Structure of Fe-species in Fe-ferrierite

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Zeolites

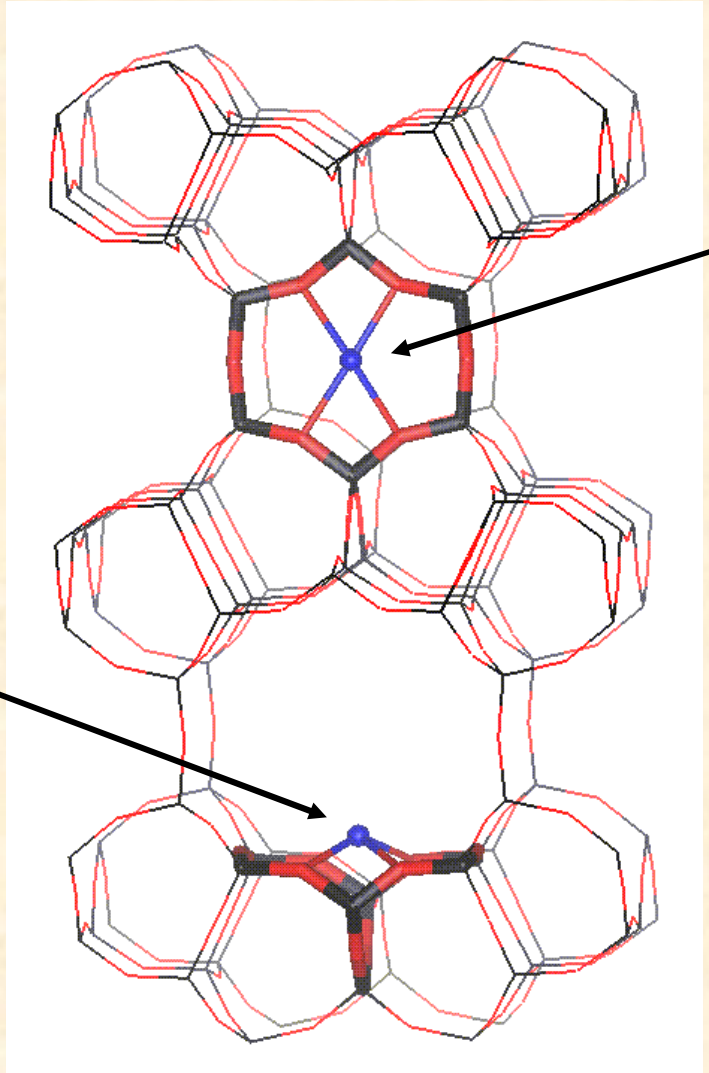
- $(Si^{IV}_2O_4) \rightarrow (Si_{2-x}Al^{III}_xO_4)M^{II}_{x/2}$

$(M^n_{2/n}\, Al_2O_4)x\ (SiO_2)y\ H_2O$

- vast internal surface

- catalytic reactions
(NO_x reduction to Nitrogen)

