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MÖSSBAUER INVESTIGATIONS OF NATURAL AND SYNTHETIC TOCHILINITE AND VALLERIITE

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The main task and objects of investigations

The main task of investigations

The investigation of structure of iron-magnesium tochilinite and valleriite; the research of magnesium relative content in the initial mixture influence on synthetic tochilinite structure.

Subjects of investigations

1. Samples obtained as a result of the tochilinite synthesis process under different conditions (temperature of synthesis and Fe/Mg ratio in the initial mixture).
2. Samples of natural tochilinite.
3. Samples of natural and synthetic valleriite.

Methods of investigations

^{57}Fe Mössbauer spectroscopy; the model fitting and extraction of hyperfine parameter distribution functions.

Conditions of tochilinite synthesis process

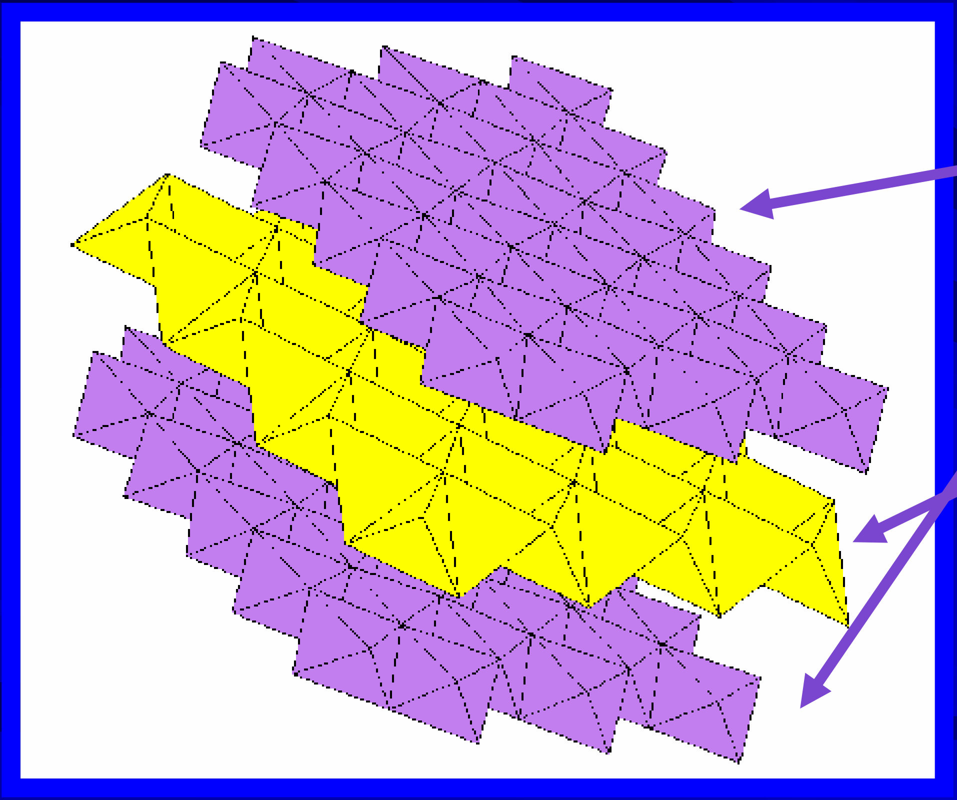
Tochilinite synthesis process was realized by interaction of Fe(II)-hydroxide with H_2S in alkaline medium at different temperatures and Fe/Mg ratio in the initial mixture.

№ series	t_s, °C	content of Fe (ν_{Fe}), mol	content of Mg (ν_{Mg}), mol	relative content of Mg (n_{Mg}), %
I	160	$15\cdot10^{-3}$	$(0.67\div4.17)\cdot10^{-3}$	4.30÷21.80
II	160	$11\cdot10^{-3}$	$(1.54\div8.23)\cdot10^{-3}$	12.3÷42.80
III	180	$15\cdot10^{-3}$	$(0.67\div3.46)\cdot10^{-3}$	2.30÷21.80
IV	180	$11\cdot10^{-3}$	$(0.50\div2.63)\cdot10^{-3}$	4.30÷22.10

Structure of tochilinite

Chemical formula: $2Fe_{1-x}S{\cdot}n(Mg,Fe,Al)(OH)_2$

$0.08 \leq x \leq 0.28$; $1.58 \leq n \leq 1.75$

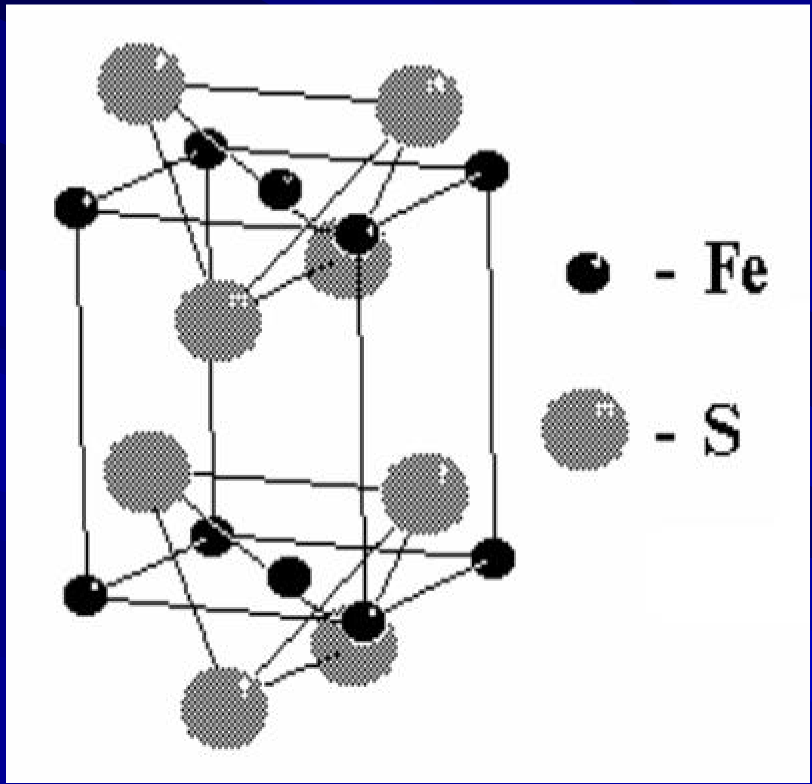


Brucite-like layers
$(Mg,Fe,Al)(OH)_2$

Sulfide layer
$Fe_{1-x}S$

C1
a_{tch} = 5.37 Å, b_{tch} = 15.60 Å,
c_{tch} = 10.72 Å

Structures of mackinawite and brucite



Mackinawite

FeS

P4/nmn, z = 2

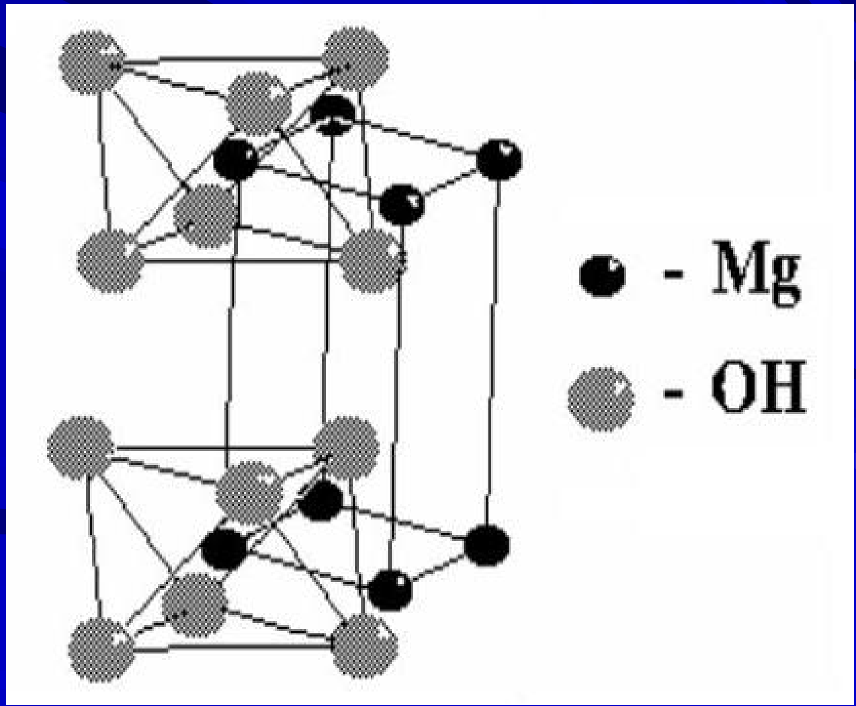
$a_m = b_m = 3.679$ Å, $c_m = 5.047$ Å

Brucite

$Mg(OH)_2$

$P\bar{3}m1$, z = 1

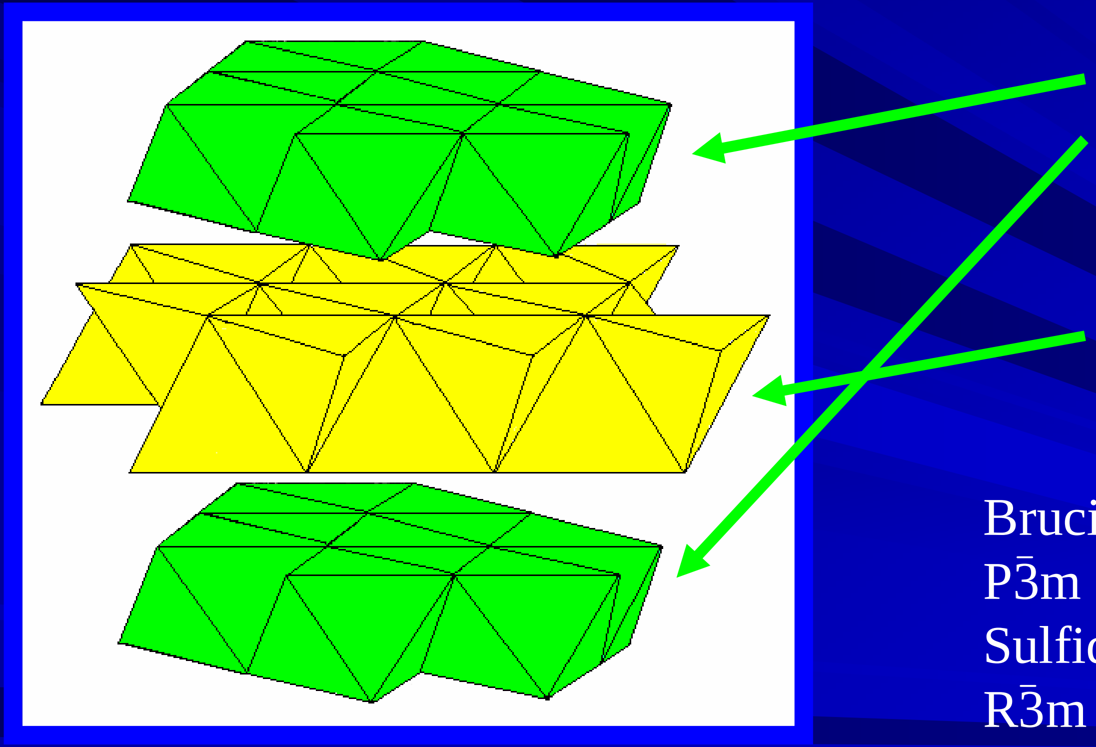
$a_{br} = b_{br} = 3.258$ Å, $c_{br} = 4.605$ Å



