

1 Textures and chemical composition of magnetite from iron
2 oxide-copper-gold (IOCG) and Kiruna-type iron oxide-apatite (IOA)
3 deposits and their implications for ore genesis and magnetite
4 classification schemes

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Abstract

23 Textural and compositional data of magnetite from Igarapé Bahia, Alemão, Sossego,
24 Salobo, and Candelaria iron oxide-copper-gold (IOCG) and El Romeral Kiruna-type
25 iron oxide-apatite (IOA) deposits show that some magnetite grains display oscillatory
26 zoning or have been reequilibrated by oxy-exsolution, coupled dissolution and
27 reprecipitation (CDR) reactions, and/or recrystallization. Textures formed via CDR
28 are most widespread in the studied samples. The original oscillatory zoning was likely
29 derived from the crystal growth during fluctuating fluid compositions rather than
30 variation in temperature and oxygen fugacity. The oxy-exsolution of ilmenite in
31 magnetite is attributed to increasing oxygen fugacity and decreasing temperature with
32 alteration and mineralization, resulting in product magnetite with lower Ti and higher
33 V contents. Recrystallization of some magnetite grains is commonly due to
34 high-temperature annealing that retained primary compositions. Two different types
35 of CDR processes are defined according to textures and chemical compositions of
36 different generations of magnetite. The first generation of magnetite (Mag-1) is an
37 inclusion-rich and trace element-rich core, which was replaced by inclusion-poor and
38 trace element-poor rim (Mag-2). The third generation of magnetite (Mag-3),
39 inclusion-poor but trace element-rich, occurs as veins replacing Mag-2 along fracture
40 or grain margin. Type 1 CDR process transforming Mag-1 to Mag-2 is more extensive
41 and is similar to those reported in skarn deposits, whereas type 2 CDR process is local,
42 transforming Mag-2 to Mag-3. During type 1 CDR process, minor and trace elements
43 Si, K, Ca, Mg, Al, and Mn in magnetite are excluded and Fe contents increase to

1 45 various extents, in contrast to the type 2 CDR process which is characterized by
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3 46 increased contents of Si, K, Ca, Mg, Al, and Mn. Type 1 CDR process is possibly
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6 47 induced by the changing fluid composition and/or decreasing temperature during
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9 48 progressive alteration and ore formation, whereas type 2 CDR process can be
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12 49 interpreted as post-ore replacement due to a new pulse of magmatic-hydrothermal
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15 50 fluids.

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17 51 The identification of magnetite core (Mag-1) with igneous origin and rim (Mag-2)
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20 52 with magmatic-hydrothermal origin in the Sossego IOCG and El Romeral IOA
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23 53 deposits supports a fluid changing from magmatic to magmatic-hydrothermal during
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26 54 IOCG and IOA formation and indicates a genetic link between these two deposit
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29 55 types. Large dataset here further demonstrate that magnetite is susceptible to textural
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32 56 and compositional reequilibration during high-temperature magmatic and
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35 57 magmatic-hydrothermal processes. The reequilibrated magnetite, particularly that
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38 58 after CDR processes, has geochemical patterns that may be different from its
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41 59 precursor, complicating the application of discrimination plots for genetic and
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44 60 provenance interpretation. Therefore, in situ chemical analysis of magnetite combined
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47 61 with textural characterization is necessary to understand the origin of magnetite in
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50 62 IOCG and IOA deposits.

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53 63 **Keywords:** Magnetite textures; Trace elements; Dissolution and reprecipitation;
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56 64 Discriminant diagrams; IOCG-IOA

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66 Introduction

1 67 Magnetite is an important component in a variety of iron ore deposits, including iron
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3 68 skarns, iron oxide-copper-gold (IOCG), iron oxide-apatite (IOA), banded iron
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6 69 formations (BIF), and magmatic Fe-Ti oxides (Dupuis and Beaudoin, 2011). A range
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9 70 of minor and trace elements such as Al, Ti, Mg, Mn, Zn, Cr, V, Ni, Co, and Ga can be
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12 71 incorporated into the inverse spinel structure of magnetite (Buddington and Lindsley,
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15 72 1964; Frost and Lindsley, 1991; Dupuis and Beaudoin, 2011; Nadoll et al., 2014).
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17 73 Magnetite formed from melt/fluids with various compositions or formed under
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20 74 different physicochemical conditions has characteristic textures and compositions
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23 75 (Buddington and Lindsley, 1964; Toplis and Corgne, 2002; Dupuis and Beaudoin,
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26 76 2011; Dare et al., 2012; Nadoll et al., 2014; Tan et al., 2016a). Based on trace element
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29 77 composition of magnetite, a series of discriminant diagrams have been proposed to
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32 78 distinguish magnetite with different origins, e.g., magmatic vs. hydrothermal (Dare et
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35 79 al., 2014, 2015; Knipping et al., 2015b) or derivation from different deposit types
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38 80 (Loberg and Horndahl, 1983; Singoyi et al., 2006; Dupuis and Beaudoin, 2011;
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41 81 Nadoll et al., 2014, 2015; Knipping et al., 2015b; Makvandi et al., 2016b; Huang et al.,
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44 82 2019). These diagrams have been widely used in subsequent studies (Huang et al.,
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47 83 2013, 2014, 2015a, b, 2016, 2018; Chen et al., 2015; Chung et al., 2015; Liu et al.,
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50 84 2015; Zhao and Zhou, 2015; Velasco et al., 2016; Broughm et al., 2017; Pisiak et al.,
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53 85 2017).

54 86 Magnetite has long been considered to be resistant to mechanical breakdown and
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56 87 chemical alteration and thus can be used for provenance and petrogenetic studies
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59 88 (Grigsby, 1990; Dare et al., 2014; Nadoll et al., 2014) and mineral exploration
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1 89 (Dupuis and Beaudoin, 2011; Boutroy et al., 2014; Sappin et al., 2014; Makvandi et
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4 90 al., 2015, 2016a, b; Pisiak et al., 2017). However, recent studies have shown that both
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6 91 texture and trace element composition of igneous and hydrothermal magnetite can be
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9 92 significantly modified via coupled dissolution-reprecipitation (CDR) processes (Hu et
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12 93 al., 2014, 2015; Heidarian et al., 2016; Wen et al., 2017; Yin et al., 2017; Huang et al.,
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14 94 2018). Infiltration of mixed basinal brines and meteoric waters that already dissolved
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17 95 evaporites was proposed as an important mechanism to induce CDR reaction of
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20 96 magnetite in skarn deposits (Hu et al., 2014, 2015; Huang et al., 2018) and
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23 97 Chadormalu IOA deposit (Iran) (Heidarian et al., 2016). Wen et al. (2017) proposed
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26 98 the crystallization of titanite results in fracturing and pressure solution of igneous
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29 99 magnetite to form hydrothermal varieties. Yin et al. (2017) attributed CDR reaction of
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32 100 skarn magnetite to an increased oxygen fugacity and co-crystallized sulfide at
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35 101 far-from-equilibrium or local equilibrium conditions. Therefore, the factors inducing
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38 102 CDR processes of magnetite from different geological environments remain
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41 103 controversial. Both IOCG and IOA deposits contain large volumes of distinctly
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44 104 low-Ti iron oxides within rocks that have undergone extensive alkali-calcic
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47 105 metasomatism by hydrothermal fluids (Williams et al., 2005; Corriveau et al., 2016)
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50 106 and may have multiple stages and/or origins of ore-forming fluids (Knipping et al.,
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53 107 2015a, b; Heidarian et al., 2016; Broughm et al., 2017; Rojas et al., 2018). For
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56 108 example, Knipping et al. (2015a, b) identified three types of magnetite that are
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59 109 magmatic and hydrothermal in origin and proposed a new model for the formation of
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62 110 IOA deposits by flotation of magmatic magnetite suspensions. Therefore, detailed