Fe- ferrierite



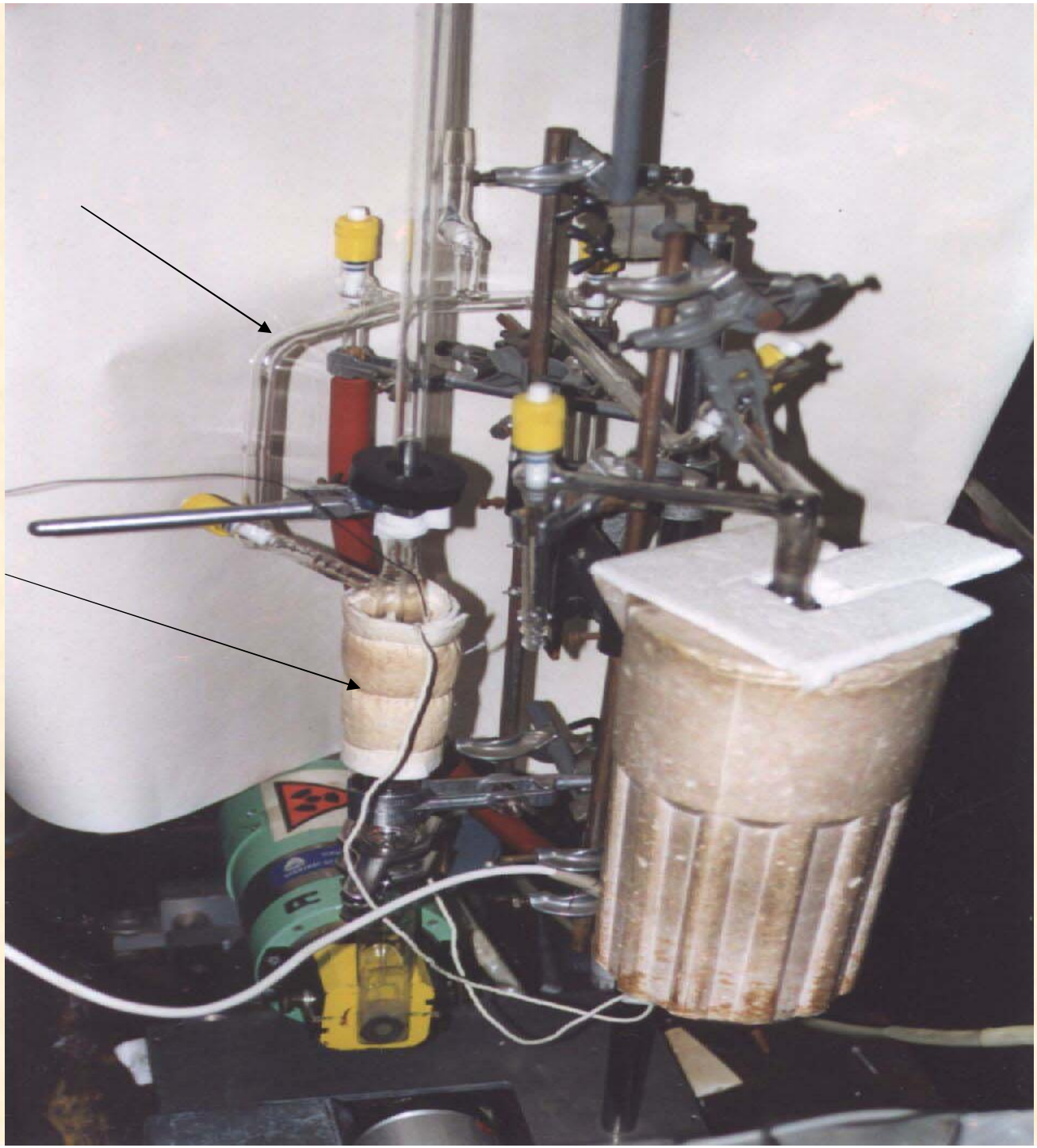
Fe cations in ferrierite

~7wt % of Fe
Si/Al ~ 8.5

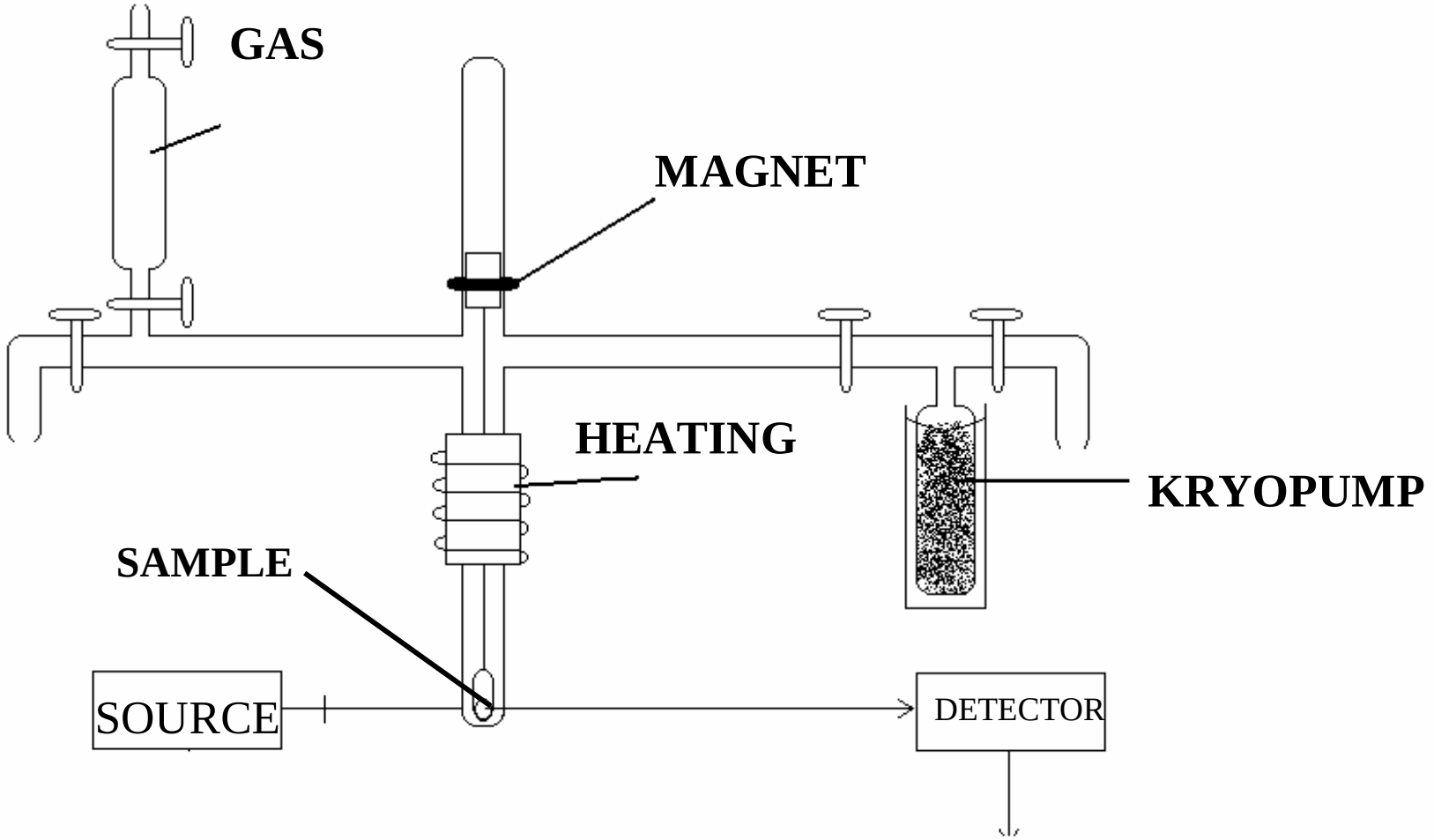
Measurements

- In sito measurements
- 57C source in Rh matrix.
  Calibration with α-Fe.
- measurements on Fe^{57} enriched samples
- The aim is to distinguish different Fe-forms (valence; position).

I N S I T O



APPARATUS FOR MÖSSBAUER SPECTROSCOPY



States of measurement

1) **fresh sample**: measured in air at room temperature
2) **dehydration**: measured at room temperature in vacuum
   -evacuated at 450^{o}C for 3 hours.
3) **oxidation with O_2**: measured at RT in vacuum
   - evacuated at 450^{o}C for 3 hours.
