

LOWER ECCA SHALE D.T.A. CURVES—A THERMO-DYNAMIC INTERPRETATION

By J. A. DRENNAN

Abstract

Typical D.T.A. peak systems yielded by the fresh lower Ecca shales in the Durban and Pietermaritzburg areas are presented. The theoretical course of recrystallisation for these rocks is derived from chemical thermodynamic data. These theoretical results agree well with experimental observation.

Carbon is found to dictate the course of recrystallisation on the basis of overall chemical rather than detailed mineralogical composition.

1. Introduction

The findings reported in this paper are based on observations made on a number of samples taken from fresh lower Ecca shale exposures at Avoca, Briardene, Cato Manor, Illovo and at Town Hill, near Pietermaritzburg.

The variable composition of these samples always falls within the mineral suite:

carbon:	1.5-5%
quartz:	20-35%
siderite:	0-50%
chamosite:	0-28%
illite:	10-45%

Chemically the compositional variations are as follows:

SiO ₂ :	38-64%
Al ₂ O ₃ :	6-23%
Fe ₂ O ₃ :	3-29%
MgO	} 3.5-10%
CaO	
K ₂ O	
Na ₂ O	
TiO ₂	

The principal mineral hosts for iron are the authigenic minerals, chamosite and siderite. Detrital illite plays only a minor rôle in this respect.

The most striking feature of the bed to bed variations of these shales is their erratic iron content. There appears to be a relation between the pH of the lower Ecca deposition environment and the diagenetic redistribution of iron between the siderite and chamosite components of the mineral suite. This has been discussed elsewhere (Drennan 1964).

2. Characteristic D.T.A. Curves

The apparatus used to obtain the D.T.A. curves illustrated in Figure No. 1 was a sensitive, well stabilised automatic machine with provision for an oxidizing or inert furnace atmosphere.

The curves illustrated are typical of the curves obtained from the various types of shale sampled. These samples can be described as follows:

Sample No. 1. A highly ferriferous shale (20.8% Fe) with its iron content distributed fairly evenly between the siderite and chamosite components.

Sample No. 2. A largely detrital shale (3.6% Fe) with some chamosite and no siderite.

Sample No. 8. A ferriferous shale (10.8% Fe) with the major portion of the iron content accommodated by the chamosite component and no evidence of siderite.

Sample No. 27. A highly ferriferous shale (24.5% Fe) with the major portion of its iron content accommodated by the siderite component.

Several features of these curves are quite normal and will not be discussed. These are the 100° C. endotherm common to all eight curves, the exothermic oxidation of carbon between 350° and 700° C. on the four curves produced under oxidizing conditions, and the endothermic dehydroxylation of chamosite and illite.

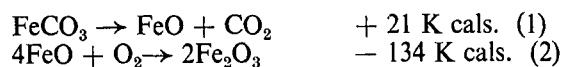
The feature of immediate interest is the 730° C. exotherm exhibited by the highly ferriferous samples Nos. 1, 8 and 27 in an inert atmosphere. There is, in fact, a peak system here as the 730° C. exotherm is invariably preceded by a slight endotherm with a maximum at about 675° C. Both peaks are absent when oxidizing conditions prevail in the furnace. It can be seen from the corresponding thermograms that there is no question of interference by other peak systems.

Because it only appeared with an inert furnace atmosphere, the 730° C. exotherm could not be attributed to an oxidation. It thus represented a crystalline phase inversion or a recrystallisation. This was examined by repeatedly reversing the heating cycle of the D.T.A. apparatus between 600° and 850° C. while an inert atmosphere was maintained in the furnace. This showed that the peak was not reversible and thus pointed to a recrystallisation.

3. Chemical Thermodynamic Aspects

3.1 The Dissociation of Siderite

The most widely accepted explanation for the characteristic endo-exothermic D.T.A. peak system yielded by the siderite dissociation under oxidizing conditions is due to Rowland and Jonas (1949). They assumed that these two peaks were accounted for by the reactions:

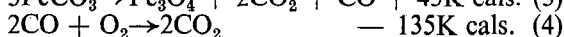
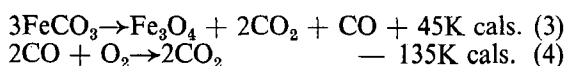


Experiments with pure natural siderite during the present work indicated that this mineral does not dissociate to the transient wustite (FeO) stage indicated by equation No. 1, even in an atmosphere of pure carbon monoxide. X-ray diffraction analyses of the

solid dissociation product indicated that dissociation and subsequent quenching in pure dry nitrogen or carbon monoxide produced magnetite with a small quantity of wustite. When dissociation took place in air the solid product was found to be magnetite with a small quantity of hematite.

