

Science Paper

Oxygen Isotopes of Iron Oxides as a Diagnostic Tool for Iron Formation-Hosted High-Grade Magnetite-Hematite Deposits

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Coarse-grained granoblastic magnetite-hematite and sheared platy hematite iron orebodies comprise several small deposits (5 to 30 Mt each) on the eastern margin of the São Francisco Craton, bordering the Ediacaran–Cambrian Brasiliano Orogenic belt. Three main mineralization stages are associated with the Brasiliano Orogeny: (1) syn- to the late-collisional stage (*ca.* 580–560 Ma) with development of lens-shaped schistose orebodies along thrust planes. (2) late- to the post-collisional stage (*ca.* 560–530 Ma) with the formation of massive magnetite bodies by contact metamorphic-metasomatism with pegmatite. (3) Post-tectonic stage with crystallization of granular hematite associated with late pegmatite (*ca.* 530–490 Ma). In order to better evaluate the fluid oxygen signature of each mineralization stage, new oxygen isotopes measurements were performed on ore bodies associated with the three stages. These stages are followed by changes in the oxygen isotope signature, with a progressive decrease of the $\delta^{18}\text{O}$ from the iron formation (1.7 to 8.1‰) to high-grade ore (-1.6 to 2.6‰) that appears to be a common aspect of the mineralization of iron formations. In the present cases, magmatic fluids ($\delta^{18}\text{O}$ from 4.6 to 13.1‰) have imprinted a relatively “heavier” signature than the most hypogene iron formation high-grade ores worldwide that was progressively modified by meteoric water percolated along extensional fractures. The iron oxides from the contact zones of pegmatitic yielded intermediate $\delta^{18}\text{O}$ values (1.8 to 5.0‰), indicating a higher magmatic fluid/rock ratio.

1. Introduction

Iron formation-hosted iron deposits are a major source of this metal worldwide. Although the protolith is still expressively rich in iron, holding around 30 to 35 wt.% Fe (Klein, 2005) various upgrade processes involving ascending hot fluids (hypogene) and descending meteoric water (supergene) may combine to transform the iron formation (IF) to a high-grade ore through the development of mineralogical, textural, and chemical changes that are closely related to the protolith, geotectonic environment, fluid source and path characteristics (Hagemann et al., 2016). Based on the investigations of a large number of deposits worldwide Hagemann et al. (2016) propose four genetic end-member models for iron formation-hosted high-grade iron deposits involving both hypogene and supergene processes: (1) Carajás-type model, hosted in iron formations of the Algoma Type associated with volcano-sedimentary sequences, which typically undergo hydrother-

mal alteration by early magmatic ($\pm$ metamorphic) fluids and ancient “warm” meteoric water; (2) Hamersley-type (and the Quadrilátero Ferrífero metamorphic variety) is syn-orogenic, developed in Lake-Superior-type IF sequences, with mineralization fluids sourced by early basinal ($\pm$ evaporitic) brines, metamorphic fluids and ancient “warm” meteoric water; (3) Urucum-type, hosted by glaciomarine IF in continental graben-type basins with possible diagenetic to metamorphic hypogene mineralization by basinal fluids; (4) Capanema-type, for supergene enriched IF with no evidence for deep hypogene roots. The present research addresses a unique and previously unexplored category, focusing on iron deposits hosted within Lake-Superior-type iron formations situated in high-grade metamorphic terranes, often in close proximity to magmatic intrusions. This distinct and unconventional type of iron formation-hosted mineralization defies categorization within the established genetic interpretations. Here is introduced a new model that accounts for the complex in-

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terplay between geological factors, including magmatic intrusions, metamorphic processes, and other unique environmental conditions.

The IF-bearing sequence of Orosirian/Statherian age (2.0–1.7 Ga) of the Serra da Serpentina Group stretches along the eastern border of the Southern Espinhaço fold-thrust belt (Rolim et al., 2016; Rosière et al., 2021; Silveira Braga et al., 2015). The IF hosts lens-shaped schistose, specularitic and massive coarse-grained magnetite-hematite high-grade orebodies (>60 wt. % Fe). The mineralization took place during the syn- to post-collisional phases of the Ediacaran to Cambrian Brasiliano orogeny with the consolidation of the São Francisco craton (Gomes et al., 2018; Rosière et al., 2021; Silveira Braga et al., 2020) and developed at distinct depths and stages of the evolution of the orogen, accounting for the different morphologic and genetic types described in the area (Silveira Braga et al., 2021). In the upper greenschist metamorphic distal foreland domains of the Araçuaí-West Congo Orogen specularitic orebodies are concentrated along thrust planes, whereas, the eastern Guanhanes Tectonic Block is dominated by coarse-grained magnetite-hematite bodies hosted by coeval iron formations of amphibolite facies tectonically enclosed by gneissic rocks (Barrote et al., 2017; Gomes et al., 2018; Silveira Braga, Rosière, Santos, Hagemann, McNaughton, et al., 2019; Silveira Braga et al., 2020, 2021). The orebodies are intersected by numerous quartz and anatectic pegmatites veins (Silveira Braga et al., 2020).

The oxygen isotopes composition of iron oxides is a useful proxy to genetically classify high-grade iron ore deposits and to provide a suitable tool for determining the interaction of hydrothermal fluids and iron formations (Gutzmer et al., 2006; Hagemann et al., 2016; Thorne et al., 2009). The interaction of the IF with aqueous metamorphic and subsequently with meteoric fluids from the shallow crust typically causes decrease of the $\delta^{18}\text{O}_{\text{fluid}}$ value in the sequentially generated iron minerals components of high-grade iron ore (Gutzmer et al., 2006; Hensler et al., 2014; Powell et al., 1999; Thorne et al., 2009). Unlike most IF-hosted iron deposits, host rocks in the eastern Espinhaço fold-thrust belt (ES) and Guanhanes Tectonic Block (GB) have undergone a long period of hypogene Fe mineralization associated with a far-field circulation of large volumes of high-temperature, high-salinity fluids, associated with the anatexis of older granites (Gomes et al., 2018; L. A. R. de Oliveira et al., 2017; Silveira Braga et al., 2020), before being subsequently modified by descending meteoric fluids. The upgrading processes affected iron formations over a large area of previously consolidated continental crust during the Brasiliano orogeny and imprints a distinct isotopic signature in the ore compared to the four end-members models proposed by Hagemann et al. (2016).

In this work, we compare the oxygen isotope data obtained from several iron ore bodies of the Espinhaço-Guanhanes area (ES-GB, [fig. 1](#)), across the eastern border of the Southern Espinhaço fold-thrust belt (Morro Escuro and Passabém deposits), to the Guanhanes Tectonic Block (Liberdade, Cuité and Horto-Baratinha deposits), with published results from several deposits hosted by iron formation

worldwide with the purpose of understanding the conditions and documenting a characteristic signature for the mineralization.

The newly acquired oxygen isotope data, in conjunction with previous whole-rock and mineral chemistry data, field mapping, petrography, and isotope/geochronology studies, covers the entire spectrum of magmatic-to-metamorphic hydrothermal mineralization system of the hypogene iron mineralization of the ES-GB area, delivering exciting findings and setting out relevant facts upon the uniqueness of the origin of the iron ore bodies and association with the evolution of the Araçuaí-West Congo Orogen and the Eastern Brazilian Pegmatite Province. We discuss possible causes of changes in the oxygen isotope composition of the different iron oxides generations during iron ore mineralization, as well as its relationship with the regional tectonic and magmatic events, thereby establishing geological-geochemical parameters to define a new genetic model.

2. Geological setting

Tectonic slivers of iron formations interlayered with sandy to pelitic metasedimentary rocks are widespread at the eastern margin of the São Francisco Craton bordering the Ediacaran–Cambrian Araçuaí orogenic belt ([fig. 1](#)). They are enclosed in Archean and Paleoproterozoic orthogneissic rocks of the Guanhanes Tectonic Block (GB) and are correlated with the more continuous upper greenschist to lower amphibolite metamorphic iron formation units, named regionally as itabirites of the Serra da Serpentina in the southern domain of Espinhaço Supergroup ([fig. 1](#)). A lower Statherian maximum deposition age for the iron formations is constrained by detrital zircon ages from sandy-pelitic units (SHRIMP U-Pb ages with uncertainties quoted at the 1 σ level: 1668 $\pm$ 23 Ma (Silveira Braga et al., 2015); 1666 $\pm$ 32 Ma (Rolim et al., 2016); 1671 $\pm$ 20 Ma (Silveira Braga, Rosière, Santos, Hagemann, McNaughton, et al., 2019).

The GB represents the deeper crustal roots of the Southern Espinhaço fold-thrust belt upthrust on the thin-skinned Espinhaço Supergroup during the Ediacaran–Cambrian Brasiliano orogeny. It comprises Archean TTG (tonalite–trondhjemite–granodiorite) terranes with magmatic U-Pb SHRIMP ages between 2867 $\pm$ 10 Ma to 2713 $\pm$ 7 Ma (L. C. da Silva et al., 2002), tectonic outliers of metamorphic Orosirian–Statherian iron formation-bearing supracrustal units (Carvalho et al., 2014; Rolim et al., 2016; Silveira Braga et al., 2015; Silveira Braga, Rosière, Santos, Hagemann, McNaughton, et al., 2019) and Statherian granitic plutons of the voluminous Borrachudos Suite (Magalhães et al., 2018; L. C. da Silva et al., 2002; Silveira Braga, Rosière, Santos, Hagemann, McNaughton, et al., 2019).

All units were intruded by post-tectonic Ediacaran–Ordovician pegmatite bodies in the period between 630 to 480 Ma (Gomes et al., 2018; Pedrosa-Soares et al., 2011; Silveira Braga, Rosière, Santos, Hagemann, McNaughton, et al., 2019; Silveira Braga et al., 2020). They comprise the Eastern Brazilian Pegmatite Province, one of the most significant pegmatite fields worldwide, subdivided into dis-