   - oxygen (p=100 Torr) infused.
   - sample kept in an environment of O_2 at **450^{o}C for 30 min**.
4) **oxidation by N_2O**:measured at room temperature in vacuum
   - evacuated at 450^{o}C for 3 hours.
   - N_2O (p = 100 Torr) was infused.
   - sample kept in an environment of N_2O at **250^{o}C for 30 min**.
5) **oxidation by O_2 + re-oxidation by N_2O**: … RT+vacuum
   - environment of oxygen at **450^{o}C for 30 min**.
   - environment of N_2O at **250^{o}C for 30 min**.

Fitting

We decomposed all spectra in a **common set of 6 sub-spectra**.

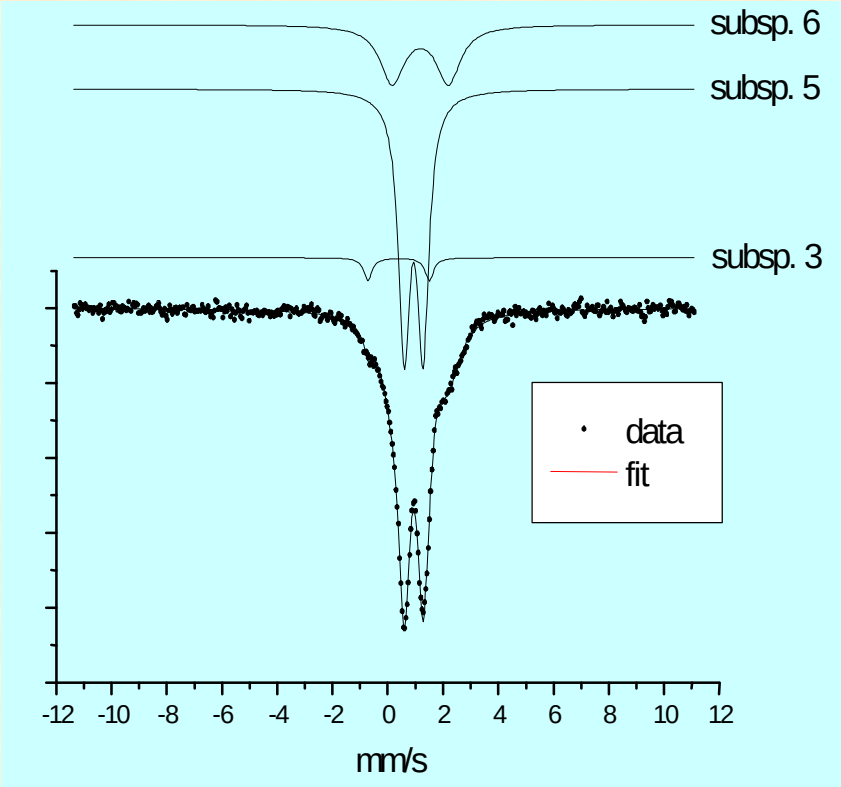
Our aim was to assign each sub-spectrum to
a **position** of iron in the sample
and the iron **valence**.

