

A Mössbauer study of samples from an oil well

O.D. Rodrigues, R. Garg, E. Galvão da Silva^a, M.F. de Jesus Filho^b,
U.B. Jayanthi^c, A.M.G. Figueiredo^d and V.K. Garg

*Departamento de Física, Universidade Federal do Espírito Santo,
29060-900 Vitória, ES, Brazil*

^a *Departamento de Física, Universidade Federal de Minas Gerais,
31270 Belo Horizonte, MG, Brazil*

^b *Departamento de Química, Universidade Federal de Minas Gerais,
31270 Belo Horizonte, MG, Brazil*

^c *Instituto Nacional de Pesquisas Espaciais, 12201 São Jose dos Campos, SP, Brazil*

^d *Instituto de Pesquisas Energéticas e Nucleares, São Paulo, SP, Brazil*

Seven different samples obtained from the Petrobras Oil Well 1-ICA-1BA from depths down to 1872 m have been studied by Mössbauer spectroscopy, X-ray diffraction and neutron activation analysis. The X-ray diffraction showed the presence of clay minerals, feldspar, calcite, pyrite, quartz, dolomite, andrite and others. The neutron activation analysis has been used to obtain the iron concentration in the samples. The Mössbauer spectra were obtained both at room and liquid nitrogen temperatures. Spectra are complex in nature indicating multiple sites or mixture of iron containing minerals. The spectra at 85 K could be least squares fitted are resolved up to four doublets with typical values of $IS(Fe) = 1.4, 1.21, 1.16, 0.40$ and $QS = 3.62, 2.82, 2.37, 0.61$ mm/s respectively. They have slightly large line widths except for the first doublet. Two samples also showed the presence of hematite.

1. Introduction

Depending upon the time and the type of organic matter, sediments that are rich in organic matter may form oil; sediments rich in terrestrial plants etc. tend to form coal. A good source rock for the formation of oil must contain appropriate kind of organic matter and must have undergone an appropriate diagenesis (maturation). The optimum production of oil takes place in a relatively short interval of maturity. The oil and gas migrate from source rock to reservoir rock. The characterization of the source rock is an important part of the estimation of hydrocarbon reserves [1]. The source is generally analysed by organochemical analysis. The effect of catalysis of clay minerals in the formation of oil is an important feature of a good source rock. Degree of maturation (diagenesis) of organic matter could also be a significant parameter in source rock characterization. Mineral analysis of the source rock is, therefore, very informative [2–5].

Morup and Lindgreen [6] studied the content of iron in inorganic minerals

from North Sea by Mössbauer spectroscopy and suggested that the presence of ankerite (Fe, Mg, Ca) CO₃ is related to the maturity of source rock. In this report we present results on seven different samples obtained from PETROBRAS oil well 1-ICA-1BA from depths down to 1872 m, that have been studied by Mössbauer spectroscopy, powdered X-ray diffraction, and neutron activation analysis.

2. Experimental and results

Neutron activation analysis

100 mg of each sample was irradiated for 8 h in a flux of neutrons ($\sim 10^{12}$ n cm⁻² s⁻¹) along with a standard sample. The measurements of induced radiation was done after seven days with gamma ray spectroscopy. The obtained iron concentration is given in table 1.

X-ray diffraction

X-ray diffractographs were obtained at the Research Center of Petrobras using powdered samples. The minerals obtained after peak analysis are given in table 1.

Mössbauer spectroscopy

Mössbauer spectra were recorded in the standard transmission geometry with Co⁵⁷/Rh source. All the seven samples gave Mössbauer parameters (table 2) that

Table 1

Neutron activation analysis (iron concentration) and X-ray diffraction identification.

Sample	Sample depth (m)	Iron (± 0.04 , %)	XRD
A ^a	915	2.42	X-ray diffraction analysis indicated the presence of clay minerals, quartz, calcite, dolomite, pyrite, feldspar, andrite and others in varying concentrations in all the samples.
B ^b	1722	0.99	An analysis of clay minerals indicated that mostly it is illite, and in much smaller quantity smectite.
C	1752	1.10	
D	1797	0.61	
E	1803	2.07	
F	1824	1.46	
G	1872	3.66	

^a Source rock.