A more dynamic investigation was made by mounting a sample of pure siderite on the platinum ribbon element of an X-ray diffraction furnace which was flooded with a stream of pure carbon monoxide to prevent oxidation of any transient wustite to magnetite. The furnace was mounted in the X-ray goniometer to oscillate about the peak angle for the 311 reflection from magnetite. The temperature was then raised steadily while the reflected intensity of the X-ray beam was recorded. This indicated that the 311 magnetite peak grew rapidly from the background between 400° and 450° C. and then disappeared just as abruptly between 500° and 550° C.

It does seem that the typical D.T.A. peak system for the siderite dissociation under oxidizing furnace conditions can be explained by the equations:

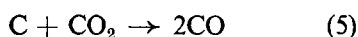


This reaction exhibits a greater free energy change per mole FeCO_3 than the conventional one and both CO_2 and CO were detected when dissociation occurred in a pure dry nitrogen stream. Further, the calculated heats of reaction for the two equations are compatible with the characteristics of the D.T.A. curve which requires a surplus of exothermic heat over endothermic heat per mole FeCO_3 .

It is not proposed to dwell on the dissociation mechanisms of siderite in various environments as there is some doubt that published thermodynamic data on this compound is reliable. On the basis of experimental observation alone, however, it is possible to conclude that the principal solid dissociation product of the reaction in an inert or reducing atmosphere is magnetite and not wustite as might be expected from previous publications.

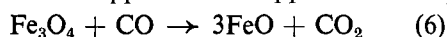
3.2 The Stability of Iron Oxide in the Presence of Solid Carbon

In a confined space containing excess carbon, there is a particular equilibrium ratio of carbon dioxide to carbon monoxide for any temperature. This can be more clearly expressed as % CO in the $(\text{CO} + \text{CO}_2)$ component of the confined atmosphere. By applying chemical thermodynamic data to the simple equation:



the curve shown in Figure No. 2 was obtained. From this it can be seen that if the temperature of a confined atmosphere in contact with excess carbon is raised from 400° to 850° C. the $(\text{CO} + \text{CO}_2)$ component of the gases will change from almost pure CO_2 to over 98.5% CO.

A similar approach was applied to the equation:

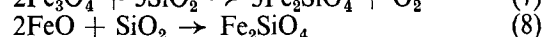
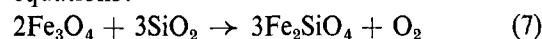


when it was found that the equilibrium % CO in the $(\text{CO} + \text{CO}_2)$ component of a gas in contact with magnetite falls with rise in temperature.

The results of calculations for equations Nos. 5 and 6 are plotted in Figure No. 3 for the narrow temperature range 630°, 700° C. From this it is apparent that below 665° C. the equilibrium composition of the gaseous phase in contact with excess carbon will favour the formation of magnetite. Due to the natural increase of CO with rise in temperature, however, a point is reached at 665° C. above which magnetite becomes unstable and tends to be reduced to wustite. This reduction of magnetite can be shown to be an endothermic one of approximately 7 K cal./mole Fe_3O_4 at 665° C.

3.3 The Recrystallization of Fayalite

By applying chemical thermodynamic data to the two equations:



it is apparent that reaction No. 7 will not proceed significantly in the temperature range 298 to 1500° K. In contrast, reaction No. 8 will proceed exothermally over the entire temperature range provided kinetically favourable conditions exist.

4. The Recrystallization Mechanism

4.1 The $\text{FeO} - \text{Fe}_2\text{O}_3 - \text{Al}_2\text{O}_3 - \text{SiO}_2$ Quaternary System

To understand the 730° C. recrystallization mechanism it is necessary to consider the high temperature phase relationships of silica, alumina and iron oxide in the presence of carbon. Because of the various states of oxidation which can be assumed by iron it is necessary to refer to the $\text{FeO} - \text{Fe}_2\text{O}_3 - \text{Al}_2\text{O}_3 - \text{SiO}_2$ quaternary system. This system is illustrated in Figure No. 4 as a regular tetrahedron with one oxide component at each apex. By confining the discussion to this system the lesser oxide components are being ignored. Most of these occur in relatively small quantities and have little effect on the course of recrystallization. An exception is found in carbon, however, which has an influence out of all proportion and to a great extent unrelated to its degree of occurrence.

Of the oxide components in the above quaternary system, Al_2O_3 and SiO_2 are thermodynamically stable in the presence of carbon within the temperature range being considered. The iron oxides on the other hand are not. It follows therefore that as the conditions within a D.T.A. sample containing these four oxides and carbon vary, the equilibrium phase relationships of the total sample can be expressed in terms of a subsystem represented by the ternary join between the Al_2O_3 and SiO_2 apexes of the tetrahedron and a point on the binary $\text{FeO} - \text{Fe}_2\text{O}_3$ join. In consequence of this, the composition and stability of the combined iron oxide component of the system in the presence of carbon, controls the course of recrystallization during heating.

