

# Use of Mössbauer Spectroscopy to Study Indiana Oil Shales

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## Introduction

Oil shales are recognized as being a potential source of petroleum for the immediate future. Indiana may have a source of valuable oil in its New Albany shale which is located in the southern and western regions of Indiana. Shales are sedimentary rocks formed in shallow seas which are mixtures of inorganic minerals and organic materials. The major organic constituent of the shales is kerogen which can be extracted from the rock and refined to produce petroleum products. Kerogen is a complex, acid-insoluble organic polymer which is formed from the decomposition of plants buried in the sediments. The process by which plant materials decompose and reform into kerogen as the sediments are compressed into shale is not well understood. In particular, the minerals in the shales which surround the organic material may or may not play a catalytic role in kerogen formation.

Investigations by the Indiana Geological Survey have shown that the New Albany shale has a number of characteristic rock formations which reflect the organic content of the shale. There is a black shale rich in organic material with a high potential for petroleum development, a greenish-gray shale which is poor in organic material, and brown shales with an organic content between those of the black shales and the green shales. Despite the obvious color differences in the shales, there are few mineralogical differences. For this reason, standard mineralogical techniques cannot be used in trying to determine the relationship of the minerals present in the shales to the formation of kerogen (Cliff, 1980 Lineback, 1970 and Shaffer and Chen, 1981).

It has been hypothesized that the organically rich oil shales were formed in an anoxic environment. The kerogen poor shales were formed in an environment high in oxygen which supported the presence of burrowing animals who ate the plants before the kerogen could be formed (Maynard, 1982). On this basis it is expected that minerals in the organic-rich shales will be in a reduced state related to those in organic-poor shales. This study reports an attempt to determine whether  $^{57}\text{Fe}$  Mössbauer spectroscopy can be used to study differences in the mineralogy of Indiana oil shales.

## Methods

Mössbauer spectroscopy is the resonant absorption and emission of gamma-rays. In order for a nucleus to resonantly absorb or emit high energy gamma radiation, it must recoil to conserve momentum. If the nucleus is found in a crystal lattice which can recoil as a whole to conserve momentum while taking very little energy from the gamma radiation, resonant absorption and emission can occur. The probability of this happening depends upon the energy of the gamma, the bonding of the nucleus in the lattice, and the temperature of the lattice. The most useful Mössbauer nuclide for the study of geological materials is  $^{57}\text{Fe}$  because iron is abundant in all geological materials; the nuclide has a convenient low energy gamma transition at 1.4. KeV; and its parent nuclide  $^{57}\text{Co}$  has a long half life and is convenient to handle.

When resonant absorption and emission of gamma radiation occur, the very narrow half widths of the nuclear transitions allow detection of the minute changes in the energies of nuclear levels brought about by the interaction of the atomic electrons

and the nuclear charge distribution. If the source nucleus and the absorbing nucleus are bound in different lattices, the energy levels of the source nucleus will not exactly match those of the absorbing nucleus. Energy is added to or subtracted from the gamma radiation from the point of view of the absorbing nucleus by moving the absorbing lattice relative to the source and using the Döppler shift to alter the energy of the emitted radiation. Transmission of radiation is measured as a function of the relative motion of the source and absorber.

Three parameters are measured from these absorption spectra which, coupled with the well-studied properties of the  $^{57}\text{Fe}$  nucleus, present quantitative information on the chemical state of iron in the absorber. The isomer shift of the center of the resonance spectrum measures the electron density at the site of the nucleus. Its value is characteristic of different iron-bearing minerals. The splitting of the nuclear levels due to the interaction of the nuclear quadrupole moment and the electric field gradient of the atomic electrons produces an absorption doublet whose splitting measures the asymmetry of the electron charge distribution at the crystal sites where iron is bound. Finally, the interaction of the magnetic moment of the iron nucleus with the magnetic field produced by atomic electrons produces a six line absorption spectrum which is not observed in Mössbauer spectra of shales recorded at room temperatures.

