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Article

Maghemite in brazilian iron ores: quantification of the magnetite-maghemite isomorphic series by x-ray diffraction and the rietveld method, and confirmation by independent methods

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Maghemite (γ-Fe2O3) is a mineral formed from magnetite oxidation at low temperatures, an intermediate metastable term of the magnetite to hematite oxidation and could be mixed with both. It has magnetic susceptibility similar to magnetite, crystal structure close to magnetite with which it forms a solid solution, while compositionally it equals hematite. Maghemite is thus easily misidentified as magnetite by X-ray diffraction and/or as hematite by spot chemical analysis in iron ore characterization routines. Nonstoichiometric magnetite could be quantified in samples of Brazilian soils and iron ores by the Rietveld method using a constrained refinement of the X-ray patterns. The results were confirmed by reflected light microscopy and Raman spectroscopy, thus qualitatively validating the method. X-ray diffraction with the refinement of the isomorphic substitution of Fe2+ by Fe3+ along the magnetite-maghemite solid solution could help to suitably characterize maghemite in iron ores, allowing for the evaluation of its ultimate influence on mineral processing, by affecting its surface and breakage properties.

Keywords: Iron ore; Maghemite; Nonstoichiometric magnetite; X-Ray diffraction; Ore characterization.

1. Introduction

Iron ore concentrates and pellets are a major export product of Brazil. Its mineralogy is generally simple, the main iron-bearing minerals are hematite and magnetite in the Carajás (state of Pará, northern Brazil) ore, and hematite with goethite in very variable amounts and rare magnetite in the one from the Quadrilátero Ferrífero (state of Minas Gerais, southeast of Brazil), as well as diverse gangue minerals.

The conversion of magnetite to hematite or goethite may pass through the metastable isostructural phase maghemite [1,2], which generally leads to the coexistence with a product called nonstoichiometric magnetite [3] consisting of a solid solution with varying atomic ratios of Fe2+:Fe3+. Magnetite can have a range of oxidation states dependent upon the amount of structural Fe2+, which can be discussed quantitatively as the magnetite stoichiometry (x = Fe2+/Fe3+, atoms). For magnetite with an ideal Fe2+ content (assuming the Fe3O4 formula), the mineral phase is known as stoichiometric magnetite (x

= 0.50). As magnetite becomes oxidized, the Fe2+/Fe3+ ratio decreases ($x < 0.50$), with this form denoted as nonstoichiometric or partially oxidized magnetite. When the iron is completely oxidized ($x = 0$), it is maghemite (γ-Fe2O3) [4].

The surface properties of magnetite and maghemite differ by the presence of vacancies to compensate the oxidation state of up to 1/3 of the Fe atoms, which could have implications for ore beneficiation operations and subsequent steelmaking processes. This mineralogical conversion can also affect the breaking and surface properties of iron ore particles. Thus, the correct identification and quantification of these minerals is essential to determine the ore textures and surface properties.

In addition to benefits for steel industry, the accurate identification of maghemite also can help in the reconstruction of mineralization processes in BIFs (banded iron formation) and other iron ore deposits. The magnetite-hematite oxidation can occur in two ways: supergenic enrichment that comprise successive oxidations of the primary mineral and originating goethite and a metastable phase such as maghemite (or nonstoichiometric magnetite) [5]. The second way is through metamorphism and deformation, when magnetite oxidizes directly to hematite, without originating (or at least not preserving) maghemite [6-7]. The temperature is another influential factor in maghemite genesis. In high temperatures (over 600ºC), the transformation is direct to hematite. On the other hand, in lower temperatures the oxidations products of magnetite are subordinate of its origins. In natural magnetite samples, when oxidized between 200ºC and 500ºC, the final product are grains constituted of a preserved core of magnetite with the surface covered by hematite layers [6].

Maghemite has a magnetic susceptibility similar to that of magnetite [8] and is a polymorph of hematite; it is thus easily misinterpreted as magnetite or hematite by most mineralogical methods, and it is believed that maghemite may be misidentified as magnetite and/or hematite in iron ore characterization routines. Although several methods for the mineral and textural characterization of iron ores have been developed in recent years, e.g. [9], none of them considers maghemite. The development of a microstructural technique for the identification of maghemite would open the possibility of adding such technique in some of the methods established for the characterization of iron ores.

