TEXTURAL CHARACTERIZATION OF IRON OXIDES AGGREGATES OF QUADRILÁTERO FERRÍFERO, MG. BRAZIL[1]

The phase transformation of magnetite to haematite and its textural implications

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Abstract

The samples studied in this paper were derived from the iron oxide facies of iron formations (IFs) of the Quadrilátero Ferrífero, southeastern Brazil. The rich-iron oxide varieties of the IFs can be regarded as Fe-O systems because they consist predominantly of aggregates of haematite and magnetite crystals. The study was based on carefully selected samples in which magnetite crystals occur as isolated large crystals set in a matrix of haematite grains. An electron microscope equipped with an EBSD system were used to investigate the transformation that occurs along the crystallographic planes {111} of the magnetite producing a characteristic triangular pattern of interlocking lamellae of transformed haematite crystals. EBSD analyses show that the magnetite and the new haematite crystals, martite, share crystallographic planes of highest atomic density, e.g. {111} and (0001).

Key words: Textural characterization; EBSD; Magnetite; Haematite; Phase transformation.

CARACTERIZAÇÃO TEXTURAL DE AGREGADOS DE ÓXIDO DE FERRO DO QUADRILÁTERO FERRÍFERO, MG, BRASIL

Transformação de fases de magnetita para hematita e suas implicações texturais

Resumo

As amostras estudadas nesse artigo derivam-se de formações ferríferas, FFs, fácies óxido, do Quadrilátero Ferrífero, sudeste do Brasil. As variedades de FFs podem ser consideradas como sistemas Fe-O porque consistem predominantemente de agregados de hematita e magnetita. O estudo foi baseado em amostras cuidadosamente selecionadas onde cristais de magnetita ocorrem como cristais isolados mergulhado numa matriz de grãos de hematita. Um microscópio eletrônico equipado com um sistema EBSD foi utilizado para investigar a transformação que ocorre ao longo dos planos cristalográficos {111} da magnetita produzindo um padrão triangular característico de lamelas intercruzadas de cristais de hematita. Análises de EBSD mostram que a magnetita e os novos cristais de hematita, martita, compartilham planos cristalográficos de mais alta densidade, exemplo {111} e (0001).

Palavras-chave: Caracterização textural; EBSD; Magnetita; Hematita; Transformação de fases.

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INTRODUCTION

Magnetite and haematite are the most common minerals, representing the Fe-O system. However, native Fe and wüstite could be considered two other members of that system. They are rare and require specific pressure and temperature conditions to be stable in geological systems. Maghemite is another mineral also rare in crustal environment. It is not predicable in natural phase stability diagrams but it is present in laboratorial experiments. Wüstite is uncommon in crustal rocks at temperature below 570ºC and high pO_2 fugacity becomes this mineral unstable. Actually, temperature and pO_2 fugacity define de amount of vacancies of Fe^{3+} in the wüstite lattice. High pressure, suggested by the occurrence of wüstite in mantle or nucleus conditions in the Earth, is an important factor related to the stability of minerals in the system Fe-O. A further essential principle, which controls the crustal rareness of wüstite, is its first tendency to react forming iron minerals from the silica-system instead of iron oxides. It is incorporated in silicates before to define itself as one oxide. Wüstite is highly reactive with quartz of hypo-saturated system in silica.(1) The vacancies occurrence is also described in the maghemite (©-Fe_2O_3), a structural analogue of magnetite, although with only Fe^{3+}.(2) In this mineral, the ion Fe^{3+} occupies a spinel lattice where occur vacancies eventually filled with alternative ions to stabilize the crystallographic spinel structure. A synchrotron study of maghemite(3) also described this kind of crystalline defect. Maghemite is observed at nearly 17GPa when haematite, a stable phase (〈-Fe_2O_3), starts to crystallize. The complete transformation is noticed at 27GPa and a new irreversible stable phase is observed (〈-Fe_2O_3) the haematite (2). Even though it is huge the sway of pressure on these transformations, haematite is not only under the influence of it. To haematite really establishes itself as a stable phase, it is required a system with high pO_2 fugacity (1). In the other hand, another Fe-O system-phase, the magnetite, is stable in a wide range of pressure and temperature condition, whereas monoclinic transformations are described in high-pressure conditions.(4)

Since the majority of the studies on the transformation in the system Fe-O are based essentially on the crystallographic aspect of a single-phase lattice, this study attempt to establish a relationship between the original lattice of the primary phase and the transformed one. To do that, initially a brief review of the current theory of phase transition will be provided and that will be focused in the crystal chemistry aspects of the system Fe-O, in particular to the natural occurrence of iron oxide minerals (ferritic-spinel magnetite) in iron formations in the southern Brazil. In addition, the crystallographic control on transition between the haematite and magnetite crystals using electron diffraction technique (EBSD) will be evaluated. Therefore the main objective of this study is to investigate the textural aspects of the phase transformation magnetite-haematite in rock samples from a crystallography viewpoint with the aid of EBSD.