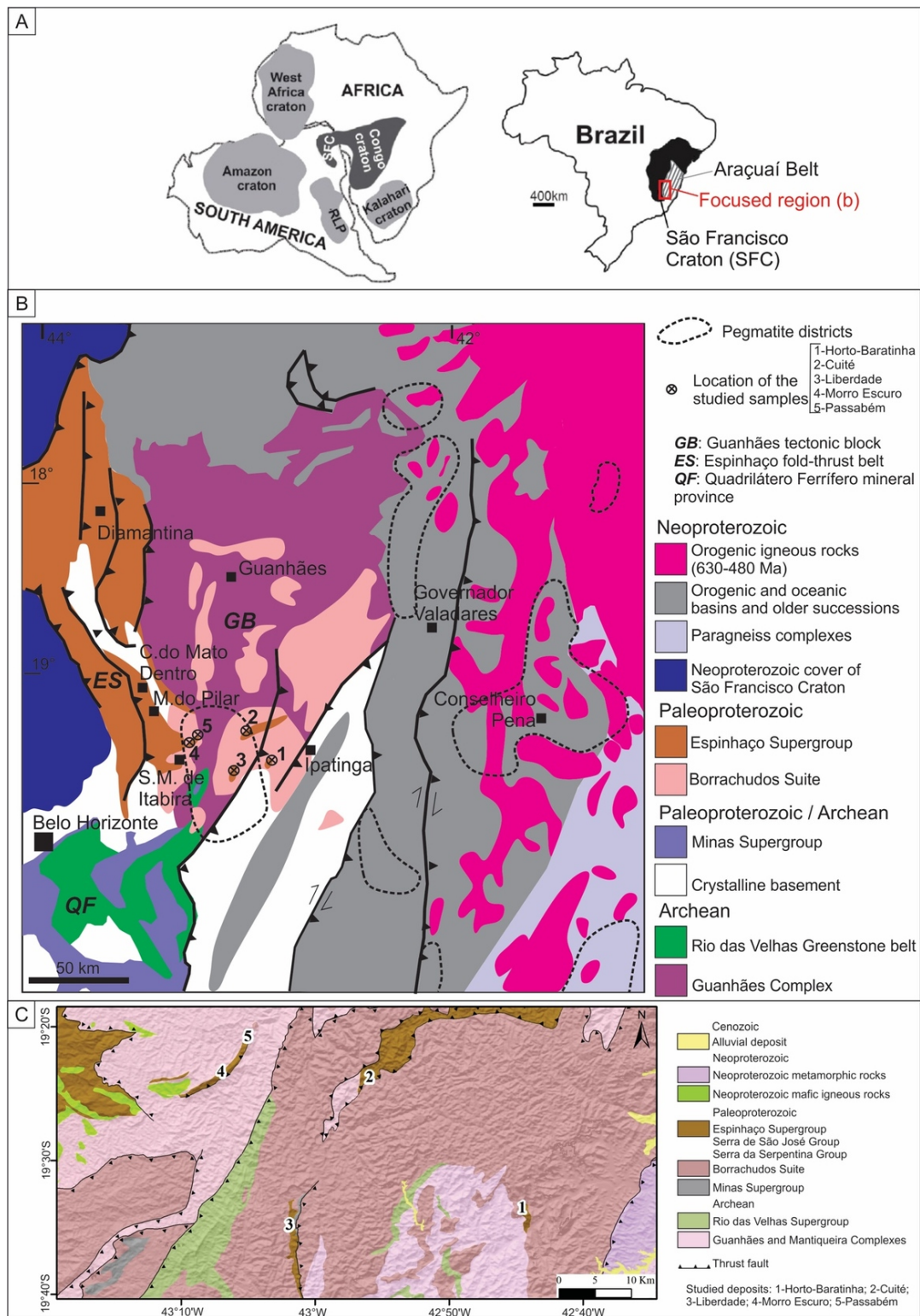


Figure 1. (A) Geotectonic configuration of the São Francisco-Congo Craton (Alkmim et al., 2006) and Araçuaí Orogenic Belt. (B) Simplified geological map of the SE Araçuaí Orogen, modified from Pedrosa-Soares et al. (2011), showing the location of the studied samples. (C) Geological map of the study area (modified after Grossi-Sad et al., 1997; A. A. K. Oliveira & Leite, 2000; Pinto & Silva, 2014; S. L. da Silva, 2000).

tricts encompassing several pegmatite populations (fig. 1). The studied area is located in the Santa Maria de Itabira district, which contains Ediacaran-Cambrian pegmatites crystallized by anatexis of granitic rocks of the Borrachudos

Suite (Pedrosa-Soares et al., 2011; Silveira Braga et al., 2020).

The itabirites of the Espinhaço-Guanhanes area are metamorphic iron formations recrystallized to upper greenschist and amphibolite facies and comprise a monotonous se-

quence of quartz-hematite rocks with lesser magnetite-martite (fig. 2C–D, 3A, D, 4A–B). The primary banding of the iron formation is generally transposed to a regional schistosity, with extensive obliteration of sedimentary/diagenetic structures and the development of a structural layering. The layering is defined by the alternation of millimeter wide bands of quartz and iron oxides (fig. 3A, D, 4A–B), comprised of strongly oriented platy hematite crystals and subordinate granoblastic domains (Gomes et al., 2018; Silveira Braga et al., 2015; Silveira Braga, Rosière, Santos, Hagemann, McNaughton, et al., 2019). The grain size noticeably increases eastwards from sub-millimeter to millimeter.

The tectonic and metamorphic setting of the iron formation-bearing sequences of the ES-GB (Southern Espinhaço fold-thrust belt and Guanhões Tectonic Block) at the eastern São Francisco Craton precludes a clear recognition of the primary characteristics of these rocks and hampers the interpretation of the pre-tectonic mineralogical and textural changes. The ductile deformation and development of a penetrative foliation defined by elongated hematite plates (lamellar hematite) support an interpretation of a metamorphic-tectonic origin for all iron oxides species and paragenesis (Rosière et al., 2013; Rosière & Rios, 2004). The mineralogy and geochemistry of the ES-GB itabirites outside the mineralized zone are largely homogeneous with an overall low detrital content and the geochemical signature, in particular the REE contents, is typical of a Lake Superior-type iron formation (Gomes et al., 2018; Silveira Braga et al., 2015; Silveira Braga, Rosière, Santos, Hagemann, McNaughton, et al., 2019).

3. Iron ore deposits

Similar to the iron formations, the platy hematite-rich, high-grade orebodies bordering the Southern Espinhaço fold-thrust belt (ES) exhibit a schistose fabric comprised mostly of hematite and have undergone a syn-tectonic mineralization by selective removal of quartz by hydrothermal fluids (Silveira Braga et al., 2021). In the Guanhões Tectonic Block (GB), high-grade, elongated schistose bodies occurs in discrete zones, comprised by thick platy, lamellar and granular-textured hematite. The hematite fabric intergrows with hypidioblastic magnetite that is progressively oxidized to brown-pink kenomagnetite (nonstoichiometric magnetite – (Kullerud et al., 1969)) and hematite pseudomorphs after magnetite composing a fabric here named kenomagnetite-martite. Although a schistose fabric is ubiquitous in the iron formations, irregular massive high-grade orebodies commonly develop at the contact zones with pegmatite intrusions comprised by coarse-grained magnetite and hematite grains. The magnetite crystals are commonly intergrown with equant grains of well-crystallized hematite (Gomes et al., 2018; L. A. R. de Oliveira et al., 2017; Silveira Braga, Rosière, Santos, Hagemann, McNaughton, et al., 2019; Silveira Braga et al., 2020). The deposits discussed here are located along a W-E section across the Guanhões Block from the eastern boundary of Southern Espinhaço fold-thrust belt to the tectonic contact with the Paleoproterozoic Mantiqueira Complex basement (fig. 1).

Morro Escuro and Passabém: The Morro Escuro and Passabém deposits are located at the westernmost limit of the sampled area (fig. 1). They are placed in an ENE-WSW elongated allochthonous inlier block, bound by SE-verging back-thrusts in contrast with the regional W-facing structure of the eastern border of the Southern Espinhaço fold-thrust belt (Carvalho et al., 2014; Silveira Braga et al., 2015). The metasedimentary sequence is comprised of schists, quartzites, conglomerates and iron formation obliquely intersected by numerous meter-long and dm-wide shear zones. In both deposits, the iron formation displays the usual schistose fabric comprised by, aside from lamellar hematite, discontinuously distributed kenomagnetite-martite that grows mimetically along the foliation. The iron formation host centimeter thick lenses of quartz-free, high-grade, schistose hematite ore associated with boudins of quartz veins (Silveira Braga et al., 2015), (fig. 2C, D, F). Coarse-grained magnetite-rich quartz veins are present, parallel to, or crosscutting the foliation (fig. 2C, 3E). Pegmatite bodies are scarcely distributed, occasionally observed intersecting amphibolite-rich layers (fig. 2E).

Liberdade: In the Liberdade deposit (fig. 1) the iron formation occurs as internally folded and sheared lenticular bodies structurally interlayered with quartz schist and sillimanite-bearing banded paragneiss (Gomes et al., 2018). The high-grade bodies are discontinuous, 5 to 30 m-thick, mostly massive, with subordinate schistose domains (fig. 2B and 3G–H). The shape of the orebodies is broadly controlled by the foliation, bordered by elongated pegmatite boudins of variable thickness and interfingered iron oxide-quartz veins (fig. 2A–B, 3B). The iron ore fabric comprises more or less equant grains of granoblastic hematite occasionally containing few relics of kenomagnetite and mm-size elongated platy hematite (Gomes et al., 2018), concentrated in discontinuous foliated domains, overgrown by coarse-grained hypidioblastic kenomagnetite-martite crystals (fig. 2B).

Cuité: The metasedimentary sequence at Cuité is located along the same structural trend of the Liberdade deposit (fig. 1). Like in Morro Escuro-Passabém, the sequence is enclosed as a tectonic slice in a granitic pluton of the Borrachudos Suite between SE-verging back-thrusts (fig. 1) and display similar structural and textural features although with relatively coarser grain size. The sequence comprises mica-schist structurally interlayered with iron formation, schistose and granoblastic, tabular-shaped orebodies as well quartz and kaolinized pegmatite schlieren smeared in the schistosity planes (fig. 2H). The maximum thickness of the orebodies on the order of tens of meters and three ore assemblages were identified, exposing an intricate internal arrangement of lamellar-granular hematite domains (schistose ore, fig. 2H), massive magnetite-martite (fig. 3E, 4C) and granular hematite (fig. 4D).

Horto-Baratinha: The Horto-Baratinha deposit is located at the eastern limit of the study area (fig. 1). The iron formation is associated with quartzite, quartz mica-schist, and para-amphibolite exposed by the mine works as a <40 m wide continuous layer between the upper and lower schists units. The strata are folded with the develop-

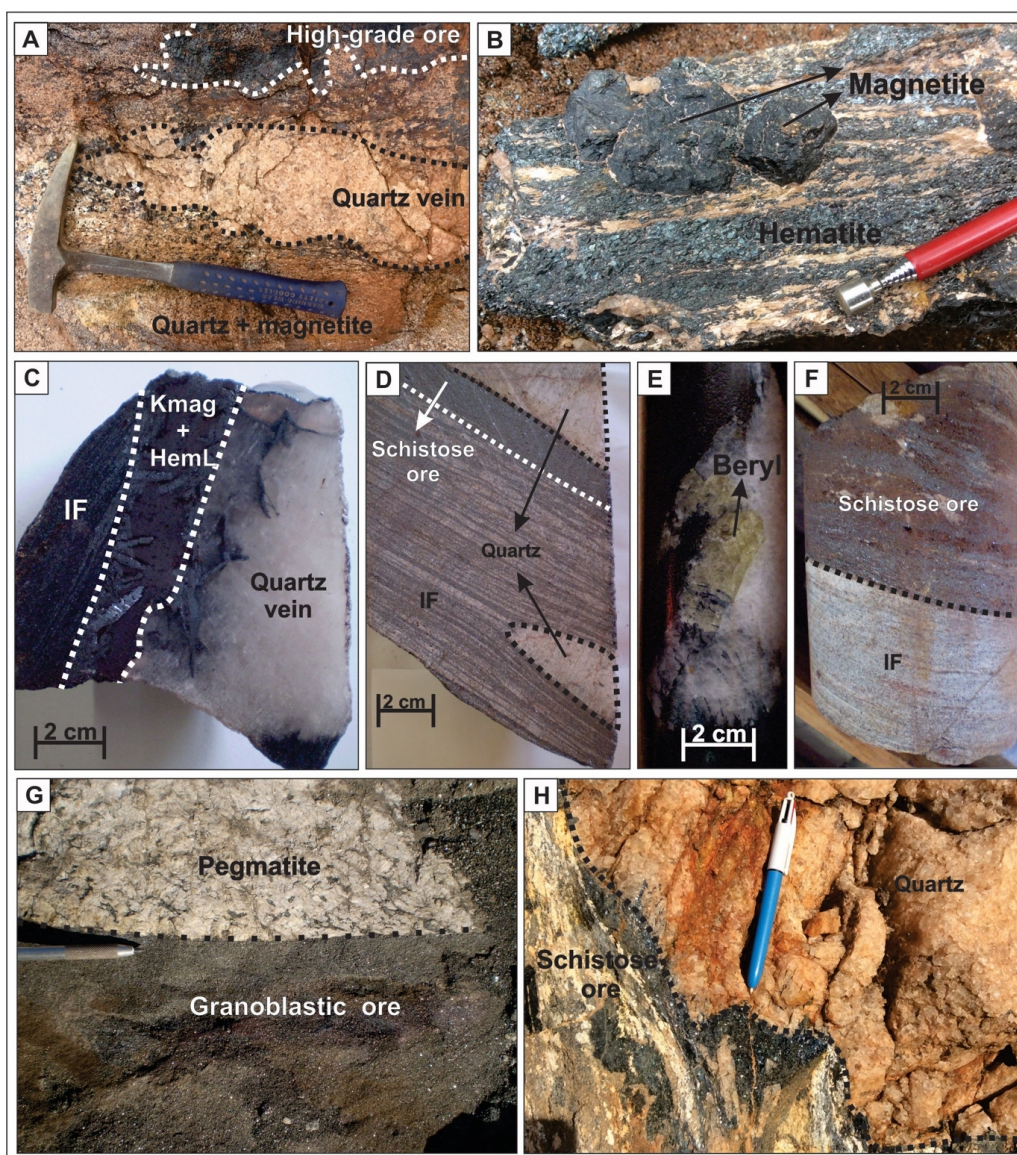


Figure 2. Macroscopic aspects of the deposits. (A) Coarse grained quartz-vein and disseminated magnetite in iron formation at the contact with granoblastic, high-grade ore in the Liberdade deposit. (B) High-grade iron ore from the Liberdade deposit, composed mainly of granular hematite and cm-large magnetite granoblasts. (C) Coarse grained sheaves of ilmenite overgrowing magnetite rich iron formation (IF) at the contact with quartz vein. Drillcore sample from Morro Escuro deposit. (D) Cm-long hematite plates comprise the foliation in schistose iron formation. Drillcore sample from Morro Escuro. (E) Beryl crystals in pegmatite vein. Drillcore from Morro Escuro. (F) Contact zone of schistose iron formation and lense of high-grade ore. Passabém deposit. (G) Contact zone of pegmatite and granoblastic ore. Baratinha deposit. (H) Foliated iron oxide concentration in the contact zone with quartz boudin from Cuité deposit.