Structure of valleriite

Chemical formula: $CuFeS_2 \cdot \{n(Mg,Fe)(OH)_2 + m(Al,Fe)(OH)_3\}$

$1.3 \leq n \leq 1.6$; $0 \leq m \leq 0.3$

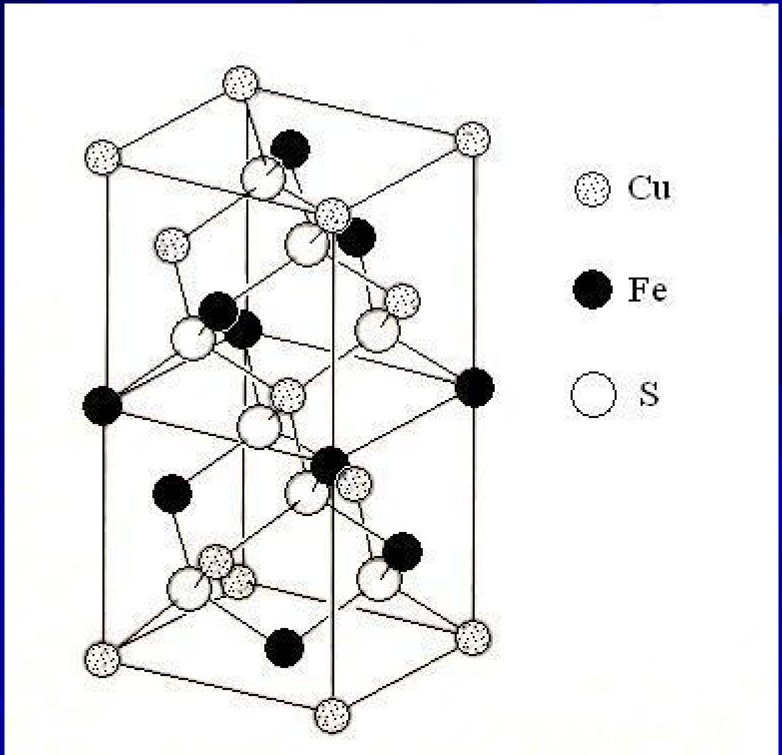


Brucite-like layers
$\{(Mg,Fe)(OH)_2 + (Al,Fe)(OH)_2\}$

Sulfide layer
$CuFeS_2$

Brucite-like layers:
$P\bar{3}m$ $a = b = 3.07$ Å, $c = 11.37$ Å
Sulfide layers:
$R\bar{3}m$ $a = b = 3.792$ Å, $c = 34.10$ Å

Structure of chalcopyrite

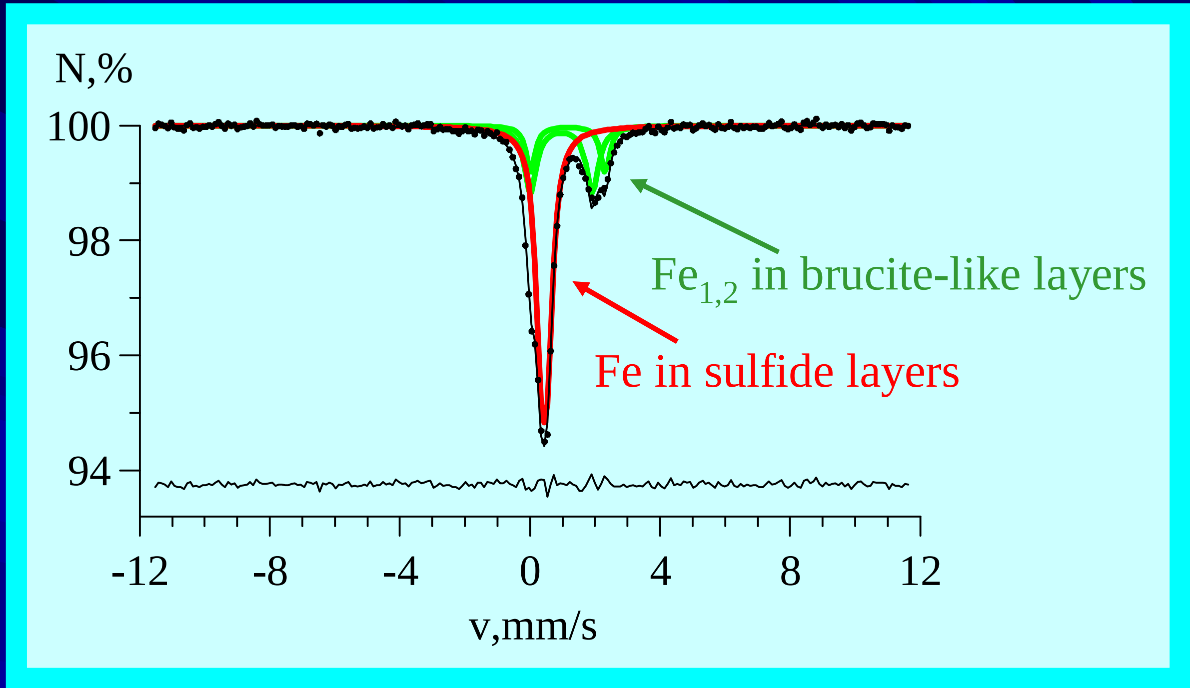


$CuFeS_2$

$I\bar{4}2d$

$a_{ch} = b_{ch} = 5.25$ Å, $c_{ch} = 10.32$ Å

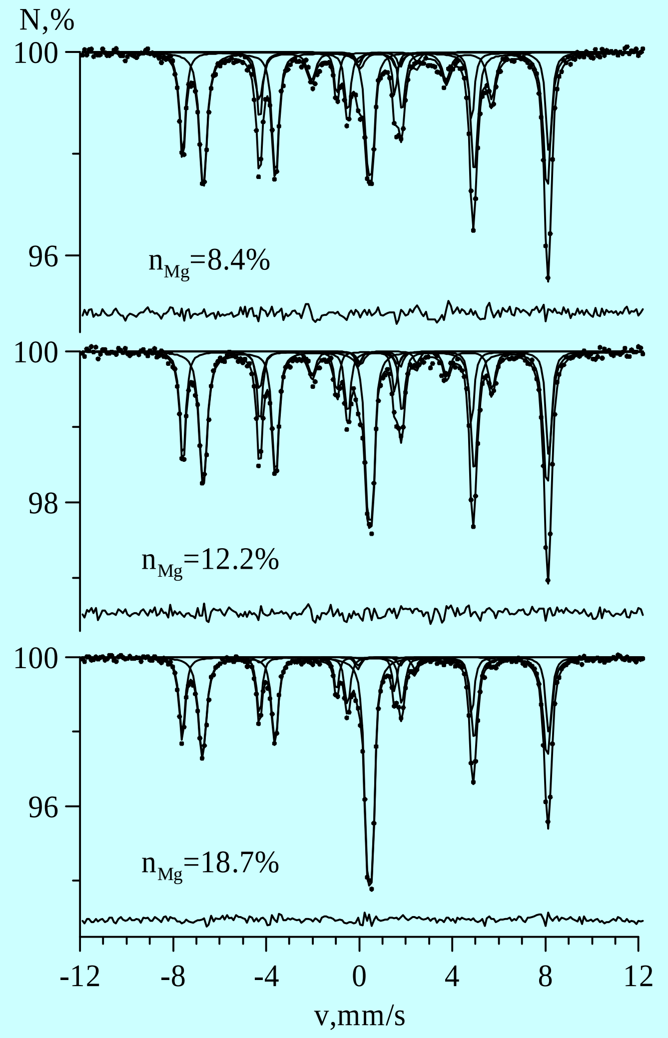
Mössbauer spectrum of synthetic tochilinite

