

A study of the Iron chemical bond by the Mössbauer effect in the Ferromanganese concretions of the Black Sea

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One of the most efficient methods for identifying the chemical bonds in various combinations is the « Mössbauer effect ». As for the study of the nature of iron chemical bond in the various compounds, the Mössbauer effect offers the following advantages :

1. The resonance absorption occurring only with the ^{57}Fe nuclei, the information thus obtained, namely the electric field gradient, the electron density and the magnetic field at the nucleus, are exclusively related to this nucleus. Therefore, if the sample is a mixture of several substances, these will not affect the form of the Mössbauer spectrum, except when the substance is a chemical compound of iron, other combinations having no effect whatever.

2. ^{57}Fe presents the best combinations for obtaining this effect, since the Debye-Waller factor « f » is large (« f_{max} » = 1, while for ^{57}Fe we have « f » = 0.5 - 0.8) even at room temperature; thus it is possible to obtain spectra with measurable effects even in the case of small natural iron concentration in mixtures having only 5 % and even 1 % Fe, with resonance widths of 10^{-8}eV which is much smaller than that of most elements manifesting this effect.

In this work, we endeavoured to identify the chemical bond of the iron in the ferromanganese concretions collected in the Black Sea along the romanian coast, in comparison with those of the Pacific Ocean, by studying the Mössbauer spectra of ^{57}Fe from the iron natural isotopic mixture.

Experimental Part and Results

The Mössbauer spectra were carried out with the help of an automatic Mössbauer spectrometer with a negative feedback allowing to obtain 20 Hz rectangular velocities of the ^{57}Co source. The standard spectrum of natriumnitroprussiate, $\text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})]$ as well as the sample spectra of ferromanganese concretions and goethite, were carried out at room temperature, i.e. 25 - 30° C.

We made use of a 0.5 microcurie source of ^{57}Co embeded in a palladium lattice and a scintillation detection device with a NaI(Tl) crystal 1 mm thick. The isomeric shift of the ^{57}Co source in Pd in regard to that of natriumnitroprussiate is equal to 0.422 mm.s^{-1} and the natural width of the natriumnitroprussiate resonance line is equal to 0.2 mm.s^{-1} [1]. The thickness of the absorbants — finely grounded concretions or goethite sample — was chosen so as to not exceed 30 - 80 mg.cm^{-2} in order to obtain spectra with the smallest relative errors in regard to the value of Mössbauer effect (absorbant thickness sufficient to reduce an « e » times the 14.4 keV gamma quanta intensity of the ^{57}Fe , (« e » being the base of natural logarithms) [2]. The time necessary to draw a spectrum varied from 2 to 6 hours, while the corresponding parameters are to be found in Table 1.

The parameters errors were analytically computed by the formulae given in [3], where $\sigma \chi_0$, $\sigma \varepsilon$ and $\sigma \Gamma$ are the standard errors, respectively those of the Mössbauer resonance position (χ_0) of the effect value (ε) and of the resonance width (Γ) with respect to the source of ^{57}Co in palladium. N_0 represents the number of points along the resonance line width, while N_F is the number of pulses in out of resonance, i.e., which were not absorbed by resonance.

$$\sigma \chi_0 = \frac{0.8 \Gamma}{\varepsilon \sqrt{N_0 N_F}} \quad ; \quad \sigma \varepsilon = \frac{1.6}{\sqrt{N_0 N_F}} \quad ; \quad \sigma \Gamma = \frac{2.26}{\varepsilon \sqrt{N_0 N_F}}$$

Conclusions

From the spectra obtained and from the experimental results recorded in Table 1, the following conclusions can be drawn :

1. The ferromanganese concretions in the Black Sea and those in the Pacific Ocean, have similar chemical structures.

2. The large widths of resonance we have obtained, much larger than those of natriumnitroprusiate, are chiefly due to the gradient fluctuations of the electric and magnetic fields appearing in the ^{57}Fe nuclei together with a possible *Goldanski-Kariaghin effect* [1], [4].

3. The small values of the chemical isomeric shifts and of the quadrupolar splittings prove that the Fe valency is 3+ in these combinations having the structure of the goethite $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, or $(\text{FeOOH})_2$ in good agreement with the data of other researchers' results [5], or goethite in considerable quantity mixed in small amounts with ferromanganites [6]. We mention that our « goethite sample » was an old piece of cast-iron used previously for water network and analysed by means of X-ray diffraction using Debye-Scherrer method which allowed us to identify the characteristic goethite peaks on the spectrogram.

4. The absence of the divalent iron in the concretions was also confirmed by the fact that in a previous analysis the manganese was present in the form of MnO_2 which being an oxidiser transformed the divalent iron into trivalent iron [6], excluding the presence of reduced iron.

5. From the standpoint of the Mössbauer effect, the divalent iron presents in regard to the natriumnitroprusiate considered as a standard, a 1.5 - 1.6 mm.s^{-1} shift, while that of the trivalent iron is a 0.7 - 0.8 mm.s^{-1} shift (1, p. 268), and in our concretion samples of the Black Sea, the isomeric shift is 0.55 - 0.57 mm.s^{-1} .

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TABLE 1. — Mössbauer spectra parameters of ^{57}Fe obtained with the source of ^{57}Co in palladium for sodiumnitroprussiate (N^o 1), ferromanganese concretions (FeMn conc.) in the Black Sea (N^o 2-5), in the Pacific Ocean (N^o 6) and for the goethite (N^o 7).

No. Absorbant	Absorbant thickness mg.cm ⁻¹	Resonance position 10 ⁻² mm.s ⁻¹		Amplitude resonance %		Resonance width mm.s ⁻¹	
		1	2	1	2	1	2
1 Natrium-nitroprussiate	30	- 129.8	+ 41.4	8.2 ± 0.2	9.1 ± 0.2	0.3 ± 0.01	0.27 ± 0.01
2 FeMn conc. Phase II Black Sea (Sulina)	50	- 28 ± 1	+ 54 ± 1	3.2 ± 0.1	3.8 ± 0.1	0.50 ± 0.02	0.50 ± 0.02
3 FeMn conc. Phase II Black Sea (Constantza)	50	- 21 ± 1	+ 50 ± 1	4.0 ± 0.1	4.3 ± 0.1	0.55 ± 0.02	0.50 ± 0.02
4 FeMn conc. Phase II Black Sea (Constantza)	50	- 28 ± 1	+ 60 ± 1	2.9 ± 0.1	3.4 ± 0.1	0.55 ± 0.02	0.45 ± 0.02
5 FeMn conc. Phase I Black Sea (Constantza)	80	- 33 ± 2	+ 60 ± 2	1.3 ± 0.07	1.3 ± 0.07	0.50 ± 0.04	0.50 ± 0.04
6 FeM conc. Pacific Ocean (Callaos)	50	- 22 ± 1	+ 54 ± 1	4.7 ± 0.15	4.8 ± 0.15	0.55 ± 0.02	0.55 ± 0.02
7 Goethite (cast-iron)	30	- 32 ± 1	+ 58 ± 1	5.2 ± 0.2	4.7 ± 0.2	0.50 ± 0.02	0.55 ± 0.02

