Iron Oxides of Fazendão Deposit, East Border of Quadrilátero Ferrífero, Minas Gerais, Brazil

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Abstract. The iron oxides highly influence the soil structure and aggregation of mineral particles in soil. They also play an important role in some economical variables, as those related to the use of land for agriculture practices or mineral exploitation, in ore mining activities. About 60 % of all industrial activities on iron processing in Brazil is based on ores mined in the geodomain of Quadrilátero Ferrífero, state of Minas Gerais, Brazil. Samples of a mining area for iron, the Fazendão Deposit in the east border of Quadrilátero Ferrífero have been studied in an attempt to contribute to a better understanding of the key chemical and mineralogical pathways related to the formation and transformation of iron oxides, involving hematite. From powder diffraction patterns, it is confirmed that hematite is the main mineralogical phase in all samples. The total iron contents were found to range between 65.15 and 70.00 mass%. The saturation magnetization values, $\sigma = 6.9$ and $2.1$ JT$^{-1}$ kg$^{-1}$, are significantly measurable only for the two samples showing some evidences of magnetite. 298 K-Mössbauer data confirmed the dominant occurrence of hematite in all samples, along with magnetite for the two samples showing non-zero magnetization. 110 K-Mössbauer data indicate that the hematite in all samples undergoes the Morin transition ($T_M \approx 260$ K), as expected for the relatively pure oxide. Maghemite could not be detected in any sample. New numerical analysis are now being performed, using Rietveld refinement of XRD data, in an attempt to obtain crystallographic results that could indicate more reliable evidences about the mechanisms of formation of hematite, particularly in the magnetic samples, for which the precursor is presumably magnetite.

1. Introduction
Iron oxides are found in large proportions in nature, being the most abundant metal oxides in soils. They rank second in the mineralogical occurrence order in the clay fraction of tropical and sub-tropical pedosystems, following the kaolinite group [1].

Iron oxides play an important influence on some critical properties of the geo-superficial layer, such those related to the use of land for agriculture practices or involved in the genesis of iron ore deposits [2]. About 60 % of all starting material used in industrial processing of iron in Brazil comes from exploitation of mines in the geodomain broadly known as Quadrilátero Ferrífero, in the state of Minas Gerais, Brazil. Itabirite is the dominant metamorphical hematite-rich rock of that area [3].
name “itabirite” has more commonly been applied in this sense to the metamorphosed banded iron formations (BIFs) of the Cauê Formation [4], but its use also comprehends similar BIFs of other parts of Brazil and western Africa. This denomination is also used to generically describe [5] any massive rock with a granular to schistose fabric, composed primarily of specularite, granoblastic hematite and, more locally, magnetite (Fe₃O₄), a primary oxide, which tends to be converted to hematite presumably via two main broad chemical mechanisms [6]: (i) by direct oxidation or (ii) through an intermediate formation of maghemite (γFe₂O₃).

The main objective of this work was to contribute to a better understanding of the key chemical and mineralogical pathways related to the formation and transformation of iron oxides, involving hematite, in a mining area for iron, the Fazendão Deposit, in the Quadrilátero Ferrífero geo-province.

2. Experimental

Nine samples were collected from sampling sites in that mine (geographical coordinates of the mineral deposit 20° 07’ 51.71” S 43° 25’ 00.09” W), in the east border of Quadrilátero Ferrífero, state of Minas Gerais, Brazil. The samples were analyzed with conventional chemical analytical methods, as redox titration (dichromatometry), for total iron contents, and with physical techniques, namely powder X-ray diffraction, ⁵⁷Fe Mössbauer spectroscopy at 298 K and 110 K and saturation magnetization (σ) measurements, with a portable magnetometer [7] under a fixed magnetic field of ~0.3 tesla.

3. Results and Discussion

From powder X-ray diffraction patterns (radiation CoKα), hematite appears to be the main mineralogical phase in all samples (Figure 1). The corresponding rhombohedral-hexagonal cell parameters for hematite [8], as obtained from Rietveld refinement of powder X-ray diffractometry patterns, are presented in table 1.

Table 1. Rhombohedral-hexagonal cell parameters for hematite

| Parameters / Samples | a/Å | b/Å | c/Å |
|----------------------|-----|-----|-----|
| FZ-01                | 5.038(1) | 5.038(1) | 13.750(1) |
| FZ-02                | 5.035(6) | 5.035(6) | 13.748(5) |
| FZ-03                | 5.039(2) | 5.039(2) | 13.750(5) |
| FZ-04                | 5.034(7) | 5.034(7) | 13.75(3) |
| FZ-05                | 5.029(5) | 5.029(5) | 13.74(3) |
| FZ-06                | 5.03(3) | 5.03(3) | 13.74(7) |
| FZ-10                | 5.032(8) | 5.032(8) | 13.74(3) |
| FZ-11⁺               | 5.035(9) | 5.035(9) | 13.752(6) |
| FZ-12⁺               | 5.035(9) | 5.035(9) | 13.749(4) |

*Samples with magnetite

Figure 1 - XRD pattern from FZ-01 sample  [Hm = hematite; Mt = magnetite; Qt = quartz]
From volumetric determinations (dichromatometry), the total iron contents were found to range between 65.15 and 70.00 mass%, as shown in Table 2. These results agree with previously reported data on related materials of this same area [9,10].

