Mössbauer's spectroscopy applied on kaolinitic clays.

Study of Fe^{3+} influences on final color of ceramic bodies

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Kaolin

- Name comes from Chines locality Kao-Ling (高嶺土) original meaning – „High Mountain Ridge“
- Material is used for the production of porcelain, paper, tires, medicaments etc.
- Basic material for all geopolymer reactions.
- Kaolin origins from feldspars
- Main component is kaolinite (accompanied by quartz, rests of feldspar, eventually micas and limited proportions of iron and titanium oxides).

Kaolinite

- chemical composition:

  $Al_2O_3\ 2SiO_2\ 2H_2O$

- Double layered structure changing regularly the layers of tetrahedral (Si_2O_5) and octahedral ($Al_2(OH)_4$)
- Fe^{3+} izo-morphologically substitutes aluminum ion

Kaolin composition changes through the thermal treatment

Changes formulated by (Brindley and Nakahira-1959) and generally used in ceramic industry :

- 580 °C dehydration (– H_2O)
- 925 °C spinel ($2Al_2O_33SiO_2$) $+SiO_2$
- 1050 °C mullite phases ($2Al_2O_32SiO_2$)$+SiO_2$
- 1200 °C mullite ($3Al_2O_32SiO_2$) $+SiO_2$

P.S. The ceramic technology never worked with changes at aluminum ion coordination after the loss of lattice waters and before the spinel appears.

Mullite

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Fe^{3+} in kaolin

- Commonly used rules:
- Fe^{3+} changes color in clays [pink-red to dark brown].
- By the rising temperature color change to the darker shades.
- Industry of the porcelain production resolves the color problem by reduction atmosphere use during the firing. (Changing by this way the coloring ferric oxide to discoloring ferrous oxide).
- These rules and industrial experiences **are not valid** generally.

Study of waste kaolinic clay

- Clay „S2“ supplied by EXIMOS a.s.
- Clay is by-product of washed sandstone beside getting white sand for glass production.
- Unfortunately clay has no farther use and fills the deposit ponds. [30000 t/year]
- Clay change color according to the treatment temperature.
- Raw material – yellow (content of Fe_2O_3 = 2.57 wt.%)
- 750°C brick reddish
- 1000 °C – light red
- 1100 °C – white, slightly gray shade
- 1180 °C - white

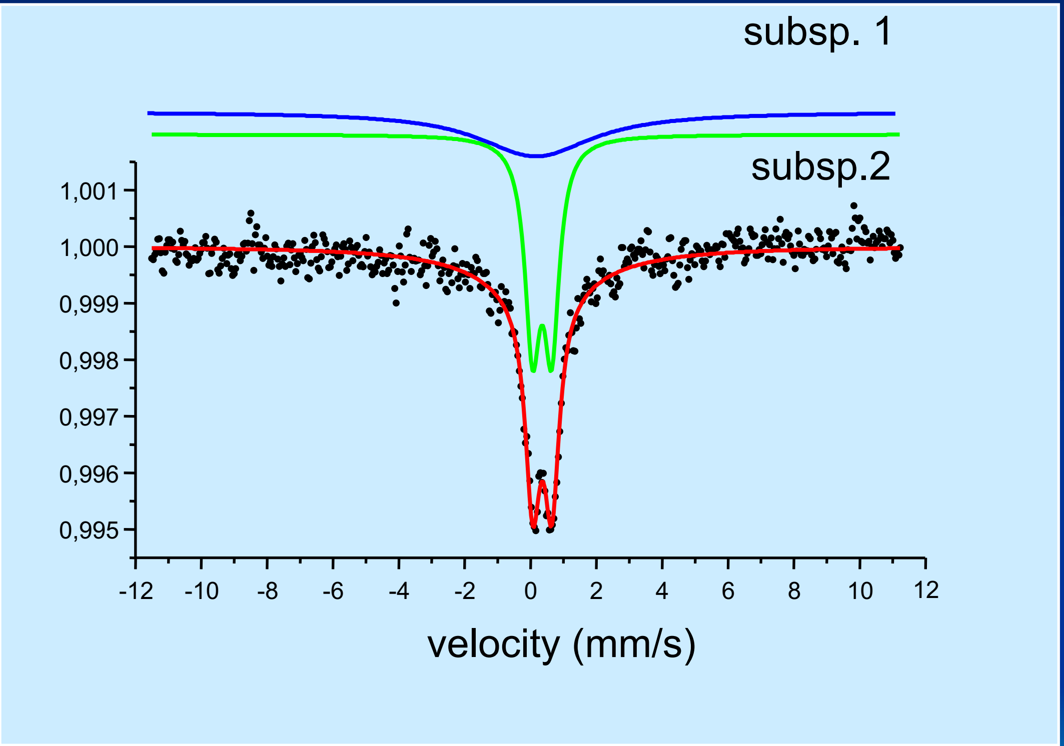
Mössbauer's spectroscopy

- Analysis by Mössbauer spectra:
- reflects resonant absorption and emission of gamma rays in solids.
- Typically, three types of nuclear interactions may be observed: isomer shift, also called chemical shift in the older literature; quadrupole splitting; and magnetic hyperfine splitting

