

Magnetite formation by the reduction of hematite with iron under hydrothermal conditions

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Abstract

The formation of magnetite by the reduction of hematite with iron in the presence of aqueous solution at 350–570°C, 1–2 kbar pressure, takes place by two reactions: (1) the oxidation of iron metal with water, and (2) the reduction of hematite with hydrogen. The overall oxidation-reduction reaction is accelerated by increased temperature, pressure, and solution acidity. The oxidation of iron occurs by a replacement and armoring mechanism, whereas hematite reduction occurs by reductive dissolution of hematite and direct precipitation of magnetite from the bulk solution. The initial rapid rate of the hematite reduction may render unreliable an oxygen isotope geothermometer calibrated using the reaction.

Introduction

The reduction of hematite to magnetite at elevated temperatures and pressures in the presence of water can be represented by the equation:



Magnetite can also be formed at high temperatures in the presence of water by the reduction of hematite with iron metal. The reaction can be expressed by the equation:



Little is known about the mechanisms of reactions (1) and (2) under hydrothermal conditions. However, several studies have been made on the reduction of hematite at or near one atmosphere pressure, using a variety of reducing conditions: CO/CO₂, H₂, H₂/H₂O, and Fe/H₂O (McKewen, 1960; Kawaski *et al.*, 1962; Endom *et al.*, 1964; Heizmann and Baro, 1966; Nabi and Lu, 1968; Hara *et al.*, 1969). These studies have shown that magnetite initially forms as a surface layer on the hematite reactant, and then gradually replaces the hematite. The kinetics of reaction are controlled by diffusion of gases to and from the hematite-magnetite interface, through the coating magnetite layer. Topotaxial influences on the mechanism of the reduction of single crystal hematite have also been determined (Heizmann and Baro, 1966; Moineau and Baro, 1967; Baro and Heizmann, 1969; Moineau and Baro, 1971). The epitaxial relationship between the two minerals is such that planes of oxy-

gen with compact stacking are parallel for both phases, with iron atoms apparently having little or no effect on relative orientations.

The purpose of this note is to present observations on the mechanisms of magnetite formation by the reduction of hematite with iron under hydrothermal conditions at 350°–570°C, 1–2 kbar pressure, and to indicate possible consequences of these mechanisms for a magnetite-water oxygen isotope geothermometer calibration (Bertenrath *et al.*, 1973). The iron-magnetite-wustite triple point is at 575°C (Huebner, 1971), and the experimental upper temperature limit was chosen so as to eliminate the possibility of wustite formation.

Experimental methods and observations

The solid reactants were weighed out according to the stoichiometry of equation (2). The solids used were: iron (metal) powder (Fisons Ltd.); iron metal shavings, approximately 1mm long (British Chemical Standards No. 260/3) and iron (III) oxide > 99.995 percent (Koch Light Ltd.). Solutions were either water or dilute hydrochloric acid. Experimental charges consisted of 50–60 mg solid and 800–1000 mg solution sealed inside 0.006" thick walled gold capsules. All experiments were performed inside stainless steel cold-seal bombs, using water as the pressure medium. Reaction products were examined by X-ray powder diffraction using iron filtered CoK α radiation. This method could not satisfactorily detect the small amounts of iron in products, but visual examination

with a moderate-power binocular microscope sufficed for this purpose. The molar proportions of magnetite to hematite were estimated from the relative intensities of the magnetite 311 reflections and the hematite 104 reflections. For this purpose a calibration curve was prepared by X-ray diffraction of mixtures containing known amounts of magnetite and hematite. Scanning electron microscopy was employed in determining the nature of the reaction mechanisms.

Experimental results are summarized in Table 1. The estimates of magnetite/hematite proportions are given as percent magnetite yield, as determined from the stoichiometry of equation (2). Temperatures are quoted $\pm 5^\circ\text{C}$, pressure ± 200 bars; and the stated reaction times are from when the bombs equilibrated at temperature (run-up times were approximately 45 min.). The following observations can be made with respect to the data presented in the table. (1) The reaction of iron powder with hematite is accelerated by increasing temperature, pressure and solution acidity. (2) Extensive magnetite formation ($\geq 60\%$) occurs in reactions of short duration (0.25–0.5 hours). Iron metal constitutes only 11 percent of the total iron of the reactants, thus the bulk of the high magnetite yields must come from the reduction of hematite. Additionally, Matthews (1974) has shown that only slight oxidation of iron metal powder ($\leq 20\%$) occurs under similar experimental conditions. Substantial magnetite formation must occur during the run-up period.