ment of a dome and basin pattern (Silveira Braga, Rosière, Santos, Hagemann, McNaughton, et al., 2019). Pegmatite occurs as metric to several tens of meters-wide dikes and sills crosscutting the granites and metasedimentary rocks. Pegmatite bodies are coarse-grained (>5 mm), undeformed, and rich in iron oxide crystals at the contact zone with the iron formation (Figs. 2G, 3C, 4E–F). The high-grade iron orebodies occur as irregular and discordant bodies with dimensions from meter to tens of meters, associated with the pegmatite (Silveira Braga, Rosière, Santos, Hagemann, & Salles, 2019). The ore fabric is granoblastic, coarse-grained (0.01 mm–3.0 mm), comprised of granular hematite and

kenomagnetite-martite (fig. 3I) which overprints and obliterates the structure of the IF. Accessory minerals such as ilmenite, quartz, carbonate, chlorite, amphiboles, biotite, talc, apatite, and muscovite are observed mainly at the contact with pegmatite intrusions Silveira Braga, Rosière, Santos, Hagemann, McNaughton, et al., 2019).

Geothermobarometric calculations indicate a minimum temperature of 512 °C (± 50 °C) and a maximum pressure of 5.9 ± 1 kbar in the metasedimentary sequence of Morro Escuro and Passabém deposits (Silveira Braga et al., 2015). A minimum and maximum temperatures of respectively 550 °C (± 50 °C) and 690 °C (± 50 °C), with an estimated pressure

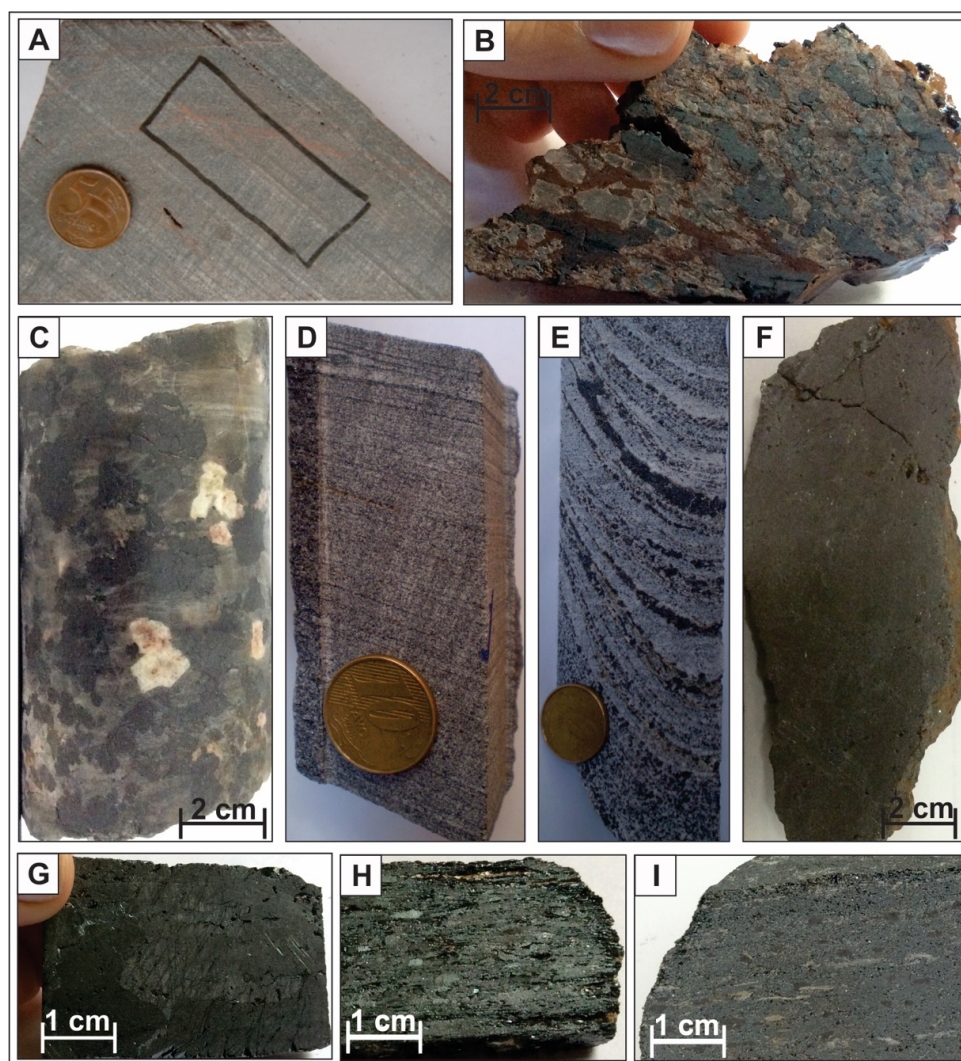


Figure 3. Macroscopic features of the studied samples. Schistose iron formations (samples M-181,45 (A) from Morro Escuro and P-13-001 (D) from Passabém deposit) with mm-thin tectonic layering comprised by alternating quartz-rich and iron oxides-rich bands. (B) Quartz vein containing blasts of magnetite and martite (sample FLPRO35 from Liberdade deposits). (C) Magnetite-rich pegmatite, containing cm-large magnetite crystals near the contact with iron formation (sample B-S54 from Baratinha deposit). (E) Quartz vein containing granoblastic magnetite. (sample P-5-002 from Passabém deposit) (F) Coarse-grained magnetite-martite ore (sample C-R10 from Cuité deposit). (g) Coarse-grained magnetite/hematite ore (sample FLPRO34c from Liberdade deposit). (H) Medium- to coarse-grained schistose ore with granular and lamellar hematite (sample FLPRO38 from Liberdade deposit) (i) Medium- to coarse-grained magnetite/hematite schistose ore (sample B-R31 from Baratinha deposit).

of around 6 kbars were calculated for the Horto-Baratinha deposit (Silveira Braga, Rosière, Santos, Hagemann, McNaughton, et al., 2019). This temperature gradient points to an eastward increasing metamorphic grade (fig. 1). Fluid inclusion homogenization temperatures were calculated by Gomes et al. (2018) for two generations of quartz-hematite veins that crystallized during the Brasiliano orogeny, associated with the silica leaching from iron formations in the areas around the Liberdade and Morro Escuro deposits (fig. 1). According to the authors, the first generation of veins (Vp1) crystallized from high-salinity (26.5 ± 1 wt% NaCl_{eqv}), high-temperature fluids (329 ± 15 °C) that indicate a significant contribution of anatexis. Thermometric studies of the second generation of veins (Vp2), on the other hand, delivered lower salinity (wt% of NaCl_{eqv} between 2.74 ± 1.5 and

12.7 ± 1) and lower temperature fluids (between 145 ± 5 °C and 260 ± 5 °C) trapped in the quartz, that indicate crystallization at a lower crustal level. Oliveira et al. (2017) obtained similar low- to moderate homogenization temperatures (91 to 228 °C) from aqueous-saline fluids (6.3 and 13.7 wt% NaCl_{eqv}) in quartz veins from the Morro do Pilar and Conceição do Mato Dentro deposits (fig. 1).

4. Sampling and analytical methods

Nineteen samples of iron formation, high-grade ore bodies, and quartz/pegmatite veins, containing lamellar/platy and granular hematite, and kenomagnetite-martite, from five iron ore deposits across the Guanhanes Block and Southern Espinhaço fold-thrust belt were selected for oxygen

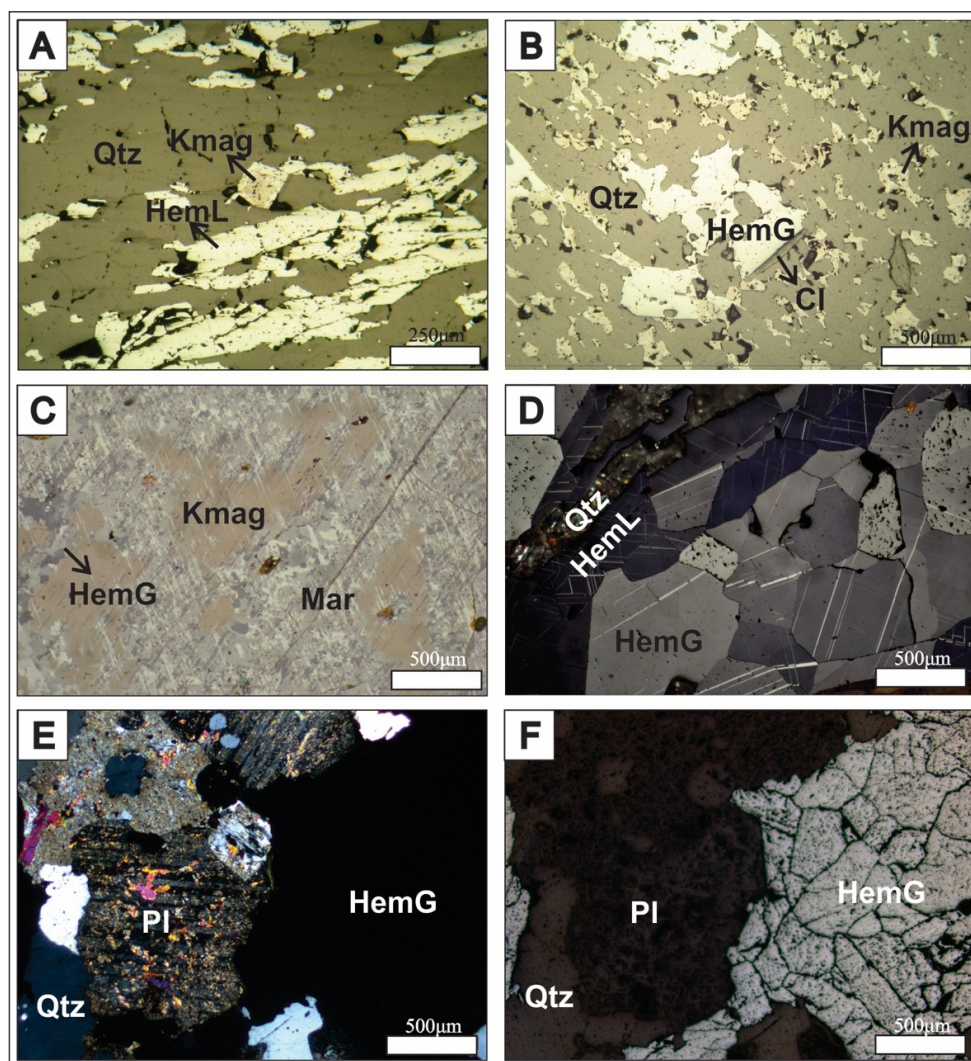


Figure 4. Microscopic features of the studied samples. (A) Lamellar hematite defining the foliation in schistose iron formation overgrown by magnetite with oxidized rims to hematite/martite. Sample M-181,45 (Morro Escuro deposit), reflected, plane-polarised light. (B) Hidioblastic granular hematite and magnetite overgrow earlier hematite crystals in iron formation. Sample M-3-501 (Morro Escuro deposit) reflected, plane-polarised light. (C) Coarse-grained partially martitized kenomagnetite in high-grade ore. Sample C-R04 (Cuité deposit), reflected, plane-polarised light. (D) Granular and lamellar hematite with twin-lamellae intergrown with quartz in high-grade ore. Sample C-R10 (Cuité deposit), reflected, partially crossed-polarised light. (E) and (F) plagioclase, quartz and hematite in pegmatite. Sample B-S27 (Baratinha deposit), E - transmitted light, crossed-polarised light; F - reflected light, plane-polarised light.

