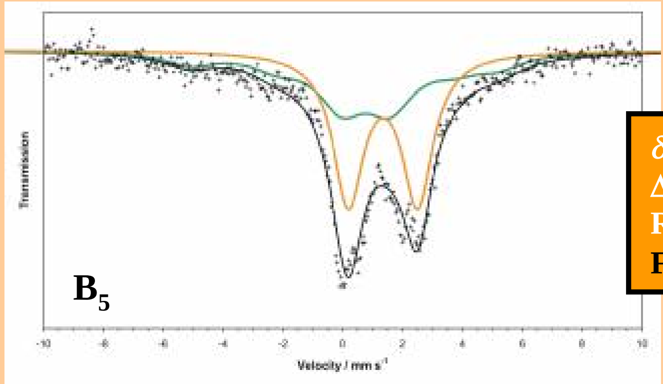
Phase composition of samples B_1-B_{12} (RT MS)



177 ºC (B_5)-179 ºC (B_6): $FeC_2O_4 \cdot 2H_2O$: 54.6 → 19.2 %, γ-Fe_2O_3 : 0 → 39.3 %

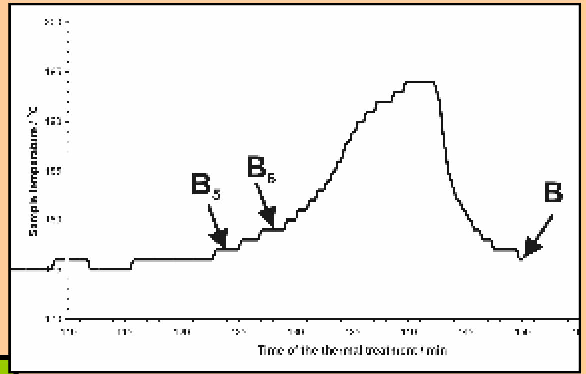
IFMS of B_5, B_6 and B: origin of the temperature effect

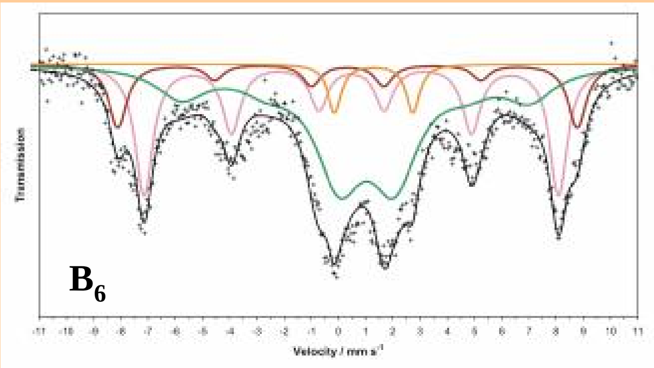
IFMS (50 K, 5 T) of samples B_5, B_6 and B – origin of exoeffect



δ = 1.35 mm/s
ΔE_Q = 2.31 mm/s
RA = 55.5 %
$FeC_2O_4{\cdot}2H_2O$

δ = 0.41 mm/s
ΔE_Q = -0.74 mm/s
H = 32.1 T
RA = 25.0 %
am-Fe_2O_3





δ = 1.30 mm/s
ΔE_Q = 2.88 mm/s
RA = 4.6 %
$FeC_2O_4{\cdot}2H_2O$

δ = 0.84 mm/s
ΔE_Q = -0.42 mm/s
H = 39.7 T
RA = 51.9 %
am-Fe_2O_3

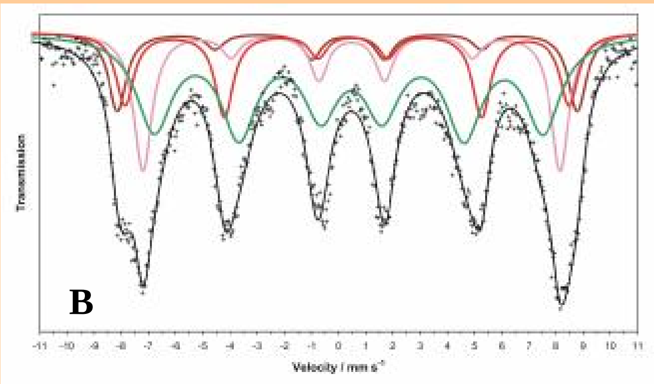
δ = 0.34 mm/s
ε_Q = 0 mm/s
H = 52.5 T
RA = 12.7 %
γ-Fe_2O_3 (A)