In the reactions in which iron metal shavings and hematite were the solid reactants, the shavings could be recovered from the experimental products, coated with a surface layer of magnetite, but otherwise unreacted. The products remaining after the extraction of the iron shavings contained both magnetite and hematite at 350° and 465°C , but at 555°C only magnetite was detectable. Similar observations were made in several experiments in which iron powder was reacted with hematite; whereas all hematite had undergone conversion to magnetite, traces of unreacted iron remained in the product.

SEM micrographs illustrating the mechanisms involved in the iron-hematite reaction are given in Figures 1 and 2. Two distinct generations of magnetite crystals can be observed: (a) irregular, tightly packed, magnetite crystals, surrounding the iron metal grains (Fig. 1), (b) well formed, loosely packed, magnetite crystals, often revealing extremely well developed crystalline habits (Fig. 2). No obvious orientated relationships exist between the type (b) crystals.

TABLE 1. Experimental results

| $T^\circ\text{C}$ | t.hrs | P.kb | Solid reactants | Solutions | Products | Yield % |
|-------------------|-------|------|-------------------------|-------------|-------------------------------|---------|
| 355 | 166 | 1 | Fe shavings Hematite | 0.01M.HCl | Magnetite Hematite Iron | 80 |
| 355 | 166 | 1 | " " | 0.001M.HCl | Magnetite Hematite Iron | 60 |
| 360 | 97 | 1 | Fe powder Hematite | 0.01M.HCl | Magnetite Hematite Iron | 80 |
| 360 | 510 | 1 | " " | " " | Magnetite Hematite Iron | 90 |
| 360 | 510 | 1 | " " | 0.001M.HCl | Magnetite Hematite Iron | 80 |
| 365 | 455 | 2 | " " | " " | Magnetite Iron (s)* | |
| 360 | 0.25 | 2 | " " | Water | Magnetite Hematite Iron | 60 |
| 365 | 455 | 2 | " " | " | Magnetite Iron (s) | |
| 360 | 650 | 1 | " " | " | Magnetite Hematite Iron | 75 |
| 365 | 1940 | 1.5 | " " | " | Magnetite | 100 |
| 465 | 116 | 1 | Fe shavings Hematite | Water | Magnetite Hematite Iron | 65 |
| 460 | 48 | 1 | Fe powder Hematite | 0.01M.HCl | Magnetite | 100 |
| 460 | 136 | 1 | " " | 0.001M.HCl | Magnetite | 100 |
| 455 | 358 | 1 | " " | 0.0001M.HCl | Magnetite | 100 |
| 460 | 0.5 | 1 | Fe powder Hematite | Water | Magnetite Hematite Iron | 60 |
| 460 | 48 | 1 | " " | " | Magnetite Hematite Iron | 80 |
| 455 | 358 | 1 | " " | " | Magnetite Iron (s) | |
| 455 | 515 | 1 | " " | " | Magnetite Iron (s) | |
| 555 | 166 | 1 | Fe shavings Hematite | Water | Magnetite Iron | |
| 545 | 0.5 | 1 | Fe powder Hematite | Water | Magnetite Hematite Iron | 75 |
| 570 | 267 | 1 | " " | " | Magnetite | 100 |
| 540 | 367 | 1 | " " | " | Magnetite | 100 |
| 565 | 534 | 1 | " " | " | Magnetite | 100 |

*(s) indicates that only traces of iron are present in the reaction product.

Magnetite crystallizes in the isometric system, and most commonly shows octahedral and dodecahedral form. These habits can be recognized in some of the idiomorphic crystals shown in Figure 2.