^b Reservoir rock.

Table 2
Mössbauer parameters (IS is with respect to α -Fe).

Sample	T (K)	Site	IS ± 0.05 (mm/s)	QS ± 0.05 (mm/s)	Γ ± 0.02 (mm/s)	A (%)	H_{int} ± 0.6 (kOe)
A	85		1.40	3.62	0.22	12	
			1.21	2.82	0.36	26	
			1.16	2.37	0.35	8	
			1.40	0.61	0.33	54	
B	RT	Fe ²⁺ (I)	1.33	3.36	0.36	8	
		Fe ²⁺ (II)	1.14	2.28	0.48	36	
		Fe ³⁺	0.25	0.70	0.44	39	
		hematite	0.38	-0.20	0.41	17	500
	85		1.41	3.55	0.23	7	
			1.22	2.82	0.37	39	
			1.17	2.42	0.35	10	
		hematite	0.42	0.69	0.45	22	
		hematite	0.48	-0.24	1.02	22	523
C	85		1.37	3.58	0.22	7	
			1.20	2.76	0.36	31	
			1.15	2.34	0.35	9	
			0.39	0.61	0.31	53	
D	85		1.33	3.63	0.23	4	
			1.19	2.79	0.29	19	
			1.18	2.39	0.31	10	
			0.39	0.59	0.29	67	
E	85		1.40	3.62	0.22	13	
			1.21	2.81	0.32	29	
			1.19	2.42	0.32	12	
			0.42	0.62	0.41	46	
F	85		1.39	3.62	0.25	30	
			1.22	2.80	0.31	28	
			1.20	2.45	0.31	16	
			0.40	0.61	0.36	26	
G	RT		1.35	2.91	0.27	9	
			1.09	2.34	0.48	53	
			0.26	0.70	0.43	22	
			0.34	0.23	0.23	6	
		hematite	0.36	-0.32	0.57	10	503
G	85		1.43	3.59	0.23	5	
			1.24	2.74	0.38	27	
			1.17	2.42	0.35	8	
			0.41	0.66	0.50	41	
		hematite	0.48	-0.12	0.47	20	510

are similar, although morphologically samples looked somewhat different. All the samples were analysed both at room temperature and 85 K. Sample B and sample G showed magnetic spectra corresponding to hematite ($\alpha\text{-Fe}_2\text{O}_3$). Since samples B and D contained lower concentrations of iron recording of Mössbauer spectra for these samples took more time. Initially all the spectra were least squares fitted for three doublets (two of Fe(2+) and one of Fe(3+)). This resulted in large linewidth of the Fe(3+) doublets. Therefore, four doublets were least squares fitted which resulted in considerable improvement of the fitting (table 2, 85 K data). The typical least squares fitted spectra are depicted in fig. 1. The iron content present in the