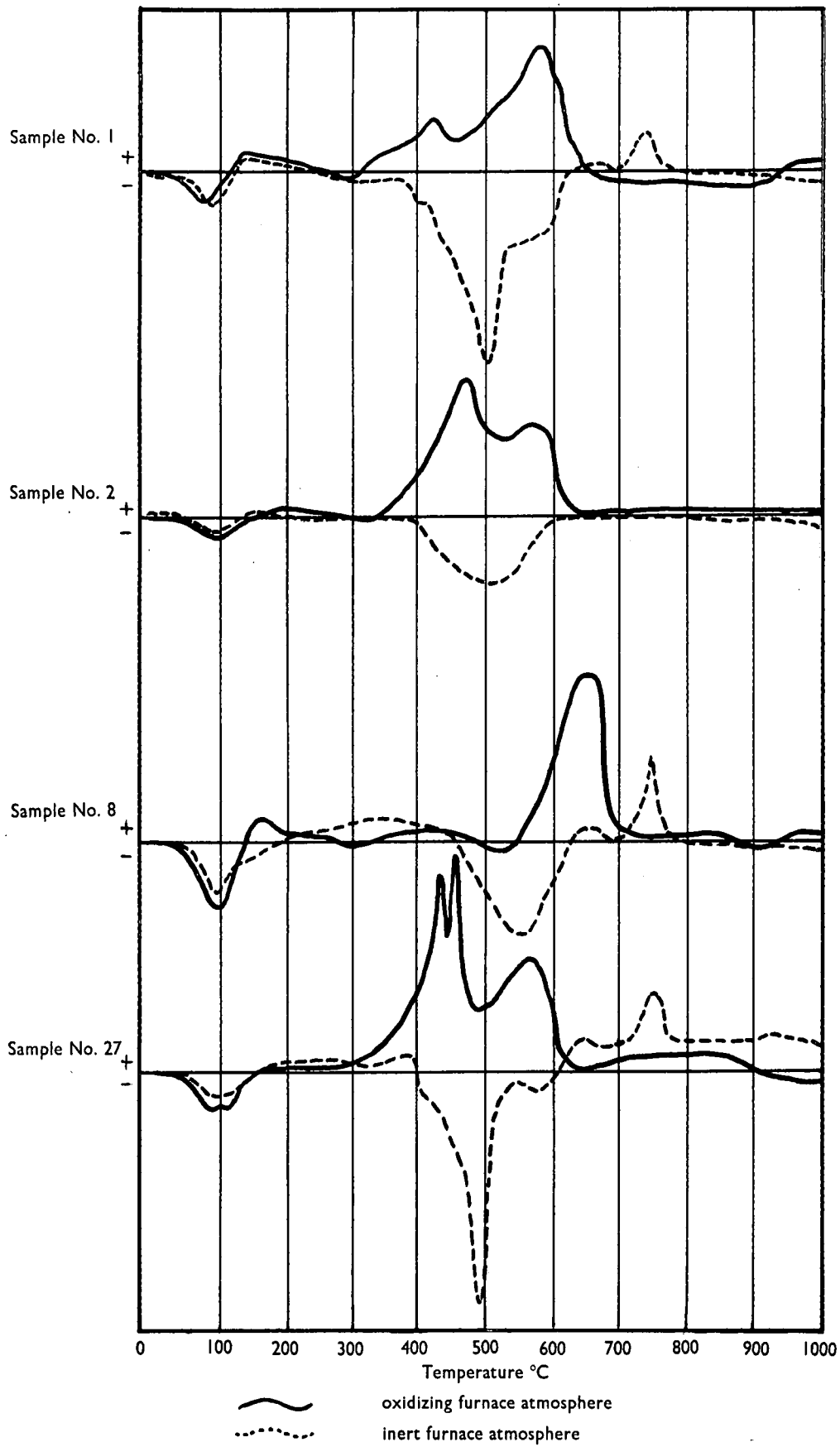


FIG. 1 D.T.A. CURVES OF TYPICAL SHALES
Heating-Rate.— 10° C/min.

4.2 The Initial Ternary Join

It is apparent from section 3 that subsequent to dehydroxylation the iron oxide component of the unoxidized D.T.A. sample will consist of:

1. A highly crystalline magnetite; the solid dissociation product of siderite, and;
2. An amorphous iron oxide contained by the dehydroxylated chamosite. The calculated stability of iron oxide in the presence of excess carbon indicates that this amorphous iron oxide should have a composition approaching that of magnetite.

Immediately subsequent to dehydroxylation therefore the equilibrium phase relationship for an unoxidized Ecca shale body can be expressed in terms of the $\text{Fe}_3\text{O}_4\text{-Al}_2\text{O}_3\text{-SiO}_2$ ternary join of the main quaternary system. The characteristics of this subsystem indicate that these three oxides are compatible.