Discussion

The experimental observations indicate that magnetite formation proceeds non-stoichiometrically. Reduction of hematite to magnetite occurs more rapidly than the oxidation of iron. Complete reaction is achieved in conditions of enhanced T , P , and solution

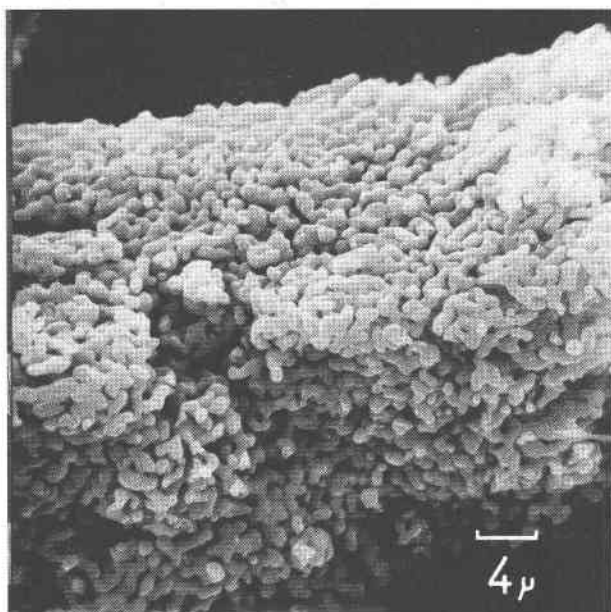
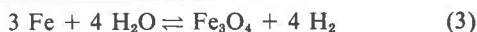


FIG. 1. Magnetite crystals surrounding an iron metal grain. Product from reaction of iron with hematite in water after 0.5 hours at 545°C.

acidity. This independence in the chemical behavior of the two solid reactants, together with the SEM observations, suggests that two reactions are occurring:

Oxidation of iron metal with water



Reduction of hematite with hydrogen



In oxidation–reduction terms, the two reactions are proceeding in opposite directions. (3) occurs so as to increase $f(\text{H}_2)$, and hence decrease $f(\text{O}_2)$; whereas (1) results in increased oxygen fugacity. Effectively (1) and (3) are two opposed $f(\text{O}_2)$ buffer reactions.

The ‘slow step’ of the overall reaction is the oxidation of iron. Since, according to the above equations, the iron oxidation provides the source of hydrogen for the hematite reduction, it would be expected that the kinetics of (1) are controlled by those of (3). However, if the join hematite–capsule water is itself considered to contain an oxidation–reduction couple, undergoing partial reaction, then additional hematite reduction occurs over that taking place by stoichiometric reaction. An alternative proposal is that the non-stoichiometric reaction progress is a consequence of hydrogen diffusion from the pressure medium through the capsule walls into the reacting

system. Eugster and Wones (1962) note that the effects of hydrogen diffusion from a pressure medium buffered by bomb walls are only noticeable at temperatures greater than 700°C. Specifically, Huebner (1971) states that the hematite–magnetite $f(\text{O}_2)$ buffer is stable for 2–3 days at 750°C. At the lower temperatures of this study, hydrogen diffusion rates must be significantly slower than at 700°C, particularly so since reasonably thick-walled gold tubing was used. The non-stoichiometry is evident at all temperatures in runs of only 0.5 hours duration; this clearly cannot be a consequence of hydrogen diffusion from the pressure medium. It is reasonable to conclude that hydrogen diffusion through capsule walls is of secondary influence on experimental phenomena.

Matthews (1974) found that increasing temperature and solution acidity accelerated the oxidation of iron metal. Consequently, the rate of generation of hydrogen by the oxidation reaction will also be increased by higher temperature and solution acidity. McKewen (1960) found that the rate of hematite reduction in hydrogen–water vapor mixtures at 1 atmosphere is proportional to the partial pressure of hydrogen. Thus, the rate-enhancing effects of temperature and solution acidity on the iron–hematite reaction could have a dual origin. The production of magnetite from the oxidation of iron is increased, but also, because of the corresponding increase in $f(\text{H}_2)$,