Mössbauer's spectroscopy

- **Isomer shift** describing a shift in the resonance energy of a nucleus due to the transition of electrons
- **Quadrupole splitting** reflects the interaction between the nuclear energy levels and surrounding electric field gradient
- The ground to excited state transitions appear as two specific peaks in a spectrum, sometimes referred to as a "doublet".
- **Magnetic hyperfine splitting** Magnetic (hyperfine splitting) is a result of the interaction between the nucleus and any surrounding magnetic field. In the majority of cases only 6 peaks can be monitored in a spectrum produced by a hyperfine splitting (BHF).

Mössbauer's spectra of the raw material sample „S2“

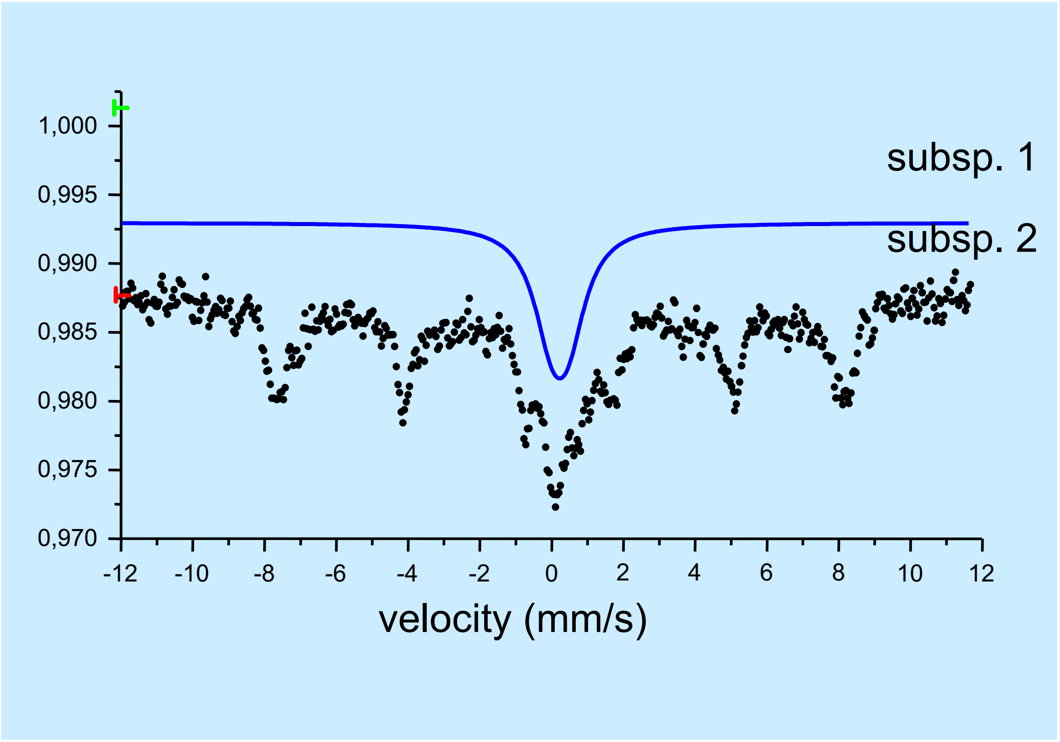


	Subsp. 1	Subsp. 2
IS δ	**0.30 mm/s**	**0.36 mm/s**
QUA ΔE_Q	**0.08 mm/s**	**0.58 mm/s**

- Clay do not contain hematite
- Fe^{3+} in form of hydro ferric oxide (FeO(OH)) lepidokrokite

Mössbauer's spectra clay „S2“

Sample fired at 750°C



	Subsp. 1	Subsp. 2
IS *δ*	**0.37 mm/s**	**0.27 mm/s**
QUA ΔE_Q	**- 0.22 mm/s**	**0.46 mm/s**
BHF	**48.9 T**	