1 111 studies on textures and chemical compositions of magnetite from IOCG and IOA
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3 112 deposits would shed light on the factors controlling chemical processes such as CDR
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6 113 and formation mechanisms for these deposits.
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9 114 In this study, we present combined textural and compositional data for magnetite
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11 115 from five IOCG and one IOA deposits. Iron oxide-copper-gold deposits include the
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14 116 Igarapé Bahia, Alemao, Sossego and Salobo deposits in Brazil, the Candelaria deposit
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17 117 in Chile, whereas IOA deposit is represented by the El Romeral deposit in Chile. The
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20 118 objectives of this study are to (1) characterize the textures and composition of IOCG
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22 119 and IOA magnetite, (2) constrain the process and possible mechanism involved in the
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25 120 formation of IOCG and IOA deposits, and (3) evaluate the applicability of the existing
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28 121 magnetite major and trace element discrimination diagrams.
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32 33 34 123 **Geology of the Selected Deposits and Sample Information**

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36 124 Nine samples are collected from five IOCG deposits and one sample is from El
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39 125 Romeral IOA deposit (Table 1). These deposits are mainly distributed in Carajás
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42 126 Mineral Province (CMP) of Brazil and Chilean iron belt. The detailed geology and
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45 127 geochemistry description of the selected deposits can be found in literature. Herein,
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48 128 we focus on the deposit information such as host rock, hydrothermal alteration,
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51 129 mineral assemblages, and the composition and temperature of ore-forming fluids.
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56 131 *Sossego*

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58 132 The Sossego Cu-Au deposit in CMP of Brazil is hosted by granite, granophyric
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1 133 granite, gabbro, and felsic metavolcanic rocks (Monteiro et al., 2008a, b; Xavier et al.,
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3 134 2012). It consists of two major groups of orebodies, Sequeirinho–Pista–Baiano (SPB)
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6 135 and Sossego–Curral (SC), with distinct types of hydrothermal alteration. The SPB
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9 136 orebodies are characterized by deep-emplaced magnetite-(apatite) and
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12 137 albite-actinolite-rich zones, whereas the SC orebodies have predominant potassic and
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15 138 chlorite alteration typical of shallow crustal levels (Monteiro et al., 2008a). The
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18 139 deep-emplaced Neoproterozoic IOCG-forming events in SPB reflect coupling of ductile
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21 140 sinistral transpression with NNE-directed oblique shortening and Neoproterozoic
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23 141 magmatism (~2.7 Ga), whereas the shallow-emplaced Paleoproterozoic IOCG
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26 142 mineralization may be related to the emplacement of ~1.88 Ga A-type granites that
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29 143 caused regional circulation of magmatic and externally derived fluids along crustal
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32 144 discontinuities (Moreto et al., 2015). Two samples 080 and 084 are collected from the
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35 145 SC orebodies. Sample 080 is composed of magnetite, chalcopyrite, apatite, actinolite,
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38 146 quartz, and calcite (Fig. 1A) or consists of magnetite, chalcopyrite, ilmenite, apatite,
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41 147 chlorite, calcite, and talc (Fig. 1B). Ilmenite occurs as euhedral grain associated with
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44 148 magnetite or exsolution lamellae within magnetite (Fig. 1B). Sample 084 has a
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47 149 mineral assemblage of magnetite, apatite, actinolite, quartz, and chalcopyrite (Fig.
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50 150 1C).

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52 152 *Igarapé Bahia*

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55 153 The Igarapé Bahia Cu-Au deposit in CMP of Brazil is hosted by Archean low-grade
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58 154 metamorphosed volcano-sedimentary rocks (Tazava and De Oliveira, 2000).
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1 155 Hydrothermal alteration at Igarapé Bahia includes (1) Fe metasomatism leading to the
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3 156 formation of grunerite, fayalite, and/or Fe oxides (magnetite and/or hematite), (2)
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6 157 carbonate alteration (mainly siderite), (3) chalcopyrite and bornite, (4) quartz-poor
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9 158 gangue, (5) low REE, and (6) enrichment in U and Co from early to late (Tazava and
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12 159 De Oliveira, 2000; Tallarico et al., 2005; Dreher et al., 2008). This deposit was
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15 160 derived from magmatic-hydrothermal fluids related to Archean A-type granites
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18 161 (Tallarico et al., 2005). The mixing between high-temperature, high-salinity magmatic
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21 162 fluids and meteoric fluids is the main mechanism for the Cu-Au mineralization
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24 163 (Tallarico et al., 2005). One sample F392 from this deposit has a mineral assemblage
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27 164 of magnetite, chalcopyrite, siderite, and chlorite (Fig. 1D).

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30 166 *Alemao*

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34 167 The Alemao Cu-Au deposit in CMP of Brazil is hosted by Archean
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37 168 metavolcano-sedimentary rocks similar to neighboring Igarapé Bahia deposit. The
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40 169 orebody is conformably emplaced at the interface between volcanic rocks and the
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43 170 overlying sedimentary domain (Ronze et al., 2000). Hydrothermal alteration at
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46 171 Alemao includes (1) Fe metasomatism leading to the formation of grunerite, fayalite,
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49 172 and/or Fe oxides (magnetite and/or hematite), (2) intense chloritization (Mg and Fe
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52 173 chlorite), (3) biotitization, (4) chalcopyrite and bornite, (5) intense carbonate
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55 174 alteration (mainly siderite), and (6) local silicification and tourmalinization from early
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58 175 to late (Ronze et al., 2000). This deposit was considered to be related to
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61 176 magmatic-hydrothermal system similar to that responsible for IOCG deposits in CMP

1 177 (Ronzê et al., 2000). One sample Alemao from this deposit has a mineral assemblage
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3 178 of magnetite, apatite, quartz, calcite ± chlorite (Fig. 1E, F). Some magnetite grains
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6 179 show obvious core-rim textures composed of inclusion-rich core and inclusion-poor
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9 180 rim (Fig. 1E). Chalcopyrite inclusions are common in magnetite.