Abbreviations: HemG = granular hematite, HemL = lamellar hematite, Kmag = kenomagnetite, Qtz = quartz, Cl = chlorite, Pl = plagioclase, Ms = muscovite.

isotope analyses (table 1). Centimeter-sized fragments of texturally and mineralogically homogeneous samples were crushed using an agate mortar and pestle to a size where iron oxide fragments were released. The fragments were carefully handpicked under the microscope avoiding gangue minerals until a concentrate of at least 2 mg of material per sample.

The oxygen isotope composition was measured at the University of Göttingen, Germany, by laser fluorination in combination with gas chromatography and gas source mass spectrometry. All measured values are reported in per mil relative to the Vienna Standard Mean Ocean Water (V-SMOW) standard. Details regarding the current system are described in Pack et al. (2016). San Carlos olivine, NBS-28

quartz and the UWG-2 Gore Mountain garnet (Pack et al., 2016; Valley et al., 1995) were used as standards. The uncertainty (1σ precision) for $\delta^{18}\text{O}$ is 0.1‰, which is associated with analytical precision and was determined based on replicates of internal standards, demonstrating the reproducibility of the instrument. Analytical accuracy was assessed using the standard results (23 measurements), with values ranging between 94.4% and 99.9% (using the accuracy equation of Harouaka et al. (2020)). Precision was measured by the analysis of duplicate samples, obtaining a value of 0.68% for the relative standard deviation (RSD). The low RSD value indicates a low probability of contamination by gangue minerals, once they were carefully avoided during handpicking and, if present, would be het-

Table 1. Summarized details of the analyzed samples.

Sample ID	Lithotype	Location	Minerals analyzed		
			HemL	HemG	Kmag/Mar
B-R27	Granular (hematite and magnetite) ore	Horto-Baratinha		X	X
B-R28	Itabirite	Horto-Baratinha	X		
B-R31	Granular (hematite and magnetite) ore	Horto-Baratinha		X	X
B-R62	Itabirite	Horto-Baratinha	X		
B-S11	Granular and lamellar hematite ore	Horto-Baratinha		X	
B-S27	Pegmatite	Horto-Baratinha		X	
B-S54	Pegmatite	Horto-Baratinha			X
C-R04	Granular magnetite ore	Cuité			X
C-R10	Granular and lamellar hematite ore	Cuité		X	
FLPRO32	Quartz vein	Liberdade		X	
FLPRO33	Quartz vein	Liberdade			X
FLPRO34c	Granular (hematite and magnetite) ore	Liberdade			X
FLPRO35	Quartz vein	Liberdade			X
FLPRO38	Granular and lamellar hematite ore	Liberdade	X		
M-181,45	Itabirite	Morro Escuro	X		
M-2-501	Itabirite	Morro Escuro			X
M-3-501	Itabirite	Morro Escuro		X	X
P-13-001	Itabirite	Passabém	X		X
P-5-002	Quartz vein	Passabém			X

Abbreviations: HemL= lamellar hematite, HemG = granular hematite, Kmag = kenomagnetite, Mar = martite.

erogeneously distributed and generate high RSD values. To verify any possible contamination by gangue minerals XRD analysis were complementarily conducted in some iron oxides concentrate samples. The handpicked fragments were crushed again with the agate mortar to reach grain size <200 μm , and taken to XRD analysis. The concentrate was spread on a glass slide using acetone and analyzed with a Panalytical 'Pert PRO MPD diffractometer (PW3040/60), equipped with a $\text{CuK}\alpha$ source of the Centro de Pesquisa Professor Manoel Teixeira da Costa (CPMTC) of Universidade Federal de Minas Gerais (UFMG). Scanning ranges from 5.01 to 69.99° 2 θ ; 40 kV and 45 mA; 0.02° step size and 1.0 s scan step time; continuous scan type; divergent slit size of 0.9597°; 0.76 mm receiving slit size. The results certify the purity of all iron oxide samples, with no peaks indicating the presence of gangue minerals above glass background (fig. 5).

5. Results

5.1. $\delta^{18}\text{O}$ of iron oxide samples

The $\delta^{18}\text{O}$ values of all iron oxides vary from -1.6 to 8.1‰ (table 2 and fig. 6). The heaviest signatures were obtained in iron oxides from iron formation (1.7 to 8.1‰), followed by veins (1.8 to 5.0‰) and ore bodies (-1.6 to 2.6‰). Thin lamellar hematite (HemL) from the least altered iron formation displays a wide range of values between 1.7 to 8.1‰, with the higher values obtained from Morro Escuro (6.2‰) and Passabém (8.1‰) iron formation. Contrastingly, the analyses of thick platy hematite from high-grade

orebody, collected at the Liberdade deposit, yielded much lower $\delta^{18}\text{O}$ value (0.8‰).

Kenomagnetite-martite (Kmag/Mar) fragments were sampled from high-grade iron orebodies of all deposits and iron formations layers from Morro Escuro and Passabém. The $\delta^{18}\text{O}$ isotope analyses from iron formations delivered values between 3.4–3.7‰ (Morro Escuro) and 4.7–5.0‰ (Passabém). The $\delta^{18}\text{O}$ values obtained from high-grade iron ore vary from -1.5 to 6.7‰. The lowest $\delta^{18}\text{O}$ values were identified in the Cuité high-grade ore (-1.5 and -0.3‰) followed by Liberdade (0.2‰) and Horto-Baratinha (0.5 and 0.7 ‰) orebodies. The kenomagnetite-martite fragments sampled from pegmatite and quartz veins yielded higher values than the samples from high-grade orebodies (1.8 to 5.0 ‰), varying from 1.8 to 1.9‰ in the Horto-Baratinha pegmatite, 3.2–3.3‰ in the Liberdade quartz vein, and 4.7–5.0‰ in the Passabém quartz vein.

The $\delta^{18}\text{O}$ signature obtained from granular hematite crystals (HemG) from ore varied from -1.6 to 6.1‰. The highest $\delta^{18}\text{O}$ values were found in well-developed hypidiomorphic crystals from quartz-veins exposed in the Liberdade deposit (3.1‰) and in the iron formation from Morro Escuro (4.7 and 6.1‰). The lowest were identified in the sample of massive high-grade ore from Cuité (-1.6 and -1.5‰). The $\delta^{18}\text{O}$ values of hematite from Horto-Baratinha vary from 0.6 to 2.6‰ in the high-grade ore body and 2.4 to 2.5‰ in the pegmatite vein.

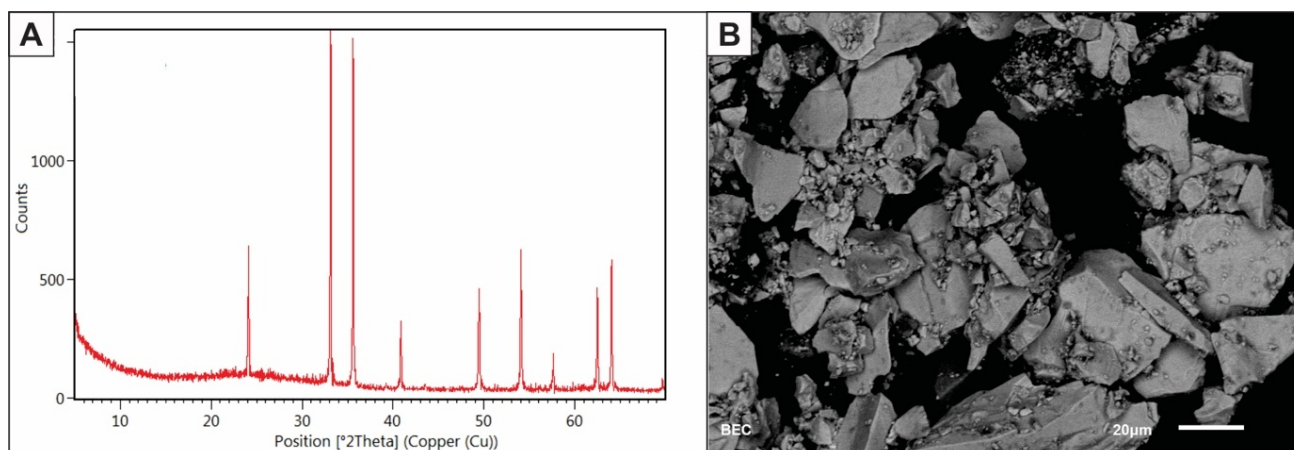


Figure 5. Controlling contamination procedure, example of sample B-S11. (A) XRD result where all peaks correspond to hematite. (B) Backscattered electron image of crushed handpicked grains analyzed by XRD.

5.2. Oxygen isotopes in equilibrium with hydrothermal fluid

In this study, the fractionation curve of Yapp (1990) (eq 1), Zheng (1991) (eqs 2 and 3), and Bao and Koch (1999) (eq 4) were applied for the calculation of $\delta^{18}\text{O}_{\text{fluid}}$ values (fig. 6) in equilibrium with the different iron oxides of the iron formation and related high-grade ores. Yapp (1990) conducted experiments to determine the α -T (T – temperature) relation in the hematite-water system, in which the mineral was synthesized at temperatures ranging from 62 °C to 120 °C. The α represents the fractionation factor or isotopic partition coefficient for two chemical compounds for two species (A and B) where $\alpha_{AB} = R_A / R_B$, being $R = ^{18}\text{O}/^{16}\text{O}$, $1000 \ln \alpha_{AB} = \delta_A - \delta_B$. The authors consider that the hematite-water curve is approximately parallel to the magnetite-water curve at temperatures of < 200 °C. In fig. 6 we included the values calculated for $\delta^{18}\text{O}_{\text{fluid}}$ associated with magnetite at a temperature of 350 °C just for comparison. Zheng (1991) and Zheng and Simon (1991), using a modified increment method, obtained a semi-theoretical calibration of oxygen isotope fractionation, producing hematite-water and magnetite water α -T relations significantly different from the data obtained by Yapp (1990). To investigate the temperature dependence of the fractionation between water and hematite, akaganeite, and goethite at near-surface temperatures, Bao and Koch (1999) have experimentally synthesized ferric oxide at six temperatures, ranging from 35 to 140 °C, and obtaining a greater hematite-water temperature sensitivity than in the goethite-water system.

$$1000 \ln^{18} \alpha_{\text{min-H}_2\text{O}} = 1.63 \cdot 10^6 \cdot T^{-2} - 12.3 \quad (1)$$

$$1000 \ln^{18} \alpha_{\text{min-H}_2\text{O}} = (2.69 \cdot 10^6 \cdot T^{-2}) + (-12.82 \cdot 10^3 \cdot T^{-1}) + 3.78 \quad (2)$$

$$1000 \ln^{18} \alpha_{\text{min-H}_2\text{O}} = (3.02 \cdot 10^6 \cdot T^{-2}) + (-12.00 \cdot 10^3 \cdot T^{-1}) + 3.31 \quad (3)$$

$$1000 \ln^{18} \alpha_{\text{min-H}_2\text{O}} = 0.733 \cdot 10^6 \cdot T^{-2} - 6.914 \quad (4)$$

The calculation of the $\delta^{18}\text{O}_{\text{fluid}}$ values were based on the fluid inclusion homogenization temperatures of 150 and 350 °C obtained by Gomes et al. (2018) and Oliveira et al. (2017) (fig. 6). The $\delta^{18}\text{O}$ values of the mineralizing fluids estimated from the curves of Yapp (1990) and Bao and Koch (1999) are remarkably similar, with a difference of 0.4‰ for a temperature of 150 °C. For the temperature of 350 °C, the difference increases to 3.1‰. Both equations were determined experimentally for hematite at temperatures below 140 °C. The results for magnetite at 350 °C were extrapolated.

