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PETROLOGY OF SPENT SHALE: PREAMBLE ON OXYGEN FUGACITY

By

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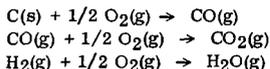
INTRODUCTION

The green River Formation in Colorado, Wyoming, and Utah is well-known for its hydrocarbon content and unique assemblage of minerals. With the increasing need for a petroleum substitute, this area has been investigated for future exploitation. Extraction of the organic compounds from oil shale is accomplished by retorting. Several possible schemes for retorting shale have been proposed (1, 2, 3). The internal conditions of these retorts will be greatly affected by the mineral matrix of the shale. By monitoring the mineral matrix of the shale, questions on retort efficiency and environmental problems may be addressed.

The question this paper will start to investigate is how closely the mineralogy of spent shale may be thermodynamically linked to the conditions that prevailed within the retort. Shales from the Green River Formation contain high amounts of reactive minerals. For example, carbonates are especially prone to decomposition at elevated temperatures and varying atmospheric compositions.

Are these minerals reacting to the products that would be dictated by the thermodynamics? During metamorphism, there are two important factors that will dramatically affect mineralogy: these are temperature and  $O_2$  fugacity. The temperature of a system may be monitored using thermocouples or other devices; however, no such device easily measures  $O_2$  fugacity. "Fugacity" for gas solutions is the same as activity for liquid solution (4). There are primarily two approaches for determining the fugacity of  $O_2$  in a system. The gaseous composition of the system may be determined from which the fugacity is calculated. Alternatively, known redox couples in solid systems such as  $Fe^{2+}$  and  $Fe^{3+}$  are used to determine the  $O_2$  fugacity in the vapor over the solid.

Campbell and others (5) have studied the gaseous compositions within several retorts and have published results on  $CO(g)$ ,  $CO_2(g)$ ,  $H_2(g)$ , and  $H_2O(g)$  contents as a function of temperature. The reactions of primary concern are:



The iron-containing minerals within unretorted and retorted shales have been studied by Melchior (6, 7). Changes of the iron-containing minerals were observed at various temperatures and internal retorting conditions. Of particular interest, the changes in the mineral pyrite were examined. Are the  $O_2$  fugacities derived from the gases and those determined by the iron-containing minerals consistent?

DISCUSSION

The chemistry of iron is complex; it can be stable as  $Fe^0$ ,  $Fe^{2+}$ , and  $Fe^{3+}$ . The oxidation state of Fe is sensitive to the oxidation-reduction potential of the system and should dictate what oxidation state of Fe is present. Geochemically, the  $Fe^{2+}$  and  $Fe^{3+}$  species exist in minerals. Melchior (6) has investigated the speciation of iron in minerals within oil shale. The results of this study show that iron in the  $2^+$  state predominates. The minerals pyrite ( $FeS_2$  (cubic)), siderite ( $FeCO_2$  (orthorhombic)), and ankerite ( $(Fe, Mg, Ca)(CO_3)_2$ ) were all detected in unretorted shale using Mössbauer effect spectroscopy. The presence of these minerals indicate that the environment of deposition and development of the shale was relatively reducing and of low energy.

Once removed from these conditions, the minerals are susceptible to change. During retorting, changes occur rapidly and should mimic those observed under metamorphism. The chemical changes of the minerals siderite and pyrite under varying conditions have been investigated (8-10). The chemistry of iron in metamorphic environments has also been exhaustively investigated by Eugster and others (11-13). They have presented the Fe-O-Si buffer system based on mineralogy and varying temperature and redox conditions. The  $O_2$  fugacity within a geologic system may be

obtained from the mineralogy. Within the Fe-O-Si system, fayalite (FeSiO<sub>4</sub>) may be present under the least oxidizing conditions, while hematite (Fe<sub>2</sub>O<sub>3</sub>) is present under the most oxidizing conditions. Figure 1 has been reproduced from Eugster (11,12) and displays the Fe-O-Si buffer system.

In addition to the information on Fe speciation of minerals in unretorted shales, Melchior (6) has determined the speciation of Fe in retorted shales. Table I displays the results of this study for combustion-type retorts. The results show that much of the iron that existed in the 2<sup>+</sup> state within the unretorted shale has been converted to the 3<sup>+</sup> state during retorting. The minerals siderite and ankerite underwent conversion prior to conversion of the pyrite. The question of pyrite conversion is essential to answering the ecological questions which abound concerning trace element mobility.