4.3. The Final Substitution of a Boundary Subsystem

It has been shown (section 3.2, Figure No. 3) that above 665°C . magnetite becomes thermodynamically unstable in an atmosphere in equilibrium with excess carbon. Theoretically this instability gives rise to an endothermic reduction of magnetite to wustite. It follows therefore that with increase in temperature through 665°C ., the $\text{Fe}_3\text{O}_4\text{-Al}_2\text{O}_3\text{-SiO}_2$ ternary join ceases to represent the equilibrium phase relationships of the shale. Endothermic reduction of magnetite to wustite causes the iron oxide apex of the initial ternary join to move along the binary $\text{FeO-Fe}_2\text{O}_3$ join (Figure No. 4) towards the FeO apex of the tetrahedron. At temperatures approaching 730°C ., the equilibrium content of carbon monoxide in the gaseous phase of the unoxidized shale sample becomes so high that the solid phase relationships are established in the $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2$ boundary system.

Two $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2$ systems have been derived. The most recent one is the equilibrium system reported by Schairer & Yagi (1952). This system includes iron cordierite as a recrystallization product. These workers point out, however, that iron cordierite only crystallizes with some reluctance even after seeding of melts with cordierite crystals. When considering a dynamic solid state recrystallization therefore, it is best to refer to the metastable $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2$ system derived by Schairer (1942) for possible high temperature phase relationships. This system is illustrated in Figure No. 5 and contains only four compatibility triangles instead of the six exhibited by the equilibrium system.

4.4 The Compositional Range

If the compositions of the lower Ecca shales are recalculated for the $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2$ system, it is found that these fall in a scatter along the heavy line ABC, joining the two binary compositions 63.5% FeO , 36.5% SiO_2 — 27.5% Al_2O_3 , 72.5% SiO_2 (Figure No. 5).

Now although the endothermic reduction of magnetite to wustite above 665°C . maintains a state of equilibrium between the iron oxide component and

the gaseous phase of the shales, it leads to a system of incompatible oxides. This is demonstrated by the compatibility triangles depicted in Figure No. 5. These indicate that if a level of equilibrium is to be re-established above 665°C ., then any wustite formed from magnetite must recrystallize with silica and alumina to form fayalite and hercynite. Theoretically therefore, wustite can only exist in a transient form between 665°C ., when it is produced from magnetite, and approximately 730°C ., when it recrystallizes with silica and alumina to re-establish a metastable oxide assemblage.

From Figure No. 5 it can be seen that the point B represents an important discontinuity in the recalculated compositional range of the shales. In the range AB any composition must recrystallize to fayalite, hercynite and silica. In the range BC recrystallization will lead to hercynite, mullite and silica. This explains to some extent why the 675°C endo-exothermic D.T.A. peak system is only exhibited by highly ferriferous shales. In the high iron range AB, the recrystallization of fayalite is thermodynamically valid and exothermic. Data is not available for hercynite so it is not clear whether recrystallization of this compound contributes to the 730°C exotherm. It probably does to a smaller extent than fayalite. Mullite on the other hand is known to recrystallize only relatively slowly in clays as conditions become kinetically favourable above 900°C . It appears therefore, that only those recalculated shale compositions falling in the range AB (Figure No. 5) will provide the typical peak system exhibited by samples No. 1, 8 and 27 in Figure No. 1.

4.5 Experimental Confirmation

The following experimental observations provide confirmation of the postulated recrystallization mechanism:

1. X-ray diffraction traces of ferriferous shales heated in the presence of excess carbon to temperatures of 650°C . exhibit a strong magnetite peak system.
2. X-ray diffraction traces of shales heated in the presence of excess carbon to 950°C exhibit peak systems which confirm recrystallization according to the compatibility triangles of Schairer's metastable $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2$ system.
3. The observed temperature of the D.T.A. endotherm at 675°C . is just 10°C . above the theoretically predicted temperature for the endothermic reduction of magnetite to wustite.
4. The exothermic recrystallization of fayalite from wustite and silica is indicated by the 730°C D.T.A. exotherm with ferriferous samples.
5. Heating the shales under oxidizing conditions eliminates the recrystallization peak system.
6. The exhibition of the recrystallization peak system correlates with the recalculated $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2$ chemical composition rather than with mineralogical composition.

5. Conclusion

It is concluded that the 675°730° C. endo-exothermic D.T.A. peak system exhibited by ferriferous lower Ecca shales in an inert furnace atmosphere is due to the following recrystallization mechanism:

1. Dissociation of siderite and dehydroxylation of the clay minerals lead to a stable oxide assemblage made up largely of Fe_3O_4 , Al_2O_3 and SiO_2 . These oxides are compatible with one another and in equilibrium with the gaseous phase of the shale.
2. With increasing temperature the presence of excess carbon causes the carbon monoxide content of the gaseous phase of the shale to increase in accordance with the chemical thermodynamic characteristics of the equation:

$$\text{C} + \text{CO}_2 \rightarrow 2\text{CO}.$$
3. Above 665° C. the content of carbon monoxide in the gaseous phase of the shale reaches a level

which causes magnetite to become unstable. This oxide is consequently reduced endothermally to wustite. This is indicated by the 675° C. endotherm observed on the D.T.A. curves.