According to Yapp's equation (1990), the calculated $\delta^{18}\text{O}_{\text{fluid}}$ values for the fluid in equilibrium with the lamellar hematite (HemL) from the high-grade ore, yielded an average of 4.0‰ for 150 °C and 8.9‰ for 350 °C. The $\delta^{18}\text{O}_{\text{fluid}}$ values obtained from iron formation are higher than from iron ore, exhibiting an average of 7.7‰ for 150 °C and 12.6‰ for 350 °C (fig. 6). The $\delta^{18}\text{O}$ values of the fluid in equilibrium with composite kenomagnetite-martite (Kmag/Mar) from the veins are not very different from the platy crystals in iron formation with an average of 6.5‰ for 150 °C and 11.4‰ for 350 °C, using Yapp (1990), and 11.5‰ for 150 °C and 350 °C using Zheng (1991). The $\delta^{18}\text{O}_{\text{fluid}}$ values for Kmag/Mar calculated using the equation of Zheng (1991) at 150 °C and 350 °C are similar. For fluid in equilibrium with Kmag/Mar from the iron ore, the values average 3.1‰ for 150 °C and 8.0‰ for 350 °C, applying Yapp (1990), and 8.1‰ for 150 °C and 350 °C according to the calculations following Zheng (1991). The $\delta^{18}\text{O}_{\text{fluid}}$ values for Kmag/Mar from the iron formations have an average of 7.8‰ for 150 °C and 12.7‰ for 350 °C, making use of Yapp (1990), and 12.8‰ for 150 °C and 350 °C applying Zheng's equation (1991).

The average $\delta^{18}\text{O}$ value of the fluid in equilibrium with vein-hosted granular hematite (HemG) at 150 °C is 5.9‰ and 10.8‰ at 350 °C (fig. 6A). Granular hematite from the high-grade iron ore, on the other hand, display calculated average $\delta^{18}\text{O}_{\text{fluid}}$ values of 3.8‰ for 150 °C and 8.7‰ for 350 °C. When comparing Horto-Baratinha and Cuité iron ore samples, the $\delta^{18}\text{O}_{\text{fluid}}$ values display different ranges, with the first exhibiting higher values (3.7‰ to 5.8‰ for

Table 2. Oxygen isotope results of different paragenetic iron oxide generations from IF and high-grade ore bodies of Guanhões Block and Southern Espinhaço belt. The $\delta^{18}\text{O}$ values are shown in per mil relative to Vienna Standard Ocean Water.

Rock sample ID	Analysis code	Location	Lithotype	Analysed mineral	$\delta^{18}\text{O}$ (‰)
B-R28	B_03	Baratinha	Itabirite	HemL	1.7
B-R62	B_06	Baratinha	Itabirite	HemL	3.2
				duplicate	3.3
B-R27	B_01	Baratinha	Granular (hematite and magnetite) ore	HemG	0.8
B-R27	B_02	Baratinha	Granular (hematite and magnetite) ore	Kmag	0.7
B-R31	B_04	Baratinha	Granular (hematite and magnetite) ore	HemG	0.6
B-R31	B_05	Baratinha	Granular (hematite and magnetite) ore	Kmag	0.5
B-S11	B_08	Baratinha	Granular and lamellar hematite ore	HemG	2.5
				duplicate	2.6
B-S27	B_09	Baratinha	Pegmatite	HemG	2.5
				duplicate	2.4
B-S54	B_10	Baratinha	Pegmatite	Kmag	1.9
				duplicate	1.8
C-R04	C_01	Cuité	Granular magnetite ore	Kmag	-1.5
				duplicate	-0.3
C-R10	C_03	Cuité	Granular and lamellar hematite ore	HemG	-1.5
				duplicate	-1.6
FLPRO34c	L_03	Liberdade	Granular (hematite and magnetite) ore	Kmag+Mar	0.2
FLPRO38	L_06	Liberdade	Granular and lamellar hematite ore	HemL	0.8
				duplicate	0.8
FLPRO35	L_05	Liberdade	Quartz vein	Mar	3.3
FLPRO32	L_01	Liberdade	Quartz vein	HemG	3.1
FLPRO33	L_02	Liberdade	Quartz vein	Mar	3.2
M-181,45	M_01	Morro Escuro	Itabirite	HemL	6.2
M-2-501	M_02	Morro Escuro	Itabirite	Kmag	3.4
M-3-501	M_03	Morro Escuro	Itabirite	HemG	6.1
				duplicate	4.7
M-3-501	M_05	Morro Escuro	Itabirite	Kmag	3.7
P-13-001	P_01	Passabém	Itabirite	Kmag	6.7
P-13-001	P_02	Passabém	Itabirite	HemL	8.1
P-5-002	P_03	Passabém	Quartz vein	Kmag	4.7
				duplicate	5.0

Abbreviations: HemL= lamellar hematite, HemG = granular hematite, Kmag = kenomagnetite, Mar = martite.

150 °C and 8.6‰ to 10.7‰ for 350 °C) than the second (1.7‰ to 2.9‰ for 150 °C and 6.6‰ to 7.8‰ for 350 °C). The values of the fluid in equilibrium with HemG from the least altered itabirite show an average of 8.6‰ for 150 °C and 13.5‰ for 350 °C ([fig. 6A](#)).

6. Discussion

6.1. Iron ore genetic types and oxygen isotopic signature: hydrothermal vs. magmatic

High-grade IF-hosted iron ore systems around the world are controlled by tectonic structures, that allow large volumes of ascending and descending hydrothermal and su-

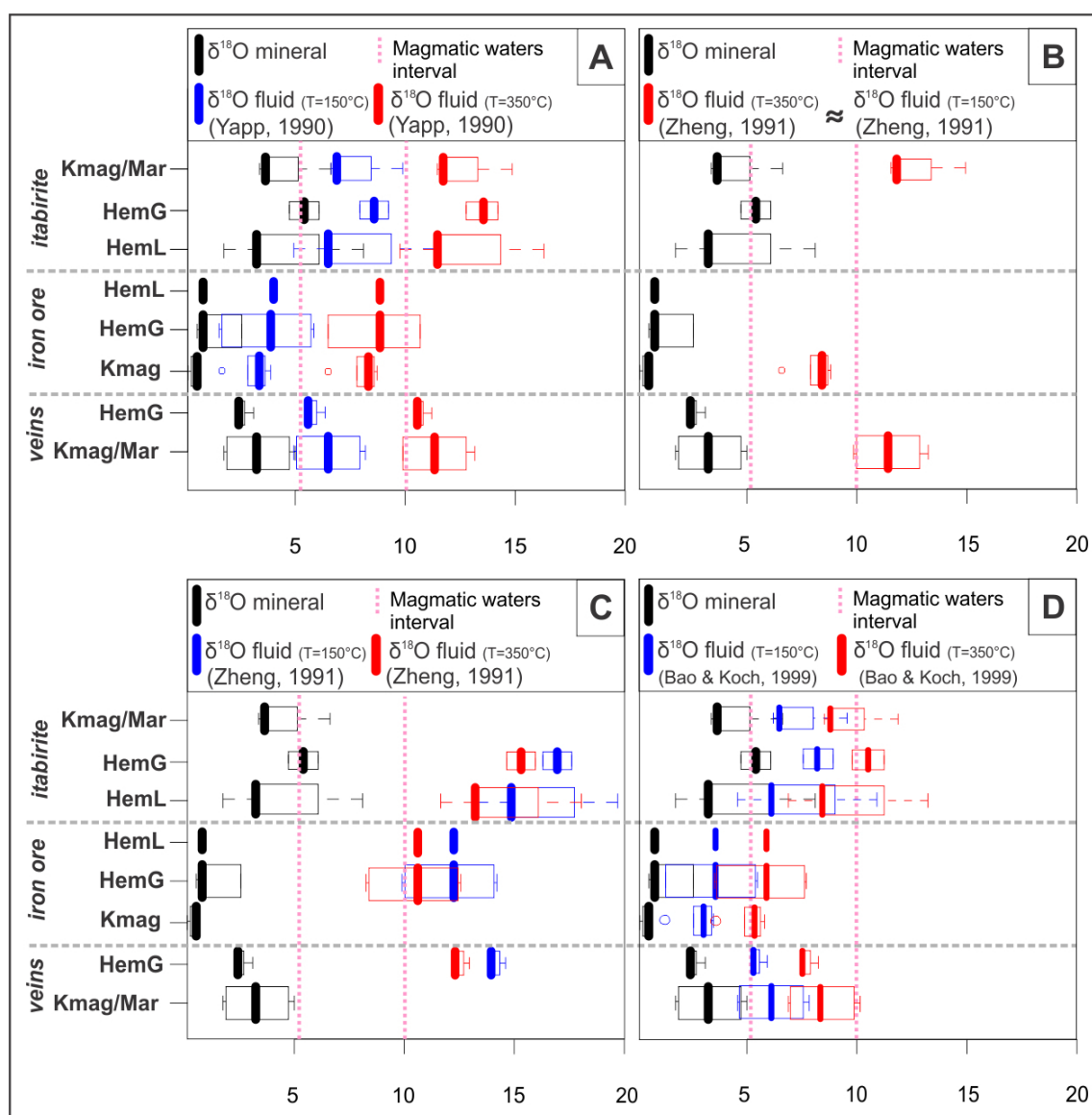


Figure 6. Box plot, showing $\delta^{18}\text{O}_{\text{mineral}}$ and $\delta^{18}\text{O}_{\text{fluid}}$ values in per mil relative to Vienna Standard Mean Ocean Water of the different iron oxide species analyzed. The fluid values were calculated using (A) Yapp (1990) equation for all iron oxides generation, (B) magnetite, and (C) hematite equations of Zheng (1991) and, (D) Bao and Koch (1999) for hematite and magnetite. The equation of Bao and Koch (1999) is defined only for hematite; values for magnetite were calculated using the same equation just for comparison. The fractionation temperature used was 150 °C and 350 °C. The magmatic waters interval of +5.5 to +10.0 ‰ is according to Taylor (1979).

Abbreviations: HemG = granular hematite, HemL = lamellar hematite, Kmag = kenomagnetite, Mar = martite.

pergene fluids to percolate (Hagemann et al., 2016). The iron deposits of the Carajás mineral province, located at the Amazon Craton, for example, are hosted by the 2.7 Ga Grão Pará Group, a greenschist metamorphic volcanic-sedimentary sequence comprised by jaspilite interlayered with basalt (Figueiredo e Silva et al., 2008). The analyses of fluid inclusion of mineralization brines trapped in quartz veins indicate the involvement of early magmatic ($\pm$ metamorphic) fluids and ancient “warm” meteoric waters circulating along a strike-slip fault zone (Hagemann et al., 2016). A progressive depletion in $\delta^{18}\text{O}$ values from the earliest hydrothermal oxide magnetite (-0.4 to $+4.3\text{‰}$) toward the latest tabular and platy hematite components (-9.5 to

-2.4‰ , [fig. 7](#)), is interpreted as the product of the mixture of descending, heated meteoric water with the ascending, modified, magmatic fluids (Figueiredo e Silva et al., 2013).