Neumann and Medeiros [3] suggested that the degree of isomorphic substitution in Fe-oxide ores through the oxidation of Fe+2 to Fe+3 in the magnetite-maghemite solid solution can be quantified using the method proposed by Gorski and Scherer [4] by using X-ray diffraction and the Rietveld method. But in light of all the mentioned difficulties, this study's approach is to first apply this proposal to samples that according to the published literature typically contain maghemite. Initially samples of red latosol (oxisol) were analyzed, as the presence of maghemite in these soils is widely documented, particularly when they are derived from basalts. In addition, this material is readily available, occurring in diverse regions of Brazil, particularly in the southeast, south, as well as the central-west of Brazil [10]. Also, iron ore samples from Quadrilatero Ferrifero were tested, as some authors [11,12] describe maghemite and mainly non-stoichiometric magnetite in itabirite rocks and gangue iron ore in different localities of this region. After validation of this analytical technique through Raman spectroscopy coupled to a reflected light microscope (Raman microprobe), it was applied to Brazilian iron ores samples following the same methodology.

2. Materials and Methods

2.1 Materials

This work was carried out in two stages, using the same method, respectively, with:

(i) 3 soil samples (Guaíra, Ilha Grande, Mato Grosso) and 3 samples from the Quadrilatero Ferrífero (Guanhães, Guanhães 2, Espinhaço);

(ii) 10 iron ore samples from each, the northern (N4WN) and southern (N4WS) segments of the N4W iron ore mine in Carajás. Although all were analyzed, only three for each segment are presented, as the results are very similar for all.

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2.2 Methods

The samples were concentrated with a ferrite magnet (Alnico V). The ferromagnetic fractions were homogenized and 4 g and 1 g of each were split with a rotary sampler for X-ray diffraction analysis and for making a polished section, respectively.

For X-ray diffraction analysis, the samples were ground in a McCrone Micronizing Mill with agate grinding media and 15 mL of water for 10 min. The suspensions of ground samples were discharged into PTFE Petri dishes and dried overnight at 60°C. After drying, the samples were gently reground with agate mortar and pestle, and backloaded into sample holders, in order to reduce preferential orientation, and analyzed on a Bruker-AXS D4 Endeavor X-ray diffractometer, using Ni-filtered Co$K\alpha$ radiation. Quantitative analyzes were performed by refinement of the total multiphase spectrum method, known as the Rietveld method [11-13], with Bruker-AXS Diffrac.Topas 5.0 software. The crystal structure files of the phases were sourced from the Bruker-AXS and COD (Crystallographic Open Database) databases, with implementation for the restricted refinement of isomorphic substitutions in goethite [12-14], hematite [13-15] and the solid solution magnetite-maghemite [3].

For microscopy, the 1 g samples were cold-mounted in epoxy resin, ground and polished to a mirror finish. The polished blocks were analyzed on reflected light microscope (Zeiss Axioimager M2.m) and Raman microprobe. A Horiba Jobin-Yvon LabRam 800HR spectrometer coupled to an Olympus BX-41 polarizing microscope was employed, using a 632.8 nm excitation laser with neutral density filters to reduce the laser power to 0.7 mW in order to avoid oxidation [14-16]. Even reducing the laser power, the spectra had to be measured quickly, for three accumulations of 2 s each, since the decrease in the intensity of the maghemite diagnostic vibrations was observed for longer measurement times.

3. Results and Discussions

3.1 First Stage

The six samples used in the first stage showed varied mineralogy, as shown in Table 1. The differentiation of magnetite and maghemite in X-ray diffractograms is qualitatively difficult, since both have a very similar crystal structure and share most of the peaks; low intensity diagnostic peaks may not be observed when the amount of maghemite is subordinate to that of magnetite in the sample. However, the oxidation of magnetite, being transformed into maghemite, can be calculated by the Rietveld method refinement, which can deal with the superposition of peaks. The method implemented by Neumann and Medeiros [3] is based on the difference in the scattering coefficient between atoms and vacancies of bivalent and trivalent iron, constrained by the linear variation of the size of the crystallographic axis of the unit cell, as determined by Gorski and Scherer [4], establishing a relationship with x (chi, stoichiometric ratio of Fe2+:Fe3+) equal to $a = 0.1094\ x + 8.3424$.