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14 182 *Salobo*

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17 183 The Salobo Cu-Au-Ag deposit in CMP of Brazil is hosted by the Archean
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20 184 volcano-sedimentary rocks consisting of amphibolite, metagraywacke, banded iron
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23 185 formation, and quartzite (Requia and Fontboté, 2000). The ore-bearing,
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26 186 magnetite-rich rocks are the product of strong Fe–K alteration at high temperatures
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29 187 (550–650°C) and have been deformed and mylonitized (Lindenmayer and Teixeira,
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32 188 1999; Requia and Fontboté, 2000; Requia et al., 2003). The Fe–K alteration is
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35 189 replaced by widespread chlorite alteration (<370°C) accompanied by the formation of
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38 190 calcite, epidote, albite, sericite, quartz, and fluorite (Xavier et al., 2012). The main
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41 191 Cu-Au ores were probably formed by high temperature, highly saline, oxidized,
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44 192 sulfur-poor, near-neutral pH fluids (Requia, 2002), related to Archean (~2.57 Ga)
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47 193 granite magmatism (Requia et al., 2003). The main Cu-Au mineralization was
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50 194 overprint by ~2.45 Ga hydrothermal activity, indicating a protracted tectono-thermal
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53 195 event for the evolution of the Salobo deposit (deMelo et al., 2017). Total
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56 196 homogenization temperatures of highly saline fluid inclusions in quartz range from
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59 197 173°C to 485°C and geothermometry from post-ore stage chlorite yields a
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62 198 temperature of 350°C (Réquia and Xavier, 1995). Sample SAL2 from this deposit is

1 199 composed of magnetite, chalcopyrite, grunerite, and quartz (Fig. 1G), whereas sample
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3
4 200 11CC051 consists of magnetite, chalcopyrite, chlorite, and quartz (Fig. 1H).
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9 202 *Candelaria*

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11 203 The Candelaria Cu-Au-Ag deposit in the southeast of Copiapó, Chile is the largest

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13 204 IOCG deposit in the Punta del Cobre belt (Marschik and Fontboté, 2001). This

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15 205 deposit is hosted by Early Cretaceous volcanic and volcanoclastic rocks. Alkali

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17 206 metasomatism is widespread in Candelaria, including sodic (albite and/or marialitic

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19 207 scapolite) or K-Fe (biotite and/or K-feldspar) alteration related to ore formation

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21 208 (Marschik and Fontboté, 2001; Marschik et al., 2003). The Cu-Fe (chalcopyrite +

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23 209 magnetite ± hematite) ores are associated with biotite-potassium feldspar ± calcic

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25 210 amphibole ± epidote alteration at Candelaria (Marschik and Fontboté, 2001).
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29 211 Magnetite tends to be associated with potassic assemblages and hematite is common

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31 212 in sodium metasomatized rocks, which are interpreted in terms of more internal and

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33 213 high-temperature vs. external and low-temperature portions of the ore-forming

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35 214 hydrothermal system (Marschik and Fontboté, 2001). The bulk of the magnetite

36
37 215 probably formed at temperatures of about 500°C to 600°C, whereas the main sulfide

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39 216 stage followed with formation of pyrite and chalcopyrite at temperatures of >470°C to

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41 217 328°C (Marschik and Fontboté, 2001). Magmatic fluids or non-magmatic fluids

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43 218 equilibrated with magmatic silicates were dominant during the main copper

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45 219 mineralization, which are mixed with a non-magmatic fluid (e.g., basinal brines or

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47 220 meteoric waters) during the late stages of hydrothermal activity (Marschik and
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1 221 Fontboté, 2001). Ore formation was broadly coeval with batholithic granitoid
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3 222 intrusions and with regional uplift, suggesting a magmatic fluid contribution into the
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6 223 hydrothermal system (Marschik and Fontboté, 2001). Sample 367A from this deposit
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9 224 consists of magnetite, K-feldspar, actinolite, and minor albite and biotite (Fig. 1I).
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11 225 Sample PC98102 is composed of magnetite, chalcopyrite, and minor chlorite, biotite,
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14 226 and monazite (Fig. 1J). Sample PC1492 has a mineral assemblage of magnetite,
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17 227 chalcopyrite, K-feldspar, actinolite, chlorite, and apatite (Fig. 1K).
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229 *El Romeral*

25 230 The ~110 Ma El Romeral deposit (Rojas et al., 2018) is one of several IOA deposits
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28 231 (e.g. Cerro Negro Norte, Los Algarrobos, Los Colorados) that form the Chilean iron
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31 232 belt. The deposit is hosted by Late Palaeozoic metasediments cut by Early Cretaceous
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34 233 andesite porphyry and diorite (Bookstrom, 1977). The hydrothermal alteration in this
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37 234 deposit is represented by actinolitization, chloritization, argillization, and martitization
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39 235 (Bookstrom, 1977). Magnetite deposition was accompanied by pervasive
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42 236 actinolitization, followed by chloritization and alteration of previously actinolitized
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45 237 diorite and phyllite. Altered rocks within and around the orebodies contain magnetite,
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48 238 actinolite, plagioclase, diopside, clinozoisite, titanite, chlorapatite, marialitic scapolite,
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51 239 tourmaline, chlorite, pyrite, calcite, mica, and clays (Bookstrom, 1977). The deposit
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54 240 was considered to be produced by magmatic-hydrothermal fluids derived from the
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56 241 Romeral diorite (Bookstrom, 1977; Rojas et al., 2018) or basin-derived,
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59 242 non-magmatic brines (Mathur et al., 2002). One sample El Romeral from this deposit
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1 243 consists of magnetite, actinolite, and minor chlorite and biotite (Fig. 1L).
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6 245 **Analytical Method**

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9 246 All samples were prepared as standard polished thin sections and subsequently

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11 247 examined using optical microscopy and back-scattered electron (BSE) imaging to

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13 248 characterize the mineralogical and textural relationships. BSE was done using a

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15 249 HITACHI S-3400N scanning electron microscope (SEM) attached with an Oxford

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17 250 Instruments Energy+ energy dispersive spectrometer (EDS) hosted at the Université

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19 251 du Québec à Montréal (UQAM). Major and minor/trace element analyses of

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21 252 magnetite were conducted at Université Laval using a CAMECA SX-100 electron

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23 253 probe microanalyzer (EPMA), equipped with five wavelength-dispersive

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25 254 spectrometers. Major element Fe was determined using a 5- μ m diameter beam with a

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27 255 voltage of 15 kV and a current of 20 nA. A series of minor and trace elements were

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29 256 measured, including K, Ca, Al, Si, Ti, Mg, Mn, Cr, V, Sn, Cu, Zn, Ni, and P, using

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31 257 5- μ m diameter beam with a voltage of 15 kV and a current of 100 nA. Analytical

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33 258 conditions are similar to those described by Dupuis and Beaudoin (2011). Calibration

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35 259 was achieved using a range of natural and synthetic standards, comprising simple

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37 260 oxides (GEO Standard Block of P and H Developments) and natural minerals

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39 261 (Mineral Standard Mount MINM 25–53, Astimex Scientific) (Jarosewich et al., 1980).