Table 2. Total iron content from volumetric determinations ($\sigma$ = standard deviation over the mean, estimated from results of three determinations)

| Sample   | Iron content (% Fe ± $\sigma$) |
|----------|---------------------------------|
| FZ–01    | 65.15 ± 0.04                    |
| FZ–02    | 68.69 ± 0.04                    |
| FZ–03    | 70.00 ± 0.01                    |
| FZ–04    | 68.51 ± 0.05                    |
| FZ–05    | 68.74 ± 0.04                    |
| FZ–06    | 67.69 ± 0.04                    |
| FZ–10    | 68.07 ± 0.05                    |
| FZ–11    | 67.93 ± 0.02                    |
| FZ–12    | 65.93 ± 0.05                    |

The saturation magnetization values observed are consistent with the values for natural hematite, $\sigma \sim 0.1$ T$^{-1}$ kg$^{-1}$, except for two samples, for which $\sigma = 6.9$ and 2.1 J T$^{-1}$ kg$^{-1}$ (samples FZ-11 and FZ-12, respectively). In these two samples, crystals of magnetite could be optically observed from microscope examination of thin petrographic sections; results were confirmed from data of XRD and $^{57}$Fe Mössbauer spectroscopy at 298 K. They were then chosen to be treated with sodium dithionite-citrate-bicarbonate (DCB) [11], in an attempt to selectively remove hematite and concentrate the magnetic phase.

298 K-Mössbauer data also confirmed the dominant occurrence of hematite in all samples (Figure 2, table 3), along with some magnetite for the two samples showing non-zero magnetization (Figure 3).

**Figure 2** - 298 K-Mössbauer spectrum for sample FZ-01 and FZ-02

**Figure 3** - 298 K-Mössbauer spectrum for sample FZ-11 and FZ-12 (magnetic samples)
Table 3. Mössbauer Parameters for samples FZ-01, FZ-02, FZ-11 and FZ-12 (δ = isomer shift relative to α-Fe; ε = quadrupole shift; $B_{hf}$ = hyperfine field; Γ = line width; AR = relative area of the subspectrum)

| Sample | Temperature/K | δ/mm s$^{-1}$ | ε/mm s$^{-1}$ | $B_{hf}$/T | Γ/mm s$^{-1}$ | AR/% |
|--------|---------------|---------------|---------------|------------|--------------|------|
| FZ-01  | 298           | 0.3(7)        | -0.21(1)      | 51.5(2)    | 0.32(9)      | 100.2(2) |
|        | 110           | 0.4(8)        | 0.41(1)       | 54.7(6)    | 0.37(7)      | 100.1(1) |
| FZ-02  | 298           | 0.36(7)       | -0.2(1)       | 50.9(2)    | 0.33(8)      | 100.1(1) |
|        | 110           | 0.52(7)       | 0.41(9)       | 54.1(6)    | 0.31(1)      | 100.1(1) |
| FZ-11  | 298           | 0.375(3)      | 0.144(1)      | 49.3(1)    | 0.31(1)      | 2.0(0)   |
|        |               | 0.715(7)      | 0.37(5)       | 53.6(9)    | 0.33(2)      | 83.1(1)  |
|        | 110           | 0.468(6)      | 0.37(5)       | 50.8(0)    | 0.6(8)       | 16.9(1)  |
| FZ-12  | 298           | 0.36(8)       | -0.20(0)      | 51.6(3)    | 0.31(1)      | 85.1(5)  |
|        | 0.18(8)       | -0.02(1)      | 49.3(3)       | 0.2(9)     | 9.8(4)       |
|        | 0.63(5)       | -0.2(3)       | 54.6(1)       | 0.45(1)    | 5.0(1)       |
|        | 110           | 0.48(2)       | 0.4(1)        | 54.2(2)    | 0.37(3)      | 96.3(3)  |
|        | 0.42(1)       | -0.2(5)       | 50.9(9)       | 0.3(6)     | 3.7(3)       |

Values fixed.

110 K-Mössbauer data indicate that the hematite in all samples undergoes the Morin transition ($T_M$ ≈ 260 K), as expected for the relatively pure oxide (Figure 4 and Figure 5). The 110 K-spectrum for sample FZ-01 (Figure 4) evidences a magnetically ordered component with exceptionally high hyperfine field, $B_{hf} = 54.7(6)$ tesla, which is a somewhat unusual value for hematite at this temperature. However similar values may be found in the literature, as those reported by Spier at al. [12], for hematites at 50 K, in samples from the same banded formation of Quadrilátero Ferrífero, in Minas Gerais, of sites geographically located only about a hundred kilometers apart from our sampling area.

Figure 4 - 110 K-Mössbauer spectrum for sample FZ-01 and FZ-02

Figure 5 - 110 K-Mössbauer spectrum for sample FZ-11 and FZ-12 (magnetic samples)

4. Conclusions
Maghemite could not be detected, either from X-ray or from Mössbauer analysis, in any sample [13]. Rietveld refinement of XRD data indicates only slight, but significant, differences on dimensions of the rhombohedral-hexagonal cell, as for sample FZ-01 (which is, dominantly, specularite). This sample corresponds also to an exceptionally high hyperfine field for hematite at 110 K. New numerical analysis Rietveld refinements are now in progress, in an attempt to obtain a better crystallographic description that could indicate more reliable evidences about the mechanisms of hematite formation, particularly as they could be drawn from data for sample FZ-01 and for the
magnetic samples FZ-11 and FZ-12. Results from those calculations are expected to point also to a more accurate interpretation about subtle differences on crystallographic structures, allowing us to propose consistent models for the mineralogical transformation involving hematite in this geosystem.

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