δ = 0.48 mm/s
ε_Q = 0 mm/s
H = 47.3 T
RA = 30.7 %
γ-Fe_2O_3 (B)

Collective Crystallization Amorphous

↓

Nanocrystalline Fe_2O_3



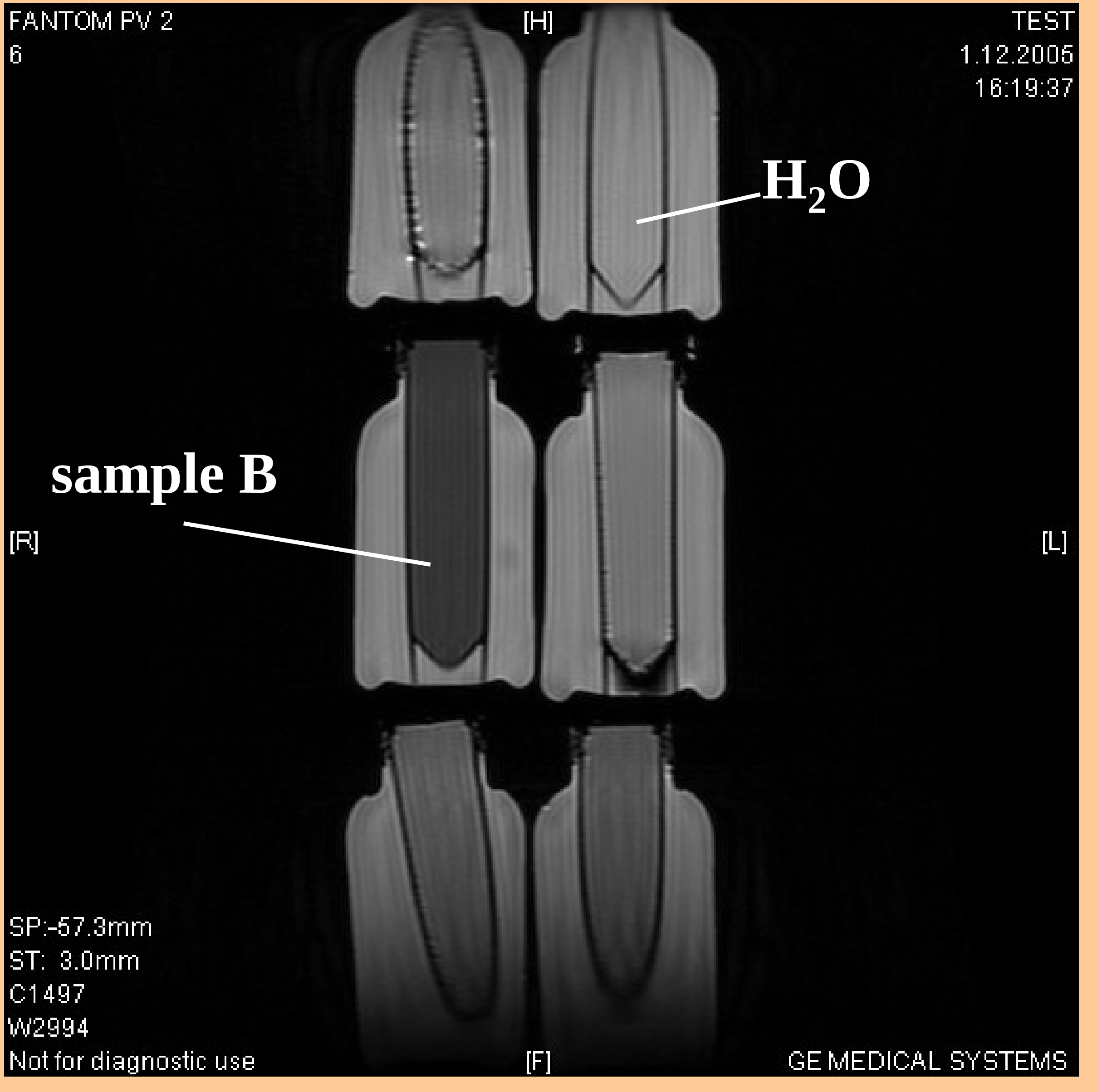
δ = 0.43 mm/s
ΔE_Q = -0.10 mm/s
H = 43.5 T
RA = 41.3 %
am-Fe_2O_3