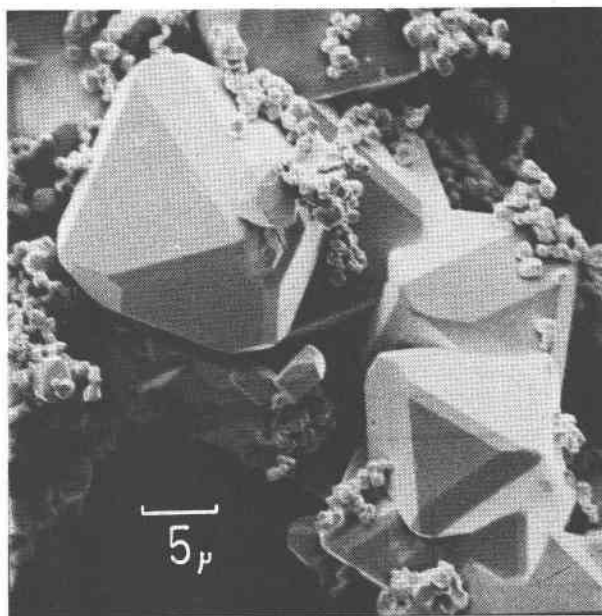


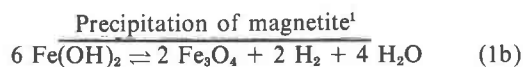
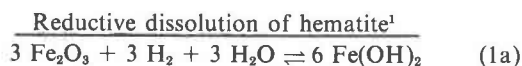
FIG. 2. Euhedral magnetite crystals formed by the reduction of hematite. Product from reaction of iron with hematite in water after 576 hours at 455°C.

the rate of hematite reduction is enhanced. The observed acceleratory effects of pressure may also be a consequence of iron oxidation being accelerated by increasing pressure.

Matthews' study revealed that magnetite initially nucleates heterogeneously from solution onto the surfaces of iron metal grains. The reaction interface then develops inwards into the iron grains, with the magnetite crystals replacing and armoring the metal. SEM examination of the iron reactant in the intermediate stages of the iron-hematite reaction invariably reveals the metal grains to be surrounded by a tightly packed layer of magnetite crystals (Fig. 1). It has also been noted previously that the iron shavings, coated with a surface layer of magnetite, can be extracted from reaction products. These observations indicate that iron oxidation in the iron-hematite reaction occurs by a replacement and armoring mechanism.

The well-formed, often idiomorphic, magnetite crystals revealed by SEM examination (Fig. 2) are formed by the reduction of hematite. The magnetite crystals are not packed together in a manner which suggests preservation of the gross morphology of the hematite grains, and contrast with the magnetite produced by the oxidation of iron, in which product crystals are tightly packed, and the gross morphologies of the reactant iron grains are preserved. These SEM observations indicate that the reduction reaction occurs through dissolution of hematite, followed by heterogeneous nucleation and growth of magnetite from solution. The magnetite growth appears to occur directly from the bulk solution, and there is no evidence to indicate that magnetite replaces and armors the hematite reactant. Nucleation of magnetite appears to be a highly favored process, as is attested by the rapid initial rate at which the hematite reduction takes place.

A further question is at what stage in the reaction does reduction occur: during dissolution of hematite, or at some later stage? Studies on the dissolution of thin films of ferric oxide at room temperature have shown that direct dissolution of the oxide is a significantly slower process than reductive dissolution (Evans, 1930; Pryor and Evans, 1949; Evans and Berwick, 1952). Holser and Schnerer (1961) found that ferrous species dominate the solution in equilibrium with magnetite under hydrothermal conditions. These observations suggest that a suitable mechanism for the hematite reduction is:



Conclusions

Magnetite formation by the reduction of hematite in the presence of water and a Ni/NiO buffer has been used in calibrating a magnetite-water oxygen isotope geothermometer at 300°–960°C (Bertenrath *et al.*, 1973). However, the evidence of this study is that the reduction of hematite in the presence of a reducing $f(\text{O}_2)$ buffer has a very rapid initial rate, with substantial magnetite formation occurring during heating of bombs up to maximum temperature. This initial magnetite formation creates a problem in the interpretation of isotopic equilibrium; for unless substantial recrystallization of magnetite takes place at maximum temperature, the oxygen isotope analysis of the solid will contain a memory reflecting the range of temperatures occurring during heating up. Early-formed magnetite crystals, though small, are frequently well-formed and sometimes euhedral; such crystals will tend to grow, but it is questionable whether they will recrystallize. In the case of the magnetite-water geothermometer calibration, the presence of memory effects of the heating-up period would tend to give low estimates of the equilibrium fractionation factor $\alpha(\text{O}^{18}/\text{O}^{16} \text{ magnetite}/\text{O}^{18}/\text{O}^{16} \text{ water})$, since $d\alpha/dT$ is positive in the range 300–960°C. Such a fractionation, when combined with another calibration (*e.g.* quartz-water) to give a geothermometer, would tend to give erroneously high temperature estimates when applied to the thermometry of natural assemblages.