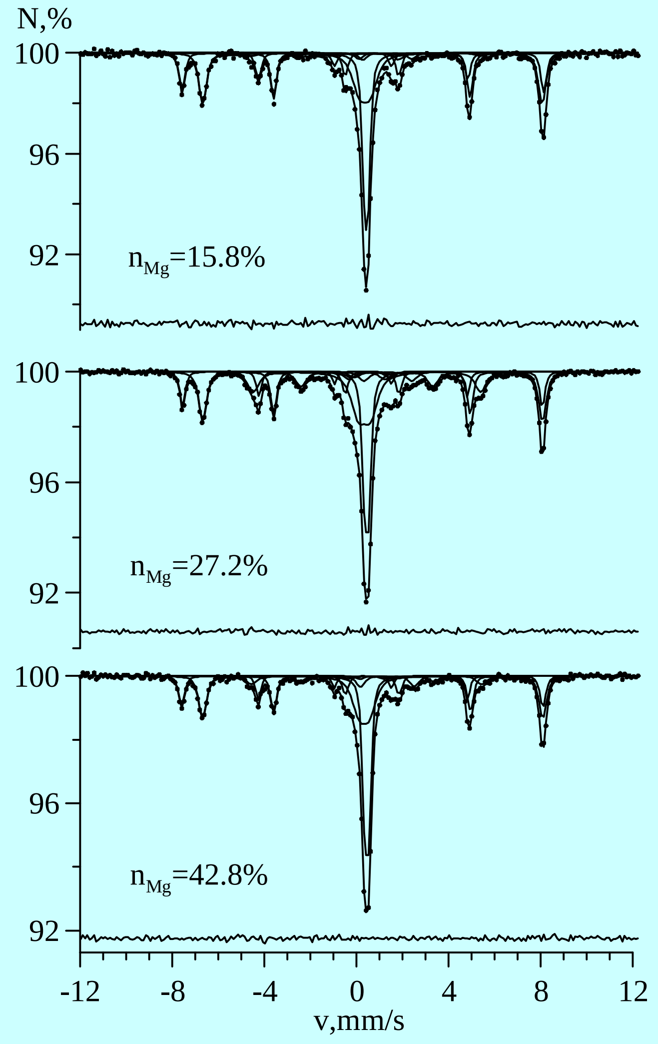


δ_s = 0.45±0.01 mm/s
ε_s = 0.08±0.01 mm/s
} sulfide layers

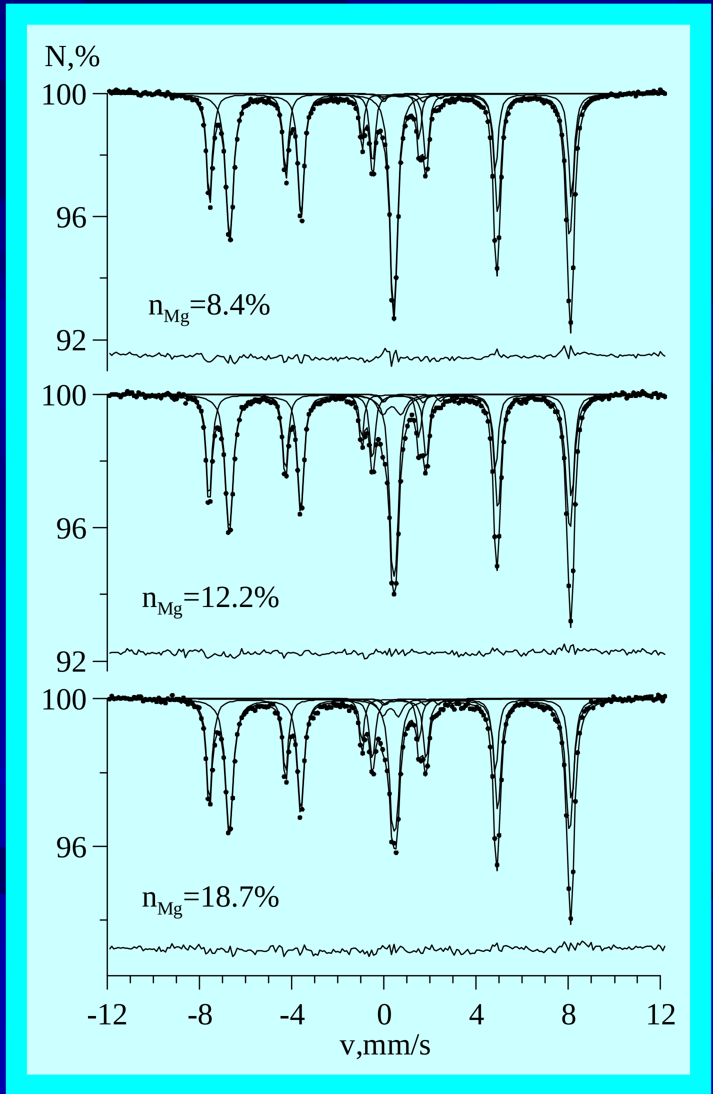
δ_{br1} = 1.12±0.01 mm/s
ε_{br1} = 1.19±0.01 mm/s
δ_{br2} = 0.87±0.02 mm/s
ε_{br2} = 0.94±0.02 mm/s
} brucite-like layers

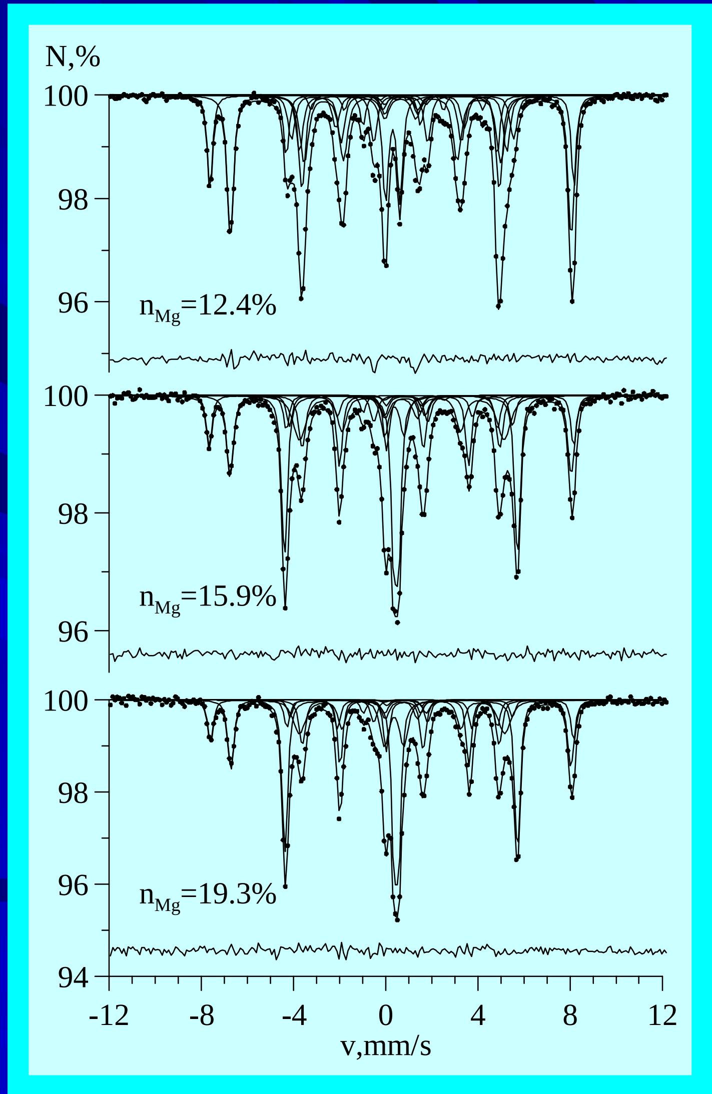
Mössbauer spectra of investigated samples of series I and II



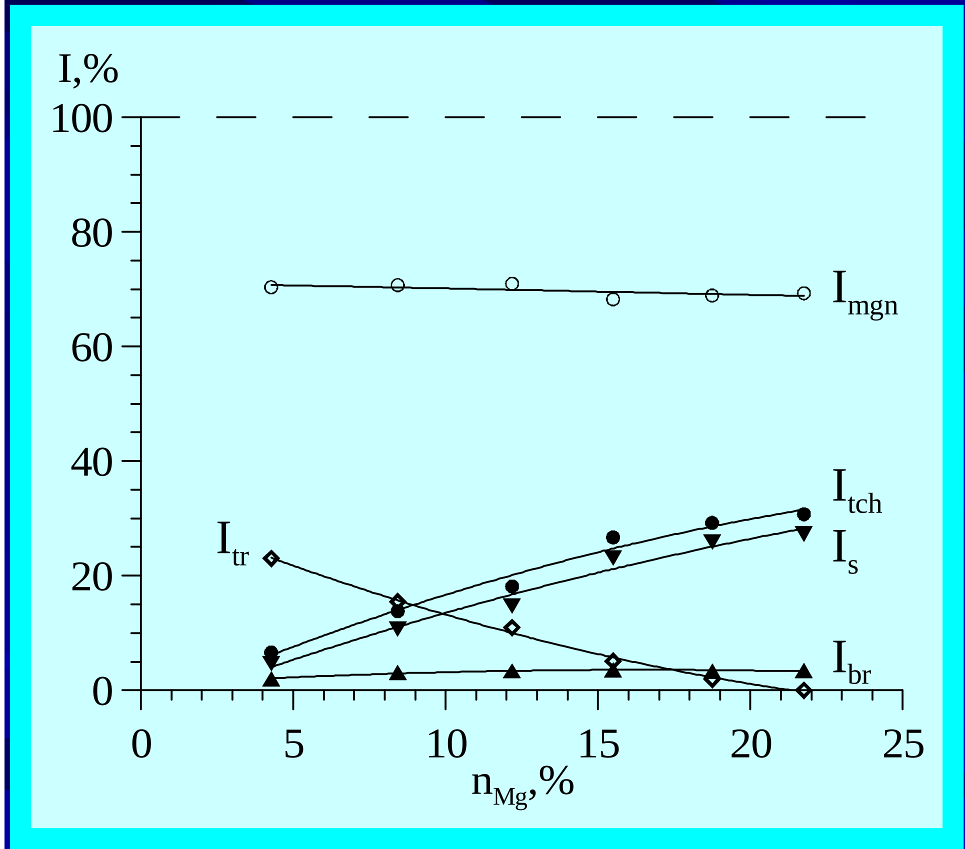


Mössbauer spectra of investigated samples of series III and IV

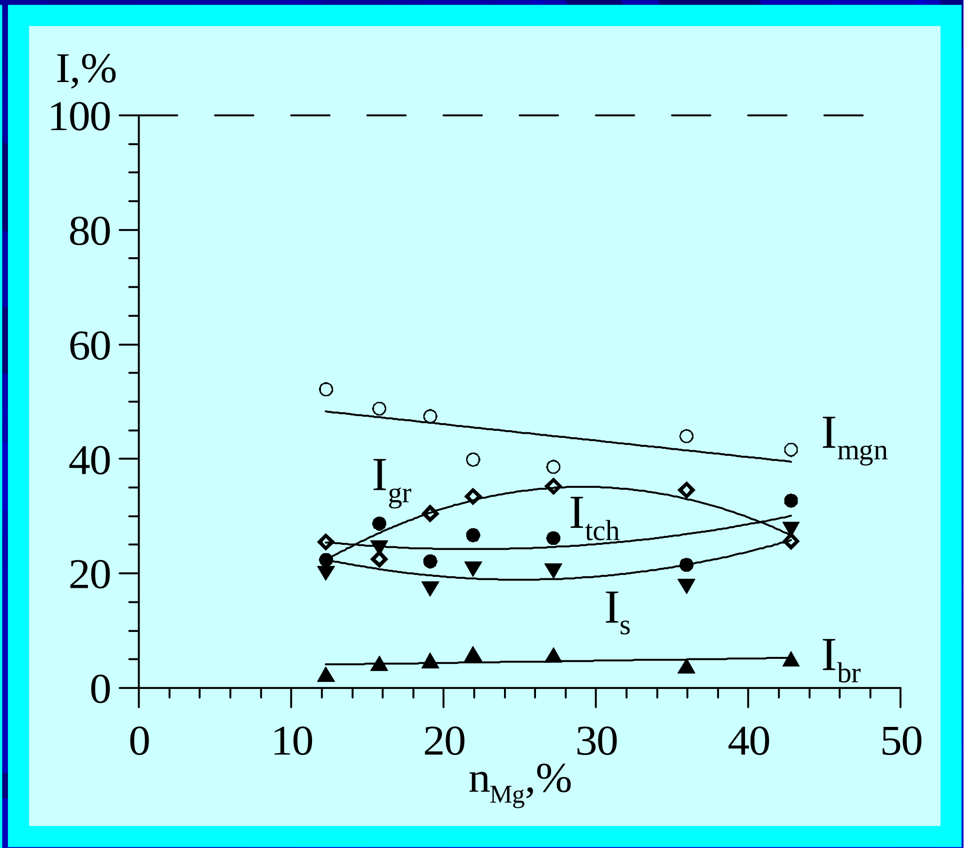




Relative intensities of ^{57}Fe nuclear subspectra of obtained phases as functions of Mg relative content in the initial mixture