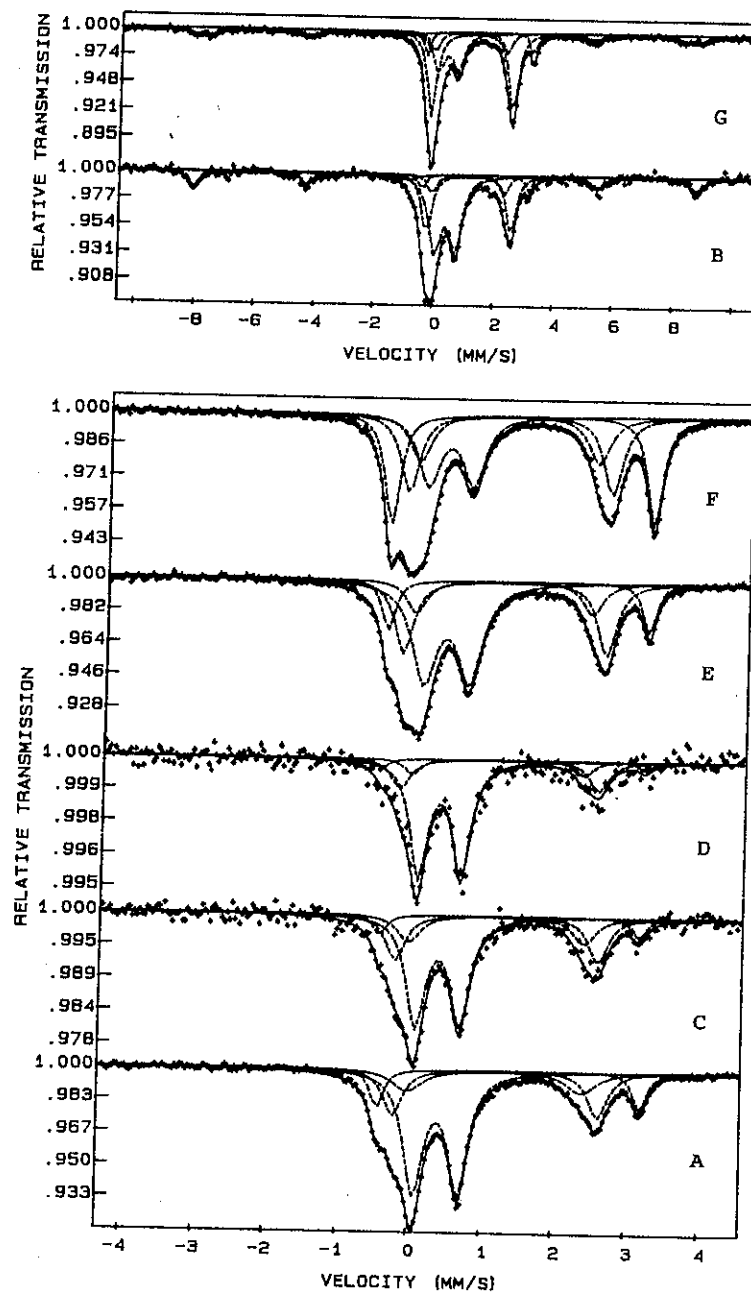


Fig. 1. Typical least squares fitted Mössbauer spectra of oil well samples at 85 K.

samples is analysed to be in the form of several different minerals.

The Mössbauer parameters at 85 K (table 2) indicate a doublet with large isomer shift and largest quadrupole splitting with sharp linewidth. The parameter of this doublet correspond to high spin Fe(2+) hydrated iron fluorosilicate [7] $[\text{Fe}(\text{H}_2\text{O})_6]\text{SiF}_6$ (QS = 3.38 mm/s and $\delta(\text{Fe}) = 1.28$ mm/s at room temperature).

The Mössbauer spectra at 85 K also contained components typical of Fe(2+) sites in clay minerals illite, and smectite [8]. The two doublets with $\delta(\text{Fe})$ values from 1.17 to 1.34 mm/s and QS values around 2.2 to 2.8 mm/s correspond to illite Fe(2+) sites [9]. It is quite possible that some sites of smectite (which is present in relatively smaller quantity as shown in X-ray diffraction) are overlapped by the presence of other doublets. The observation of slightly different Mössbauer parameters of the components of the clay minerals reflects different compositions.

All the seven samples showed an intense component with parameters corresponding to pyrite [10] (QS = 6.2 mm/s and $\delta(\text{Fe}) = 0.4$ mm/s). However, in some clay minerals similar components have also been reported [8]. Thus pyrite fraction could possibly include some Fe(3+) sites of clay minerals with Mössbauer parameters quite close to those of pyrite. But, in general, samples show that iron is mainly present as clay minerals, pyrite, and iron(II) hydrated fluorosilicate. Sample A (source rock) contains a larger quantity of clay minerals as indicated by petrographic analysis while all other samples including sample B (reservoir rock) contains traces of clay minerals. In absence of sufficient data it is not possible for us to confirm the suggestion that clay minerals help in maturation of oil in source rock. More experiments from oil well are needed to correlate characterization of source rock and maturity.

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