The samples with higher amounts of magnetite (Ilha Grande and Guanhães 2) also have maximum values of $x = 0.5$ (Table 1), indicating that in these samples the magnetite is stoichiometric, i.e. it has not undergone oxidation. These samples also bear hematite with very low Al. The magnetite in soil sample Mato Grosso is close to stoichiometry, with $x = 0.45$, i.e., around 10% of the Fe2+ has been oxidized to Fe3+. But its hematite is substituted, with 4.5% Al replacing Fe, and hydroxyl replacing oxygen. On the other hand, Guaíra shows $x = 0$, indicating maghemite as the only ferromagnetic phase, and Al-substituted hematite and goethite. Guanhães ($x = 0.194$) and Espinhaço ($x = 0.244$) are intermediate, indicating that their magnetite is partially oxidized. This section may be divided by subheadings. It should provide a concise and precise description of the experimental results, their interpretation, as well as the experimental conclusions that can be drawn.

Table 1. Rietveld quantitative phase analysis, substitutions, and magnetite stoichiometry (x) for iron ores from the Quadrilátero Ferrífero and soils.

Mineral (%p/p)	**Soil**			**Quadrilátero Ferrífero**		
	Guaíra	Ilha Grande	Mato Grosso	Guanhães	Guanhães 2	Espinhaço
Hematite(-Al)	32.5	9.5	18.8	80.4	13.1	96.3
Kaolinite	26.9	–	–	–	–	–
Gibbsite	26.5	–	–	–	–	–
Ilmenite	3.7	3.5	62.9	14.3	–	–
Anatase	3.4	–	–	–	–	–
Quartz	2.3	0.6	2	3.6	0.6	1.4
Nonstoichiometric magnetite	2.3	86.4	8.9	0.4	86.3	2.3
Titanite	1.5	–	–	–	–	–
Goethite-Al	0.9	–	–	–	–	–
Rutile	–	–	7.4	–	–	–
Talc	–	–	–	1.3	–	–
Substitutions (mol)						
Fe^{3+} hematite	0.871	1	0.9	0.98	0.992	0.979
Al^{3+} hematite	0.122	0	0.045	0.011	0.008	0.006
OH^{-} hematite	0.019	0.03	0.14	0.027	0.048	0.045
Al goethite	0.228	–	–	–	–	–
***x* magnetite**	**0**	**0.5**	**0.45**	**0.194**	**0.5**	**0.224**

Reflected light microscopy and Raman spectroscopy corroborated the detection of nonstoichiometric magnetite and maghemite in these samples. Figure 1 shows a typical Guaíra soil particle, measuring about 20 µm, euhedral and with intergrowth of various oxides, a textural phase called martite, mainly hematite pseudomorphs maintaining the magnetite habit. In this particle, hematite (Raman vibrations at 225, 293, 415, 500, 618 cm-1) and probably ilmenite (225, 390, 678 cm-1) were observed at points 1 and 2, respectively; nonstoichiometric magnetite spectra, with diagnostic bands close to 675 cm-1 at points 3 and 4; and spectra of maghemite with the doublet 667-720 cm-1 [17-18] were obtained from points 5 and 6. Point 6 is probably a mixture of maghemite and goethite (243, 293, 385, 399, 470, 543 cm-1) which is a frequently observed association. According to van der Weerd et al. [19] and Muralha et al. [20], the increase in the oxidation state in nonstoichiometric magnetite can change the main vibration from 665-670 cm-1 to higher values.