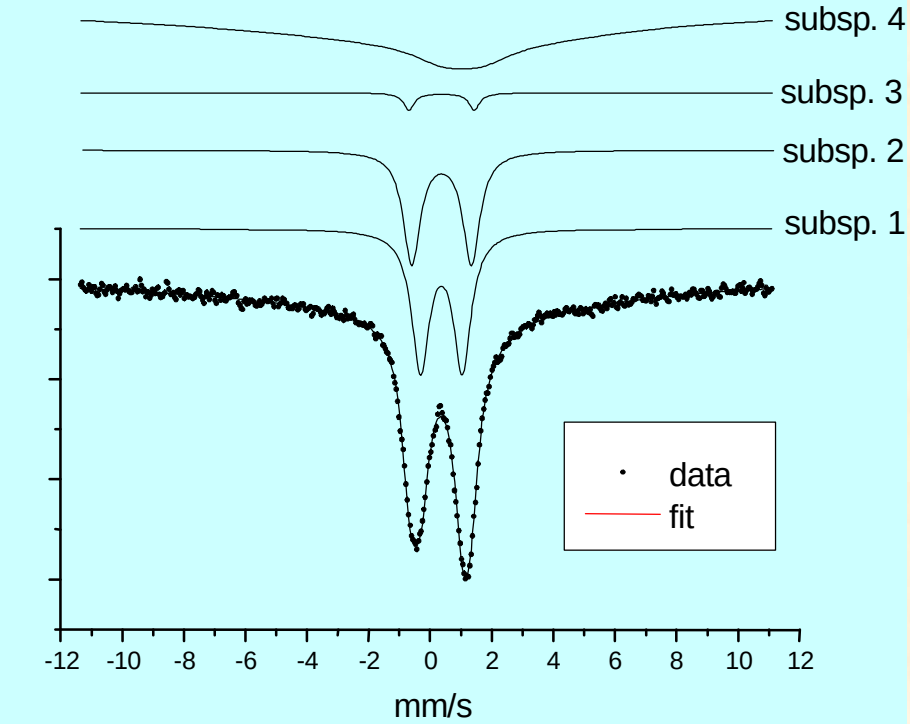
To approach this aim we used:
Mössbauer parameters and
comparison of intensities in different measurements.

Fe-ferrierite - Subspectra

	assignment	ISshift δ (mm/s)	Quadrupole splitting ΔE_Q (mm/s)	
1	Fe (3+) cationic site	0,36	1,4	
2	Fe (3+) cationic site	0,32	1,9	
3	Fe (3+) - framework	0,40	2,2	
4	Sextet-Magnetically ordered iron or iron pairs			
5	Fe (2+) - cationic site	0,9	0,7	
6	Fe (2+) - cationic site	1,2	2,0	

