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STAGES IN THE OXIDATION OF MAGNETITE

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The oxidation of magnetite on heating has received considerable attention in the geologic literature largely because of the difference in behavior of natural and synthetic magnetite. Experimental work by a number of investigators (1, 2, 3, 4, 5) invariably showed synthetic magnetite to oxidize first to gamma-Fe_2O_3 (at temperatures below the inversion) whereas natural magnetite oxidized only to alpha-Fe_2O_3, usually at more elevated temperatures.

Schmidt and Vermaas (6) conducted the most recent study of the behavior of magnetite on heating. Their differential thermal curves for natural magnetite specimens showed two distinct exothermic peaks (360–375° C. and 580° C.), the earlier of which was most pronounced in fine specimens and varied proportionally with the fineness of the material. They concluded that magnetite goes through two stages of oxidation on being heated in air, the first stage being a surface oxidation to hematite and the second stage a complete oxidation also to hematite. They state that formation of gamma-Fe_2O_3 was not detected at any stage.

The writer (7) independently studied the oxidation of magnetite by DTA with near identical results. Magnetite was observed to pass through two distinct stages of oxidation on heating in air. The first stage was shown to be related to the specific surface of the specimens. The present interpretation, however, is sufficiently different to be worthy of record.

Gheith (5) studied the oxidation of synthetic magnetite by DTA and he obtained two exothermic peaks caused by an initial oxidation to gamma-Fe_2O_3 and subsequently by the inversion from gamma to alpha-Fe_2O_3. A comparison of his curves for synthetic magnetite with those obtained from fine grained natural magnetite specimens shows a correspondence between the exothermic peak for the oxidation to gamma-Fe_2O_3 in the synthetic specimens and the first exothermic peak in the DTA curves of fine grained natural magnetite specimens. This suggests to the writer that the first peak in the DTA curves for natural magnetite may also represent oxidation to gamma-Fe_2O_3.

To investigate the nature of the first exothermic peak obtained from natural magnetite, specimens of finely ground (−250 mesh), clean magnetite from Minneville, N.Y. were heated to 430° C. and 500° C. in a differential thermal analysis unit. Both temperatures are above the first peak and below the range of the second peak for natural magnetite. The specimens after heating were brownish black and intensely magnetic. *X*-ray powder photographs of the products showed strong magnetite patterns with only a few of the strongest hematite lines.

The distribution and relative intensities of the lines in the *x*-ray photographs of these products suggested that only a very minor quantity of magnetite had become oxidized in each trial, as found by Schmidt and Vermaas (6). Chemical analysis of the ferrous iron content, however, revealed a much different situation. Whereas the original material came from a single crystal and closely approached the theoretical composition of magnetite, the specimens heated to 430° C. and 500° C. showed Fe_2O_3:Fe_3O_4 ratios of 34:66 and 45:55 respectively. This suggests that the few poorly developed hematite lines in the *x*-ray photographs of the heat treated specimens did not represent all the oxidation; that most of the oxidation below 500° C. must actually have involved a change to gamma-Fe_2O_3.

This conclusion is supported by the fact that the *x*-ray photographs of the heat treated specimens showed a distinct line broadening at high values of θ, a broadening not present in the untreated magnetite. The fact that gamma-Fe_2O_3 has slightly different cell dimensions than magnetite probably accounts for the broadening.

As a result of this differential thermal study the writer proposes that magnetite goes through the following stages during rapid oxidation:

(1) $4Fe_3O_4+O_2 \rightarrow 6$ gamma-Fe_2O_3; commencing at approximately 200° C. and culminating at about 375–400° C.

(2) Gamma-$Fe_2O_3 \rightarrow$alpha-Fe_2O_3; starting at about 375° C. and probably terminating at from 525 to 550° C. Gheith (5) found experimentally that this transition temperature is related to the temperature of formation of the gamma-Fe_2O_3.

(3) $4Fe_3O_4+O_2 \rightarrow 6$ alpha-Fe_2O_3; starting at from 550 to 575° C. The culmination and point of completion of this reaction are dependent upon the extent of reaction 1.

Reaction 1 is clearly shown by DTA studies to be related to the specific surface of the specimen. It is believed to represent a nucleation process wherein gamma-Fe_2O_3 forms on the surface of magnetite grains according to the underlying pattern. All magnetite probably becomes oxidized on the surface to gamma-Fe_2O_3 on heating, but this reaction is quantitatively unimportant in sizes coarser than 60 mesh and hence it has escaped detection in oxidation studies of natural magnetite.

Rate of oxidation appears to be an important factor in the formation of gamma-Fe_2O_3 on magnetite. Experiments conducted by the writer (7) on the oxidation of siderite illustrate the importance of reaction rates. Siderite first becomes oxidized to magnetite. Rapid oxidation of finely divided siderite at moderate temperatures in hydrothermal or dry environments resulted in the formation of gamma-Fe_2O_3. In experiments with the same materials and at the same temperatures alpha-Fe_2O_3 was the final product when the oxidation rate was retarded by CO_2 in the system. Apparently rapid oxidation favors the type of mimicry which results in the magnetite structure being preserved in the ferric oxide.

The rate of oxidation of magnetite at a given temperature and oxygen pressure is a function of the specific surface of the material and of the degree of perfection of the crystal lattice. The most pronounced difference in natural and synthetic magnetite is grain size. This alone could easily account for the differences that have been found in the behavior of the two materials during rapid oxidation. Minor structural irregularities of synthetic magnetite proposed by Starke (8) have been invoked to account for the fact that it oxidizes to gamma-Fe_2O_3, but these irregularities are probably only of secondary importance.

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THE SEPARATION OF CLAY MINERALS FROM CARBONATE ROCKS

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The separation of the clay mineral fraction of a carbonate rock is accomplished ordinarily by acid digestion. Hydrochloric acid often is preferred because it is a strong acid, forms soluble compounds and facilitates rapid solution. When insoluble silica residues are not the primary objectives of carbonate rock solution, the extent of acid reaction with the

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