TABLE I  
FeMINERALOGY PRESENT IN SPENT OIL SHALES AND OXYGEN  
FUGACITIES BASED ON THE MINERALOGY

T°C	Spent Shale Mineralogy	log f <sub>O<sub>2</sub></sub>	f <sub>O<sub>2</sub></sub>
600	Hematite, magnetite, carbonate, sulfides, clay	-14.40	3.98 x 10 <sup>-15</sup>
750	Hematite, magnetite, carbonate, sulfides, clay	-10.25	5.62 x 10 <sup>-11</sup>
935	Hematite, magnetite	- 6.20	6.31 x 10 <sup>-7</sup>
1030	Hematite, magnetite	~ 5.0	1.0 x 10 <sup>-5</sup>

Using results in Eugster (11,12), the O<sub>2</sub> fugacity within a retort vessel may be determined based on mineralogy. The presence of hematite (Fe<sub>2</sub>O<sub>3</sub>) and magnetite (Fe<sub>3</sub>O<sub>4</sub>) at those retort temperatures places the system in a distinct buffering zone. The O<sub>2</sub> fugacities for these retorts are given in Table I.

The gases CO<sub>2</sub>, CO, H<sub>2</sub>O, and H<sub>2</sub> will control the fugacity of O<sub>2</sub> in an oil shale retort. Campbell and others (5) studied the evolution of gases during oil shale pyrolysis. This study was performed to simulate conditions that may exist in surface or *in-situ* retorts. Measurements on the gaseous composition within the retort were made. From these measurements, it is possible to compute the O<sub>2</sub> fugacity based on the CO<sub>2</sub>-CO and H<sub>2</sub>-H<sub>2</sub>O couples.

The equilibrium constant for the reaction CO<sub>2</sub>(g) → CO(g) + 1/2 O<sub>2</sub>(g) is written:

$$K_f = f_{CO} f_{CO_2}^{-1/2} / f_{CO_2} \quad 1)$$

The equilibrium constant for the reaction H<sub>2</sub>O(g) → H<sub>2</sub>(g) + 1/2 O<sub>2</sub>(g) is written:

$$K_f = f_{H_2} f_{O_2}^{-1/2} / f_{H_2O} \quad 2)$$

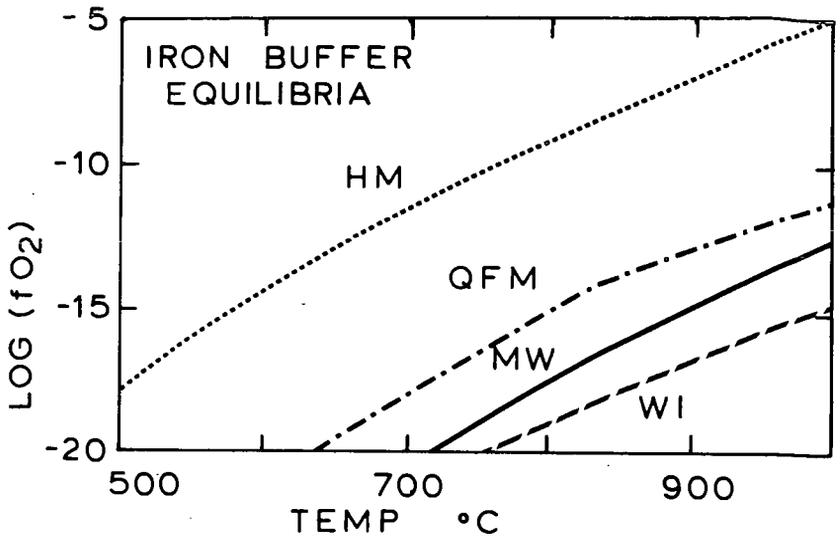
To determine the f<sub>O<sub>2</sub></sub>, we will assume that the ratios of CO<sub>2</sub>(g)/CO(g) and H<sub>2</sub>(g)/H<sub>2</sub>O(g) are equal to one. This is close to the values usually seen for most retorts (5,14). Using this assumption, it is now possible to use previously determined ΔG<sub>R</sub><sup>0</sup> values to obtain f<sub>O<sub>2</sub></sub>. Robie, Hemingway, and Fisher (15) have published ΔG<sub>R</sub><sup>0</sup> values for the species present from which ΔG<sub>R</sub><sup>0</sup> for the reactions have been calculated.