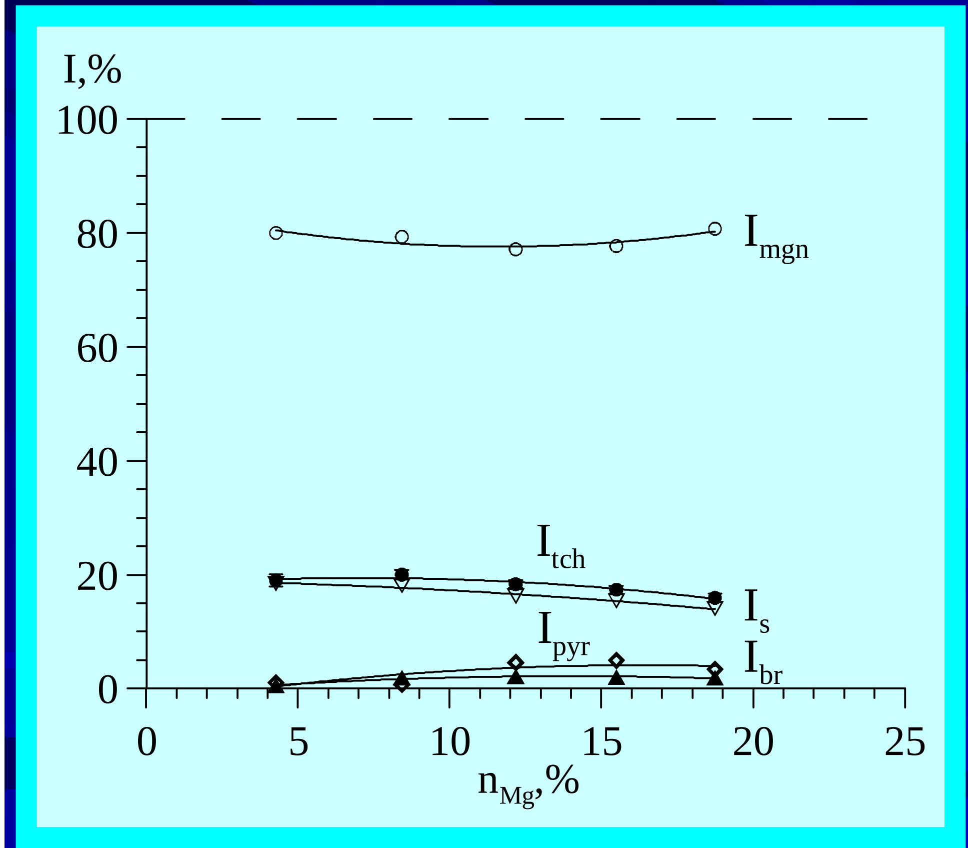


Series I

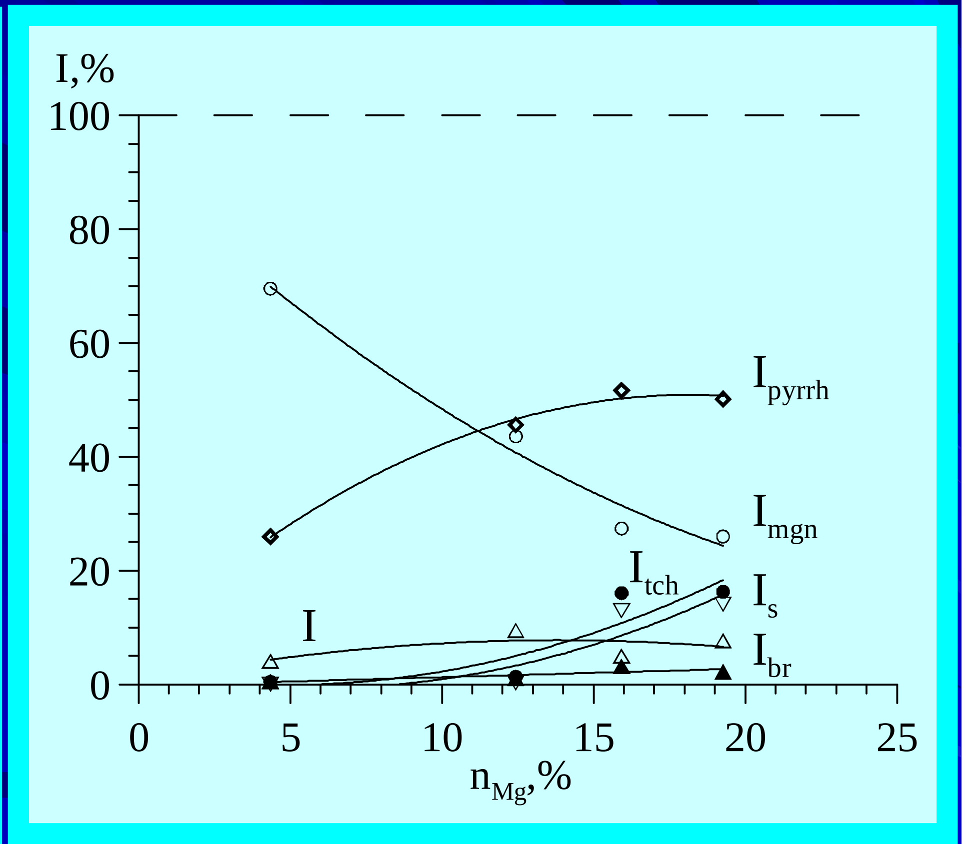


Series II

Relative intensities of ^{57}Fe nuclear subspectra of obtained phases as functions of Mg relative content in the initial mixture

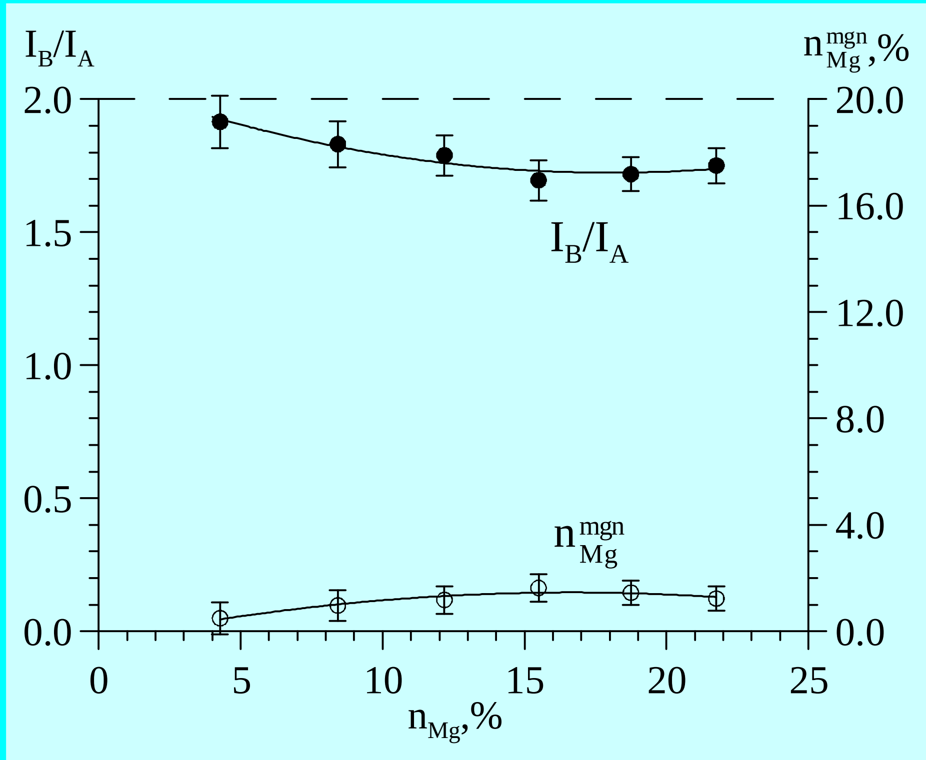


Series III

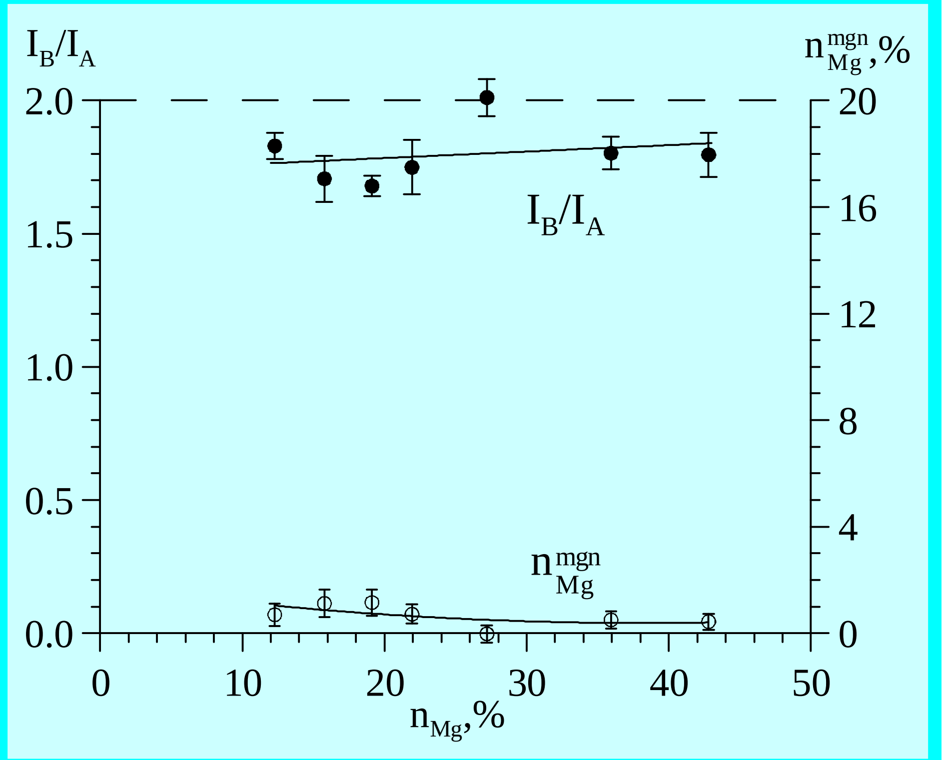


Series IV

I_B/I_A ratio of subspectrum intensities for B- and A-positions of Fe atoms in magnetite; Mg relative content in magnetite