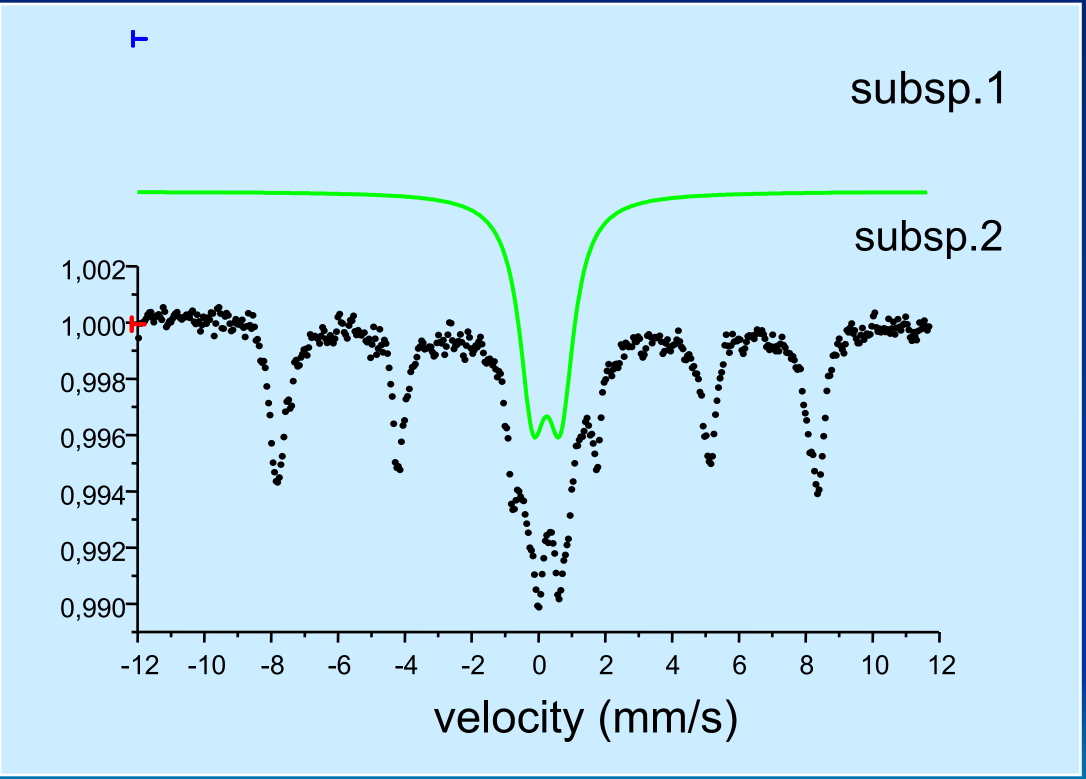
- Lepidokrokite changes to hematite (Fe_2O_3)
- Color: brick red

Mössbauer's spectra clay „S2“ explication

- Subspectrum 1 QS – quadrupole splitting (The quadrupole splitting can be used for determining oxidation state),
- value (- 0.22) shows presence of α-Fe_2O_3 because no other iron oxide phase has negative value of QS.
- Subspectrum 2 shows the paramagnetic Fe^{3+} probably bonded to aluminosilicate.

Mössbauer's spectra clay „S2“

Sample fired at 1000°C

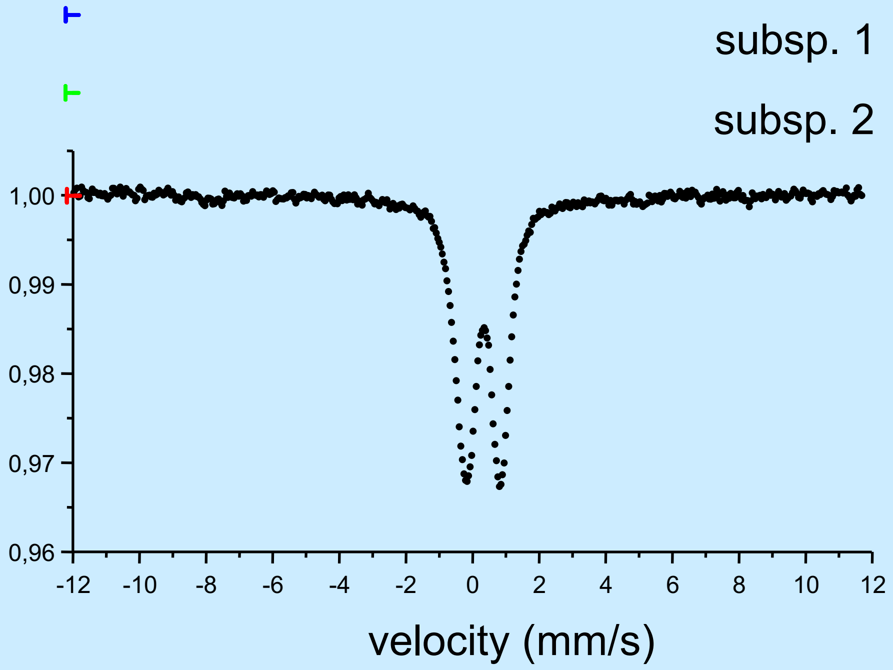


	Subsp. 1	Subsp. 2
IS δ	**0.37 mm/s**	**0.29 mm/s**
QUA ΔE_Q	**- 0.21 mm/s**	**0.82 mm/s**
BHF	**50.0 T**	