The Quadrilátero Ferrífero mineral district, on the southern portion of the San Francisco craton, southeast of Brazil, comprises Archean greenstone terranes of the Nova Lima Supergroup and the Paleoproterozoic platformal fluvial-deltaic-marine sequences of the Minas Supergroup that contain important banded iron formation-hosted, high-grade iron ore deposits (Rosière et al., 2008). The Minas Supergroup was affected by two orogenic events (2.1–2.0 Ga and 0.65–0.50 Ga) and metamorphic grade varies from greenschist facies to amphibolite (Hagemann

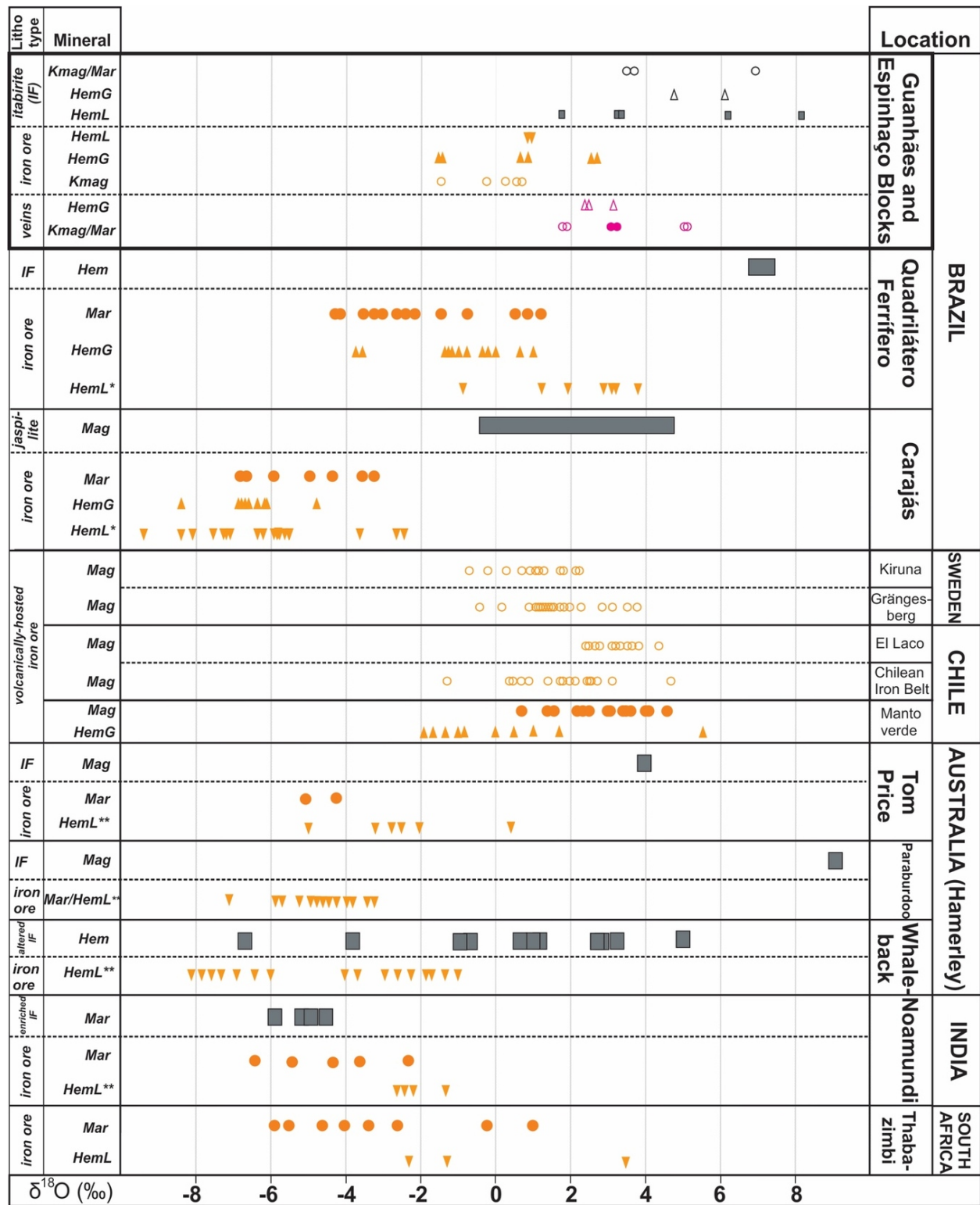


Figure 7. $\delta^{18}\text{O}$ values of different iron oxides (in per mil relative to VSMOW) from the studied samples and various high-grade iron ore deposits worldwide (modified from Hensler et al., 2014).

Abbreviations: HemG = granular hematite, HemL = lamellar hematite, HemL* = microplaty hematite + specular hematite; HemL** = platy hematite; Kmag = kenomagnetite, Mar = martite, IF = iron formation. Ore deposits data: Quadrilátero Ferrífero (Hensler et al., 2014; Hoefs et al., 1982); Carajás (Figueiredo e Silva et al., 2013); El Laco, Chilean Iron Belt and Kiruna (Nyström et al., 2008), Grängesberg (Jonsson et al., 2013), Manto Verde (Childress et al., 2020), Tom Price and Paraburdoo (Thorne et al., 2009); Mt Whaleback (Oliver et al., 2007); Noamundi (Beukes et al., 2008); Thabazimbi (Gutzmer et al., 2006).

et al., 2016; Rosière et al., 2008). Hensler et al. (2014) observed that the $\delta^{18}\text{O}$ composition of martite grains of high-grade ore ranges between -4.4 and 0.9‰ and is up to 11‰ depleted in ^{18}O relative to hematite of the banded iron for-

mation (fig. 7). According to these authors, the decrease in $\delta^{18}\text{O}$ value is again associated with the circulation of huge fluid volumes and mixture with meteoric fluids along re-

gional faults and/or large-scale folds related to the orogenic events.

The Hamersley province, located at northwest Western Australia, contains high-grade martite-microplaty hematite iron ore deposits that are primarily hosted by Paleoproterozoic banded iron formation from Hamersley Group. In Mount Tom Price, Mount Whaleback, and Paraburdoo deposits hydrothermal alteration assemblages and high-grade iron ore crosscut the magnetite-quartz rich bands. In these deposits the percolation of mineralizing fluids comprising early basinal ($\pm$ evaporitic) brines and ancient "warm" meteoric water is controlled by low angle normal faults (Hagemann et al., 2016; Thorne et al., 2009). Thorne et al. (2009) report that the $\delta^{18}\text{O}$ values of magnetite and hematite from high-grade iron ore range from -9.0 to -2.9‰ , depleted 5 to 15 per mil relative to the host banded iron formation, due to the interaction of the basinal brines and descending meteoric fluids (fig. 7). In the Kapvaal craton, South Africa, the structural styles and ore types are similar to the Hamersley deposits (Hagemann et al., 2016). The hematite-martite ores at Thabazimbi occur mainly along early normal faults or dolerite dikes that crosscut IF at high angles, with participation of basinal fluids (Hagemann et al., 2016). The martite from Thabazimbi ore bodies has $\delta^{18}\text{O}$ content between $+0.9$ to -6.0‰ whereas specularite from IF varies from $+3.4$ to 2.4‰ (Gutzmer et al., 2006), (fig. 7).

The Singhbhum craton, east of India, contain a large number of IF-hosted high-grade orebodies associated to the Paleoproterozoic Iron Ore Group. Although many aspects of the mineralization are still unclear, the hard microplaty hematite-martite ore from the Noamundi deposit are most likely formed by hydrothermal replacement of the iron formation protolith, through leaching of silica and introduction of iron by fluids of meteoric origin as proposed by Beukes et al. (2008). In Noamundi, there is an overlap of the $\delta^{18}\text{O}$ values of martite grains from both high-grade ore and the partly mineralized iron formation (fig. 7), ranging from -2.6 to -6.7‰ (Beukes et al., 2008).

The magnetite-apatite ores of the Kiruna-type, originated from iron-oxide magmas at volcanic or sub-volcanic depths, are another important iron source (Nyström et al., 2008) but formed by distinct processes, in a magmatic environment. The genetic processes involved in this ore-type includes direct magma segregation or crystallization, magma hydrothermal replacement, and hydrothermal precipitation in the sense of the iron-oxide-copper-gold (IOCG-type) deposits. The $\delta^{18}\text{O}$ mineral signatures of this type of deposit are higher than the values obtained from the majority of the IF-hosted ores, especially those intensively affected by meteoric fluids (fig. 7).

The rock assemblage of the Grängesberg deposits, in central Sweden, comprise mainly intermediate to felsic meta-volcanic rocks that crystallized at ~ 1.90 Ga in a subduction or back-arc-related tectonic setting (Jonsson et al., 2013). The $\delta^{18}\text{O}$ values of magnetite from Grängesberg ore range between -0.4 and $+3.7\text{‰}$ and magnetite of the meta-volcanic rocks display values ranging from $+4.9$ to $+9\text{‰}$ (fig. 7). The massive iron orebodies of the contemporaneous

Kiruna-Malmberget province in northern Sweden occur as large lense-shaped bodies enclosed in volcanic rocks, with the footwall composed of trachyandesitic lava and the hanging wall of rhyolitic ignimbrites and tuffs (Nyström et al., 2008).

Similar cases but in a much younger environment comprise the Chilean Iron Belt, where several magnetite-apatite deposits of Cretaceous age align along $\sim 600\text{km}$ in the Andean Cordillera. Most of these deposits are associated with coeval andesites and basalts in tectonic contact with granitoids in the north-south-trending Atacama fault zone (Nyström et al., 2008). In the magmatic-hydrothermal Mantoverde ore deposit (Childress et al., 2020), located 50 km in the Chilean Iron Belt, magnetite is the dominating mineral at depth as hematite prevails at shallow or distal levels. The Pliocene age El Laco ore, located in northern Chile, is unaffected by metamorphism, and exhibit volcanic structures and textures diagnostic of a crystallization in a cooling magmatic system, with $\delta^{18}\text{O}$ values in magnetite ranging between 2.3 to 4.2‰ (Nyström et al., 2008), (fig. 7).

Notably, the oxygen isotope signature of iron formation-hosted deposits from the ES-GB area reveals a progressive decrease in $\delta^{18}\text{O}$ values from the iron formation (1.7 to 8.1‰) to high-grade ore (-1.6 to 2.6‰), which appears to be a common trend in this type of mineralization. However, in these specific cases, the influence of magmatic fluids is evident, imparting a relatively higher oxygen isotope signature compared to most hypogene iron formation high-grade ores worldwide, with values comparable to magnetite-apatite ores of the Kiruna type. This study also underscores the uniqueness of this model, utilizing unprecedented oxygen isotope data that allowed for a more precise characterization of the presented model.

6.2. Influential factors of iron oxides oxygen signature in a hydrothermal environment

According to Clayton and Epstein (1961) a solid phase crystallizing in local equilibrium with a hydrothermal fluid has its isotopic signature depending on (a) the over-all isotopic composition of the system; (b) the chemical nature and relative amounts of the fluid and other solid phases; and (c) the temperature of the system. Although the calibration equations were at first preliminary and tentative, based on untested assumptions, with the modern laser fluorination technique the authors accepted that the isotopic composition of iron oxides records both the composition and temperature of the solutions that it forms particularly considering their resilience to dissolution.

The equation obtained by Yapp (1990) has a cross-over point with Clayton and Epstein (1961) curve at 91°C , however the switch from positive to negative values $1000\ln^{18}\alpha$ occurs at $\sim 128^\circ\text{C}$. Hayles et al. (2018) published calibration curves based on statistical thermodynamics and density functional theory for two and three oxygen isotopes thermometer for pairs of quartz, calcite, dolomite, fluorapatite, hematite, magnetite and liquid water, showing elevated temperature sensitivities as triple isotope thermometer. Similarly to the previous experiment of Bao and Koch (1999), Hayles et al. (2018) obtained only small fraction-

ations for oxygen isotopes between hematite and water at surface temperatures. The curve obtained by Hayles et al. (2018) for the systems hematite- $\text{H}_2\text{O}_{(\text{L})}$ and magnetite- $\text{H}_2\text{O}_{(\text{L})}$ ($1000\ln^{18}\alpha_{\text{mineral-water}}$ vs. temperature) lies between the theoretical results from Zheng and Simon (1991) and the experimental results from Bao and Koch (1999) and Yapp (1990), with results higher than the theoretical results from Zheng and Simon (1991) by $\sim 2\text{‰}$ for magnetite, although the causes for these discrepancies are still unclear. According to Hayles et al. (2018) hematite or magnetite show promising temperature sensitivities as triple isotope thermometers showing acceptable uncertainties for surface and low-T hydrothermal environments.

Galili et al. (2019) when studying the oxygen isotope composition of marine iron oxides observed an increase in $\delta^{18}\text{O}$ values during the past ~ 2000 Ma. According to these authors, experiments with iron oxide precipitation have shown a minor temperature dependance in iron-oxide-water $\delta^{18}\text{O}$ fractionation implying that the composition of the oxides host solutions is more important in $\delta^{18}\text{O}$ signature than their temperature of formation. A relative enrichment of ^{18}O in hematite and the temperature insensitivity of the hematite-magnetite oxygen isotope fractionation was observed by Clayton and Epstein (1961) for natural samples, and Yapp (1990) in experimental data.