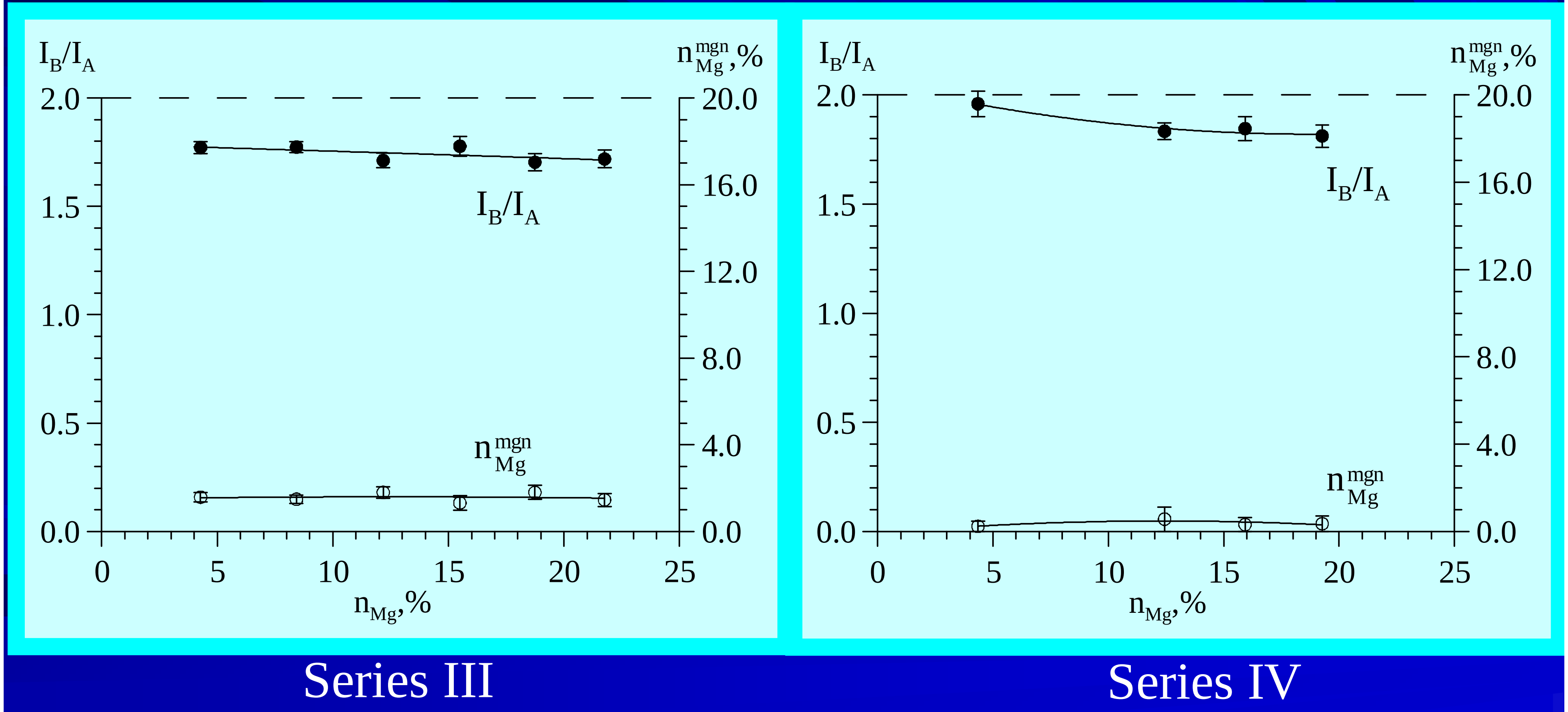


Series I

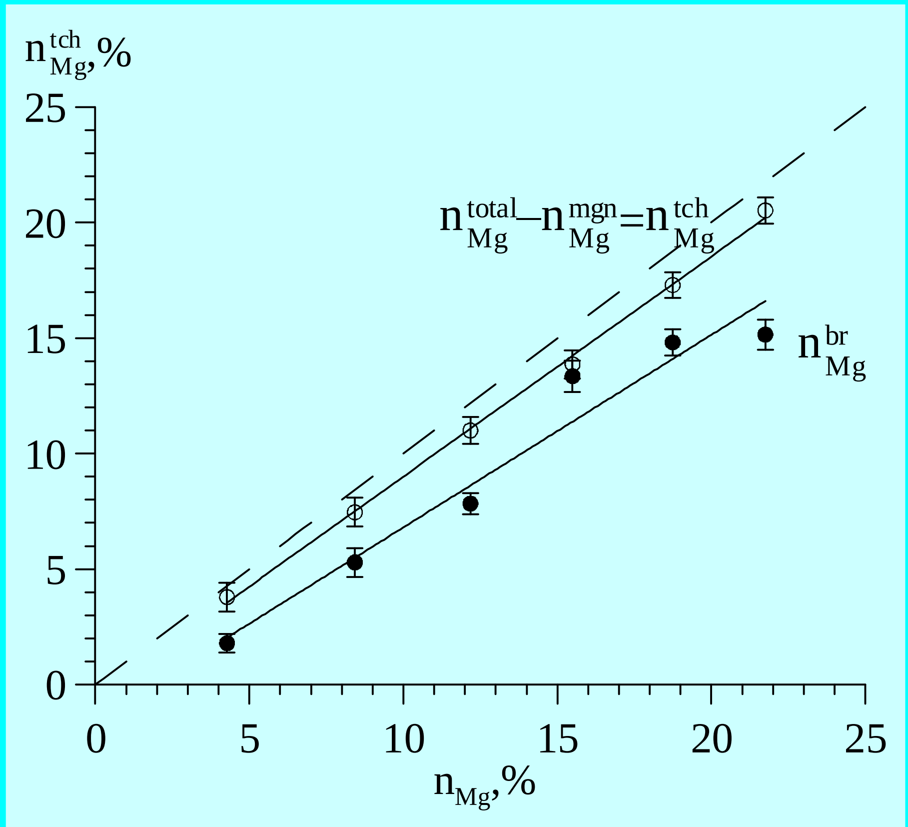


Series II

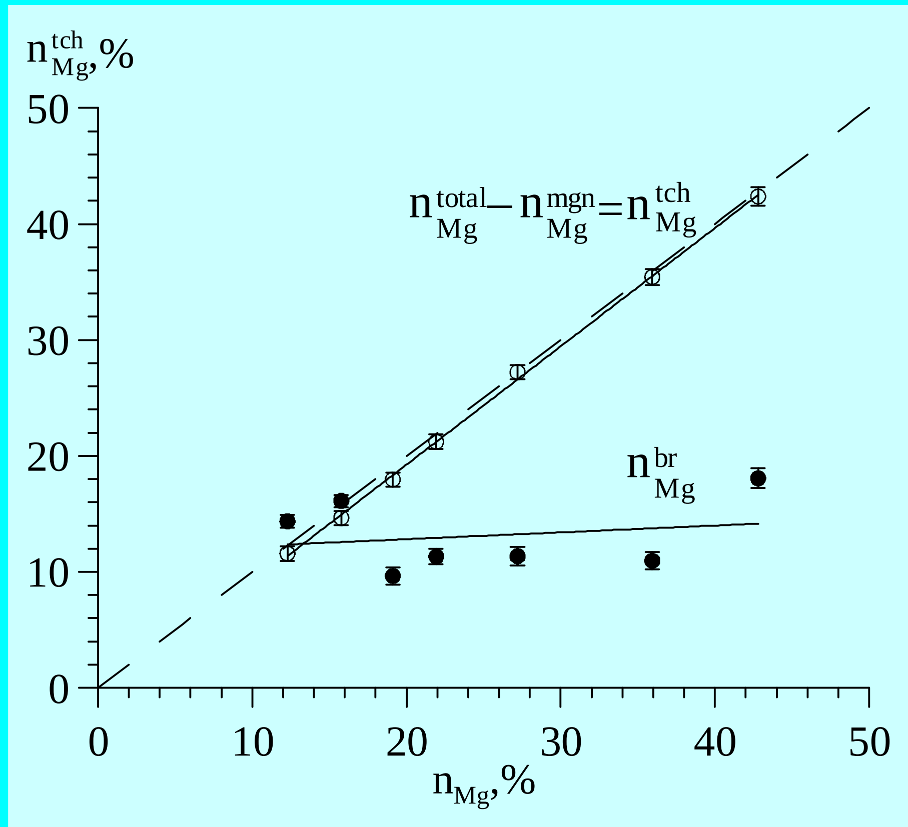
I_B/I_A ratio of subspectrum intensities for B- and A-positions of Fe atoms in magnetite; Mg relative content in magnetite



Relative contents of Mg in tochilinite as functions of Mg relative content in the initial mixture