4. The reduction of magnetite gives rise to an assemblage of incompatible oxides: FeO , Al_2O_3 and SiO_2 . Recrystallization of these oxides according to the compatibility triangles of Schairer's metastable $\text{FeO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ system must occur to re-establish a metastable condition. This recrystallization is exothermic and is indicated by the 730° C. exotherm on the D.T.A. curves.

Summary

1. Introduction

The findings reported relate to fresh lower Ecca shales from the Durban and Pietermaritzburg areas. The variable composition of these shales falls within the mineral suite: carbon, quartz, siderite, chamosite and illite.

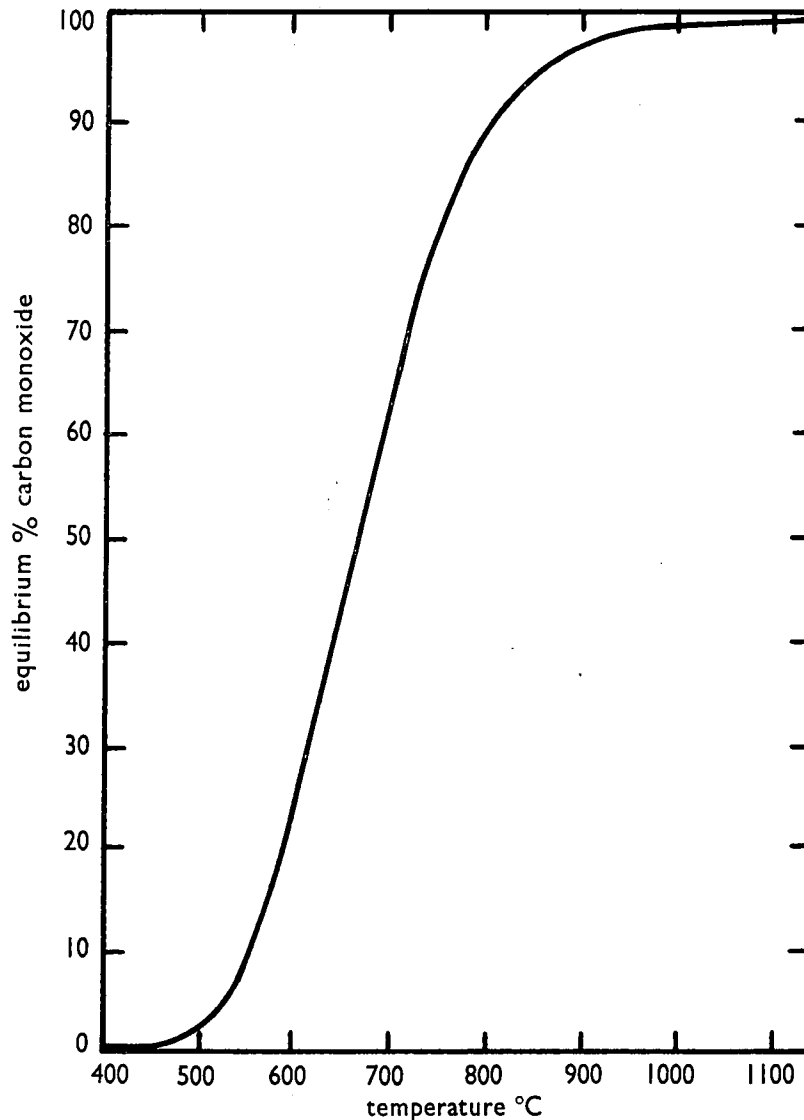


FIG. 2. EQUILIBRIUM % CO IN $\text{CO} + \text{CO}_2$ COMPONENT OF GASEOUS PHASE IN CONTACT WITH CARBON

2. Characteristic D.T.A. Curves

The feature of interest is the 675°-730° C. endo-exothermic peak system exhibited by the more ferriferous shales in an inert furnace atmosphere.

Observations indicate that this peak system arises from an irreversible recrystallization.

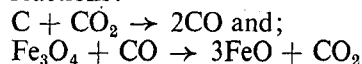
3. Chemical Thermodynamic Aspects

3.1 The Dissociation of Siderite

There is experimental and theoretical evidence that the interpretation of the mechanism of dissociation of siderite by Rowland and Jonas (1949) is incorrect. It is concluded that the solid dissociation product of siderite in an inert or reducing atmosphere is magnetite and not wustite as may be expected from previous literature.

3.2 The Stability of Iron Oxide in the Presence of Solid Carbon

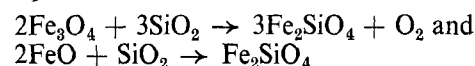
The chemical thermodynamic characteristics of the two reactions:



indicate that magnetite becomes unstable in the presence of excess carbon above 665° C. when it is reduced to wustite. This reduction is endothermic.