- Hematite starts to dissolve
- Color: Light red

Mössbauer's spectra clay „S2“

Sample fired at 1180°C



	Subsp. 1	Subsp. 2
IS δ	**0.33 mm/s**	**0.31 mm/s**
QUA ΔE_Q	**0.76 mm/s**	**1.21 mm/s**

- Change of color - discoloring
- Fe^{3+} totally incorporated into mullite lattice

Mossbauer's spectra clay „S2“

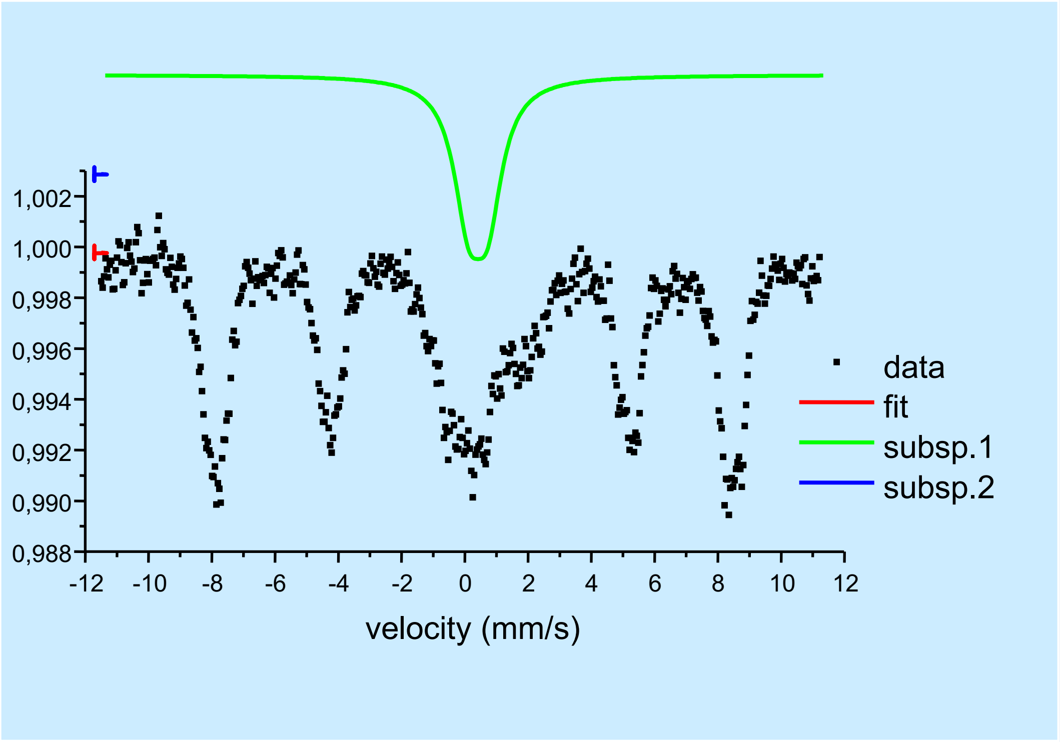
- We see the typical „doublet“–significant the presence of paramagnetic Fe^{3+} diluted in the aluminosilicate matrix at atomic level.
- Even the spectra shows the presence of Fe^{3+} ions, the incorporation means also discoloration.
- Following studies present limit of Fe^{3+}content incorporated into the aluminosilicate matrix.