FERRITIC SPINEL GROUP

The spinels are metallic oxides represented by minerals from the isometric system. Their end members have the general formula $A^{2+} B_2^{3+} O_4$ (so-called 2-3 spinels) and $A^{4+} B_2^{2+} O_4$ (so-called 4-2 spinels).(5) The cations occupy one tetrahedral and two octahedral sites per single formula. They could be divalent, trivalent and tetravalent, including Mg, Zn, Fe, Mn, Al, Cr, Ti and Si. The unit cells are relatively large with eight units per formulae each. Depending on the combination of site occupancy by different types of cations two types of spinel are possible: the inverse and normal spinel. In normal spinels, the A-cation occupies the tetrahedral site, while the two B-cations occupy the octahedral sites. In the inverse spinels, the octahedral sites are filled up with B-cations, whereas the tetrahedral sites are occupied at the same time by A-cations and B-cations.(6) The prototype mineral which represents the structural distribution of elements in a normal spinel is $MgAl_2O_4$,(7) while in the inverse-type the most important member: Magnetite has the structural formula $X(XY)O_4$. Actually, the unit cell of an inverse spinel has the octahedral site filled up with eight trivalent ions and eight divalent ions, while the remaining ions occupy the tetrahedral sites. A shallow analyze characterizes the spinel formulae as simple structures, although it is not really true because they show complex disorder patterns.(5,8-10) The spinel $MgAl_2O_4$ is described as the first stoichiometric mineral with disorder sites.(11) According to temperature variation, the cation distribution in spinel structure also varies.(8,12-14)

2-3 spinels ($MgAl_2O_4$, $MgFe_2O_4$, $FeFe_2O_4$) unit cell is smaller than the inverse types, and it becomes still smaller with increasing pressure at constant temperature. At low temperature normal spinels ($MgAl_2O_4$) show a progressively increase in disorder with increasing pressure, whereas in the inverse spinels ($MgFe_2O_4$), at the same temperature, the structure gets more ordered as the pressure rises.

For 2-4 spinels (Mg_2TiO_4, y-Mg_2SiO_4) the correlation between the crystallographic order-disorder and the pressure-temperature conditions are unclear. The elevation of temperature to the normal spinel Mg_2SiO_4 shows fewer tendencies to inversion than the 2-3 spinels.(5,15) Probably, the effects of temperature on spinel inversion are higher than those of pressure.(15) In spinels with two or more cations of variable valence (Co_2FeO_4), all sort of different volume alterations are predictable through ionic radii changes and their crystallographic site distributions.(5)

In short, the ionic distribution expected for spinels in general, is represented through the followed formula $\mathbf{(M_aFe_{1-a})^x(M_{1-a}Fe_{1+a})^yO_4}$ where 'a' is the inversion parameter. A normal spinel occurs when a = 1 and an inverse one when a=0.

CRYSTALLOGRAPHY OF MAGNETITE

The space group determination of magnetite (F3dm) is remarked to Bragg's x-ray studies of this mineral.(16) Late, Claasse (17) refined the space group and determined the oxygen parameter 'u' to F3dm. X-ray studies from Tombs and Rooksb (18) and Abrahmas and Calhou (19) was done in structures of Fe_3O_4 of low temperature. So through those first studies and several others, it is possible to observe that magnetite is a mineral from the cubic system and has a structure of ferritic inverse-spinel ($Fe^{2+}Fe_2{}^{3+}O_4$). Eight trivalent Fe-ions and eight divalent Fe-ions are in octahedral positions, while the tetrahedral sites are filled up with trivalent Fe-ions. 32 O-anions are required to the correct stabilization of the structural formula of magnetite. The oxygen ions built a cubic centered closed-packed lattice whereas the Fe-cations occupy its interstitial positions. The unit cell of magnetite has a constant of (a) = 8.396Å.(7)