3.3 The Recrystallization of Fayalite

The chemical thermodynamic characteristics of the two equations:



indicate that fayalite will only recrystallize from wustite and silica.

4. The Recrystallization Mechanism

4.1 The FeO-Fe₂O₃-Al₂O₃-SiO₂ Quaternary System

By considering the stability of the iron oxides in the presence of excess carbon it is possible to delineate a ternary join in the above quaternary system which will represent the equilibrium phase relationships of a ferriferous carbonaceous shale at any particular temperature. The stability of iron oxide in the presence of excess carbon therefore controls the course of recrystallization of a ferriferous carbonaceous shale.

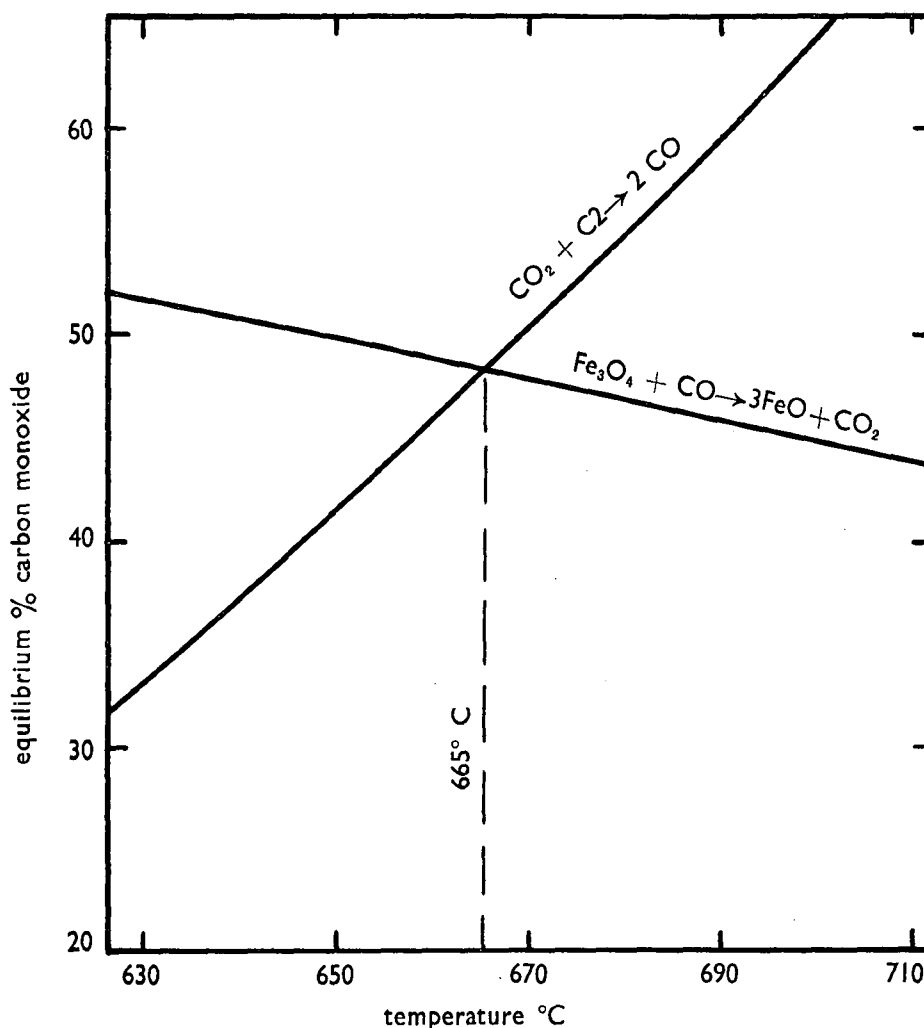


FIG. 3. EQUILIBRIUM % CO IN A CO + CO₂ MIXTURE IN CONTACT WITH CARBON

4.2 The Initial Ternary Join

Immediately subsequent to dehydroxylation the equilibrium phase relationship of the shale fall largely into the subsystem represented by the $\text{Fe}_3\text{O}_4\text{-Al}_2\text{O}_3\text{-SiO}_2$ ternary join. These three oxides are compatible and are in equilibrium with the gaseous phase of the shale.

4.3 The Final Substitution of a Boundary Subsystem

Above 665°C ., Fe_3O_4 becomes unstable in the presence of excess carbon and is reduced to wustite. At temperatures approaching 730°C . therefore, the solid phase relationships of the shale become established in the $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2$ boundary system.

The metastable $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2$ system derived by Schairer (1942) is regarded as being more applicable to the dynamic nature of a recrystallization during thermal analysis than the equilibrium system of Schairer & Yagi (1952).

4.4 The Compositional Range

Compositions recalculated for the $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2$ system, fall in a scatter along the line ABC joining the binary compositions 63.5% FeO , 36.5% SiO_2 and 27.5% Al_2O_3 , 72.5% SiO_2 (Figure No. 5).