Study of red clay material
used for the floor tiles production

- Clay – deposit „Zelec“
- Naturally dark red kaolinitic clay
- Content of Fe_2O_3 **> 10.2 wt. %**
- Color changes are practically invisible during firing:
- raw material – dark red/brown
- 750 °C red but slightly lighter than raw material
- 1000 °C similar as above
- 1180 °C very dark red/brown color

Mössbauer's spectra clay „Zelec“

Raw material

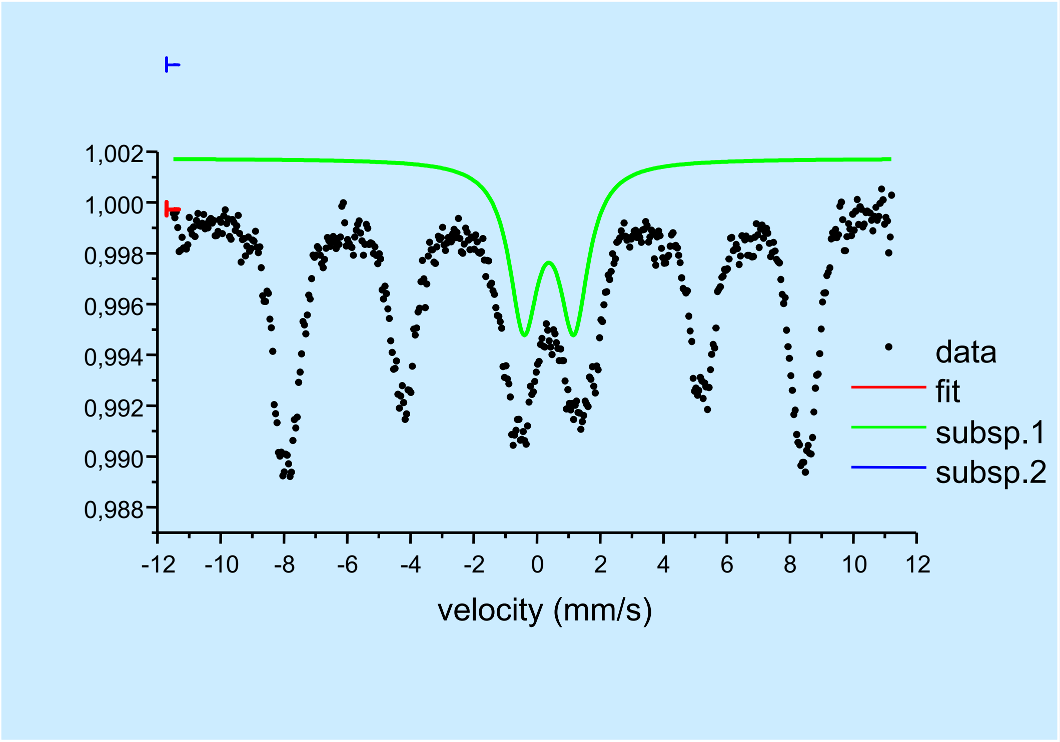


	Subsp. 1	Subsp. 2
IS δ	0.30 mm/s	0.40 mm/s
QUA ΔE_Q	0.60 mm/s	- 0.23 mm/s
BHF		50.8 T

- Clay contents hematite (α-Fe_2O_3)