Table II presents the ΔG<sub>R</sub><sup>0</sup>, K, and f<sub>O<sub>2</sub></sub> for the CO<sub>2</sub>-CO reaction, plus the f<sub>O<sub>2</sub></sub> determined based on the H<sub>2</sub>-H<sub>2</sub>O reaction. Figure 2 shows that the oxygen fugacities derived from the CO<sub>2</sub>-CO and H<sub>2</sub>O-H<sub>2</sub> couples are similar to each other but quite different from that determined by iron mineralogy.

## CONCLUSIONS

The results of this comparison have shown that there is a dichotomy between the oxygen fugacities derived by the two methods presented. This disequilibrium suggests that the mineralogic reactions are kinetically controlled. The results suggest that given sufficient time, it may be possible to promote the reaction of the iron oxides to silicates. A critical question that must be answered is if there is sufficient silica present in the matrix for Fe-silicates to form. This will be addressed in a forthcoming paper. If silicates could form, many of the trace elements thought to reside in the Fe-sulfide minerals would be incorporated into inert structures. This would eliminate some environmental problems involved with spent shale.

Future work in this area should most certainly include a study on possible catalyzing agents that would promote the formation of silicates. One agent that should strongly be considered as a catalyzing agent is steam. The presence of steam may be extremely useful in controlling silicate formation at the lower temperatures that some retorts run at.



H = HEMATITE M = MAGNETITE Q = QUARTZ  
 F = FAYALITE W = WUSTITE I = IRON

FIGURE 1  $O_2$  FUGACITY IN A Fe-O-Si BUFFER SYSTEM.

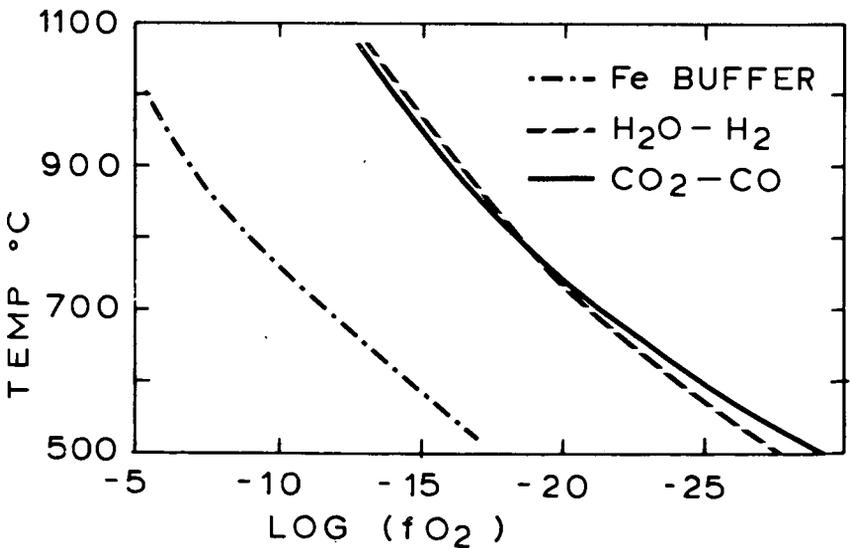


FIGURE 2.  $O_2$  FUGACITY FROM MINERAL & GAS EQUILIBRIA.

TABLE II  
THERMODYNAMIC RESULTS FOR THE CO<sub>2</sub>-CO AND H<sub>2</sub>-H<sub>2</sub>O SYSTEM

$\text{CO}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + 1/2 \text{O}_2(\text{g})$				
T°C	$\Delta G_R^\circ$ (Kcal/mole)	K	$f_{\text{O}_2}$	log $f_{\text{O}_2}$
527	50.93	$1.2 \times 10^{-14}$	$1.4 \times 10^{-28}$	-27.85
627	48.83	$1.4 \times 10^{-12}$	$1.9 \times 10^{-24}$	-23.72
727	46.75	$6.0 \times 10^{-11}$	$3.7 \times 10^{-21}$	-20.43
827	44.67	$1.3 \times 10^{-9}$	$1.8 \times 10^{-18}$	-17.74
927	42.61	$1.7 \times 10^{-8}$	$3.0 \times 10^{-16}$	-15.52
1027	40.55	$1.5 \times 10^{-7}$	$2.3 \times 10^{-14}$	-13.64

$\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g})$		
T°C	$f_{\text{O}_2}$	log $f_{\text{O}_2}$
500	$2.2 \times 10^{-28}$	-27.66
600	$1.6 \times 10^{-2}$	-23.80
700	$1.6 \times 10^{-21}$	-20.80
800	$4.4 \times 10^{-19}$	-18.36
900	$5.2 \times 10^{-17}$	-16.28

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