Yapp (2022) discusses the relation between pH and goethite-water $^{18}\text{O}/^{16}\text{O}$ fractionation obtained for synthesized goethite generating a model, which predicts that in the transition from low-pH to a high-pH, the value of $1000\ln^{18}\alpha_{\text{gt-w}}$ is relatively abrupt. Evans et al. (2013) predicted to Lake Superior BIF-hosted iron ore the conditions for the silica removal, proposing the involvement of high-pH (>9) hypersaline brines. Dymkin et al. (1984) investigated the dependence of the solubility of iron-chloride species on pH, for high temperature systems of the skarn deposits, showing that the iron has a maximum solubility acid region and a minimum in the weakly acid, neutral and alkaline regions. The differences between the pH of the fluid along the syn- to post-collisional stage of the Brazilian orogeny could therefore, influenced in $^{18}\text{O}/^{16}\text{O}$ signature. The fluid may have been more acidic in the first stages, associated with silica leaching becoming gradually less acidic along the late-collisional to the gravitational collapse (fig. 8).

6.3. Hematite and magnetite oxygen isotope fractionation behavior

The significant ^{18}O enrichment in magnetite by the interaction with hydrothermal fluids in comparison with hematite has been subject of discussion by many authors (Becker & Clayton, 1976; Zheng, 1991). Nevertheless, Hoefs et al. (1982) did not observe any considerable difference between the fractionation of these minerals in the Cauê iron formation from the Quadrilátero Ferrífero mineral province (fig. 1). Similar $\delta^{18}\text{O}$ results were obtained for magnetite and hematite fragments from the ES-GB iron formations (fig. 6 and 7) indicating a comparable behavior by the fractionation.

However, in coexisting magnetite and hematite of iron formations from the Hamersley Range, hematite shows a significant depletion of ^{18}O compared to magnetite (Becker & Clayton, 1976). Zheng (1991) also found a substantial ^{18}O enrichment in magnetite, which he attributed to crystal structural variations. According to Zheng (1991), the similar fractionation behavior observed by Hoefs et al. (1982) could be explained by differences in magnetite structure, once that magnetites with less than half of Fe^{+3} in the tetrahedral position, presenting a non-standard inverse spinel-type structure, have a lower ^{18}O index than magnetites with a completely inverse spinel-type structure.

6.4. Fluid sources and oxygen isotope signature for iron deposits

The hematite-water curve of Yapp (1990), has a cross-over point at 92°C , meaning that hematite crystals precipitating in isotopic equilibrium from an aqueous solution below 92°C should be enriched in ^{18}O , and above this temperature, they should be depleted in relation to the parent solution. The temperature of the iron oxides crystallization in equilibrium with hydrothermal fluid is commonly higher than the cross-over temperature proposed by Yapp (1990) for the majority of iron ore deposits worldwide, mainly those associated with magmatic and metamorphic fluid systems, and ancient “warm” meteoric fluids (Hagemann et al., 2016). For example, fluid inclusions trapped in specular hematite from the QF high-grade ore bodies present high-salinity and high-temperature ($\sim 345^\circ\text{C}$), compatible with magmatic hydrothermal fluids (Rosière & Rios, 2004). At Carajás, the late stage modified meteoric water are registered by many fluid inclusion trapping temperatures from $>100^\circ\text{C}$ up to 295°C (Hagemann et al., 2016).

Most iron ore deposits in the QF, Carajás (Brazil), Pic de Fon (Republic of Guinea), and Thabazimbi (South Africa) show a positive shift from lighter to heavier $\delta^{18}\text{O}_{\text{fluid}}$ values (difference of their $\delta^{18}\text{O}_{\text{fluid}}$ to their $\delta^{18}\text{O}_{\text{mineral}}$ varies between ~ 3.0 and 9.0‰), (Hensler et al., 2014). A comparable result was observed in the samples of the current study when the Yapp (1990), Zheng (1991), and Bao and Koch (1999) curves for temperatures of 150°C and 350°C were used (fig. 6, table 3). When utilizing the Zheng (1991) equations (eqs 2 and 3), a shift to significantly higher $\delta^{18}\text{O}_{\text{fluid}}$ values is observed when compared to Yapp (1990) and Bao and Koch (1999) (eqs 1 and 4), which could be due to the uncertainty underlying the semi-theoretical calibration utilized by Zheng (1991), (fig. 6). The values corresponding to the Hayles et al. (2018) curve are in the middle of those obtained using the Yapp (1990), Bao and Koch (1999), and Zheng (1991) equations.

The $\delta^{18}\text{O}_{\text{fluid}}$ values obtained in our calculations for the iron oxides from high-grade ore and veins from Horto-Baratinha, Cuité, Liberdade, and Passabém deposits using the equations of Yapp (1990) and Bao and Koch (1999) fit in the range of magmatic waters between $+5.5$ and $+10.0\text{‰}$ (Taylor, 1979), (fig. 6A and D). The higher $\delta^{18}\text{O}_{\text{fluid}}$ values calculated for 350°C (Yapp equation) comply with the partial mixing of magmatic and other fluids sources contempo-

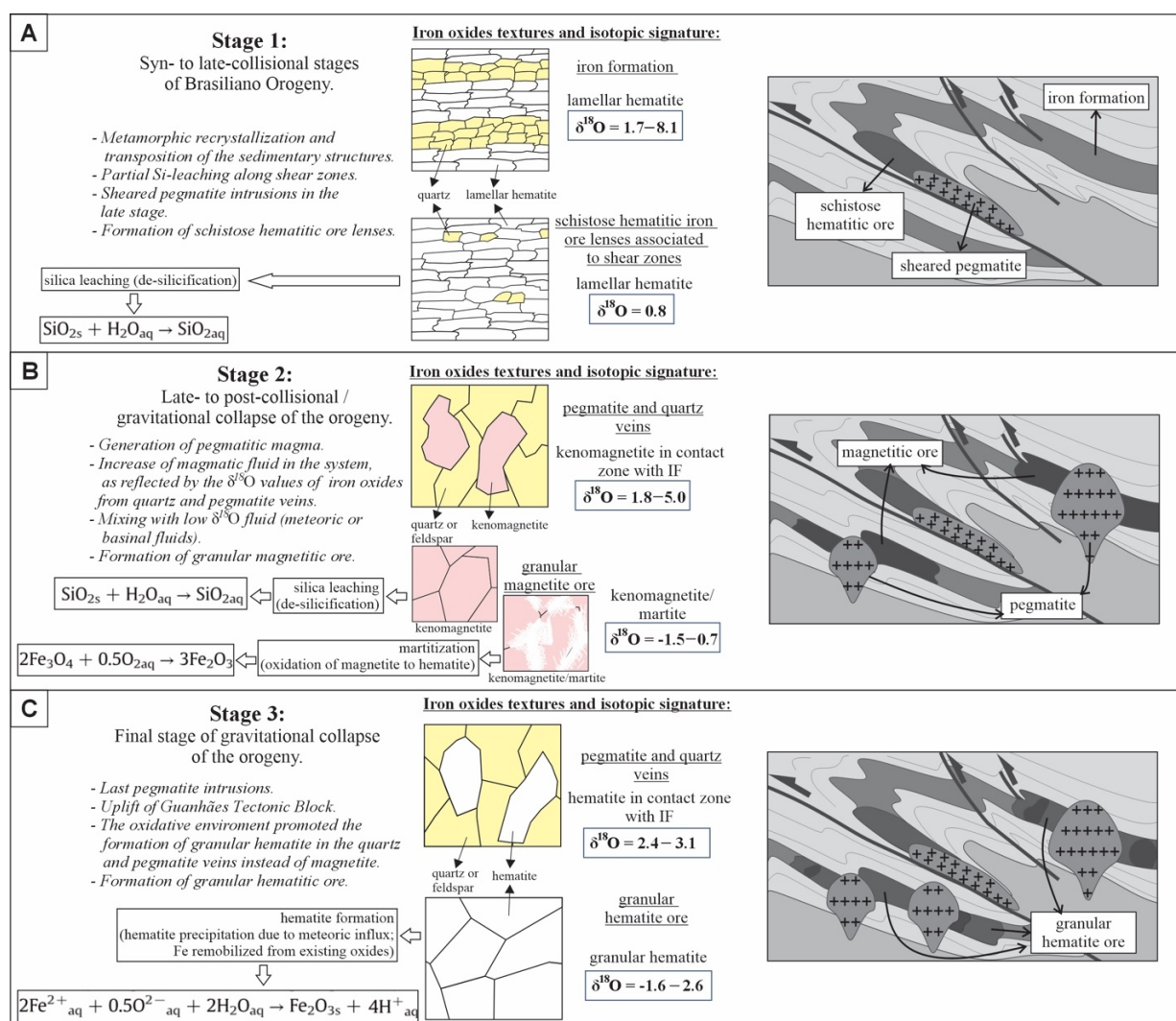


Figure 8. Genetic model of iron mineralization with the textural and oxygen isotopic evolution of Guanahães Block and Southern Espinhaço Belt divided into three phases (A), (B) and (C), associated with distinct stages of the Brasiliano orogeny. Key chemical reactions from Hagemann et al. (2016).

Table 3. Intervals of the oxygen isotope results of different paragenetic iron oxide generations from IF and high-grade ore bodies of Guanahães Block and Southern Espinhaço belt. The $\delta^{18}\text{O}$ values are shown in per mil relative to Vienna Standard Ocean Water. The calculated $^{18}\text{O}/^{16}\text{O}$ fluid range represent the values obtained based on curves from Yapp (1990), Zheng (1991), Zheng and Simon (1991), Bao and Koch (1999).

Rock	Mineral	$\delta^{18}\text{O}_{\text{mineral}}$ (‰)	$^{18}\text{O}/^{16}\text{O}_{\text{fluid}}$ (T=150°C)	$^{18}\text{O}/^{16}\text{O}_{\text{fluid}}$ (T=350°C)
IF	HemL	1.74 – 8.12	4.56 – 19.61	9.00 – 17.98
	Kmag	3.40 – 6.72	6.22 – 14.91	8.48 – 14.89
High-grade ore	HemL and HemG	-1.55 – 2.64	1.27 – 14.13	3.48 – 12.50
	Kmag	-1.48 – 0.68	1.34 – 8.86	3.55 – 8.85
Pegmatite and quartz veins	Kmag/Mar	1.76 – 5.01	4.58 – 13.19	6.79 – 13.18
	HemG	2.40 – 3.12	5.22 – 14.61	7.43 – 12.99

Abbreviations: HemL= lamellar hematite, HemG = granular hematite, Kmag = kenomagnetite, Mar = martite.

aneously with the late-collisional phase of the Brasiliano orogeny (fig. 8).

6.5. $\delta^{18}\text{O}_{\text{mineral}}$ signature of iron oxides from iron formations

The foliated iron formation of the Serra da Serpentina Group located in the Morro Escuro tectonic inlier in the ES-GB area, host the westernmost deposits of Morro Escuro and Passabém, and is considered representative of the regional widespread least altered units as indicated by whole-rock and mineral chemistry data (e.g., Gomes et al., 2018; Silveira Braga et al., 2015) comparable with other similar metamorphic iron formations such as the Cauê Formation of the Paleoproterozoic Minas Supergroup that outcrop in the Quadrilátero Ferrífero District further south (Spier et al., 2007). The $\delta^{18}\text{O}_{\text{mineral}}$ signature of the iron oxides (table 2) vary from +3.4 to +8.1‰ and the corresponding $\delta^{18}\text{O}_{\text{fluid}}$ calculated values at 350 °C varies from +11.5 to +16.2‰ (according to equation in Yapp, 1990). They fall in the same range found in the Cauê iron formation (Hoefs et al., 1982) (fig. 7), but are higher than the values obtained from the least altered samples collected in the Horto-Baratinha deposit ($\delta^{18}\text{O}_{\text{mineral}}$ +1.7 to +3.3‰ and $\delta^{18}\text{O}_{\text{fluid}}$ +9.8 to +11.4‰). The bulk-rock minor and trace element concentrations of the iron formations from these deposits are nevertheless chemically indistinguishable from other occurrences from the GB-ES belt (Silveira Braga et al., 2021) leading to the conclusion that the lower $\delta^{18}\text{O}_{\text{mineral}}$ of hematite from Horto-Baratinha is probably related to local variations in the characteristics of the syn-orogenic regional metamorphic fluids and unassociated with the mineralization.