Mössbauer's spectra clay „Zelec“

Sample fired at 750°C

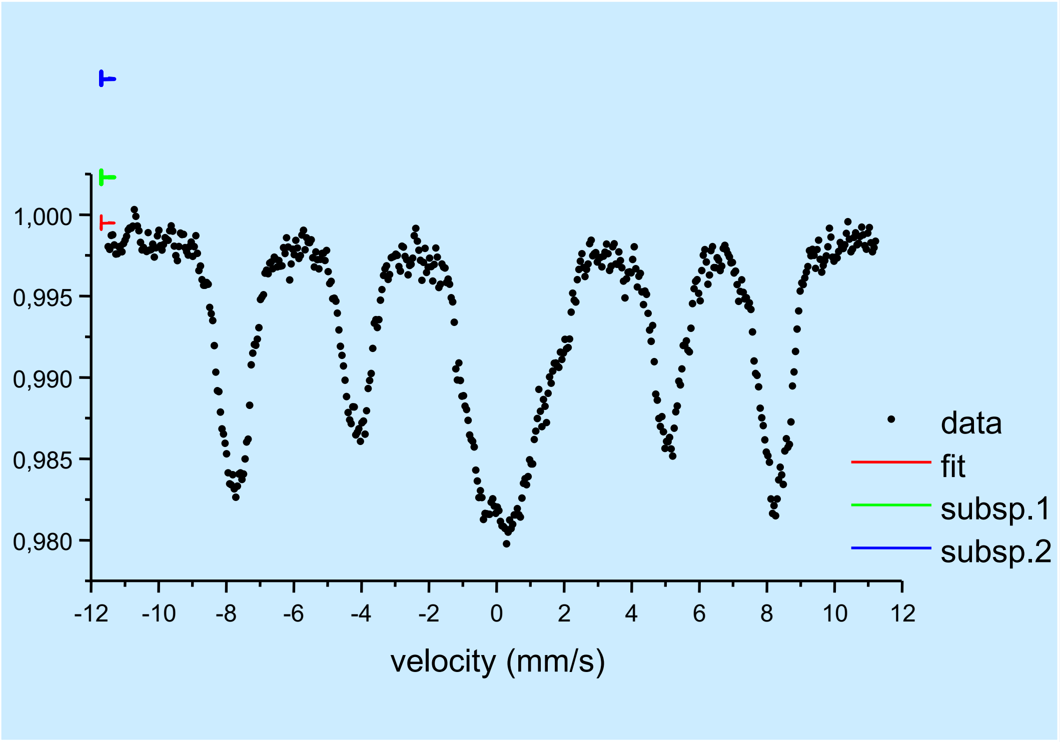


	Subsp. 1	Subsp. 2
IS δ	0,38 mm/s	0,38 mm/s
QUA ΔE_Q	1,53 mm/s	- 0,23 mm/s
BHF		50,8 T

- Hematite confirmed

Mössbauer's spectra clay „Zelec“

Sample fired at 1000°C

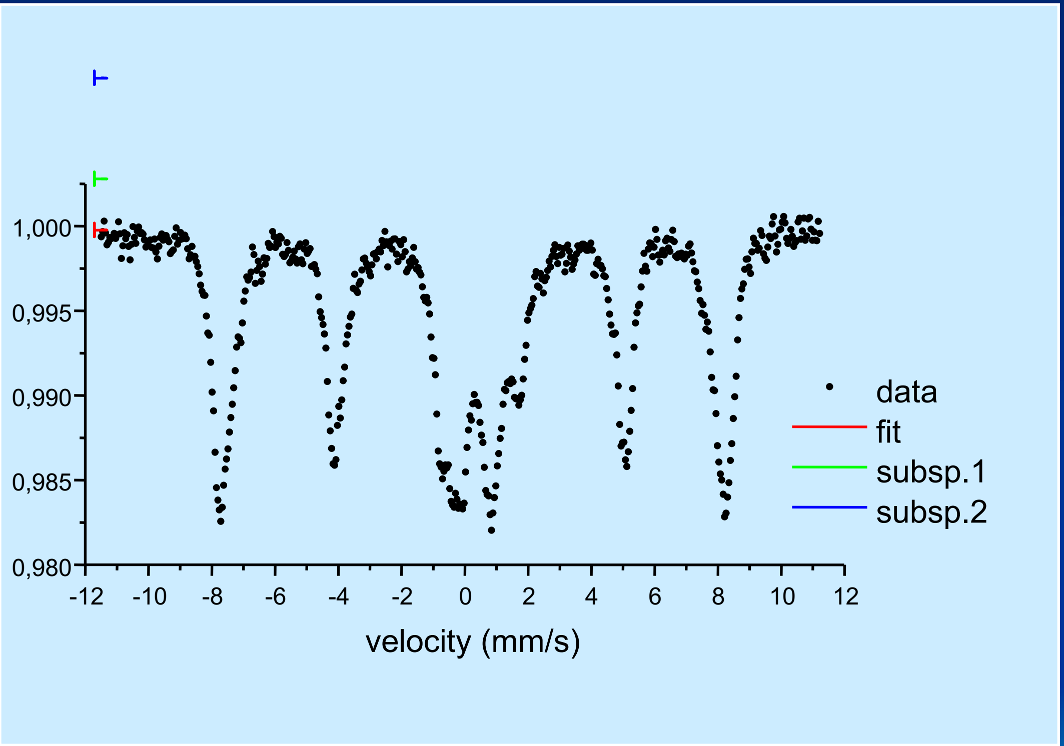


	Subsp. 1	Subsp. 2
IS δ	0.28 mm/s	0.37 mm/s
QUA ΔE_Q	0.82 mm/s	-0.23 mm/s
BHF		49.7 T

- Hematite content still confirmed

Mossbauer's spectra clay „Zelec“

Sample fired at 1180°C



	Subsp. 1	Subsp. 2
IS δ	**0.30 mm/s**	**0.37 mm/s**
QUA ΔE_Q	**1.10 mm/s**	**- 0.21 mm/s**
BHF		**49.3 T**