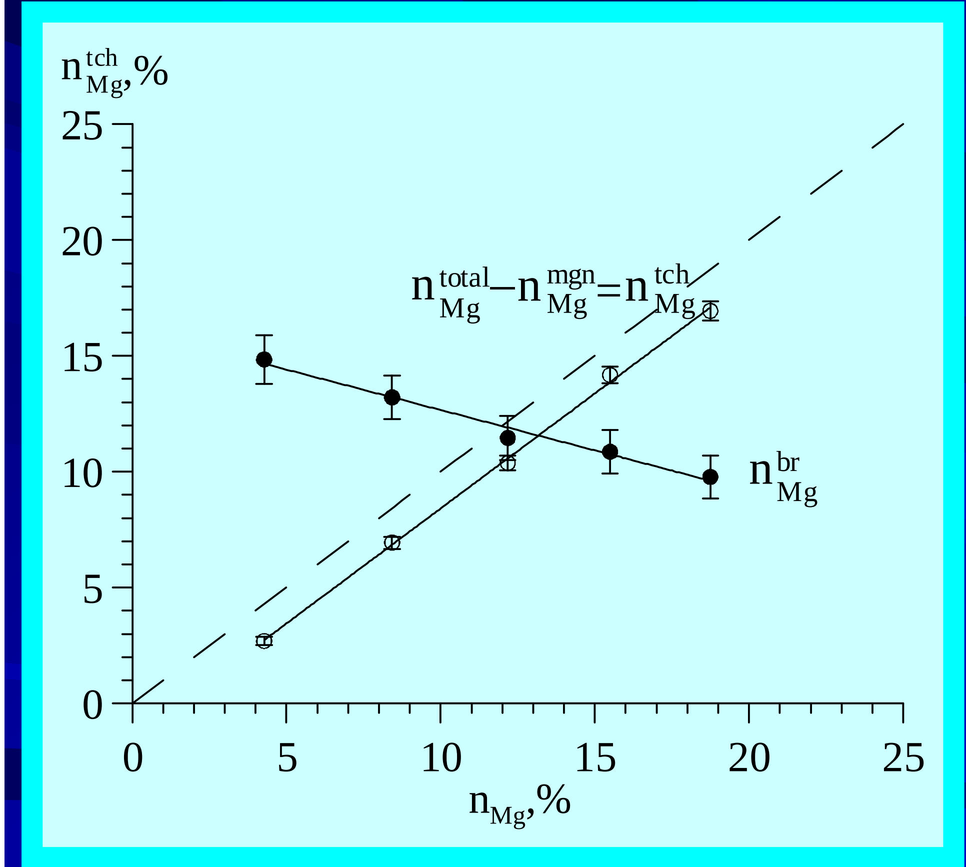


Series I

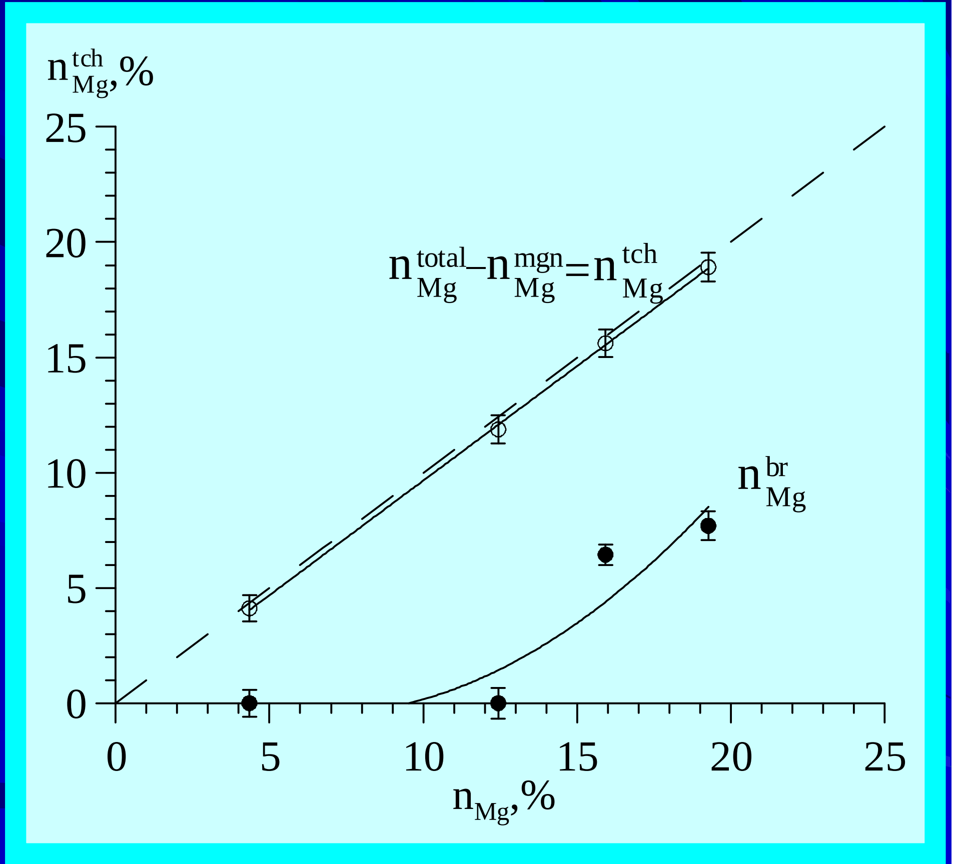


Series II

Relative contents of Mg in tochilinite as functions of Mg relative content in the initial mixture