δ = 0.38 mm/s
ε_Q = –0.21 mm/s
H = 48.7 T
RA = 10.5 %
α-Fe_2O_3

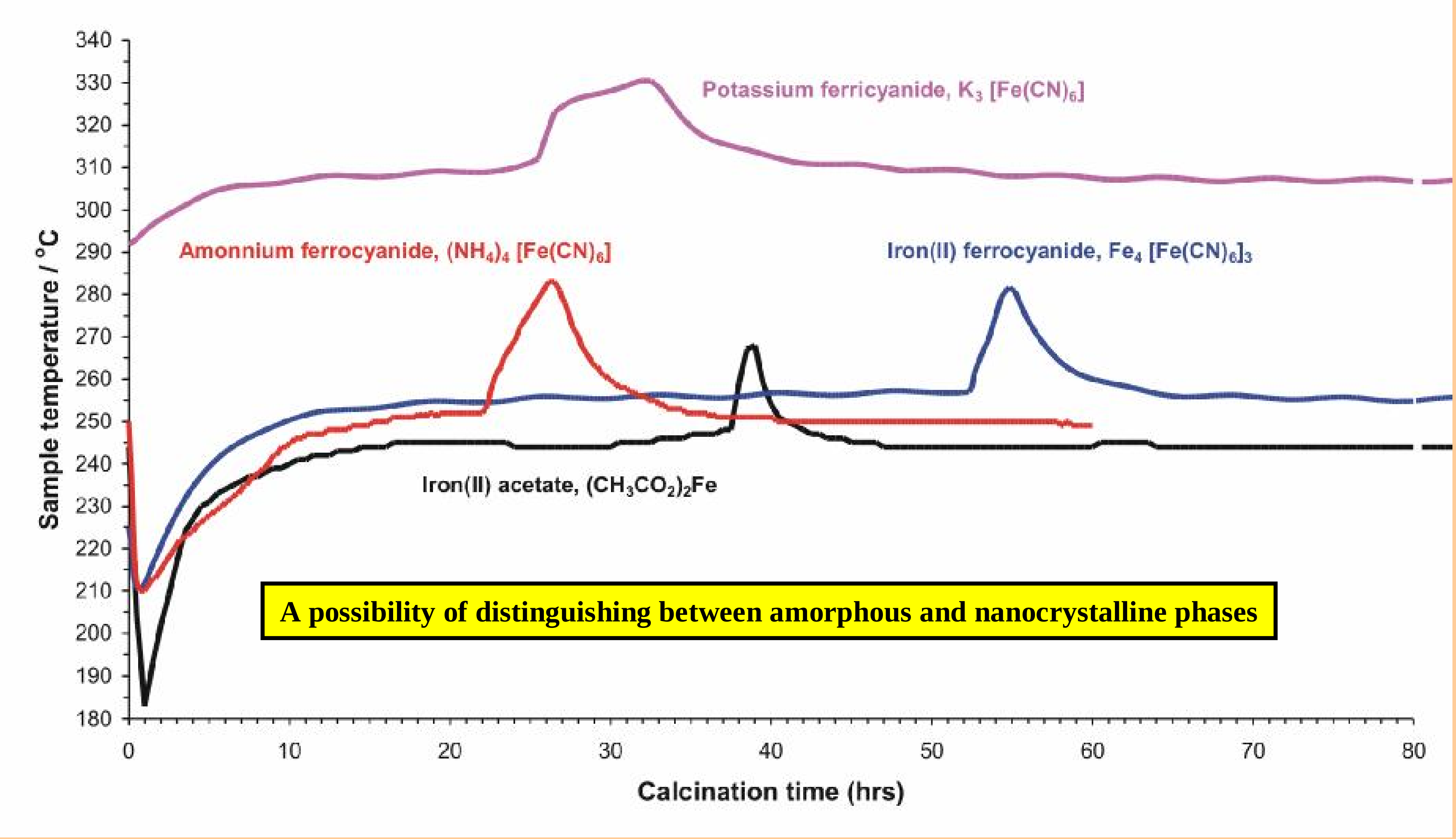
δ = 0.48 mm/s
ε_Q = 0 mm/s
H = 47.5 T
RA = 18.4 %
γ-Fe_2O_3 (B)