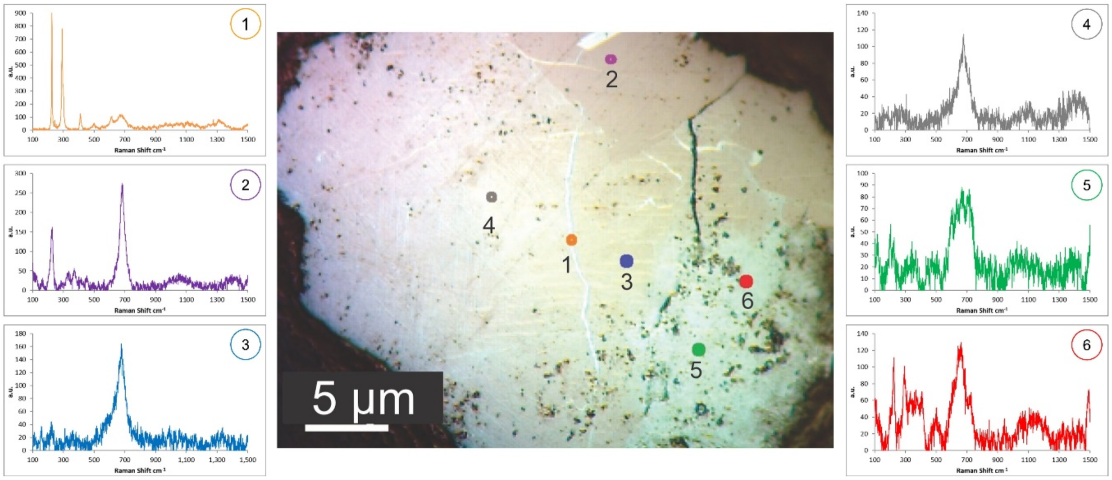

Figure 1. Guaíra soil particle observed by reflected light microscopy, and Raman spectra with di-agnostic vibrations of (1) hematite (225, 293, 415, 500, 618 cm-1); (2) ilmenite (225, 390, 670 cm-1); (3 and 4) nonstoichiometric magnetite (675 cm-1); (5) maghemite (667, 720 cm-1); (6) maghemite and goethite intergrowth (243, 293, 385, 399, 470, 547 cm-1).

3.2 Second stage

Table 2 presents the quantitative analysis by the Rietveld method of representative samples from mines N4WN (AM-01A, AM-01B and AM-01H) and N4WS (AM-02A, AM-02C and AM-02J) in Carajás. The mineralogy comprises hematite, goethite, magnetite/maghemite, quartz, kaolinite and gibbsite. While the main ferromagnetic phase in N4WN has an oxidation state close to that of maghemite (x = 0.057, 0.069, and 0.071), in mine N4WS its oxidation state is closer to that of magnetite (x = 0.340, 0.399, and 0.413).

Table 2. Rietveld quantitative phase analysis, substitutions, and magnetite stoichiometry (x) for iron ores from Carajás.

Mineral (%p/p)	**N4WN**			**N4WS**		
	AM-01A	AM-01B	AM-01H	AM-02A	AM-02B	AM-02E
Kaolinite	1.5	1.4	1.4	0.2	0.3	0.2
Quartz	0.6	0.7	0.7	0.5	0.7	0.4
Goethite-Al	5.8	6.2	5.6	18.1	18.1	18.4
Hematite-Al	87.6	87.3	87.7	77.4	77.3	77.7
Nonstoichiometric magnetite	4.5	4.4	4.5	3.4	3.3	3.0
Gibbsite	0.0	0.0	0.0	0.4	0.4	0.3
Substitutions (mol)						
Fe^{3+} hematite	0.971	0.972	0.971	0.964	0.963	0.963
Al^{3+} hematite	0.004	0.005	0.005	0.005	0.006	0.006
OH^- hematite	0.074	0.069	0.072	0.094	0.096	0.095
Al goethite	0.007	0.011	0.011	0.033	0.032	0.036
***x* magnetite**	**0.069**	**0.057**	**0.071**	**0.413**	**0.340**	**0.399**

Reflected light microscopy analysis revealed that in the N4WN polished section the magnetite domains (pinkish gray) are very scarce, in contrast to N4WS, in which these domains are more common (Figure 2). It agrees with the Rietveld analysis, as in the N4WN samples the predominant magnetic phase is maghemite, due to it x values close to 0. It is worth mentioning that the identification of maghemite on a reflected light microscope is a difficult and laborious task, as there is no consensus on its characteristics, especially its color, which may be described in the literature [21-23] as light gray, bluish gray, white to bluish gray, bluish white, lilac, pinkish brown, and brownish gray. Meurant [24] developed an empirical color scale to determine the oxidation stage of the magnetite in which the stoichiometric magnetite is pinkish gray, turning brownish pink as its degree of oxidation increases, until it becomes light blue when completely transformed into maghemite. However, Morris [5], based on the observation of samples from the Hamersley deposits, BIFs from Brazil and Liberia, stated that, in practice, iron ores generally exhibit their oxidized magnetic phases with a brownish pink color, and the bluish colors, typically found in the literature, are observed only in some samples. Therefore, because of this difficulty, either supposed magnetite domain (pinkish gray), nonstoichiometric magnetite (also pinkish gray) and maghemite domain (bluish gray) in the grains should be verified by other analytical techniques, such Raman spectroscopy.