Iron constitutes several percent by weight of the shales and they are therefore readily studied by Mössbauer spectroscopy. Karl and Zuckerman (1981) and Cole *et al* (1978) have used this technique to identify iron-bearing minerals in oil rich shales but have not studied shales with low organic content from the same formations.

In this study, four samples of New Albany shale with differing organic content were crushed and formed into absorbers whose thickness was approximately  $50 \text{ mg/cm}^2$ . Data were recorded on a conventional constant acceleration Mössbauer spectrometer using a gas-filled proportional counter and a nuclear data multichannel analyzer. The source in this study was  $^{57}\text{Co}$  diffused into a palladium matrix to produce a source gamma with a single energy. Data were fitted using a version of the variable matrix minimization procedure developed at Argonne and modified at M.I.T., Columbia and Ball State. Constraints were placed on half widths of the absorption doublets and further doublets were added to the model spectrum until further doublets failed to reduce the chi squared value of the fit.

### Results

Chemical data for four New Albany shales can be found in Table 1. The data were obtained from Nelson Shaffer of the Indiana Geological Survey. The shale sample NS79-9 is a shale rich in kerogen while sample NS79 308 is a shale poor in kerogen. The weight percent of the total carbon content in the organic-rich shale is much larger than that of the oil-poor shale. The weight percents of carbon found in the carbonate minerals of the shale also exhibit an obvious difference between the two shales. There

TABLE 1. *Chemical Data on Shales*

Weight Percent of:	C	H	N	C in $\text{CO}_2$
NS79-9	24.15	2.19	1.20	.05
NS79-57	9.42	1.41	.35	.68
NS79-308	2.31	.53	.10	.74
NS79-309	8.56	1.15	.27	.12

is a lower percentage of carbon in the carbonate minerals in the organic-rich shale than in the organic-poor shale. The low percentage of carbon in the carbonate indicates that large amounts of organic material are present.

Figure 1 shows a typical Mössbauer spectrum. The absorption spectrum consists of two unresolved doublets. The narrow doublet is characteristic of ferric iron, while the wider doublet is characteristic of ferrous iron. The solid black line shows the computer fit used to distinguish between the doublets quantitatively.