The compatibility triangles of the metastable boundary system indicate that wustite can only exist in a transient form and must recrystallize with silica and alumina to form fayalite and hercynite. Only those more highly ferriferous shales with recalculated compositions falling within the fayalite-hercynite-silica compatibility triangle can be expected to provide a recrystallization exotherm at 730°C .

4.5 Experimental Confirmation

X-ray diffraction analyses confirm the presence of magnetite before recrystallization and "fayalite, hercynite and silica" or "hercynite, mullite and silica" after recrystallization according to the compatibility triangle into which the recalculated composition of the shale falls.

The observed temperature of the 675°C . endotherm is just 10°C . above that of the theoretically predicted temperature at which magnetite begins to be endothermally reduced to wustite.

The exothermic recrystallization of fayalite is indicated by the 730°C . exotherm with ferriferous samples.

The recrystallization peak system correlates with recalculated chemical composition rather than mineralogical composition.

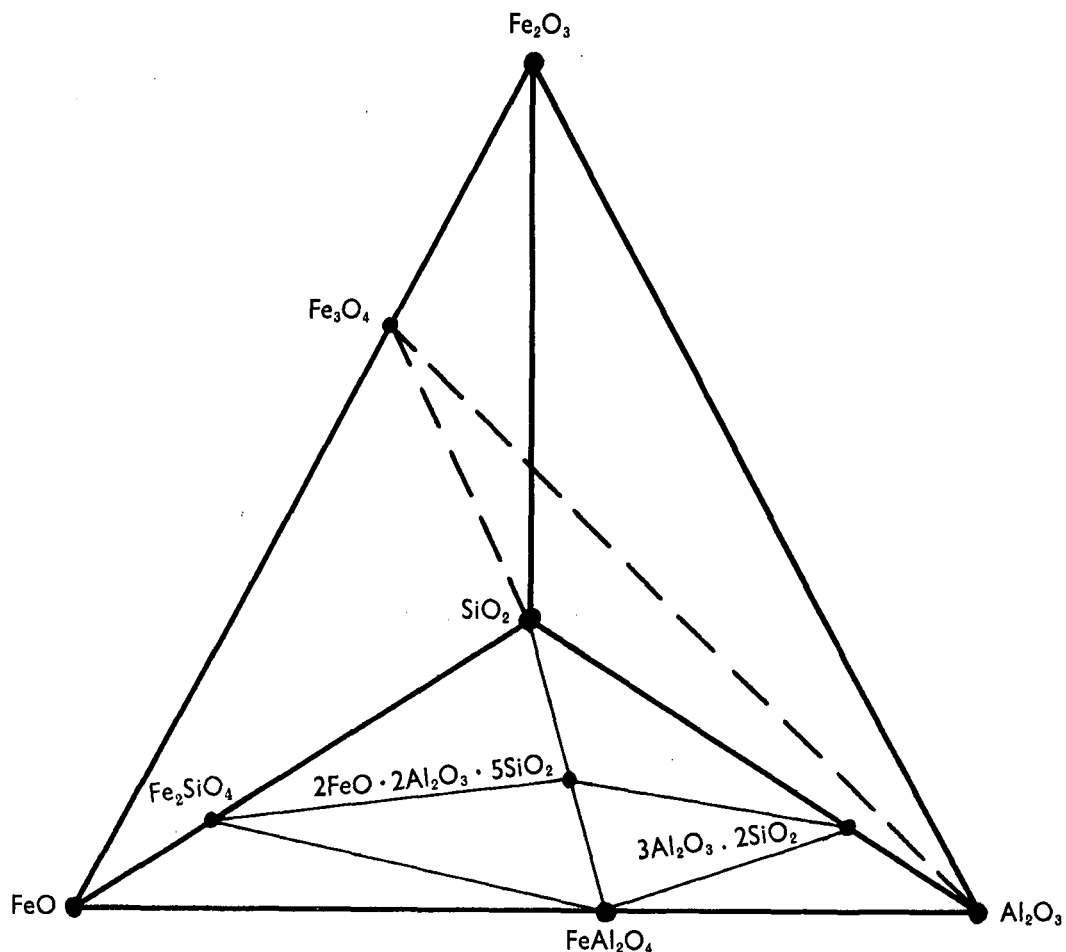


FIG. 4. THE $\text{FeO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ SYSTEM

5. Conclusion

It is concluded that the 675°730° C. endo-exothermic D.T.A. peak system exhibited by ferriferous lower Ecca shales in an inert furnace atmosphere is due to:

1. The endothermic reduction of magnetite to wustite by the gaseous phase of the shale which contains excess carbon.
2. The exothermic recrystallization of fayalite from wustite and silica.

References

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Rowland, A. R. and Jonas, C. J. (1949). "Variations in Differential Thermal Analysis Curves of Siderite," Amer. Miner., 34, pp. 550-558.