Evidence for the existence of low-temperature memory effects can be found by comparing the fractionation factors for magnetites synthesized under hydrothermal conditions at 1 kbar (a) by the reduction of hematite with iron, according to equation (2), and (b) by the oxidation of iron metal with water. A magnetite synthesized in this study ($T=565^\circ\text{C}$, $t=534$ hours) gives a fractionation factor $10^3 \ln \alpha = -7.83$; whereas a magnetite produced by the oxidation of iron metal powder with water, after 264 hours reaction at 560°C, gives a factor $10^3 \ln \alpha = -7.20$ (analytical details can be found in the Appendix). Both reactions involve magnetite formation by solu-

¹ The inclusion of ferrous hydroxide as solution species is for the purposes of satisfying the stoichiometries of equations (1a) and (1b). The true nature of the ferrous solution species existing in hydrothermal conditions is not known. However, it is possible to write equations similar to (1a) and (1b) using alternative representations for the ferrous solution species; $\text{Fe}(\text{H}_2\text{O})_6^{2+}$, *etc.*

tion and precipitation, with the inherent possibility of establishing isotopic equilibrium between the product phases. However, whereas extensive magnetite formation occurs during the run-up period of the hematite-iron reaction, only minor magnetite formation ($\sim 20\%$) occurs during the run-up of the iron oxidation (Matthews, 1974). The difference between the two fractionation factors may arise from the presence of low-temperature memory effects in the isotopic analysis of the magnetite produced by hematite reduction. It is not possible to comment in detail on the calibration of Bertenrath *et al.* (1973), since they present no data in support of their fractionation curve. However, it can be noted that their curve gives $10^3 \ln \alpha \approx -7.9$ at 565°C , a value which corresponds quite closely to that obtained above from the iron-hematite reaction.

Ramdohr (1969) notes that naturally-occurring magnetite is frequently formed by the pseudomorphic replacement of hematite. This mode of formation contrasts with that observed in this study for hydrothermal conditions, in which magnetite is precipitated from the bulk solution, after the reductive dissolution of hematite. This suggests that magnetite formation by pseudomorphic replacement occurs in the absence of sufficient solution, or under P , T conditions at which diffusive processes become favored over solution and precipitation. An example of such conditions is given in the Introduction; *i.e.* high temperature and low $P_{\text{H}_2\text{O}}$. In contrast, some metamorphic magnetites are found to exhibit a well-defined crystalline habit. Octahedral magnetite associated with pyrite has been found in chlorite schists at Chester County, Vermont, and both simple and twinned octahedrons in the chlorite schist at Zillertal, Tyrol. Dodecahedral magnetite crystals have been found in the Banat region, Rumania, and at Nordmark, Sweden. At Traversella, Piedmont, well-formed magnetite occurs at a contact of limestone and diorite. The analogies between these crystal forms and those observed in this study suggest that sufficient hot solution was present to both dissolve the precursor iron solid species (commonly iron-bearing carbonate rock) and allow direct precipitation and growth of magnetite.

Appendix

Oxygen isotope analysis

Samples, as CO_2 gas, were analyzed on a 30 cm double collecting mass spectrometer described by Beckinsale *et al.* (1973). Standard reproducibility was

± 0.1 per mil or better. Oxygen was liberated from the magnetites using the BrF_5 technique of Clayton and Mayeda (1963), and from water by the guanidine hydrochloride procedure of Boyer *et al.* (1961). Analyses of the magnetites from the hematite reduction and iron oxidation respectively are $\delta_{\text{SMOW}} = 25.45$ parts per thousand and $\delta_{\text{SMOW}} = 26.10$ parts per thousand. Analyses of the water used in both reactions gave $\delta_{\text{SMOW}} = 33.51$ parts per thousand.

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