METHODS

Sample preparation

Throughout the course of the studies in iron formations, rocks samples were collected in Iron Quadrangle, Brazil. Three samples of iron formation were carefully chosen from a larger number of samples as being the most representative of transformation between magnetite and haematite phases. Small blocks were cut perpendicular to the foliation plane (formed by the basal disposition of haematite platy grains) and polished with diamond pastes before a final stage of colloidal-silica polishing (20). Previously to EBSD analysis, reflected light microscopy was used to select the most adequate microstructures. The samples were not coated with conductor material layer (e.g. carbon coat) because iron oxide minerals are able to conduct electrons, although the lapped sample surface was covered with carbon paint avoiding charging effects.

Working conditions

Crystallographic orientation data were obtained from automatically indexed EBSD pattern acquired using a Nordlys-HKL Camera System set SEM Jeol JSM-5510 and processed using the application package CHANNEL 5 (HKL). EBSD patterns were obtained using a 20kV acceleration voltage and a beam current between 60 and 65nA, 70º sample tilt at a working distance of 35mm. Samples were mapped with a step size of 0.8µm.

RESULTS AND DISCUSSION

Sample I

The sample I (Figure 1) is characterized by large subhedral magnetite crystals embedded into a matrix composed of quartz and elongate haematite grains. All the analyzed magnetite crystals are partially transformed to haematite. A couple of prismatic haematite from matrix are observed coexisting with the original magnetite crystal.

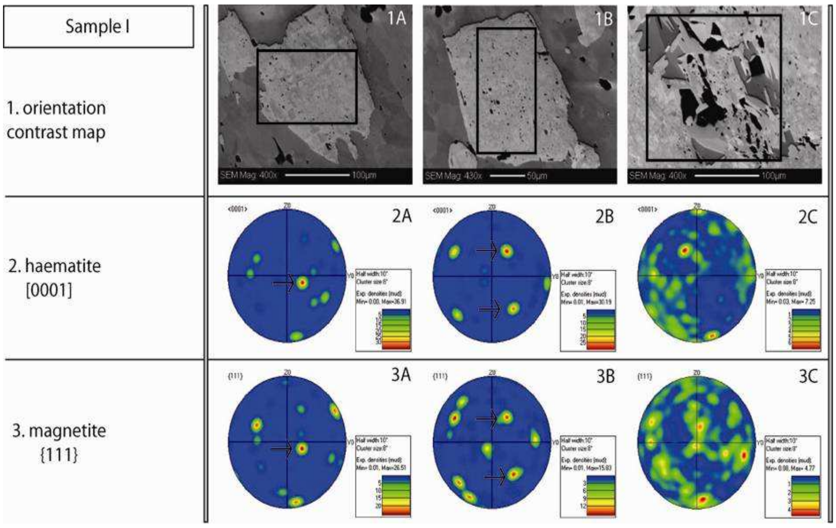

Figure 1: Former magnetite and replacement haematite crystals can be observed in the orientation contrast image (in electron forescattering image) in figures 1A, 1B and 1C. Figures 2A, B and C show stereogram figures of (0001) direction of haematite from the area marked by a rectangle on the orientation contrast image, while Figures 3A, 3B and 3C show poles of {111} planes of magnetite. Black arrows highlight the maxima densities of pole and direction figures.

Magnetite crystals are not completely euedric (Figure 1-1A, 1-1B, 1-1C) and it is very rare to find a magnetite crystal that is not at least partially transformed to haematite. The transformation follows mainly the original crystal boundaries and the octahedral plane of magnetite. The oxidation degree of these surfaces is proportional to the imperfection degree of the crystal as well as to the specific surface of magnetite (21, 22). Therefore the patterns imprinted in the magnetite crystals resulting from their transformation into haematite are characteristically of triangular shape and can be easily recognized in the optical microscope or in the forescattering images.
The haematite crystals in the matrix are tabular with regular and straight boundaries. They do not exhibit any growth relationship with the original magnetite crystals. Therefore the shape and crystallographic preferred orientation observed in the haematite grains in the matrix are features related to the regional deformation and are not directly related to the transformation processes.