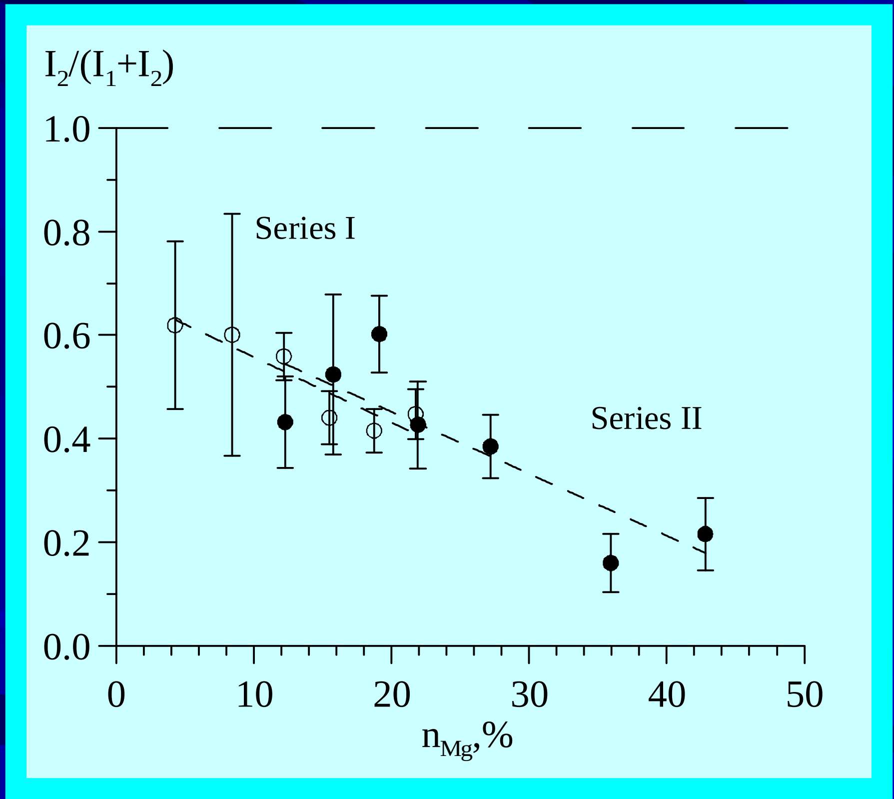


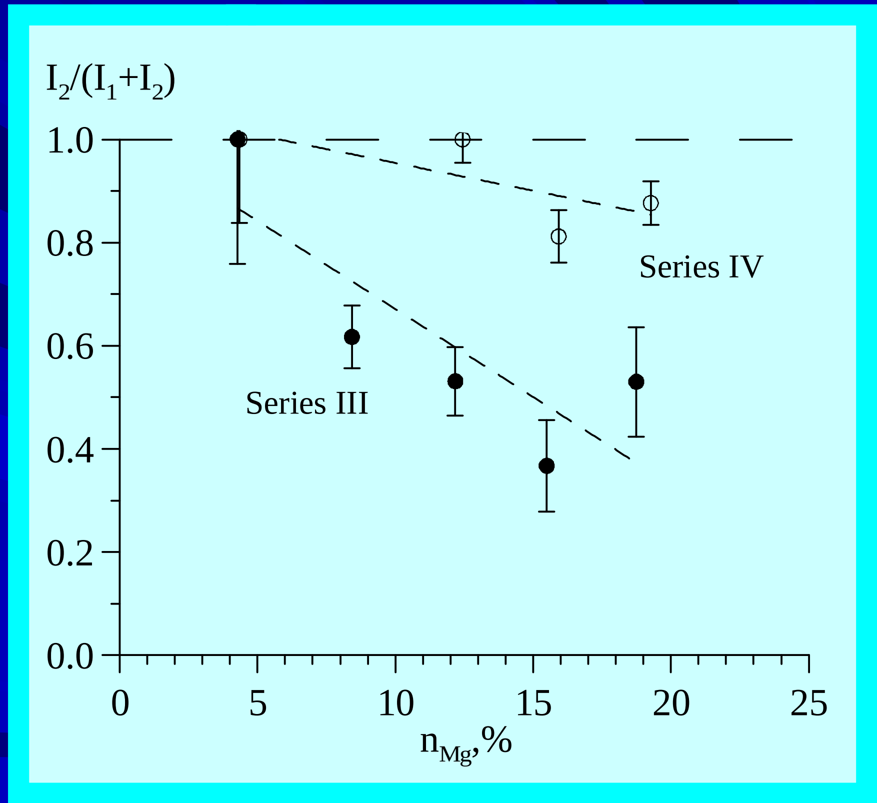
Series III



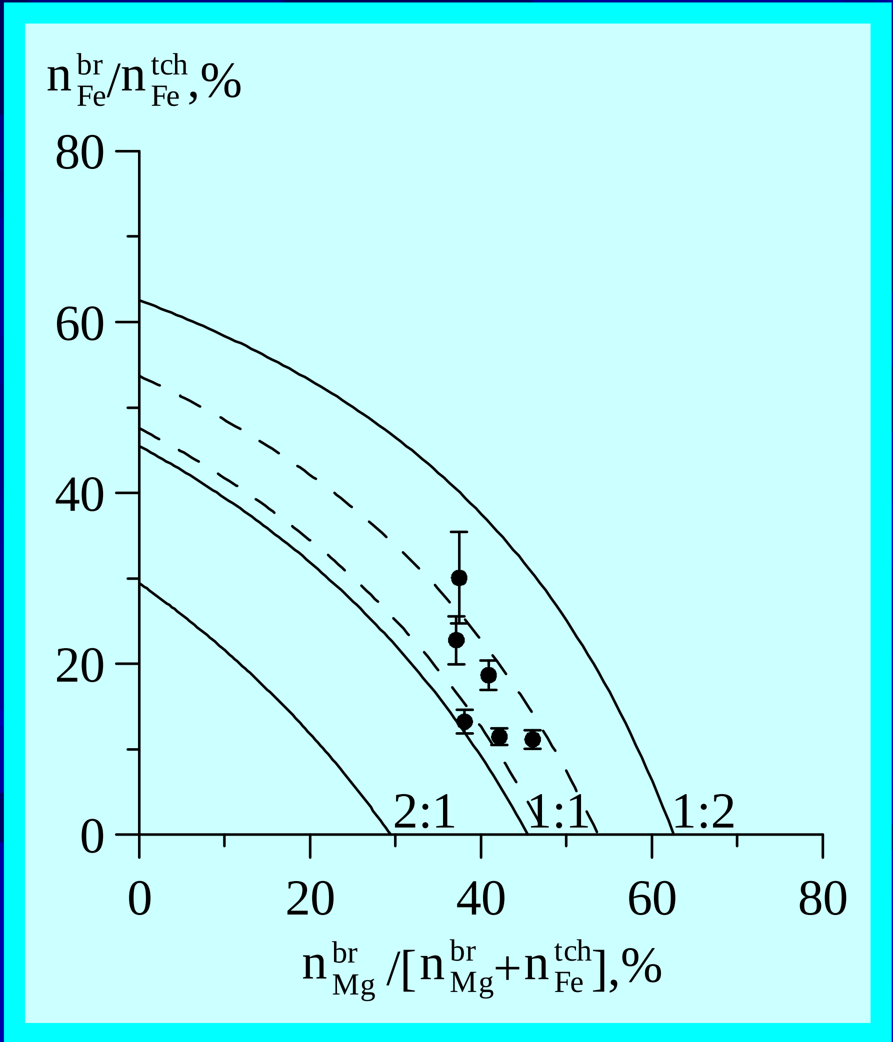
Series IV

Relative intensities of ^{57}Fe nuclear subspectra corresponding to Mg atoms positions in brucite-like layers of tochilinite





Relative content of Fe in tochilinite brucite-like layers as function of Mg relative content in tochilinite brucite-like layers



Chemical formula of tochilinite:

$$2Fe_{1-x}S\cdot 1.67k(Mg_t,Fe_{1-t})(OH)_2$$

$x = 0;\ 0.08;\ 0.28$

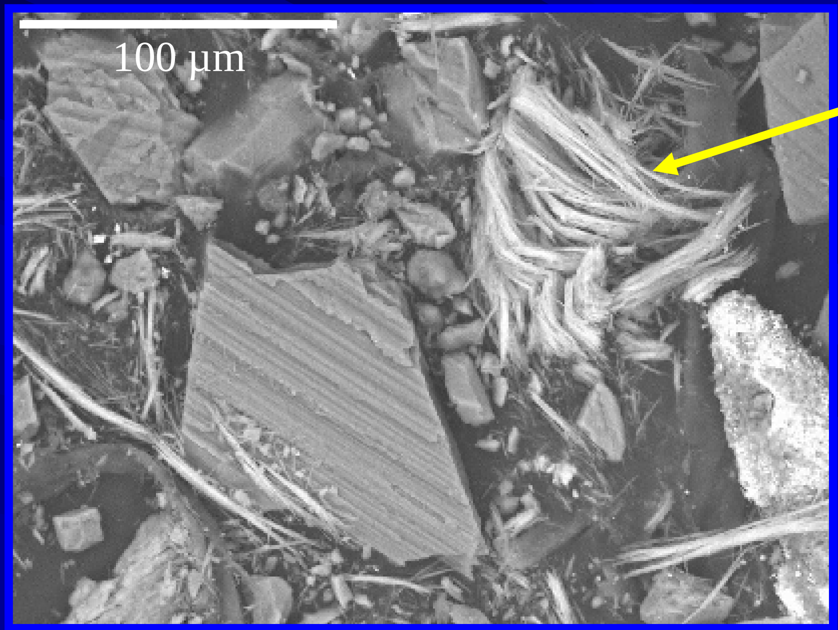
$k = 2{:}1;\ 1{:}1;\ 1{:}2$

$0 \le t \le 1$

$$\frac{n^{br}_{Mg}}{\left[n^{br}_{Mg} + n^{tch}_{Fe}\right]} = \frac{1.67\cdot k\cdot t}{\left[2\cdot(1-x)+1.67\cdot k\right]}\cdot 100\,\%$$

$$\frac{n^{br}_{Fe}}{n^{tch}_{Fe}} = \frac{1.67\cdot k\cdot (1-t)}{\left[2\cdot(1-x)+1.67\cdot k\cdot(1-t)\right]}\cdot 100\,\%$$

Pictures of samples of natural tochilinite obtained by electron-microscope methods



Tochilinite

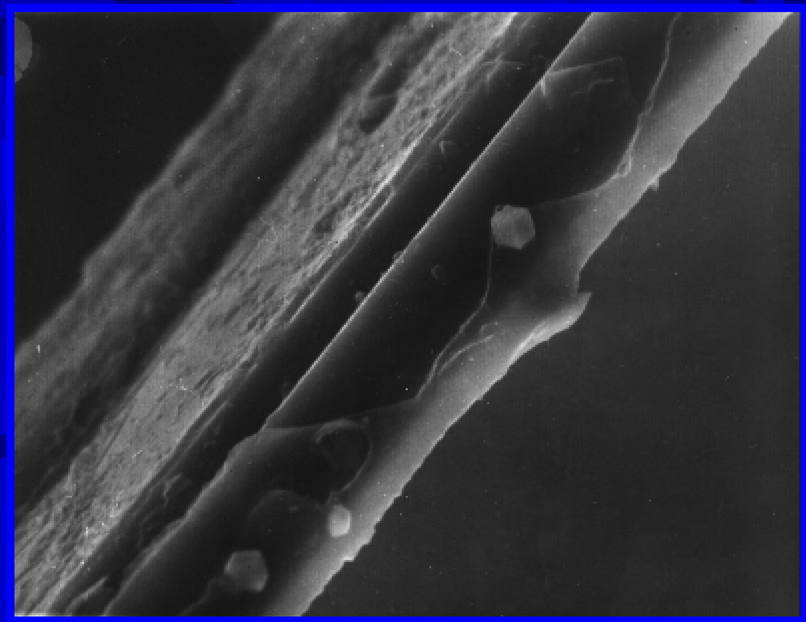
$Fe_{0.67}S \cdot (Mg_{0.75}Al_{0.25})(OH)_2$

(sample 1)

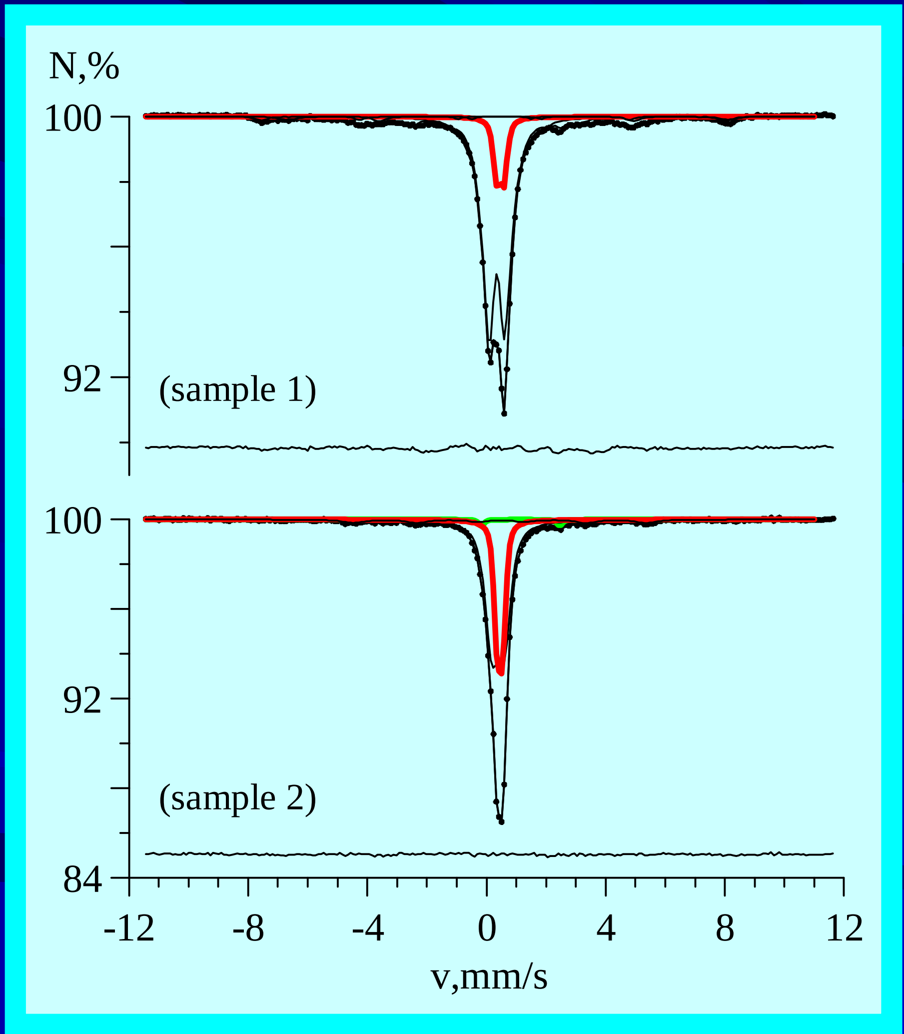
Tochilinite

$2Fe_{0.92}S \cdot 1.61(Mg_{0.81}Fe_{0.19})(OH)_2$

(sample 2, x1000)