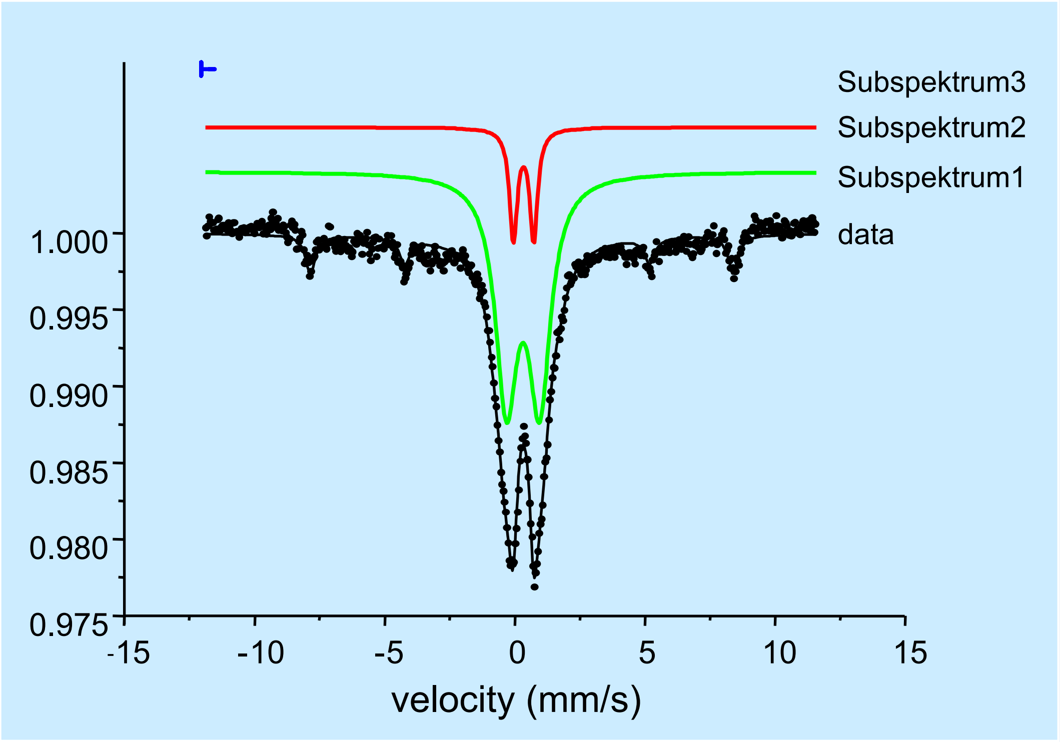
- Hematite is not dissolved in aluminosilicate matrix

The ability of kaolinite to dissolve Fe^{3+}

- Study on standard kaolin „Sedlec Ia“ used in the production of Czech porcelain.
- Fe_2O_3 content lower than 1 wt. %
- Doped by $Fe(NO_3)_3$ .9 H_2O gradually up to 5 wt. %
- Observed color changes during temperature rise:
- Presented results on samples with maximal iron content:
- 750 °C – orange/red
- 1000 °C – light skin pink
- 1180 °C – very light, practically white

