

ROLE OF PYRITE DURING THE THERMAL DEGRADATION OF KEROGEN  
USING IN-SITU HIGH TEMPERATURE ESR TECHNIQUE

By

M. Bakr<sup>1</sup>, M. Akiyama<sup>2</sup>, T. Yokono<sup>1</sup> and Y. Sanada<sup>1</sup>

Metals Research Institute, Faculty of Engineering<sup>1</sup>, and Geology  
and Mineralogy Department, Faculty of Science<sup>2</sup>, Hokkaido  
University, Sapporo, 060 Japan

INTRODUCTION

Thermal maturation of kerogen in sedimentary rocks has been studied extensively with the intent of better understanding the generation and accumulation of oil and gas (1, 2). The influence of mineral matrices on kerogen during thermal maturation has also been studied. The available in literatures have shown that the role of catalysis in pyrolysis reactions have been directed towards using minerals, such as kaolinite, montmorillonite and calcite (3-7). Analytical techniques applied in these studies did not included in-situ ESR spectroscopy. Moreover, the relationship between pyrite and kerogen has received no attention considering a possible catalytic role of pyrite on the thermal degradation of kerogen. The genetic relationship between pyrite and kerogen, in addition to the evidence that pyrite whether indigenous or added, enhances coal conversion and improves product quality under hydroliquefaction conditions (8-11) makes one wonder whether pyrite also plays a role in kerogen maturation. In this work, in-situ ESR studies between room temperature and 700 °C on the pyrolysis of kerogen in the presence and absence of added pyrite

are reported.

#### EXPERIMENTAL

Samples studied here include lignin, natural and artificial kerogen. Lignin is a pure reagent supplied from Tokyo Kashei Kogyo. Natural kerogen samples were taken from the MITI-Hamayuchi borehole and Oashizawa outcrops in Japan. Artificial kerogen was prepared from a mixture of glucose and casein (12). Pyrite is a reagent supplied from CERAC, Inc., and was checked with X-ray diffraction and Mossbauer spectroscopy before use. Procedures of Kerogen demineralization and extraction with organic solvents, have been discussed previously (13). The procedure of in-situ high temperature ESR measurements of kerogens has been described elsewhere (14). Since pyrite cannot be fully removed without specific alteration of kerogen structure, no attempts have been made to remove pyrite from the natural kerogen under investigation. Therefore the role of the indigenous pyrite cannot be justified in this study, and discussion will be focused on the added pyrite. To check the catalytic effect of added pyrite on the formation of free radicals, lignin and artificial kerogen as pyrite free materials were tested with and without addition of pyrite.

#### RESULTS AND DISCUSSION

Fig. 1 shows the temperature dependence of radical concentration for lignin with and without addition of pyrite. There are two significant points that should be mentioned:

(1) the maximum value of spin concentration for pyrite-lignin system is larger than that of the lignin one. (2) pyrite speeds up the process of radical formation, where the maximum value of spin concentration of the lignin-pyrite system is shifted significantly to lower temperature, from 575 °C to 550 °C.

In Fig. 2, the temperature dependence of radical concentration for artificial kerogen alone and the same kerogen with 10%  $\text{FeS}_2$  is illustrated. The main effects of pyrite on the thermal decomposition of kerogen are manifested by:

1. A drastic enhancement in radical concentration that starts from 225 °C and proceeds throughout the course of pyrolysis. This enhancement becomes intensive at 450 °C (the temperature of  $R_3$ ) and drops after that.
2. Speeding up the process of pyrolysis. This causes shift of the ESR maxima ( $R_1$  and  $R_3$ ) and ESR minimum ( $R_2$ ) to lower temperatures. Lowering in temperatures was measured as 25 °C for both  $R_1$  and  $R_2$ , and 50 °C for  $R_3$ .

Using the in-situ ESR technique, it has been shown that kerogen maturity and hydrocarbon generation are linked to an extent to that of free radicals therein (15). Fig. 3 demonstrates the temperature dependence of radical concentration for kerogen from Oashizawa outcrops with and without addition of pyrite (10% and 30%  $\text{FeS}_2$ ). In the 10%  $\text{FeS}_2$  system, enhancement of radical concentration starts at 275 °C and continues throughout pyrolysis. As for the 30%  $\text{FeS}_2$  system, the observed enhancement of the radical concentration starts earlier at 200 °C and becomes more pronounced than that in 10%  $\text{FeS}_2$ . Pyrite accelerates the process of radical formation in kerogen. This is manifested by shifting the temperature of the maximum value of radical concentration to lower temperature when pyrite was added. The larger the amount of pyrite is used, the more the shift in the temperature of the ESR maximum can be observed. This shift in temperature follows the sequence kerogen-30%  $\text{FeS}_2$  > kerogen-10%  $\text{FeS}_2$  > kerogen.