When compared to the positive isotopic signature delivered by least-altered, weak metamorphic iron formations worldwide, the $\delta^{18}\text{O}$ values from the ES-GB area fall in the same range (-4‰ to +5‰) proposed by Gutzmer et al. (2006), as characteristic for magnetite and hematite of these rocks. Similar results were reported for magnetite samples from the Dales Gorge Member of the Brockman iron formation collected at the Paraburdoo (8.8‰ to 13.0‰) and Tom Price (4.1‰) deposits (Thorne et al., 2009) and from the Carajás jaspilite, with magnetite values between -0.4‰ to 4.3‰ (Figueiredo e Silva et al., 2013). These are slightly higher than those found in the martite-enriched iron formation from the Noamundi mine, which delivered values ranging from -6.7‰ to -2.6‰ (Beukes et al., 2008), (fig. 7).

6.6. From iron formation to ore – the evolution of the $\delta^{18}\text{O}$ signature

The iron oxides from high-grade hydrothermal iron ore deposits always exhibit significantly lower $\delta^{18}\text{O}_{\text{mineral}}$ values than the host iron formation (Gutzmer et al., 2006; Hensler et al., 2014; Powell et al., 1999; Thorne et al., 2009). The interaction of iron oxides with meteoric fluids or basinal brines during mineralization is primarily responsible for these lowering values. The ensuing light $\delta^{18}\text{O}$ signature supports the concept that hydrothermal fluids of shallow crustal origin are key contributors to the enrichment or mineralization process of iron formation to form exceptionally large, high-grade hematite orebodies. Figueiredo e

Silva et al. (2013), supported by microchemical and fluid inclusion studies, reached similar conclusions, interpreting the exemplary progressive decrease of $\delta^{18}\text{O}$ values from the earliest hydrothermal oxide mineral magnetite (-0.4‰ to 4.3‰) toward the latest platy hematite in the gigantic Carajás Serra Norte deposits in northern Brazil (-9.5‰ to -2.4‰), as the product of progressive mixture of descending, heated meteoric water with ascending, modified magmatic fluids.

Contrastingly, the oxygen isotope signature of magnetite crystals from iron orebodies of magmatic affiliation such as the Kiruna-type (fig. 7), display relatively short-range variations with $\delta^{18}\text{O}$ values between -0.4 and +3.7‰ (Jonsson et al., 2013). Fractionation factors determine that samples <+0.9‰ cannot be in equilibrium with either magma or a magmatic fluid at high temperatures (≥ 800 °C), and magnetite crystals with lower $\delta^{18}\text{O}$ values than +0.9‰ are in equilibrium with a high- $\delta^{18}\text{O}$ fluid at temperatures of ≤ 400 °C (Jonsson et al., 2013). Triple oxygen isotope data ($^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ ratios) of magnetite from the iron-oxide-apatite (IOA) deposits of the Yazd and Sirjan areas in central Iran as studied by Peters et al. (2019), show that only a few of the magnetite samples potentially record isotopic equilibrium with the magma, leading to the conclusion that magmatic fluids exchanged O isotopes with the sedimentary country rocks at variable water/rock ratios. The presence of hematite from high-grade deposits of magmatic affinities but with lower $\delta^{18}\text{O}$ values, is also widely interpreted as crystallized in equilibrium with low temperature, descending meteoric fluids, most likely during the waning stages of mineralization. The $\delta^{18}\text{O}$ values in late-stage hematite from Mantoverde IOCG (iron oxide-copper gold) deposit, for instance, are slightly lower than magnetite (fig. 7) revealing the interaction of non-magmatic, low-temperature fluids (Childress et al., 2020).

The $\delta^{18}\text{O}$ values of the iron oxides from the investigated GB-ES high-grade iron orebodies (-1.6 to 2.6‰) fluctuate from negative to positive, but always higher than -2‰, lacking extremely negative values, which is markedly different from other IF-hosted deposits worldwide. The highest positive $\delta^{18}\text{O}_{\text{mineral}}$ values found in the mineralized areas were obtained from iron oxides grown in quartz and pegmatite veins (1.8 to 5.0‰) that fall in the ortho-magmatic range of 1 to 4 ‰ (Taylor, 1979), above the limit-value of +0.9‰ proposed by Jonsson et al. (2013) (fig. 7). These unusual values for iron formation-hosted iron ore deposits reflect an anomalous mineralization history that can only be fully understood by considering the tectonic evolution of the area. The iron enrichment history of the eastern São Francisco Craton can be divided in three deformational main stages associated with granitic suites that formed during the pre- to post collisional phases of the Brasiliano orogeny (Pedrosa-Soares et al., 2011). The mineralization events are associated with the tectonic features, alteration ages obtained from zircon grains of the country rocks and with fluid variations in terms of timing, flux rates and physicochemical conditions during the orogeny (fig. 8).

The first mineralization stage (fig. 8A) developed during the syn- and late-collisional orogenic phases (580–560 Ma)

which caused the concentration of schistose orebodies along reverse shear zones. In the western limit of the working area (fig. 1). This stage is evident in the Morro Escuro and Passabém deposits as well as further west in the Serra da Serpentina Range (Rolim et al., 2016). The oxygen isotopic signature obtained from the analyzed platy hematite crystals (HemL) is somewhat lower than that obtained from IF-hosted rock (fig. 6). Further east, in the Liberdade and in the highly deformed shear-zone-hosted Cuité deposits, massive and schistose iron ores comprise a complex tectonic fabric of isotopic light coarse-grained platy (HemL) and granular hematite (HemG), ($\delta^{18}\text{O}_{\text{mineral}} -1.6$ to 0.8 ‰) grown as elongated, stretched lenses at the cost of magnetite aggregated (fig. 8). The shift in the isotopic values from “early” magnetite to “late” hematite indicates a progressive change of the physicochemical environment due to the supply of oxidic fluids, most likely of meteoric origin, that percolated the unit during the tectonic upthrust to shallower levels. The mineralizing fluids generated from the Araçuaí Orogen during the Brasiliano orogeny (Gomes et al., 2018) were the primary conveyors of the mineralization system. They were forced upwards by pressure gradients along thrust planes in the eastern border of the São Francisco Craton (Rosière et al., 2021; Silveira Braga et al., 2021).

The second stage (fig. 8B) is associated with the late- and post-collisional phases (560 – 530 Ma). Hot hydrothermal fluids from anatectic pegmatites promoted quartz leaching and crystallization of magnetite (Kmag) crystallization leading to irregular orebodies of oxides with granoblastic fabric as seen in the Horto-Baratinha deposit (Gomes et al., 2018, 2020; Silveira Braga et al., 2020; Silveira Braga, Rosière, Santos, Hagemann, McNaughton, et al., 2019). In this deposit the magnetite grains from high-grade ore bodies (0.5 to 0.7‰) exhibit an enrichment of Mg, V, Cr, Mn, Co, Ni, Zn, and Ga compared to the hematite from IF-hosted rock (Silveira Braga et al., 2021) and the $\delta^{18}\text{O}_{\text{mineral}}$ values of magnetite are heavier than the usual iron formation-hosted deposits worldwide (fig. 7). Iron oxides (hematite and magnetite) also crystallized in the ubiquitous quartz and pegmatite veins at the contact zone with the high-grade ores, yielding $\delta^{18}\text{O}$ values in the “magmatic” range (fig. 7). The comparably lower isotopic values of the high-grade iron ore are most likely due to dilution and mixing with meteoric waters, but they are still much higher and vary in a much shorter range compared with other hypogene metamorphic deposits worldwide (fig. 7), indicating the role of magmatic fluids in the process.

The late oxidation of magnetite and new crystallization of granular hematite ($\delta^{18}\text{O}_{\text{mineral}} -1.6$ to 2.6 ‰) with anomalously high concentrations of Al, Ti, Zr, Nb, Mo, Sn, Sb, Hf, Ta, and W (Silveira Braga et al., 2021) on the massive ore characterizes the third and final stage (fig. 8C). This is associated with an increase in the intake of oxidic meteoric fluids as a result of secondary permeability generated by tectonic fracturing and opening of spaces at shallower depths during faulting. Extensional sites developed mostly by fracturing during the gravitational collapse/delamination phase of the Orogeny (~530 – 490 Ma).

In contrast to our newly proposed conceptual model, it's important to note that Genetic Model 2 Hamersley-type deposits, typically found in Lake Superior-type iron formations, exhibit distinct characteristics. While both models involve iron formations, they significantly differ in their geological context and the environmental conditions to which they are exposed. Hamersley-type deposits primarily develop in Lake Superior-type iron formations associated with the alteration by basinal and metamorphic fluids, differently from the high-temperature mixed fluids that we interpret in our new model. This distinction underscores the unique nature of our conceptual model and its potential to provide fresh insights into iron ore formation processes and its oxygen isotope signature.

7. Conclusions

The formation of the high-grade iron orebodies during the Brasiliano orogeny in the Southern Espinhaço fold-thrust belt and Guanhanês Block at the eastern border of the São Francisco Craton exemplifies a new and unusual type of mineralization of iron formations, associated with a high-grade metamorphic terrane and closely related to magmatic intrusion. The $\delta^{18}\text{O}$ data delivered by the iron oxides is diagnostic of a progressive participation of magmatic fluids in the mineralization developed by the tectonic reworking of consolidated sialic crust associated with anatectic melting during a continental collision as supported by tectonic, geochemical thermo-barometric and petrographic data. The iron mineralization of the Orosirian-Statherian iron formations of the Serra da Serpentina Group developed in a scenario of eastward increasing, positive crustal temperature gradient (fig. 8) as also indicated by whole rock and iron oxides microchemical data combined with published fluid inclusion analyses (Gomes et al., 2018; L. A. R. de Oliveira et al., 2017). The gradual participation of magmatic fluids is marked by a consistent increase in the amount of trace elements (Silveira Braga et al., 2020, 2021) in the iron oxides. The platy-shaped, thin lamellar hematite crystals from the least altered iron formation exhibit the lowest contents of minor and trace elements when compared to the oxide grains crystallized in the magnetite-martite enriched rock and associated veins (Gomes et al., 2018; Silveira Braga et al., 2021). Magnetite grains from high-grade iron ore are enriched in Mg, V, Cr, Mn, Co, Ni, Zn, and Ga and the associated coarse granular to platy-textured hematite which has anomalously high Al, Ti, Zr, Nb, Mo, Sn, Sb, Hf, Ta, and W contents (Silveira Braga et al., 2021).

Microchemical and isotopic data of recrystallization rims from zircons grains collected from the metasedimentary rocks associated with the iron formations, as well from the gneissic basement (Archean Guanhanês Complex) and from meta granitoids (Statherian Borrachudos Suite) exposed in the different iron deposits of the ES-GB area yielded U-Pb SHRIMP ages ranging from 554 to 492 Ma, younger than the core and generated during the late to post-collisional stages of the Brazilian Orogeny by interaction with magmatic-hydrothermal fluid (Silveira Braga et al., 2020). The higher $\delta^{18}\text{O}$ values (>7‰) of the zircon rims indicate the

heavy signature of magmatic fluids and are consistent with the values of the iron oxides from the studied high-grade ore deposits (fig. 6).

Our findings are consistent with other iron ore deposit-types worldwide in many aspects, such as the progressive decrease in the $\delta^{18}\text{O}$ signature from iron formation to high-grade ore. Notwithstanding, $\delta^{18}\text{O}$ values of high-grade iron ore remain remarkably higher, indicating the influence of a magmatic source in the mineralizing fluids, which become progressively lower by mixing with meteoric waters if the temperatures drop below 300–350 °C. This mixing process is evident in structurally strong deformed orebodies like Cuité and Liberdade (fig. 1) which were eventually raised to shallower depths inducing secondary porosity, increasing permeability, and allowing descending meteoric fluids to percolate. Another factor that might be relevant in lowering the isotope values of the iron oxides, and deserves future investigation, is the possibility of variation in the volume, character, and chemistry of the mineralizing fluids with changing tectonic style. Distinctively, the isotopic signature of the iron oxide crystals trapped in the rims of pegmatite and quartz veins at the contact zone with the high-grade ore was less affected by the oxidative alteration

consistently exhibiting more concentrated positive values indicating a steadily higher magmatic fluid/rock ratio.

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