δ = 0.34 mm/s
ε_Q = –0.03 mm/s
H = 52.4 T
RA = 13.5 %
γ-Fe_2O_3 (A)

Applicability: contrast agent in Magnetic Resonance Imaging

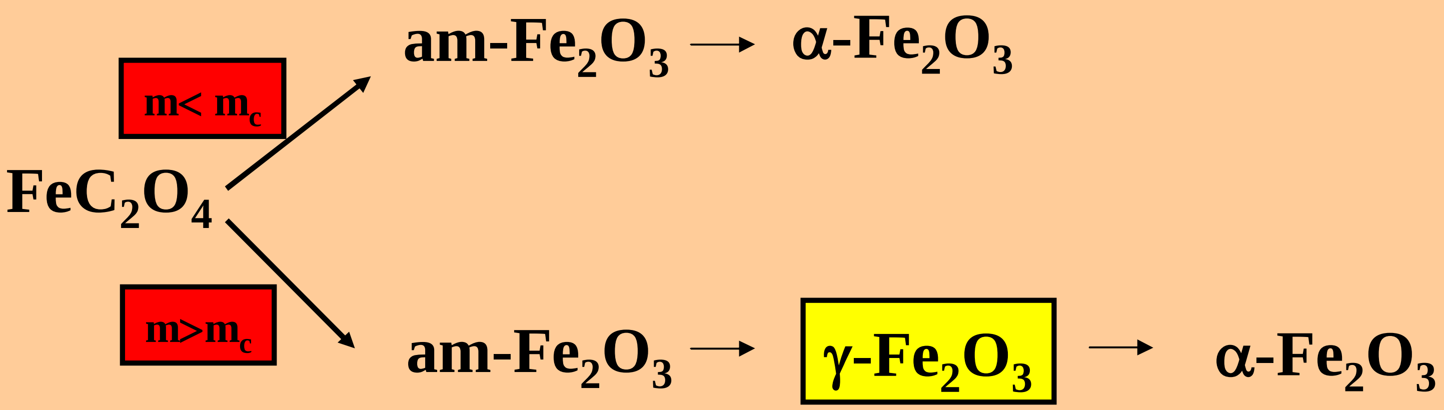


Exoeffect as a General Phenomenon



Conclusions

BASIC RESEARCH:

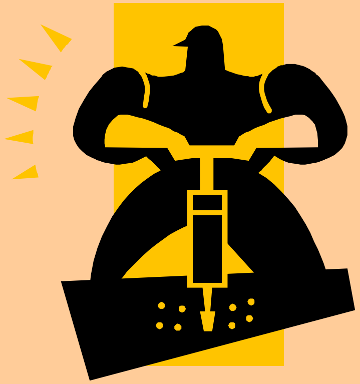


- **besides temperature, time, reaction atmosphere, precursor particle size and decomposition gases, sample layer represents another quality influencing substantially solid-state decomposition processes**
- **the formation of maghemite during the thermally induced decomposition of $FeC_2O_4 \cdot 2H_2O$ has been explained**
- **catalytic efficiency arises as a compromise of S*A* and degree of crystallinity**

APPLICABILITY:

- **low-layer samples: use in catalysis**
- **low-layer samples: preparation of hematite nanoparticles of different sizes**
- **high-layer samples: magnetic materials – contrast agent in MRI**

Many thanks to my colleagues for their help



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to you for your attention.