Five kerogen samples from MITI-Hamayuchi borehole were mixed with 10 and 30%  $\text{FeS}_2$  and examined by ESR. These samples ranges in

depth from 904 to 4499 meters, and covers the diagenesis and beginning of catagenesis. The temperature dependence of radical concentration for Hamayuchi kerogens in the presence and absence of pyrite as an additive is shown in Figs. 4 and 5 for the shallowest (No. 1) and deepest (No. 5) sample, respectively.

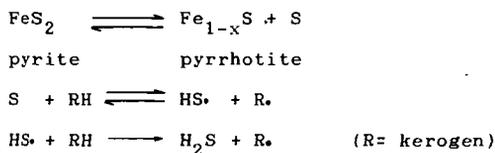
**Pyrite in the diagenesis stage.** This stage is represented by two samples (Nos. 1 and 2). In sample No. 1 (Fig. 4), the free radical concentration markedly increases in the presence of 10%  $\text{FeS}_2$  than in the case when kerogen was pyrolyzed without the additive. When 30%  $\text{FeS}_2$  was used, an incremental enhancement in reactivity over the 10%  $\text{FeS}_2$  was observed. The overall order of activity in terms of increasing spin concentration is as follows: kerogen-30%  $\text{FeS}_2$  system > kerogen-10%  $\text{FeS}_2$  system > kerogen alone, clearly indicating the strong effect of  $\text{FeS}_2$  during the pyrolysis of kerogen. Also speeding up the process of radical formation can be observed as the temperature at the positions of the maximum values of spin concentration is shifted to lower temperature when pyrite was added. Similar results were obtained for sample No. 2.

**Pyrite in the catagenesis stage.** The beginning of catagenesis is represented by three samples (Nos. 3, 4 and 5). Fig. 5 shows the results of sample No. 5. There is no noticeable change in spin concentration using 10%  $\text{FeS}_2$ , where the spin concentration in kerogen alone fraction and kerogen-10%  $\text{FeS}_2$  one is nearly the same. However, slight increase in spin concentration was observed in the presence of 30%  $\text{FeS}_2$  as is shown in Fig. 5 for sample No. 5. This results provide evidence that the effect of pyrite in this stage is either small (for 30%  $\text{FeS}_2$  system) or negligible (for 10%  $\text{FeS}_2$  system) comparing with the diagenesis stage. Similar results were obtained for samples Nos. 3 and 4.

**Decomposition of indigenous pyrite in kerogen.** Three sets of

heating experiments were carried out on kerogen sample No. 1. at 325, 375 and 450 °C in N<sub>2</sub> atmosphere. X-ray diffraction and Mossbauer showed transformation of indigenous pyrite to pyrrhotite at 450 °C.

**Decomposition of reagent pyrite.** Five sets of experiments have been conducted in N<sub>2</sub> atmosphere at 250, 375, 425, 475 and 550 °C. The transformation of pyrite to pyrrhotite was commenced at 250°C. This transformation process becomes more significant as the temperature increases to 550 °C. Thus it is evident that the large enhancement in radical concentration observed in the lignin-pyrite system (Fig. 1), artificial kerogen-pyrite system (Fig. 2) and natural kerogen-pyrite systems (Figs. 3 and 4) is consistent with the conversion of pyrite to pyrrhotite. The increase in radical concentration with FeS<sub>2</sub>, may be attributed to the nascent sulfur produced during the process of conversion of pyrite to pyrrhotite. The pyritic sulfur is a strong hydrogen acceptor, where it may abstracts hydrogen from kerogen via a free radical process. This process of radical formation may takes place as follows:



The enhancement of free radical formation via hydrogen transfer from kerogen (as a hydrogen donor) to sulfur (as a hydrogen acceptor) is illustrated in Fig. 6. Clearly, S is acting as a catalyst for generation of radicals in kerogen at these conditions. It should be noted that similar enhancement of radical formation by the catalytic effect of pyritic sulfur have been observed for coal (15).