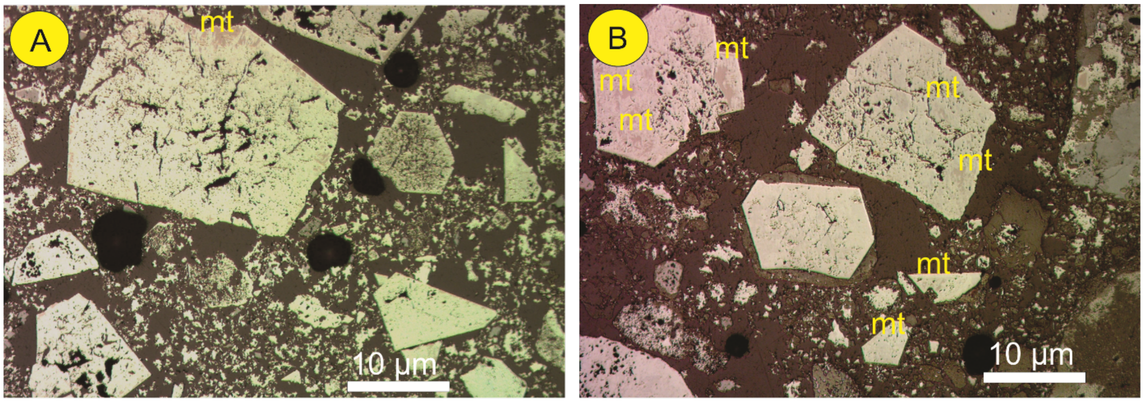

Figure 2. (a) N4WN polished section exhibit predominance of hematite (light gray) grains and few magnetite domains (mt, pinkish gray); (b) N4WS polished section, here the magnetite domains (mt, pinkish gray) are more abundant than in N4WN.

The N4WS samples are composed mainly of hematite grains, many of them the product of magnetite oxidation that is also abundant in these samples. Quantitatively, this corroborates the results of the analysis by the Rietveld method shown in Table 2. The transition from magnetite to hematite can be observed in several stages, ranging from a slight change, affecting only the edges of the magnetite grains, until grains of euhedral magnetite, completely replaced by hematite. Martite is a commonly observed texture. Maghemite, although not very abundant, has a bluish gray color and generally occurs in hematite grains close to remnants of magnetite and/or nonstoichiometric magnetite, as confirmed by Raman spectroscopy. Figure 3a and 4a shows an image of N4WS hematite grain in which magnetite and maghemite are pointed out, along with Raman spectra of maghemite. It illustrates how difficult it is to differentiate between magnetite (pinkish gray) and maghemite (bluish gray) in bright field images from reflected light microscopy.

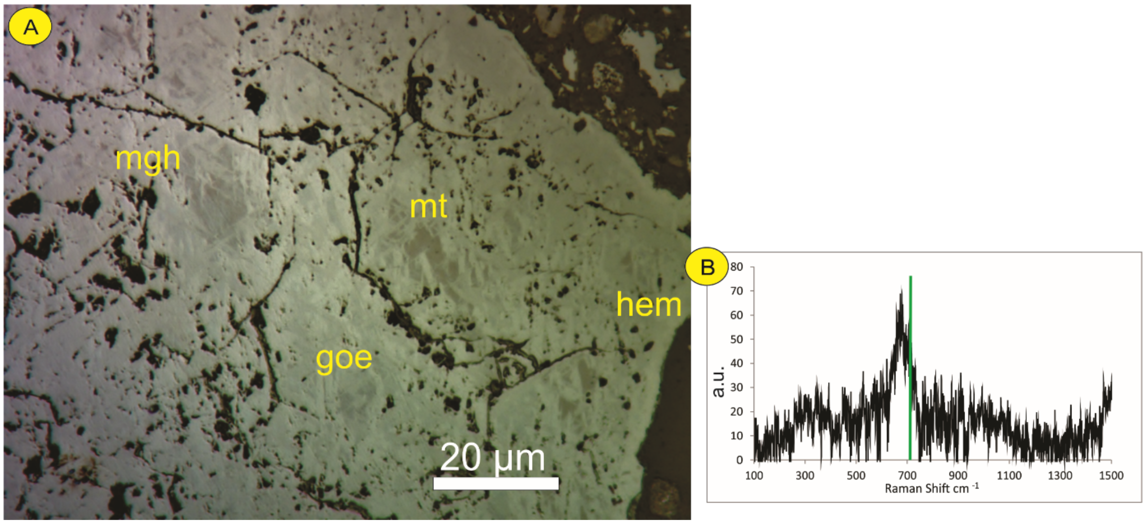

Figure 3. (a) N4WS hematite grain observed on reflected light microscope in bright field mode: hematite (hem, light gray), maghemite (mgh, bluish gray), magnetite (mt, pinkish gray) and goethite (goe, dark gray); (b) Raman spectrum of maghemite with marker at the diagnostic vibration at 720 cm-1.