Mössbauer spectra of natural tochilinite samples



$Fe_{0.67}S \cdot (Mg_{0.75}Al_{0.25})(OH)_2$

$\delta_s = 0.47 \pm 0.01$ mm/s

$\varepsilon_s = 0.12 \pm 0.01$ mm/s

$I_s = 11.6 \pm 1.0$ %

$2Fe_{0.92}S \cdot 1.61(Mg_{0.81}Fe_{0.19})(OH)_2$

$\delta_s = 0.45 \pm 0.01$ mm/s

$\varepsilon_s = 0.09 \pm 0.01$ mm/s

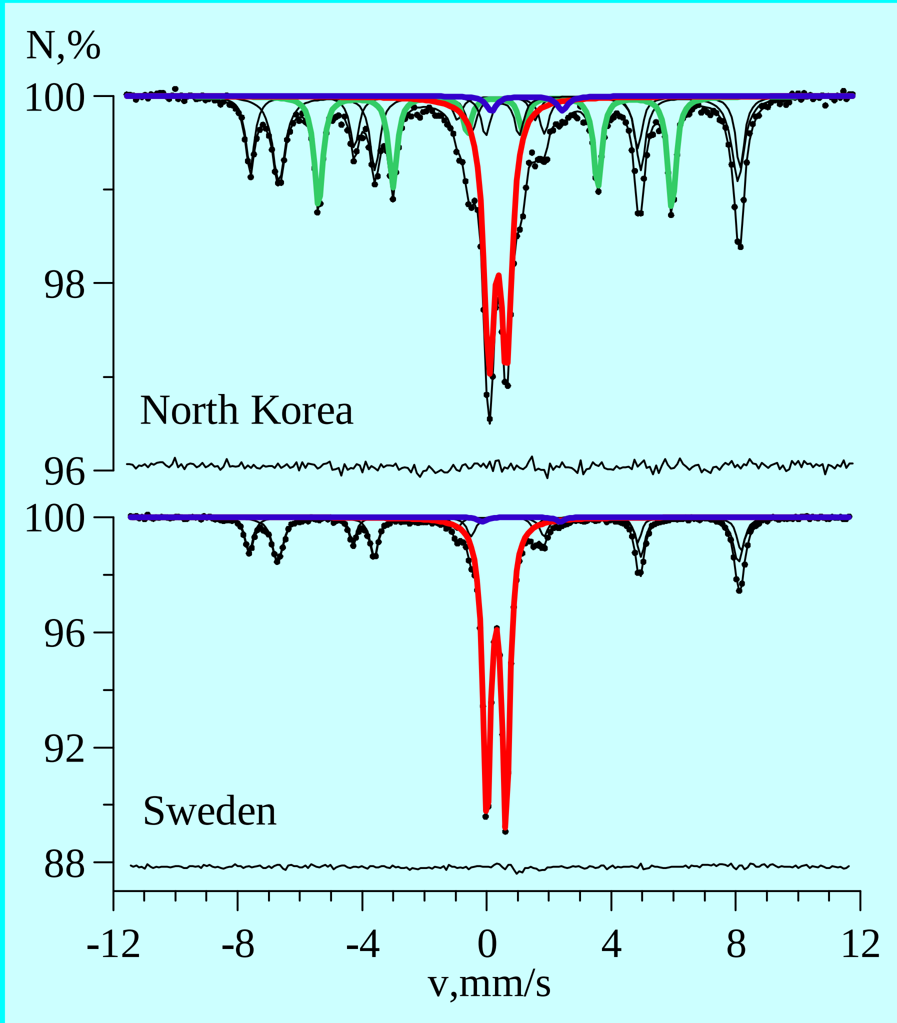
$I_s = 29.3 \pm 2.0$ %

$\delta_{br} = 1.14 \pm 0.01$ mm/s

$\varepsilon_{br} = 1.31 \pm 0.01$ mm/s

$I_{br} = 1.5 \pm 1.0$ %

Mössbauer spectra of natural valleriite samples



δ_{br} = 0.36 ± 0.01 mm/s
ε_{br} = 0.28 ± 0.01 mm/s
I_{br} = 31 ± 2 %
} Fe^{3+}– OH

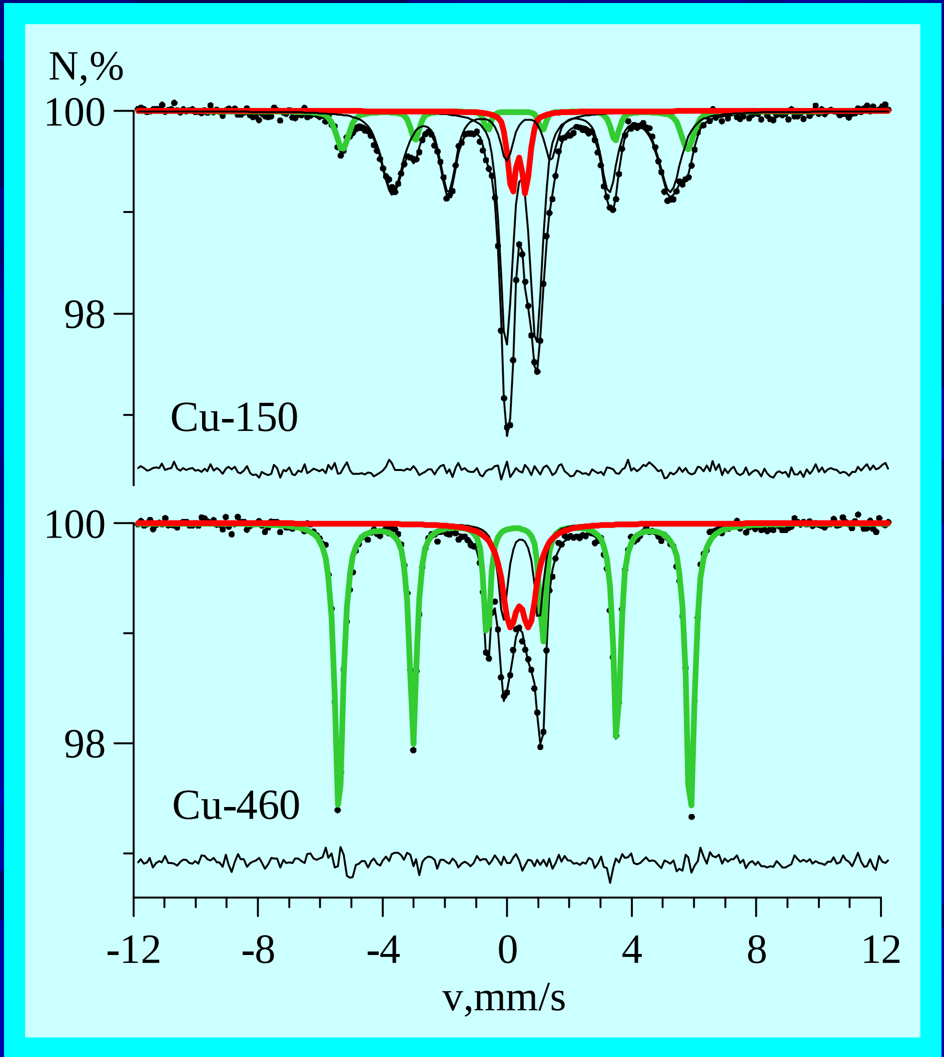
δ_{br} = 1.29 ± 0.06 mm/s
ε_{br} = 1.14 ± 0.06 mm/s
I_{br} = 2 ± 2 %
} Fe^{2+}– OH

δ = 0.17 ± 0.01 mm/s
ε = 0.00 ± 0.01 mm/s
H_n = 353 ± 1 kOe
I = 23 ± 2 %
} $CuFeS_2$

δ_{br} = 0.31 ± 0.01 mm/s
ε_{br} = 0.31 ± 0.01 mm/s
I_{br} = 59 ± 1 %
} Fe^{3+}– OH

δ_{br} = 1.10 ± 0.02 mm/s
ε_{br} = 1.25 ± 0.02 mm/s
I_{br} = 1 ± 1 %
} Fe^{2+}– OH

Mössbauer spectra of synthetic valleriite samples



δ_{br} = 0.38 ± 0.01 mm/s
ε_{br} = 0.22 ± 0.01 mm/s
I_{br} = 8 ± 2 %
} Fe^{3+}– OH

δ = 0.25 ± 0.01 mm/s
ε = 0.00 ± 0.01 mm/s
H_n = 345 ± 1 kOe
I = 11 ± 2 %
} $CuFeS_2$

δ_{br} = 0.39 ± 0.01 mm/s
ε_{br} = 0.31 ± 0.01 mm/s
I_{br} = 19 ± 2 %
} Fe^{3+}– OH

δ = 0.25 ± 0.01 mm/s
ε = 0.00 ± 0.01 mm/s
H_n = 351 ± 1 kOe
I = 68 ± 1 %
} $CuFeS_2$

Main results and conclusions

Samples of synthetic and natural iron hydroxide-sulfides: tochilinite and valleriite were investigated by Mössbauer spectroscopy methods.

Results of **tochilinite** investigations:

- Tochilinite, magnetite, troilite, greigite, pyrite and pyrrhotite were obtained in synthetic samples. Dependencies of relative content of obtained phases from Mg relative content in the initial mixture were received.
- The increase of tochilinite relative content in samples under the increase of Mg relative content in the initial mixture was observed in samples synthesized at t_s = 160°C and ν_{Fe} = 15 mmol; and in samples synthesized at t_s = 180°C and ν_{Fe} = 11 mmol in the initial mixture.
- It was shown that Mg atoms occupied one of two nonequivalent positions into brucite-like layers at entering into tochilinite structure.
- It was confirmed that in synthetic tochilinite structure equal number of sulfide and brucite-like layers conjugated.

Main results and conclusions

- The comparison of Mössbauer spectra of synthetic and natural tochilinite achieved that parameters of subspectra corresponded to sulfide and brucite-like layers in natural and synthetic tochilinite closely related.

Results of **valleriite** investigations:

- Values of hyperfine interaction parameters were determined and crystallographic identifications of ^{57}Fe nuclear subspectra was carried out.

- It was established that in brucite-like layers of synthetic vallerriite divalent Fe cations were absented in contrast to natural valleriite.