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41 262 The background was measured on one side of the peak for 15-20 s at a position free of

42
43 263 interfering element X-ray and the concentration was counted over the peak for 20-40 s

44
45 264 depending on the element. Detection limits are ~450 ppm for Fe, ~100 ppm for Zn,

1 265 ~80 ppm for Cu, ~60 ppm for Ni, 40-50 ppm for V, Cr, Mn, Sn, and 15-25 ppm for K,
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3 266 Ca, Ti, Al, Si, Mg, and P. Wavelength dispersive spectrometer (WDS) X-ray maps
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6 267 were collected using a beam diameter of 1 μm , an accelerating voltage of 15 kV, a
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9 268 beam current of 100 nA, and a counting time of 20 ms/pixel with a resolution of 512
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12 269 \times 512 pixels.

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16 17 271 **Magnetite Petrography**

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20 272 Four main textures have been recognized in the studied magnetite samples, including
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22 273 oxy-exsolution, oscillatory zoning, coupled dissolution-reprecipitation, and
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25 274 recrystallization textures (Table 1). Exsolution lamellae (trellis type or needle-like) of
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28 275 ilmenite were observed in sample 080 from the Sossego IOCG deposit (Fig. 2A, B).
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31 276 Magnetite grains in sample 080 formed during three generations. The primary
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34 277 magnetite (Mag-1) in the core, with ilmenite exsolution, is commonly overgrown by
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37 278 low-Ti magnetite at the rim (Mag-2) (Fig. 2A). The third generation of magnetite
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40 279 (Mag-3), with darker gray in BSE images (lower mean Z number), partly replaced
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43 280 low-Ti magnetite (Mag-2) and locally contains amphibole and/or rutile inclusions (Fig.
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45 281 2A). But some magnetite grains in sample 080 lack of overgrowth Mag-2 and show
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48 282 core with ilmenite lamellae (Mag-1) replaced by Mag-3 along grain margin (Fig. 2B).
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51 283 Sample 084 contains two generations of magnetite. The first generation of magnetite
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54 284 in sample 084 is composed of dark gray (Mag-1D) and light gray (Mag-1L) zones that
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57 285 image oscillatory zoning (Fig. 2C, D). Ilmenite and hercynite occur as inclusions in
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60 286 the first generation of magnetite (Fig. 2C, D). The zoned magnetite was locally

1 287 replaced by the second generation of magnetite (Mag-2) to form irregular veins (Fig.
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3 288 2C). Sample F392 from the Igarapé Bahia IOCG deposit contains two generations of
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5
6 289 magnetite (Fig. 2E). The first generation of magnetite (Mag-1) is darker under BSE
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9 290 and rich in siderite and chalcopyrite inclusions, whereas the second generation of
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11 291 magnetite (Mag-2) is smooth and inclusion-poor (Fig. 2E). Magnetite from the
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13 292 Alemao IOCG deposit shows typical replacement/dissolution-reprecipitation textures.
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16 293 Magnetite grains in this sample comprise a dark gray, inclusion-rich domain, in the
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19 294 core (Mag-1) surrounded by a rim of light gray, inclusion-poor domain (Mag-2) (Fig.
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21 295 2F). The main inclusions in Mag-1 are quartz, chlorite, and chalcopyrite (Fig. 2F). But
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23 296 some dark magnetite domains lack porosity or inclusions. Both generations of
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26 297 magnetite are crosscut by calcite veins (Fig. 2F).
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31 298 Samples 367A and PC1492 from the Candelaria IOCG deposit display
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33 299 dissolution-reprecipitation textures (Fig. 3A, B). Sample 367A contains two
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36 300 generations of magnetite. The primary magnetite (Mag-1) is dark gray and contains
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39 301 amounts of quartz inclusions, whereas secondary magnetite (Mag-2) is light gray and
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42 302 inclusion-poor (Fig. 3A). Magnetite from sample 367A shows triple junction textures
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45 303 that are typical of recrystallization (e.g., Hu et al., 2015) (Fig. 3A). Magnetite grains
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48 304 from sample PC1492 are composed of dark gray, inclusion-rich domains (Fig. 3B)
49
50
51 305 replaced along grain edges by light gray, inclusion-poor domains (Fig. 3B). Magnetite
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53 306 grains in sample SAL2 from the Salobo IOCG deposit contain dark gray (Mag-1) and
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56 307 light gray (Mag-2) domains (Fig. 3C). Some quartz inclusions occur along the
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58
59 308 boundary between two generations of magnetite. Sample El Romeral from the El
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1 309 Romeral IOA deposit contains three generations of magnetite. The first magnetite
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3 310 (Mag-1), commonly in the core, contains rutile, quartz, and chlorite inclusions and is
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5
6 311 replaced by smooth, inclusion-poor magnetite domains (Mag-2) at the rim (Fig. 3D).
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8
9 312 Mag-2 is replaced by the third generation of magnetite (Mag-3) along grain
10
11 313 boundaries (Fig. 3D). Mag-3 is darker than Mag-1 and Mag-2 in BSE images. Sample
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13 314 11CC051 from the Salobo IOCG deposit and sample PC98102 from the Candelaria
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15
16 315 IOCG deposit show triple junction recrystallization textures in magnetite (e.g., Hu et
17
18 316 al., 2015) (Fig. 3E, F). These samples contain two generations of magnetite,
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21 317 inclusion-rich (Mag-1) and inclusion-poor (Mag-2) (Fig. 3E, F).
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28 319 **Chemical Composition of Magnetite**

30 320 *Major and trace element X-ray maps*

31 321 We use WDS X-ray elemental maps to characterize chemical zoning of different
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33 322 generations of magnetite (Figs. 4-7). Sample 080 from the Sossego IOCG deposit
34
35
36 323 contains three generations of magnetite that show Ti, Al, Si, Ca and Mn zoning (Fig.
37
38 324 4A, B). Mag-1 shows higher Ti, Al and Mn contents than Mag-2 and Mag-3, whereas
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40
41 325 Mag-3 has higher Si, Ca, and Mg contents than other two generations of magnetite.
42
43
44 326 No iron zoning is observed for three generations of magnetite at 512 × 512 pixels
45
46
47 327 resolution. Sample 084 from the Sossego IOCG deposit contains two generations of
48
49
50 328 magnetite and the first generation of magnetite can be divided into dark and light gray
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52
53 329 zones (Mag-1D and Mag-1L) due to different Al, Si, Ca, and Mg contents (Fig. 5A,
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56 330 B). Titanium contents in Mag-1D and Mag-1L are heterogeneously distributed but no
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1 331 Ti zoning is observed (Fig. 5A, B). The first generation of magnetite contains ilmenite
2
3 332 and hercynite inclusions as shown by Ti and Al element maps. The second generation
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5
6 333 of magnetite (Mag-2) crosscutting Mag-1D and Mag-1L has lower Ti, Al, Si, Ca, and
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8
9 334 Mg contents (Fig. 5A). Mag-1 in sample F392 from the Igarapé Bahia IOCG deposit
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11
12 335 shows lower Fe but higher Si and Mg contents than Mag-2 (Fig. 6A). Similarly,
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14
15 336 Mag-1 from samples Alemao, 367A, and PC1492 has lower Fe but higher Si and Mg
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17
18 337 contents than Mag-2 (Fig. 6B-D). Titanium, Al, and Ca contents are indistinguishable
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20
21 338 on the X-ray maps between two generations of magnetite in these samples. Mag-3 in
22
23 339 El Romeral sample has higher Al, Si and Ca contents than Mag-1 and Mag-2 (Fig.
24
25 340 7A). Moreover, Al, Si, and Ca contents in Mag-3 increase from grain margin to
26
27
28 341 interior. Iron, Ti and Mg contents are indistinguishable between three generations of
29
30
31 342 magnetite. Mag-1 in samples 11CC051 and PC98102 from Salobo and Candelaria
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33
34 343 IOCG deposits, respectively, have slightly higher Si, Mg, and Mn contents than
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36 344 Mag-2 (Fig. 7B, C).