Fe-ferrierite after dehydration and after oxidation by O2 and reoxydation by N2O

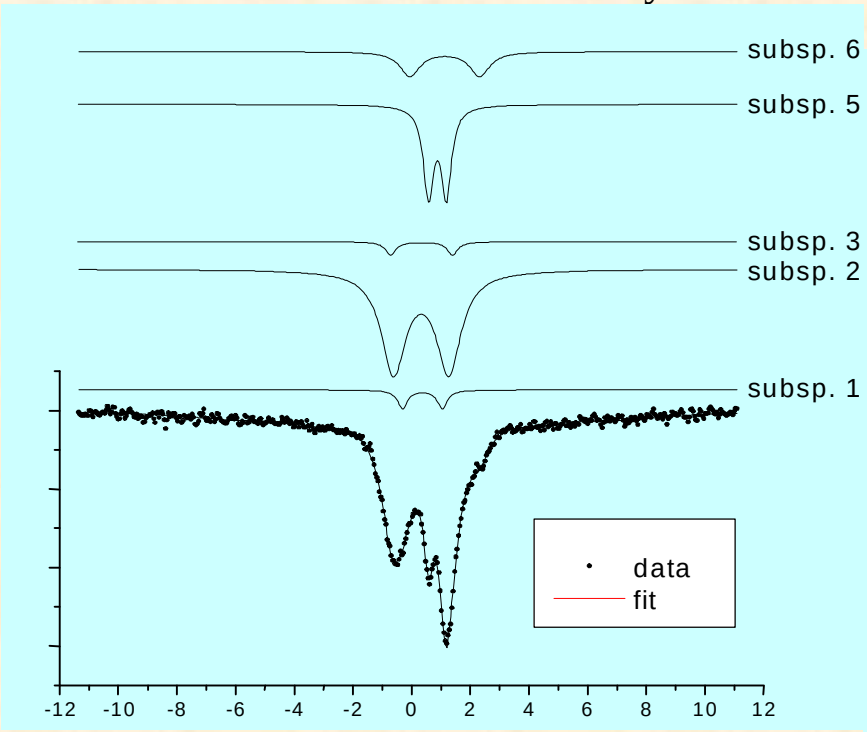


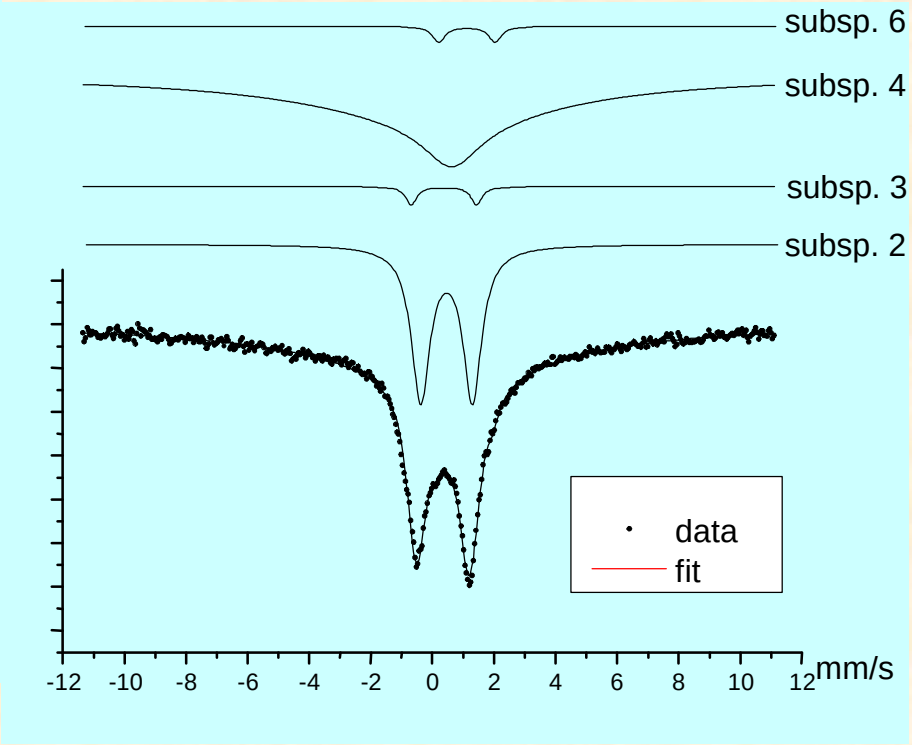


T6	δ (mm/s)	ΔE_Q mm/s)	area (%)
1			
2			
3	**0,40**	**2,23**	**4,2**
4			
5	**0,94**	**0,69**	**64,7**
6	**1,18**	**2,04**	**31,0**

T9	Δ (mm/s)	ΔE_Q mm/s)	B (T)	area (%)
1	**0,37**	**1,35**		**22,3**
2	**0,31**	**1,93**		**17,4**
3	**0,37**	**2,12**		**1,7**
4	**0,15**	**-1,77**	**24,7**	**58,7**
5				
6				