The ability of kaolin to dissolve Fe^{3+} ions

Doped Kaolin sample fired at 750°C

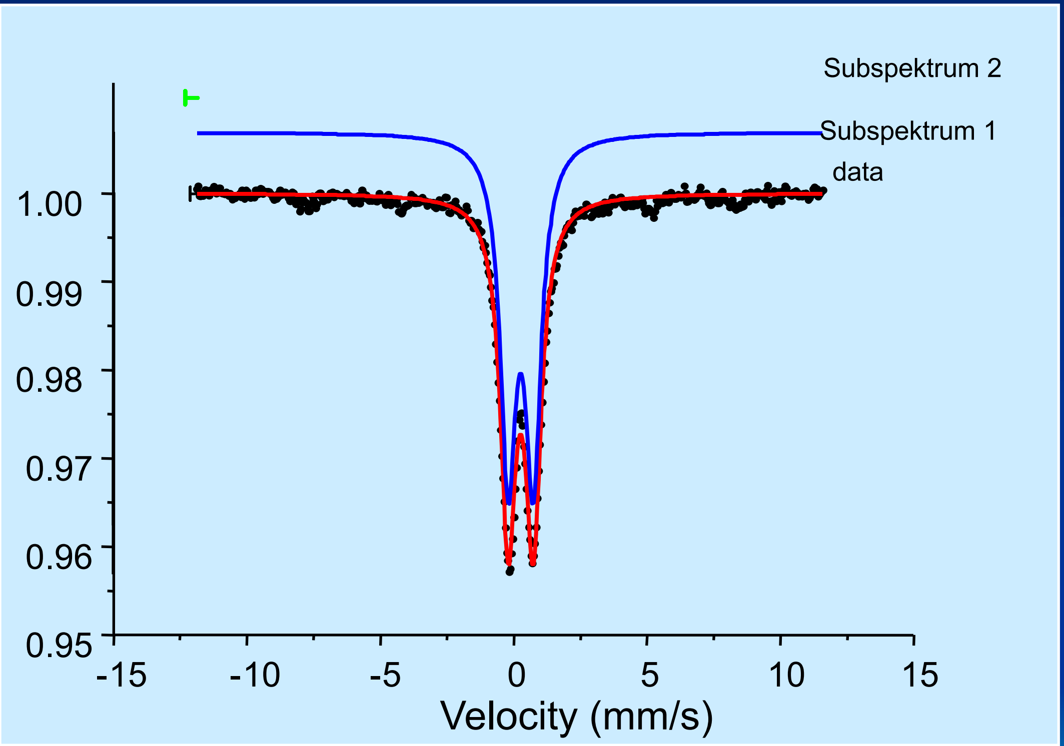


	Subsp. 1	Subsp. 2	Subsp. 3
IS δ	0.33 mm/s	0.35 mm/s	0.38 mm/s
QUA ΔE_Q	1.27 mm/s	0.78 mm/s	- 0.21 mm/s
BHF			50.5 T

- Hematite confirmed

The ability of kaolin to dissolve Fe^{3+} ions

Sample fired at 1000°C

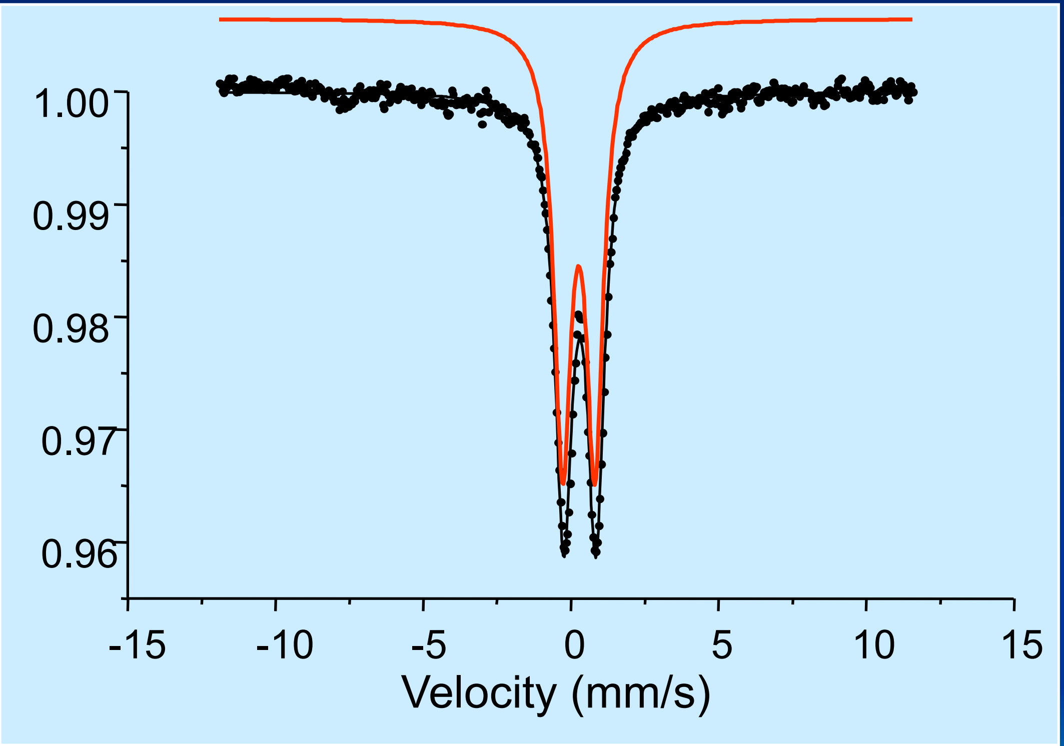


	Subsp. 1	Subsp. 2
IS δ	0.27 mm/s	0.38 mm/s
QUA ΔE_Q	0.94 mm/s	- 0.19 mm/s
BHF		50.0 T

- Hematite still occures

The ability of kaolin to dissolve Fe^{3+} ions

Sample fired at 1180°C



	Subsp
IS δ	**0.31 mm/s**
QUA ΔE_Q	**1.09 mm/s**

- Hematite completely dissolved in aluminosilicates

Conclusions

- The content of Fe^{3+} ions is not the only determination of the final color of ceramic body.
- Significant is a form of Fe^{3+} ions:

  Hematite (Fe_2O_3) always means darker colors (orange, red and brown).
- Mössbauer's spectroscopy confirms incorporation of Fe^{3+} ions in aluminosilicate matrix.
- Discoloring effect is limited by maximal amount of Fe_2O_3 in clays (5 - 6 wt. %) and temperature exceeding 1180 °C.
- Hematite originated through the firing is highly reactive due to the small and very small particles.

Thank you for your attention