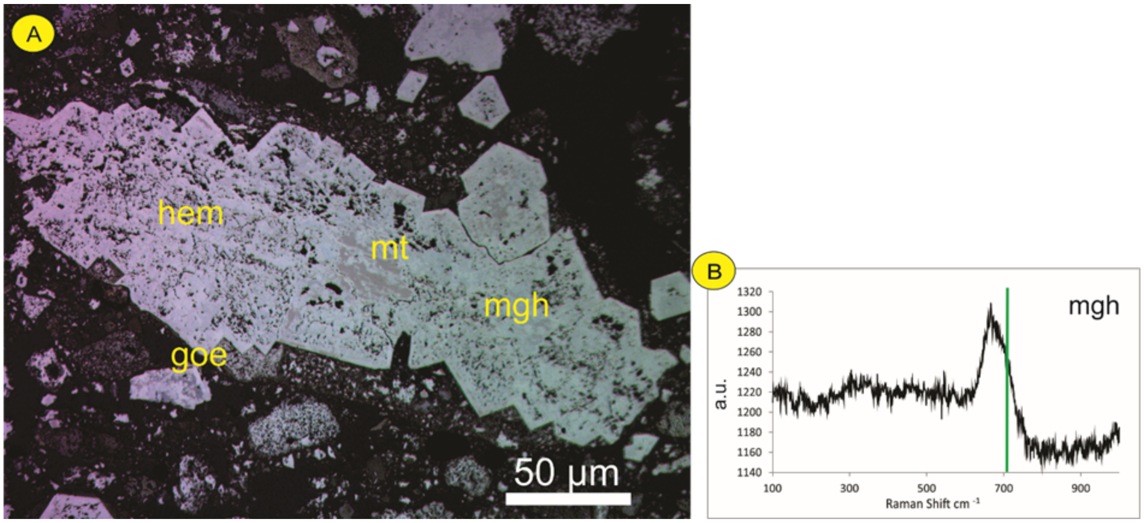

Figure 4. (a) Reflected light microscopy bright field image of a N4WS grain with intergrowth of hematite (hem, light gray), maghemite (mgh, bluish gray), magnetite (mt, pinkish gray), and goethite (goe, dark gray); (b) Raman spectrum of maghemite with marker at the diagnostic vibration at 720 cm-1.

Samples from the N4WN mine are very porous and hematite is also the predominant mineral. There are rare occurrences of pinkish gray magnetite, in line with the low levels of magnetite and the low values of x – tending to maghemite (Table 2). Magnetite is mainly interspersed with hematite (Fig. 5a), showing the magnetite-hematite oxidation reaction, and suggesting that it is actually a nonstoichiometric magnetite. Unlike N4WS samples, martite is rarely observed, probably because most of the grains of magnetite have been completely converted to hematite. Goethite is common at the edges of hematite grains. Figure 5 presents an image of an N4WN hematite grain in which a maghemite domain is identified by its Raman spectrum. Unlike N4WS samples, bluish gray maghemite is scarce in N4WN samples. However, this may be due to the fact that the supposed domains of the solid magnetite-maghemite solution are thinner than the spatial resolution of the microscope employed, but can still be detected by Raman spectroscopy.