**Hydrocarbon generation and the role of pyrite.** Hydrogen and carbon atoms crack from kerogen to form petroleum. This cracking process proceeds via free radicals formation. The more hydrogen a kerogen contains, the more hydrocarbon it can yields during cracking, and the more activity of pyrite can be observed. With increasing burial depth in Hamayuchi samples, the aliphatic hydrocarbons decrease. FT-IR data shows that the intensity of the aliphatic portion of kerogen carbon (CH) between  $3000-2700\text{ cm}^{-1}$  in sample No.1 is larger than that in sample No. 5. Elemental analysis also shows that sample No. 1 is richer in hydrogen than sample No.5. This may be the reason responsible for the activity of pyrite in sample No. 1.

#### CONCLUSION

Based on the data presented in this study, pyrite acts indirectly as a catalytic agent via sulfur. Pyritic sulfur enhances the formation of free radicals which may reflect enhancement in the hydrocarbon generation.

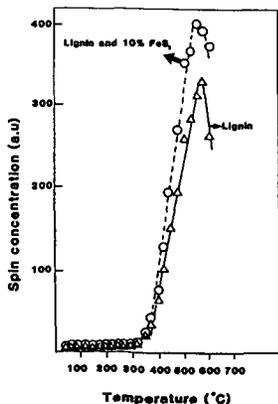


Figure 1. The temperature dependence of radical concentration of lignin in the presence and absence of  $\text{FeS}_2$ .

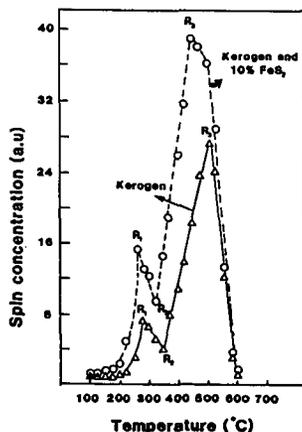


Figure 2. The temperature dependence of radical concentration of artificial kerogen in the presence and absence of  $\text{FeS}_2$ .

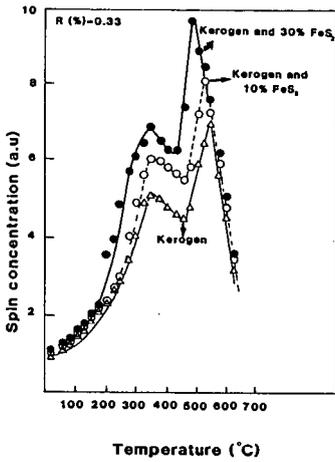


Figure 3. The temperature dependence of radical concentration of Oashizawa kerogen in the presence and absence of  $\text{FeS}_2$ .

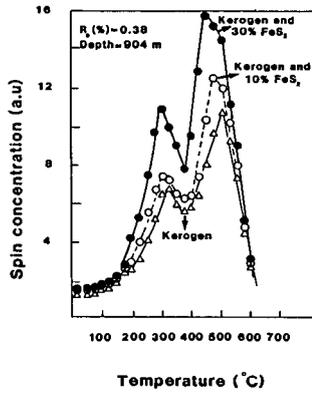


Figure 4. The temperature dependence of radical concentration of Hamayuchi kerogen No. 1 in the presence and absence of  $\text{FeS}_2$ .

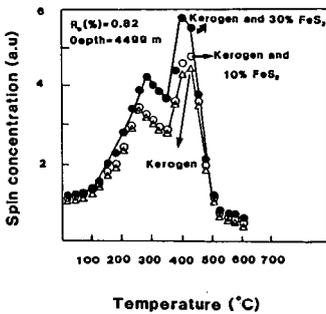


Figure 5. The temperature dependence of radical concentration of Hamayuchi kerogen No. 5 in the presence and absence of  $\text{FeS}_2$ .

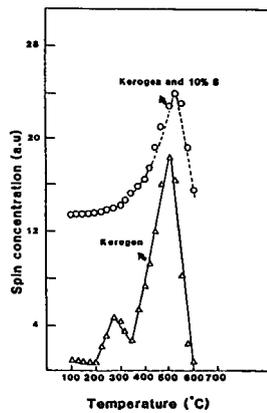


Figure 6. The temperature dependence of radical concentration of artificial kerogen in the presence and absence of sulfur.

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