Sample II

Sample II (Figure 2) is composed mainly of iron oxide minerals, although it does not exhibit elongate to tabular haematite crystals. All haematite crystals are related to the phase transformation of original magnetite. Thus, magnetite is described as crystals partially transformed to haematite (figure 2-1A, 2-1B, 2-1C, 2-1D, 2-1E), with transformation-free nuclei. Many crystals show microcracks that are controlled by planes of weakness related to cleavage and to the octahedral planes {111}. In this case, the original planes {111} are transformed into {111}-(0001) interphase boundaries. Similarly to the large crystals, in relicts of magnetite crystals, it is easily recognized the triangular shape pattern resulting from the transformation.

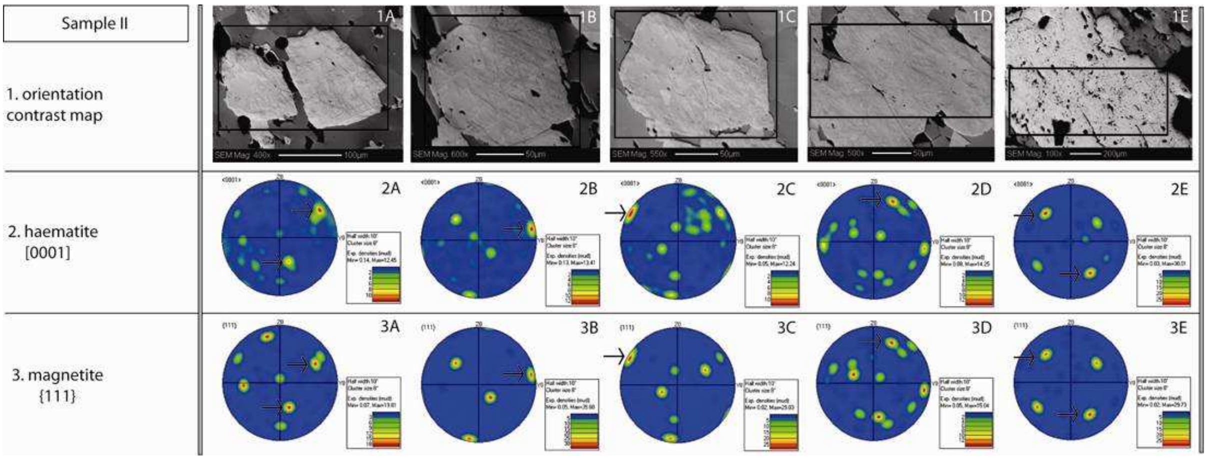

Figure 2: Magnetite crystals and new haematite crystals can be observed in electron forescattering image in figures 1A, 1B, 1C, 1D and 1E. Figures 2A, B and C show stereographic projections of the (0001) direction of haematite from the area marked by a rectangle on the orientation contrast image, while Figures 3A, 3B and 3C show poles of {111} planes of magnetite, both highlighted by black arrows.

These microstructural features result from the direct transformation of a cubic lattice into a hexagonal one. Although they have distinct structural symmetries in both crystals {111} and (0001) correspond to planes of closest packing whereby the transformation occur. For that reason the new haematite crystals inherit that orientation, e.g., the (111) directions of magnetite crystal become the (0001) of the neo-crystallize haematite.

Sample III

The sample III (Figure 3) is a rock composed only by iron oxide minerals. It is possible to observe original magnetite crystals partially transformed to haematite embedded in a matrix of prismatic haematite. The magnetite crystals are euedric, with straight boundaries. The magnetite crystals (figure 3-1A) show the classic transformation pattern, following preferentially boundaries and octahedral planes. Haematite in the matrix shows a strong shape orientation with their basal planes preferentially oriented along the same plane originating a strong planar anisotropy (parallel to the regional foliation).