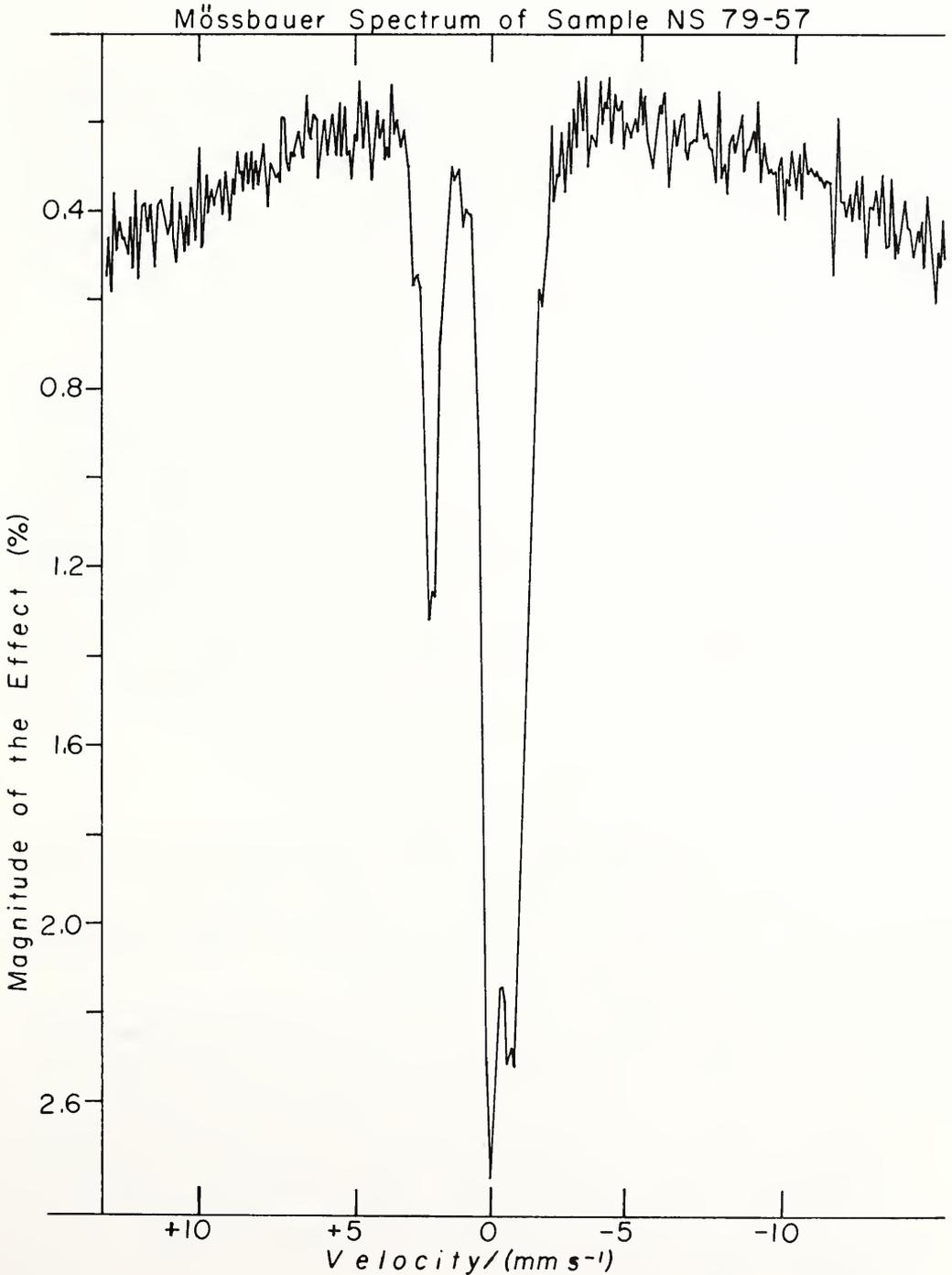


TABLE 2. *Mössbauer Parameters for Shales\**

	Q <sub>1</sub>	δ <sub>1</sub>	%	Q <sub>2</sub>	δ <sub>2</sub>	%
NS79-9	.69	.30	68	2.81	1.14	23
NS79-57	.68	.31	70	1.89	1.23	30
NS79-308	.50	.43	25	2.56	1.12	74
NS79-309	.76	.32	63	1.95	1.52	29

\* All quantities reported in mm/sec ± .10 mm/sec unless otherwise noted  
Isomer shifts (δ) are reported relative to metallic iron

The results of Mössbauer spectra taken of the four shale samples are shown in Table 2. The first group of values indicate the data from the narrow doublet representing the oxidized (ferric) iron, and the second group indicates the data from the wider doublet representing the ferrous iron. The Q column is the doublet splitting. The δ column reports the isomer shift relative to metallic iron and the amounts of ferric or ferrous iron in the shale, assuming that the absorption cross-section is identical for all chemical sites in the shale and that the iron content is proportional to the area of its characteristic absorption doublet.

### Conclusions

It was initially expected that there would be less oxidized iron than reduced iron in organic-rich shale samples such as NS79-9 and that the situation would be reversed in organic poor shales such as NS79-308. The results of this experiment contradict this simple hypothesis since experimental results show a higher percentage of oxidized iron in brown and black shales. Since this study involves only four samples, no general conclusion can be drawn concerning the mineralogy of the shales. The ferric doublet in the organic rich shales seems to be pyrite indicating, that for these samples, pyrite is associated with the presence of organic material in the shale. This is consistent with the chemical and mineralogical analyses of Levinthal and Hosterman (1982) and Maynard (1982). Further Mössbauer studies will yield detailed data on the relationship of the chemical state of iron in shales to the organic content of the shales. Such studies are currently in progress.

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