345 346 *Major and trace element compositions*

347 Full EPMA results for magnetite are presented in Table A1. Figures 8 and 9 show
348 comparative box and whisker diagrams of minor and trace elements in various
349 magnetite generations, whereas Fig. 10 shows the variations of Fe contents in
350 different generations of magnetite. In general, minor and trace elements in magnetite
351 have contents varying from below detection limits to ~2 wt% (Figs. 8, 9). For a
352 specific element, the contents vary up to three orders of magnitudes. Mag-1 in sample

1 353 080 from the Sossego deposit has Mn, Ti, V, and Cr contents of 0.01-0.07 wt%,
2
3 354 0.09-1.89 wt%, 0.17-0.21 wt%, and 0.01-0.02 wt%, respectively, higher than those of
4
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6 355 Mag-2 and Mag-3 (Table A1; Fig. 8A). Mag-3 in sample 080 shows higher Si, K, Ca,
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9 356 Al, and Mg contents (0.11-0.70 wt%, <0.01-0.07 wt%, 0.03-0.36 wt%, <0.01-0.36
10
11
12 357 wt%, and <0.01-1.89 wt%, respectively) than Mag-1 and Mag-2 (Fig. 8A). Mag-1D in
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14
15 358 sample 084 from the Sossego deposit has Si, K, Ca, Mn, Mg, and Ti contents of
16
17 359 0.17-0.65 wt%, <0.01-0.05 wt%, 0.01-0.16 wt%, 0.02-0.08 wt%, 0.07-0.18 wt%, and
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19
20 360 0.50-1.88 wt%, respectively, higher than those of Mag-1L and Mag-2 (Fig. 8B). In
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22
23 361 general, Mag-1 in samples F392, Alemao, 367A, and PC1492 has higher Si, K, Ca, Al,
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25
26 362 Mn, and Mg contents than their respective Mag-2 (Fig. 8C-F). Due to limited data for
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28
29 363 magnetite in sample SAL2 from the Salobo deposit, the statistical result of trace
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31
32 364 element composition for two generations of magnetite is unclear (Fig. 9A). However,
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34
35 365 there is a trend where Mag-1 has higher Ca, P, and V contents than Mag-2 (Fig. 9A).
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37
38 366 Mag-3 in the El Romeral sample has higher Si, Ca, Al, Mg, and Ti contents
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41 367 (0.35-0.81 wt%, 0.11-0.29 wt%, 0.29-0.65 wt%, 0.03-0.08 wt%, and 0.05-0.19 wt%,
42
43
44 368 respectively) than Mag-1 and Mag-2 (Fig. 9B). Mag-1 and Mag-2 in samples
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46
47 369 11CC051 or PC98102 from the Salobo and Candelaria deposits, respectively, have
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49
50 370 similar Al, Mn, Mg, Ti, Zn, and Ni contents (Fig. 9C, D), but Mag-1 in sample
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53 371 PC98102 has higher Si, K, and Ca contents than Mag-2 (Fig. 9D).

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55
56 372 Magnetite grains from all samples have Fe contents ranging from 65.8 to 71.4 wt%
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59 373 (Fig. 10), lower than the stoichiometric value of 72.4 wt%. Different generations of
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61
62 374 magnetite also show distinct Fe contents. Mag-3 in sample 080 has higher iron
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1 375 contents (average 70.3 wt%) than Mag-1 and Mag-2 (average 69.5 wt%) (Fig. 10).
2
3 376 Mag-1L in sample 084 has higher Fe contents (average 69.0 wt%) than Mag-1D
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5
6 377 (average 68.4 wt%), but both of them have Fe contents lower than Mag-2 (average
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8
9 378 70.4 wt%) (Fig. 10). Mag-2 in samples F392, Alemao, 367A, PC1492, and PC98102
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11
12 379 has higher Fe contents than Mag-1 (Fig. 10). Iron contents decrease from Mag-2,
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14
15 380 Mag-1, to Mag-3 in the El Romeral sample. Mag-1 and Mag-2 in sample SAL2 from
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18 381 the Salobo deposit have similar Fe contents of 70.0-70.2 wt%, whereas two
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21 382 generations of magnetite in sample 11CC051 from the same deposit also have similar
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23 383 Fe contents of 70.3-71.1 wt% (Fig. 10).
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28 385 **Discussion**

30 386 *The formation of oscillatory zoning*

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34 387 Oscillatory zoning in magnetite from the studied IOCG and IOA deposits is
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37 388 uncommon and was only observed in sample 084 from the Sossego deposit. The
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40 389 oscillatory zoning is composed of dark gray, Si-rich (Mag-1D) and light gray, Si-poor
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43 390 zones (Mag-1L) under BSE imaging (Figs. 2C, D, 11A). Similar oscillatory zoning is
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46 391 also observed in magnetite from Fe skarn deposits (Shimazaki, 1998; Ciobanu and
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49 392 Cook, 2004; Dare et al., 2014; Huang et al., 2018), the lava flows of El Laco in Chile
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51
52 393 (Dare et al., 2015), the phreatomagmatic pipe in in the Tunguska Basin of East Siberia
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55 394 (Neumann et al., 2017), and the Los Colorados iron oxide-apatite deposit of Chile
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58 395 (Knipping et al., 2015b; Deditius et al., 2018). Ciobanu and Cook (2004) interpreted
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61 396 oscillatory zoning in magnetite from the Ocna de Fier-Dognecea Fe-Cu-Pb-Zn skarn
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1 397 deposit in Romania as an example of autocatalytic surface attachment in a Liesegang
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3 398 environment, perhaps similar to experiments with minerals in solid solution series
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6 399 where end members have different solubility (Putnis et al., 1992). Chemical waves, as
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9 400 well as other types of oscillation, may develop spontaneously, especially close to
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11 401 thermodynamic equilibrium (Ortoleva et al., 1987; Chu and Ross, 1990; Hjelmfelt and
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14 402 Ross, 1991; Neumann et al., 2017). But the oscillations in chemical composition are
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17 403 seemingly incompatible with slow, near-equilibrium growth. Such compositional
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20 404 shifts appear to violate the second law of thermodynamics because systems cannot
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23 405 spontaneously reverse their growth composition to lower-entropy states at stable
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26 406 growth conditions (Shore and Fowler, 1996). This situation has given rise to various
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29 407 physical models that rely upon cyclic changes in pressure, temperature, or bulk
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32 408 composition to vary the composition of the growing crystal. Therefore, a more
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35 409 common explanation for the oscillatory zoning in magnetite is that growth zoning
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38 410 formed as a result of changes in fluid compositions and/or physicochemical
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41 411 parameters, such as temperature and oxygen fugacity, during crystal growth, which
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44 412 periodically affects the partitioning behavior of trace elements into magnetite and
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47 413 co-forming minerals (Shimazaki, 1998; Dare et al., 2015; Knipping et al., 2015b;
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50 414 Sievwright et al., 2017; Huang et al., 2018).