Schairer, J. F. (1942). "The System CaO-FeO-Al₂O₃-SiO₂," Amer. J. Sci., 25, pp. 241-274.

Schairer, J. F. and Yagi, K. (1952). "The System FeO-Al₂O₃-SiO₂," Amer. J. Sci., Bowen Volume, pp. 471-512.

Dr. Sumner: Dr. Drennan has used the X-ray technique and the differential thermal analysis technique to great advantage in explaining the differential thermal analysis curves he obtained for the various Ecca shales.

It is rather rare to have the two techniques used on one sample simultaneously and Dr. Drennan has developed a small micro-furnace for heating the sample which fits into the X-ray diffraction apparatus. The X-ray peaks of any material which might crystallize in the particular temperature range may be obtained from this combination. The combination of these techniques should be very useful in dealing with soil samples.

Professor Orchard: Dr. Drennan must be dealing with relatively unweathered Ecca shales and also weathered material. How much is inherited from the unweathered material when he examines the weathered material with regard to the minerals he mentions on page one?

Dr. Drennan: The iron minerals leach very fast as the surface is approached. The chamosites disappear almost completely, as do the siderites.

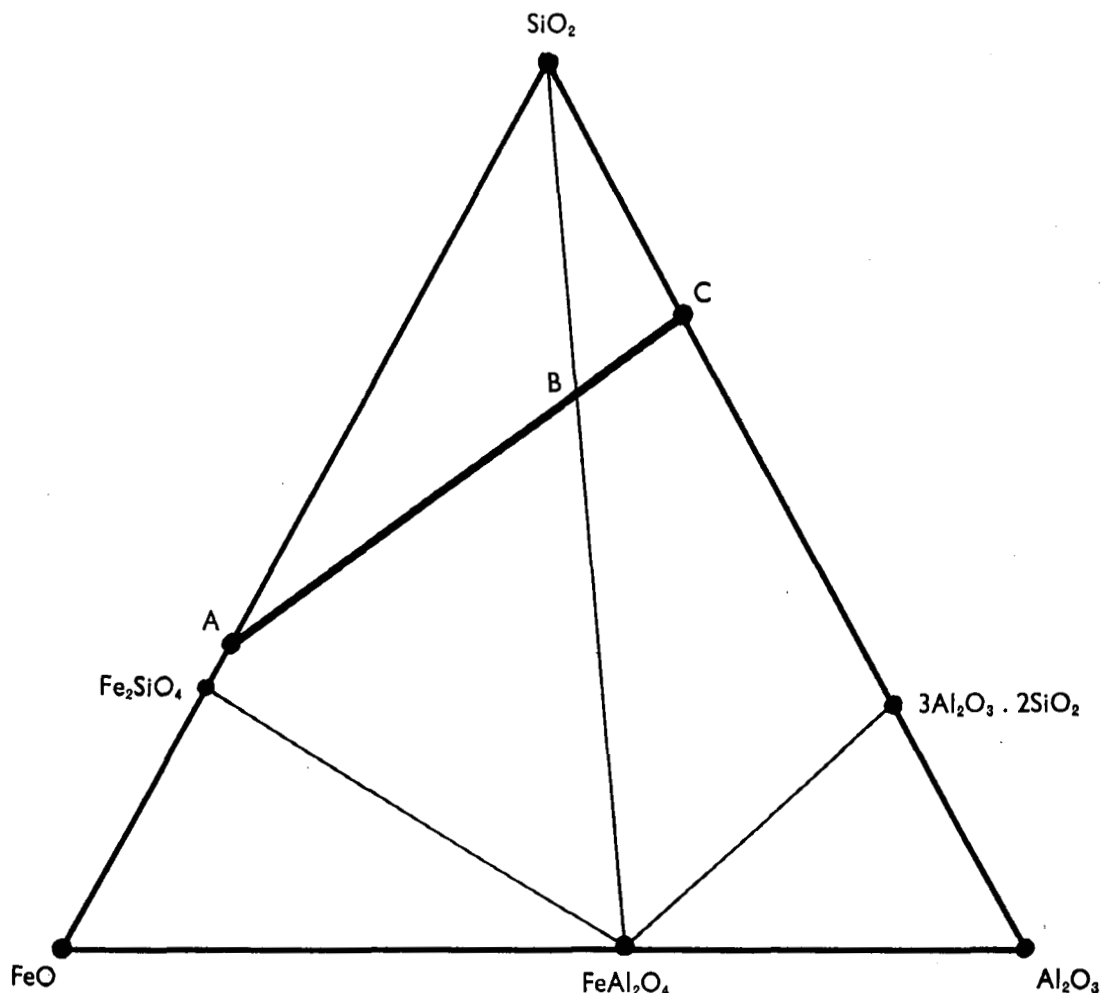


FIG. 5. THE METASTABLE FeO—Al₂O₃—SiO₂ SYSTEM