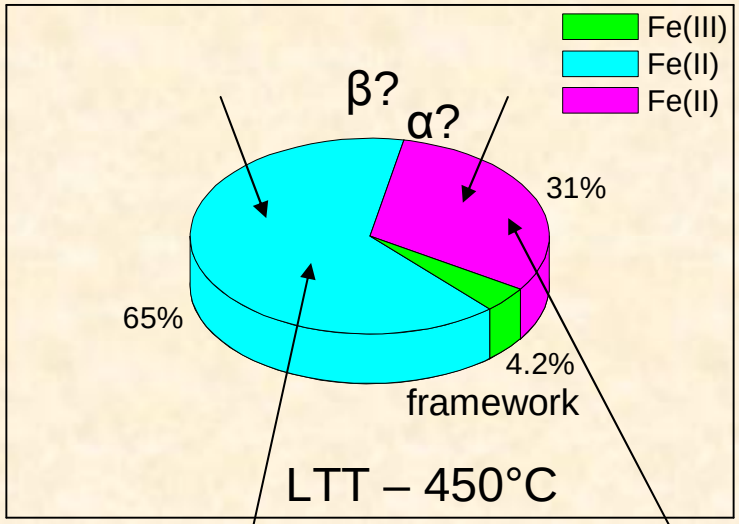
Fe-ferrierite after oxidation by O2 and after oxidation by N2O

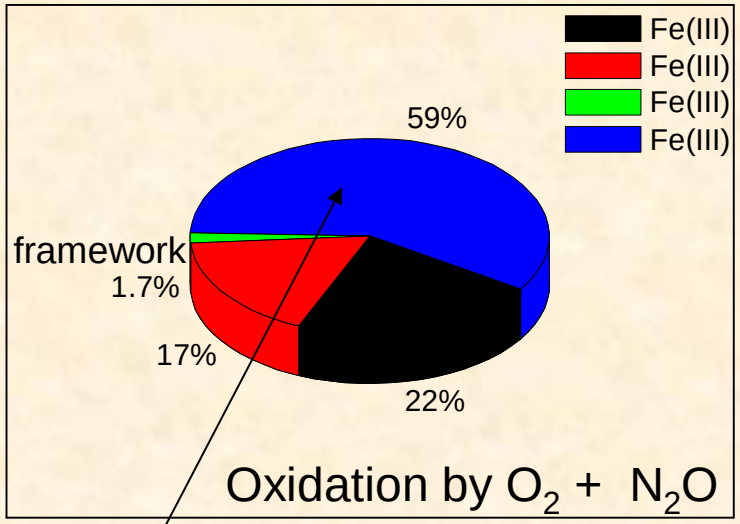




T7	δ (mm/s)	ΔE_Q mm/s)		area (%)
1	**0,36**	**1,35**		**4,2**
2	**0,32**	**1,88**		**59,3**
3	**0,37**	**2,12**		**3,3**
4				
5	**0,89**	**0,61**		**21,5**
6	**1,13**	**2,38**		**11,5**

T8	Δ (mm/s)	ΔE_Q (mm/s)		area (%)
1				
2	**0,35**	**1,67**		**27,2**
3	**0,37**	**2,12**		**1,9**
4	**0,25**	**-0,77**	**0,11**	**69,1**
5				
6	**1,06**	**1,82**		**1,9**