51 415 Oscillatory mineral zonation is usually associated with crystal growth in an open
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53 416 system, either a hydrothermal system or a melt, after a period of magma mixing or
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56 417 degassing (Holten et al., 2000). Shore and Fowler (1996) proposed extrinsic (e.g.,
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59 418 change in solution composition, pressure, or temperature) and intrinsic (e.g.,

1 419 adsorption of growth inhibitors) mechanisms to explain the oscillatory zoning in
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3 420 natural magmatic and hydrothermal minerals. Similarly, Holten et al. (2000)
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6 421 explained zonation patterns as the result of coupling between the generally nonlinear
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9 422 crystal growth dynamics and the boundary conditions imposed by externally
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11 423 controlled fluctuations. Adsorption of growth inhibitors may play an important role,
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14 424 particularly at the microscopic scale in carbonate and sphalerite that formed under
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17 425 lower temperature conditions (Shore and Fowler, 1996). However, magnetite at the
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20 426 Sossego deposit formed at a relatively high temperature (~300-500°C; Monteiro et al.,
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22 427 2008b), preventing the adsorbed species from acting as inhibitors of the crystal
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25 428 growth. For different zones of oscillatory zoning in magnetite from the sample 084,
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27
28 429 dark gray domains (Mag-1D) have higher Si, K, Ca, Mn, Mg, and Ti contents but
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31 430 lower Fe contents than light gray domains (Mag-1L) (Figs. 5B, 8B, 10). The sharp
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34 431 compositional boundaries between the alternate trace element-rich and -poor zones
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37 432 within single magnetite grain imply preservation of the original oscillatory zoning
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39 433 (Figs. 2C, D, 11A), which requires the growth rate of the crystal to be higher than
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42 434 intracrystalline diffusion (Watson and Liang, 1995). X-ray map shows that Ti does
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44
45 435 not change synchronously with Al, Si, Ca and Mg (Fig. 5A, B), indicating that Ti
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48 436 chemical behavior is different from other elements during magnetite growth. The
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51 437 contrasting behavior of Ti was also observed in oscillatory zoning of magnetite from
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53 438 Los Colorados deposit (Deditius et al., 2018) and may be related to: (1) compatibility
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55
56 439 of Ti with magnetite structure; (2) the changes in the diffusivity of Ti^{4+} in the
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59 440 near-surface environment during magnetite growth comparing with the other elements;

1 441 and (3) mobility and/or different sources of Ti (Deditius et al., 2018). No obvious
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3 442 differences in Ti contents between Mag-1D and Mag-1L in X-ray map (Fig. 5A, B)
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6 443 indicate relatively stable temperature for their formation. But point analyses indicate
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9 444 Mag-1D has higher Ti contents than Mag-1L (Fig. 8). The higher Ti contents in
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12 445 Mag-1D may be due to the unavoidable contamination by ilmenite inclusions (Figs.
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14 446 2C, D, 5A, B) or Fe-Ti oxide nanoinclusions (Deditius et al., 2018). The similar V
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17 447 contents in Mag-1D and Mag-1L of oscillatory zoning (Fig. 8B) imply relatively
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20 448 stable oxygen fugacity. Therefore, oscillatory zoning in magnetite from sample 084
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23 449 was likely derived from the crystal growth during fluctuating hydrothermal fluid
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26 450 compositions rather than variation in temperature and oxygen fugacity (Fig. 10B).

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31 452 *Reequilibration textures in magnetite*

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34 453 *Oxy-exsolution* Oxy-exsolution of ilmenite is very common in magnetite from
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37 454 igneous rocks (Frost and Lindsley, 1991; Lindsley, 1991), metamorphic rocks (Harlov,
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39 455 1992; Harlov and Hansen, 2005), and magmatic Fe-Ti-(V) and Ni-Cu-sulfide deposits
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42 456 (Von Gruenewaldt et al., 1985; Dare et al., 2012; Liu et al., 2015; Tan et al., 2016b).
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44
45 457 In contrast, in magmatic-hydrothermal environment, oxy-exsolution is absent and
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48 458 low-Ti magnetite is expected to be dominant in the IOCG, IOA, porphyry, and skarn
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51 459 deposits (Meinert et al., 2005; Williams et al., 2005; Groves et al., 2010; Dupuis and
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53
54 460 Beaudoin, 2011; Chen et al., 2015; Nadoll et al., 2015; Huang et al., 2016, 2017,
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56 461 2018). Sample 080 from the Sossego deposit show oxy-exsolution lamellae of
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58
59 462 ilmenite in primary magnetite (Mag-1) (Fig. 2A, B), similar to exsolution textures of

1 463 igneous magnetite. Primary magnetite (Mag-1) in this samples has Ti contents up to
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3 464 1.89 wt% (Table A1). The oxy-exsolution textures are also observed in the Forsyth
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6 465 (Canada), Iron Crown (Canada), Marmoration (Canada), Chengchao (China), and
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9 466 Daye (China) skarn deposits (Hu et al., 2015). Magnetite from these deposits contains
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11
12 467 up to ~1 wt% Ti (Hu et al., 2015). Since oxy-exsolution processes involve a solid
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15 468 state diffusion mechanism that is more favorable at a higher temperature when fluids
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18 469 are absent (Frost and Lindsley, 1991; Putnis, 1992, 2009), the oxy-exsolution textures
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21 470 observed in these high-temperature magmatic-hydrothermal deposits indicate a
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23 471 primary magmatic formation of some magnetite grains, as observed by Knipping et al.
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25 472 (2015 a, b) at Los Colorados.

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27
28 473 In addition to temperature, oxygen fugacity (fO_2) also significantly affects the
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31 474 solubility of Ti in magnetite (Frost, 1991; Lindsley, 1991; Sievwright et al., 2017).
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34 475 For instance, at $fO_2 < FMQ + 3$ (FMQ, fayalite-magnetite-quartz), the partition
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37 476 coefficient of Ti between titanomagnetite–melt decreases with increasing fO_2
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40 477 (Siewwright et al., 2017). Therefore, the high-Ti magnetite in the Sossego deposit may
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43 478 have originally formed at high temperatures under relatively reducing conditions,
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46 479 subsequently being modified through the exsolution of Fe-Ti oxides in response to
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49 480 increasing fO_2 and decreasing temperature during the progressive alteration and
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52 481 mineralization (Fig. 11B). This is consistent with the evolving temperatures and fluid
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55 482 compositions in the Sossego–Curral orebodies of the Sossego deposit. Monteiro et al.
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57
58 483 (2008a) showed that the Sossego–Curral orebodies experienced early K-alteration
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61 484 (460 ± 25 °C), followed by infilling of veins and breccias (400 ± 50 °C), Cu

1 485 mineralization (275 ± 25 °C), and post-mineralization veins (250 ± 25 °C). During
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3 486 these processes, fluids evolved from high-temperature formational/metamorphic or
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6 487 magmatic origin to low-temperature hydrothermal origin (Monteiro et al., 2008a).
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9 488 Oxy-exsolution of ilmenite in high-Ti magnetite results in decreased Ti and increased
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12 489 V contents in product magnetite (Fig. 12A).

