if oxidizing:[1]

$$H_2O + 3FeO = Fe_3O_4 + H_2$$

We have to date no experimental evidence that magnetite does not form directly under the appropriate conditions. The lower the temperature, the drier the hydrogen needs to be to effect reduction. In Experiment 87 run at 455°C at 2000 psi for 4 hours the solids were wüstite and iron. In experiment 89 run at 400°C at 2000 psi for 4 hours the solids were wüstite and magnetite. An extrapolation of Eastman and Evans' (1924) "best values" for the equilibrium constant from 700°C to 450°C and 400°C for the reactions,

$$FeO + H_2 = Fe + H_2O, \quad \text{and}$$

$$Fe_3O_4 + H_2 = 3FeO + H_2O,$$

yield values of the ratio $H_2O/H_2$ significantly higher than values obtained using the $H_2O/H_2$ ratios from experiment 89.

The validity of extrapolating the Eastman and Evans data to 400°C is questionable, but the magnitude of the difference between the extrapolated equilibrium ratio and our experimental $H_2O/H_2$ ratio allows for a considerable margin of uncertainty. The extrapolated ratio indicates that under the conditions of experiment 89, not only should magnetite not form, but wüstite should readily reduce to iron. Although our experiments with siderite never reached equilibrium, this discrepancy does suggest that relations in the Fe-C-H-O system differ significantly from the Fe-H-O system.

The reaction gases include appreciable methane and lesser amounts of ethane, propane, and butane. Water was present in all of the experiments.

The appearance of propane and butane can best be understood by considering the thermal stability of these hydrocarbons. The temperature necessary for siderite to react at an appreciable rate is low enough so that ethane, propane and butane are thermally stable. There is no direct evidence to indicate how these methane homologues form. Indirect evidence suggests that they do not form from methane. Some of the higher-temperature calcite and dolomite hydrogen runs were allowed to cool slowly under the reaction gases (methane, water, hydrogen) and the higher hydrocarbons did not form.

## Summary and Conclusions

Inorganic hydrocarbons up to and including butane form directly in carbonate mineral-hydrogen reactions at temperatures as low as 400°C.

[1] The fugacity of oxygen is proportional to $P_{H_2O}/P_{H_2}$.