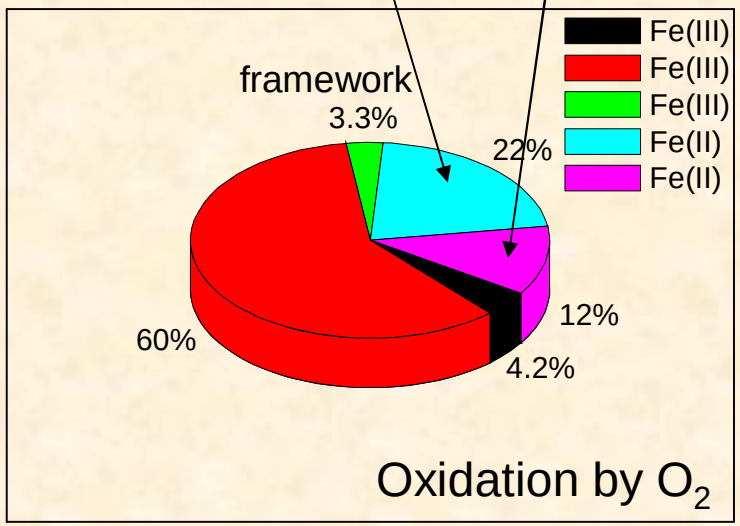


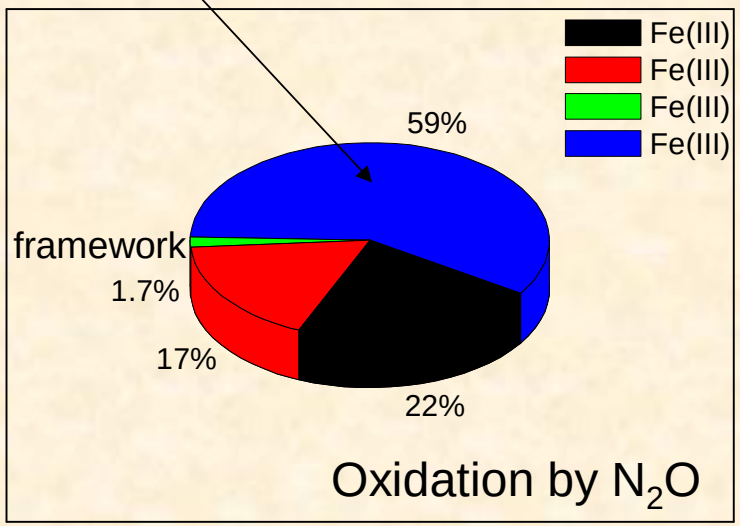


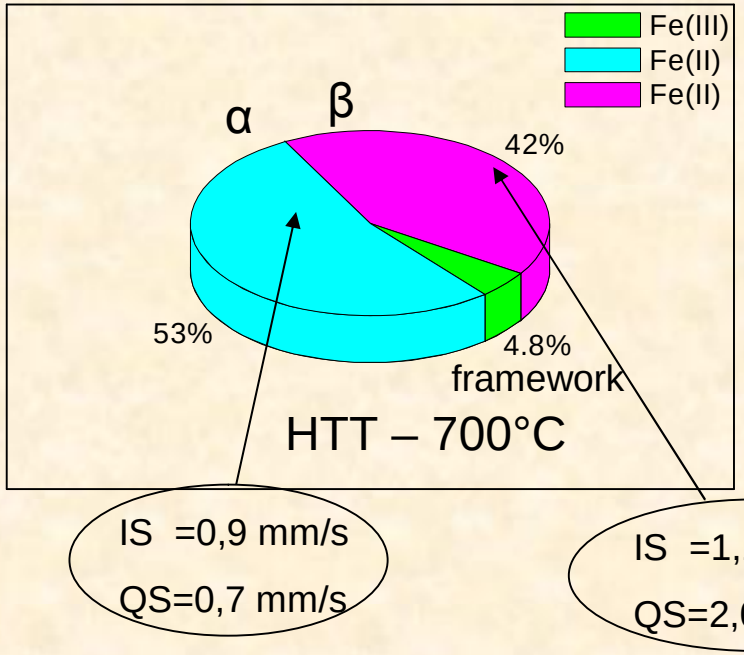
IS =0,9 mm/s
QS=0,7 mm/s

IS =1,1 mm/s
QS=2,0 mm/s

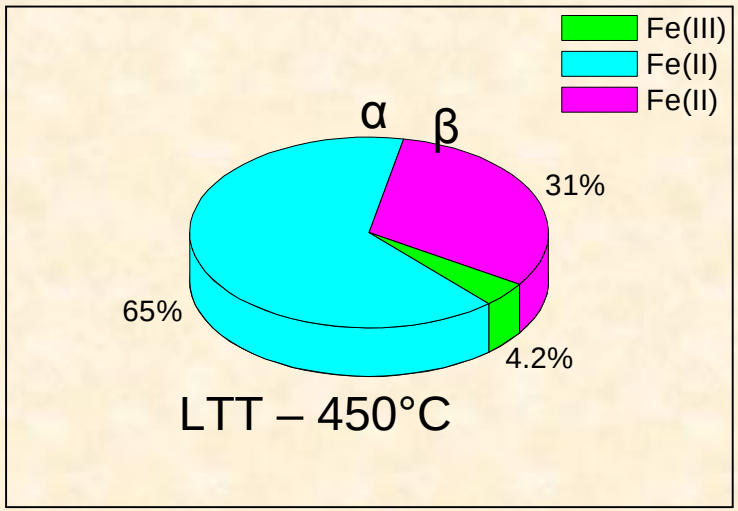
Wide sextet



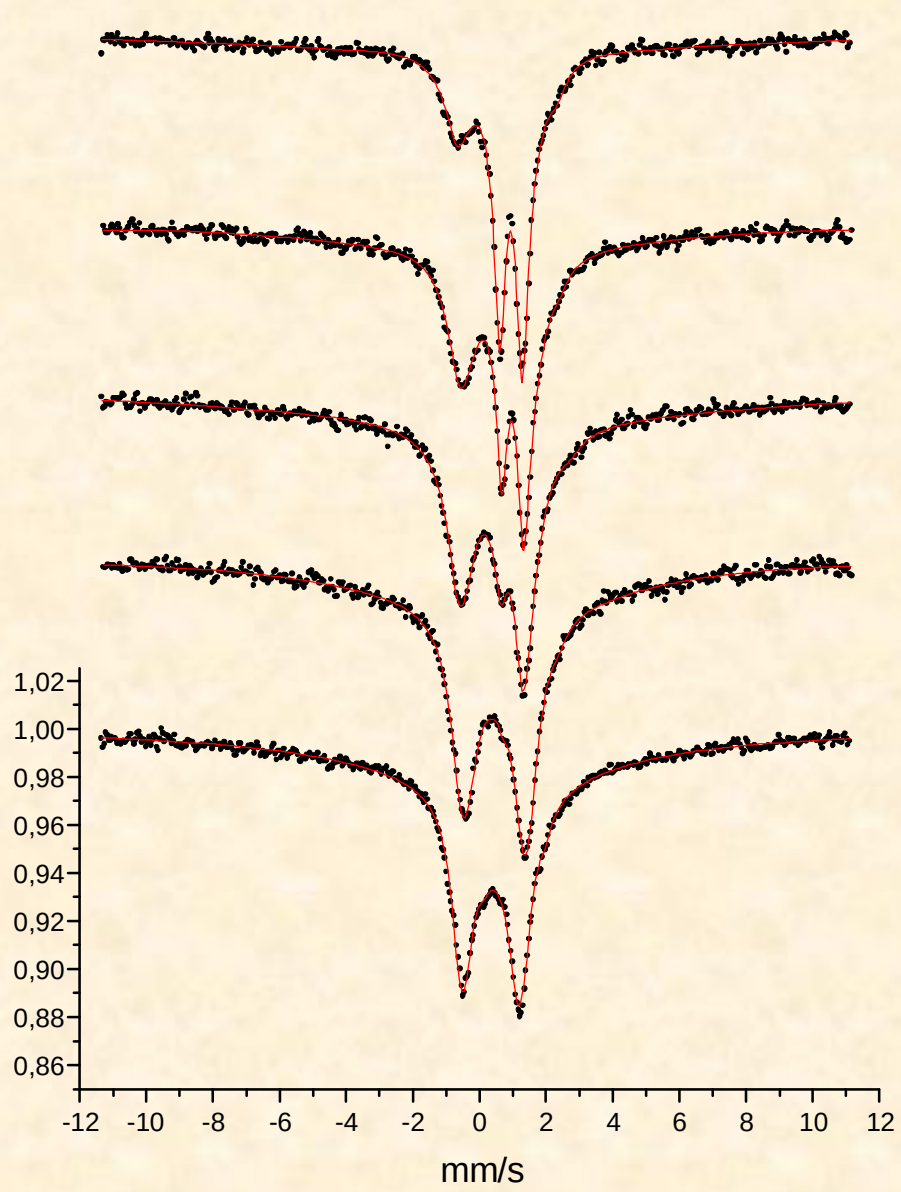




HTT	Isomer shift δ (mm/s)	Quadrupole splitting ΔE_Q (mm/s)	Relative area (%)	Fe
3	**0,37**	**2,12**	**4,8**	2+
5	**0,92**	**0,65**	**53,2**	3+
6	**1,10**	**2,05**	**42,0**	3+



T6 LTT	δ (mm/s)	ΔE_Q mm/s)	area (%)
1			
2			
3	**0,40**	**2,23**	**4,2**
4			
5	**0,94**	**0,69**	**64,7**
6	**1,18**	**2,04**	**31,0**



Reduction

Oxidation

Results

- The spectra, decomposed to six subspectra, describes all forms of iron (positions, valencies).
- Subspectra can be assignde to different valencies of iron usin Moessbauer parameter.
- In Fe-ferrierite with (Fe conc. <1%) iron is predominantly in α and β position. (no oxides)
- By compartion with IR measurements subspectra can be assigned to iron in α and β position.($I_\alpha / I_\beta \sim 3/2$)
- Intensities for and after oxidation indicate different reactivities for oxidation with N_2O and O_2