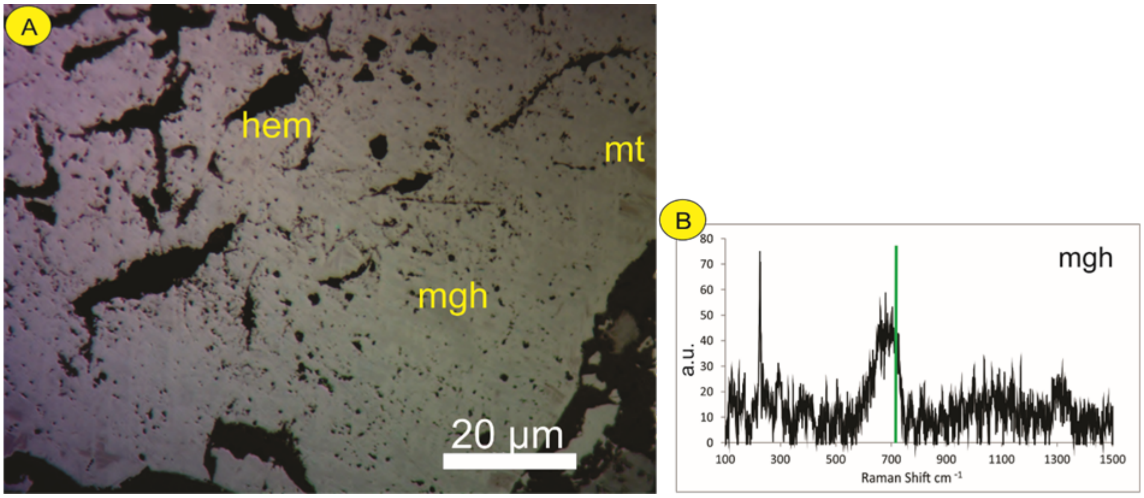

Figure 5. (a) Reflected light microscopy bright field image of a small domain of nonstoichiometric magnetite in a hematite grain from a sample from the N4WN mine; (b) Raman spectrum of nonstoichiometric magnetite and the diagnostic maghemite vibration at 720 cm-1; maghemite domain is probably below the microscope's resolution, but is still detected by the spectrometer.

4. Conclusions

Maghemite (γ-Fe2O3) is a metastable phase in the transformation from magnetite to hematite. The identification of nonstoichiometric magnetite, down to completely oxidized maghemite, is not an easy task and is not included in most mineralogical characterization routines. Chemically maghemite is identical to the coexisting hematite, therefore electron beam methods as electron energy or wavelength dispersive spectroscopy fail to recognize it. The very similar magnetic susceptibility of both minerals (k≈3000x10-3 [25]) also precludes its identification by this property. Reflected light microscopy bright field images might separate the mineral by its bluish hues, mostly in martite which is a texture witnessing transformation from magnetite to hematite as well. But quite often the maghemite domains are fine, below the resolution of optical microscopes, and might be dispersed in a hematite matrix when martite is not recognized any more. But it can be identified by Raman spectroscopy, even if not visible under the microscope and below the spatial resolution of the laser beam (~1 µm) by its diagnostic vibration at 720 cm-1.

The method proposed by Neumann and Medeiros [3] for the identification and quantification of nonstoichiometric magnetite while quantifying the whole mineralogic assembly using XRD and the Rietveld method could be tested with maghemite-rich soils, and successfully applied to iron ores. XRD is not affected (within limits) by small domains, overcoming the limitations of the image-based methods. As XRD demands a finely ground sample, adequate sampling procedures may be used, ensuring its representativity, among other advantages.

Samples from the N4WN and N4WS mines of Carajás (northern Brazil) particularly proved to be interesting from this point of view. While samples from N4WS bear nonstoichiometric magnetite with limited oxidation (χ from 0.34 to 0.41), at N4WN it is close to maghemite, with χ varying from 0.06 to 0.07. For both sample groups, however, nonstoichiometric magnetite to maghemite could be confirmed by Raman spectroscopy, thus validating the analytical results. In general, there is a wide discussion about the reconstruction of mineralization processes in BIF and other iron ores deposits. In Carajas, the most accepted model [26] proposes that both hypogene and supergene fluids are envolved in deposit genesis. However, the availability of studies approaching supergenic enrichment within this model are still scarce, and most recent works describe only hypogenic iron mineralization. According to Morris [5] maghemite and non-stoichiometric magnetite (called kenomagnetite) only will be preserved in a supergenic enrichment. The easy and fast determination of the oxidation rate along the magnetite-maghemite solid solution could open new possibilities for genetic studies not only in Carajas, but also in other iron ore deposits of the world.

The correct identification and quantification of these minerals should allow for more objective research on its implications for ore beneficiation, as surface properties and even breakage properties should be affected. The inability so far to easily detect and quantify non-stoichiometric magnetite and maghemite has so far precluded the fair evaluation of its effect on iron ore processing. This section is not mandatory but can be added to the manuscript if the discussion is unusually long or complex.

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