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17 491 *Interface coupled dissolution-reprecipitation* Dissolution-reprecipitation is a
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20 492 reaction, in the presence of a fluid, replacing an original phase with either an entirely
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23 493 new phase, or the same phase with a different composition, to reduce the free energy
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25
26 494 of a system (Putnis, 2002, 2009, 2015; Harlov et al., 2005, 2011; Ruiz-Agudo et al.,
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28
29 495 2014). When dissolution of the parent phase and precipitation of the product phase are
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31
32 496 coupled in both space and time, pseudomorphic (isovolumetric) replacement occurs in
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34
35 497 interface coupled dissolution reprecipitation (CDR) reaction (Putnis, 2009; Xia et al.,
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38 498 2009; Putnis and John, 2010; Ruiz-Agudo et al., 2014; Altree-Williams et al., 2015).
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40
41 499 CDR textures in magnetite have been observed in natural samples (Ciobanu and Cook,
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43
44 500 2004; Hu et al., 2015; Makvandi et al., 2015; Heidarian et al., 2016; Broughm et al.,
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46
47 501 2017; Wen et al., 2017; Yin et al., 2017; Huang et al., 2018) and different
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50 502 mechanisms have been proposed to explain these textures. Experimental studies also
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53 503 have demonstrated that magnetite can be dissolved by chloride-rich hydrothermal
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56 504 fluids (Chou and Eugster, 1977; Whitney et al., 1985; Ilton and Eugster, 1989) and a
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59 505 significant amount of iron can also be transported by low-density aqueous vapor in
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61
62 506 the magmatic-hydrothermal environment (Simon et al., 2004). There are some key

1 507 identifying features of CDR, as outlined by Putnis (2009), including: (1) a close
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3 508 spatial relationship between the parent and product phases; (2) a sharp reaction front
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6 509 between parent and product without a diffusional profile; (3) a permeable porosity
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9 510 generated within the product phase; (4) transfer of crystallographic structure from the
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12 511 parent to the product when an epitaxial relationship exists. Different generations of
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14 512 magnetite in samples F392, Alemao, 367A, PC1492, SAL2, and El Romeral, form
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17 513 distinct domains in one magnetite grain or occur as different grains that are spatially
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20 514 close (Figs. 2E-F, 3A-D). Moreover, sharp boundaries are observed between different
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23 515 generations of magnetite. For example, the second generation of magnetite (Mag-2) in
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25 516 sample 084 (Fig. 2C) shows lighter BSE contrast than Mag-1D and Mag-1L and
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28 517 crosscuts the zoned magnetite. Magnetite has features consistent with criteria (1) and
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31 518 (2) of CDR textures. But whether crystallographic structures between parent and
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34 519 product magnetite are same needs further transmission electron microscopy study.

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36 520 Porosity development in the product phase is a common feature of CDR, necessary
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39 521 for the propagation of dissolution within the mineral (Putnis, 2015). But product
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42 522 magnetite from samples F392, Alemao, PC1492, SAL2, and El Romeral lacks
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45 523 interconnected microscope-scale porosity (Figs. 2E-F, 3B-D). These features of
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48 524 magnetite from IOCG and IOA deposits are different from that of magnetite from
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51 525 altered granitic rocks and skarn deposits that experienced CDR processes (Hu et al.,
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53 526 2014, 2015; Wen et al., 2017; Yin et al., 2017). There are a number of factors that can
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56 527 explain lack of porosity in the product phase during CDR (Putnis and Austrheim,
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58
59 528 2013): (1) porosity is a non-equilibrium and transient microstructure and would be

1 529 expected to anneal with time due to evolving fluid composition (Putnis et al., 2005;
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3 530 Putnis, 2009; Pollok et al., 2011); (2) porosity may be restricted to the parent-product
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6 531 interface; (3) pore scale is smaller than the SEM resolution (~10 nm) (Niedermeier et
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9 532 al., 2009). Although we cannot determine which factor controls the absence of
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11 533 observable porosity in the product magnetite, the local geological conditions would
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14 534 affect the textural and compositional equilibrium between parent and product phases.
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17 535 The destruction of textural features associated with CDR processes, such as porosity
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20 536 and sharp replacement fronts, can disguise evidence of pervasive fluid infiltration
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23 537 events (Putnis and Austrheim, 2013). This textural evolution is driven both by internal
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26 538 minimization of excess energy by coarsening and by external processes in which
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29 539 continued interaction between an infiltrating fluid and the secondary mineral phases
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31 540 (Hellmann et al., 2012). Compositional and textural re-equilibration in the presence of
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34 541 a fluid phase is usually fast in terms of geological timescales, which further
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37 542 contributes to masking textural evidence for extensive fluid-mediated mineral
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39 543 alteration (Altree-Williams et al., 2015).

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42 544 It is worth noting that amounts of inclusions are found in the parent magnetite in
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45 545 samples 080, F392, Alemao, PC1492, and El Romeral (Figs. 2E-F, 3A-B). Ciobanu
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48 546 and Cook (2004) also reported a single magnetite crystal with a Si-rich, inclusion-rich
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51 547 core surrounded by a Si-rich, inclusion-free rim in skarn ores from Ocna de
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53 548 Fier-Dognecea (Romania). These textures were also observed in IOA magnetite from
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56 549 Missouri (Nold et al., 2014) and the Chilean Iron Belt (Knipping et al., 2015a, b;
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58
59 550 Rojas et al., 2018). They assigned the porous cores as igneous phenocrysts overgrown
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1 551 by pristine magmatic-hydrothermal magnetite. The ilmenite + rutile-rich core in
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3 552 sample 080 and rutile-rich core in El Romeral magnetite can be interpreted as igneous
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6 553 core because the regular distribution of ilmenite and rutile in magnetite implies an
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9 554 exsolution process at a low cooling rate probably related to a magmatic event (Rojas
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11
12 555 et al., 2018). However, the inclusions in magnetite core of samples F392, Alemao,
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14 556 and PC1492 are mainly quartz, chlorite, albite, biotite, titanite and chalcopyrite (Figs.
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17 557 2E-F, 3B), which are mainly hydrothermal in origin. EPMA analyses show that
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20 558 magnetite cores (Mag-1) have higher Si, Al, and Mg contents than massive domains
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23 559 at the rim (Mag-2) (Fig. 8C, D, F). The relatively homogenous distribution of Si, Al,
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26 560 and Mg in magnetite cores (Fig. 6A, B, D) indicates that these elements occur as
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29 561 lattice-substituted elements or nanoinclusions in magnetite (Deditius et al., 2018).
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31 562 Therefore, the silicate inclusion and trace element-rich cores in these magnetite grains
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34 563 have precipitated from Si-Al-Mg-rich hydrothermal fluids. It is suggested that the
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37 564 trace element-rich magnetite is more susceptible to fluid-assisted alteration because
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40 565 incorporation of small ionic radius cations such as Si^{4+} in magnetite would cause
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43 566 lattice defect or deformation (Hu et al., 2014). Development of smooth,
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46 567 inclusion-poor rims, in close proximity to inclusion-rich cores, thus strongly suggests
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49 568 that these formed from re-precipitation of the dissolved magnetite cores.