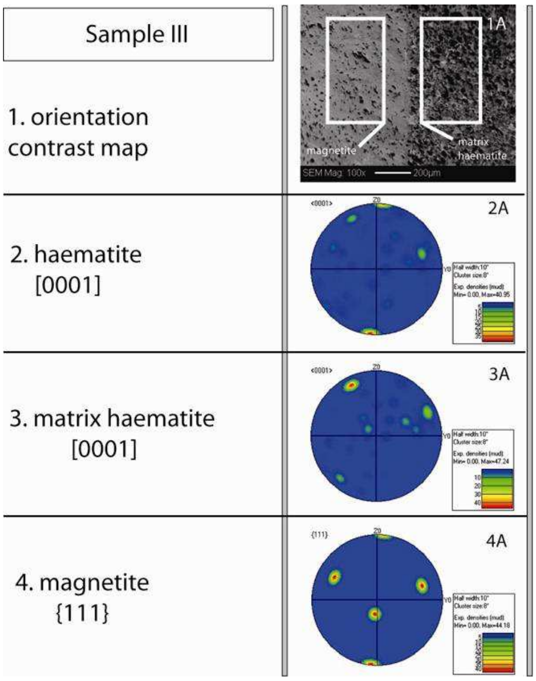

Figure 3: Single magnetite crystal partially transformed into haematite and new haematite crystals from the matrix can be observed in orientation contrast image in figure 1A. Figure 2A shows the stereogram of (0001) direction of haematite from the area marked by a white rectangle on the orientation contrast image, while Figure 3A shows the stereogram of (0001) direction of haematite from matrix. Figure 4A shows poles of {111} planes of magnetite

Crystallographic orientations

In each analyzed sample, two groups of crystallographic preferred orientation (CPO) could be distinguished. The first one refers to the CPO of haematite (0001) direction and the second to the CPO of magnetite octahedral planes {111}. The pole figures and stereograms are related to points from the area marked with a rectangle on the forescattering images.

The octahedral planes of magnetite frequently show a strong CPO because the acquisition points came from a single crystal. The (0001) direction of haematite also exhibits strong CPO.

In the sample I, it is observed (black arrows in figures 1-3A, 1-3B, 1-3C) that the maximum CPO of {111} planes of magnetite coincides with (0001) direction of haematite (black arrows in figures 1-2A, 1-2B, 1-2C) measured inside the original partially transformed magnetite crystal. However, when the (0001) haematite direction measured outside the original magnetite crystal is compared with their {111} planes, there is a clear mismatch.

In sample II, only crystals partially transformed to haematite were measured. There is a strong correlation between the direction (0001) of haematite and poles of {111} planes of magnetite (black arrows in figures 2-2 and 2-3). The maximum concentrations of those poles coincide in the pole of figures 2-2 and 2-3.

The sample III exhibits two main CPO patterns. One is related to haematite directly transformed from the magnetite crystals whereas the other is attributed to haematite grains from matrix (rectangles in figure 3-1A). Within the magnetite crystals the transformation to haematite occur along the octahedral planes. The transformed haematite crystals inherited the CCP array of the cubic magnetite crystals changing to a HCP array to rearrange the distribution of Fe^{3+} in the octahedral sites. Consequently, the preferred orientation of poles of {111} of magnetite (figure 3-4A) always coincides with preferred orientation of poles of (0001) haematite planes (figure 3-2A). This is a feature observed only in magnetite that shows microstructures of direct transformation. In the matrix, the coincidence between those two directions was not observed.

A situation like that was first suggested in the study of Lagoeiro (22) which provided microstructural evidences for the direct transformation but none crystallographic orientation data of original magnetite and new transformed haematite crystals. The crystallographic data obtained in this study also indicate that at least two generation of haematite are present in the Iron Formation rocks. One related to the transformation of magnetite crystals and the other possibility resulting from either the orientated growth of haematite crystals by precipitation direction from solution or dynamic recrystallization of originally transformed haematite crystals during the regional deformation.

Summary and Conclusions

(1) The Fe-O system has different phases, but only magnetite and haematite are important in terms of crustal rock studies. The other phases like wüstite and maghemite are not stable under main P-T conditions where crustal rocks are formed.

(2) Magnetite is the most important inverse spinel with 8 trivalent Fe-ions and 8 divalent Fe-ions in octahedral positions, while the tetrahedral sites are filled up with trivalent Fe-ions.

(3) In the Fe-O system, the presence of trivalent or divalent iron-ions is correlated with three main factors: Temperature, pressure and pO_2 fugacity.

(4) During the phase-transformation of magnetite to haematite, it is possible to note that the transition occurs through the octahedral plane {111} of magnetite. The new transformed haematite crystals inherit the orientation of the older magnetite grains. The new crystals have their basal (0001) planes preferentially oriented parallel to the {111} planes of the original magnetite grains.

(5) Haematite crystals in the matrix show concentrations of poles of basal (0001) not coincident with concentrations of poles of octahedral {111} planes of the magnetite. This suggested that at least two generation of haematite crystals in the iron rocks: one resulting from the transformation of magnetite grains and the other possibly associated with either the dissolution and precipitation of haematite platelets out of solution growing preferred oriented in the matrix or dynamically recrystallization of the newly transformed crystals.

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