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53 570 *Two types of CDR processes* Most of the studied samples contain two generations of
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56 571 magnetite, whereas samples 080 and El Romeral contain three generations of
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59 572 magnetite. According to the textures, composition of different generations of

1 573 magnetite, and formation conditions, we consider that there are two different CDR
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3 574 processes responsible for the formation of the second and third generations of
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6 575 magnetite (Fig. 11). First, magnetite grains experienced different CDR processes have
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9 576 different textures. Type 1 CDR process is the replacement process that involves the
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11 577 dissolution of Si-rich, primary magnetite (Mag-1) in the core and precipitation of
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13 578 Si-poor, secondary magnetite (Mag-2) in the rim to form core-rim texture (Figs. 2E-F,
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15 579 3A-C). Type 1 CDR process is responsible for the formation of Mag-2 in samples 084,
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18 580 Alemao, F392, PC1492, SAL2, and 367A (Fig. 11A, C-F). Type 2 CDR process is the
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21 581 replacement process that the inclusion-poor, Si-rich magnetite (Mag-3) replaced
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23 582 inclusion-poor, Si-poor magnetite (Mag-2) along fracture or grain margins (Figs.
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25 583 2A-B, 3D). Type 2 CDR process transforming Mag-2 (sometimes Mag-1 when Mag-2
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28 584 is absent, Fig. 2B) to Mag-3 is local and is responsible for the formation of Mag-3 in
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31 585 samples 080 and El Romeral (Figs. 11B, F). Second, magnetite formed by different
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34 586 CDR processes has different chemical compositions. During type 1 CDR process,
35
36
37 587 most of minor and trace elements such as Si, Ca, K, Al, Mn, Mg, and to a less extent
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40 588 Ti are excluded from the primary magnetite (Mag-1), forming the secondary variety
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42
43 589 (Mag-2) with improved iron grade (Fig. 12B). Type 1 CDR process is thus considered
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45
46 590 to be an important mechanism for increasing the iron grade in hydrothermal magnetite
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49 591 from skarn deposits (Hu et al., 2014, 2015; Yin et al., 2017; Huang et al., 2018), IOA
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52 592 deposits (Heidarian et al., 2016), and altered granitic rocks (Wen et al., 2017). In
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54
55 593 contrast to the type 1 CDR process, Mag-3 formed via the type 2 CDR process has
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57
58 594 higher Si, K, Ca, Al, Mn, and Mg contents than Mag-1 and Mag-2 (Fig. 12C).

1 595 Moreover, Mag-3 has higher Ti contents than Mag-2 (Figs. 8A, 9B).

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3 596 In addition to different textures and compositions of magnetite, different factors
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6 597 control these two types of CDR processes. Different parameters can affect the CDR
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9 598 reactions, including the fluid composition, mineral solubility, temperature and
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12 599 pressure, Eh and pH, and oxygen and sulfur fugacities (Putnis, 2002; Putnis and
13
14 600 Putnis, 2007; Xia et al., 2009; Putnis and John, 2010; Pollok et al., 2011; Makvandi et
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16
17 601 al., 2015). Infiltration of mixed basinal brines and meteoric waters that already
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19
20 602 dissolved evaporites was proposed as an important mechanism to induce CDR
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22
23 603 reaction of magnetite (Hu et al., 2014, 2015; Heidarian et al., 2016; Huang et al.,
24
25 604 2018), because these externally derived fluids contributed to an increase in salinity
26
27
28 605 and Cl⁻ contents of the ore-forming fluids, enhancing Fe solubility and consequently
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31 606 leading to disequilibrium between the precipitated magnetite and the evolving fluids
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33
34 607 (Chou and Eugster, 1977; Whitney et al., 1985; Ilton and Eugster, 1989). During type
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36 608 1 CDR process, Ti contents in magnetite slightly decrease or keep stable whereas V
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39 609 contents are constant (Fig. 8C-F), indicating that changes in temperature and oxygen
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42 610 fugacity may be not the main factor. Alternatively, variations in fluid composition
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45 611 may play an important role. Considering that type 1 CDR process is commonly
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48 612 involved in massive magnetite associated with chalcopyrite (Fig. 1E-F) that represents
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51 613 main ore formation, we consider that type 1 CDR process is induced by the changing
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54 614 or evolving fluid composition during progressive alteration and mineralization. This
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56 615 conclusion is supported by the fluid composition and evolution of individual IOCG
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59 616 and IOA deposits. For the Sossego IOCG deposit, dilution and cooling of the hot

1 617 metalliferous fluid (>500°C) by mixing with meteoric fluids have been proposed as
2
3 618 the main mechanisms responsible for the deposition of metals transported as metal
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6 619 chloride complexes (Monteiro et al., 2008b). For the Igarapé Bahia and Alemao
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8
9 620 deposits, the mixing between high-temperature, high-salinity magmatic fluids and
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11
12 621 meteoric fluids was considered to be the main mechanism for the Cu-Au
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15 622 mineralization (Ronzê et al., 2000; Tallarico et al., 2005). For the Candelaria deposit,
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18 623 dominant magmatic fluids or non-magmatic fluids equilibrated with magmatic
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21 624 silicates for the main copper mineralization were also mixed with a non-magmatic
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23
24 625 fluid (e.g., basinal brines or meteoric waters) during the late hydrothermal stages
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26
27 626 (Marschik and Fontboté, 2001). For type 2 CDR process, Ti, Si, K, Ca, Al, Mg, and
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29
30 627 Mn contents obviously increase (Figs. 8A, 9B, 12C), in contrast with the
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32
33 628 compositional variations during type 1 CDR process. The type 2 CDR process cannot
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35
36 629 be induced by evolving ore-forming fluids with lower temperature because contents
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39 630 of compatible elements such as Ti, Mg, and Mn increase (magnetite-silicate melt
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41
42 631 partition coefficients are 7.0, 2.6, and 3.0, respectively; Dare et al., 2012).
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44
45 632 Alternatively, increased temperature and/or addition of trace element-rich fluids
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47
48 633 induced this process. Type 2 CDR process commonly occurs as vein replacement
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51 634 along magnetite fracture or grain margin, it thus can be interpreted as local post-ore
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54 635 replacement due to pulse of late magmatic-hydrothermal fluids.

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56 637 *Recrystallization* Solid-state recrystallization is a process wherein new mineral
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58
59 638 grains grow from pre-existing mineral grains by solid-state diffusion of ions in

1 639 response to change in temperature, pressure, or composition of the rock system (Urai
2
3 640 et al., 1986; Hoskin and Black, 2000). This process commonly involves changing of
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5
6 641 the crystal fabric or crystal size without an accompanying change in mineral
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8
9 642 chemistry (Hoskin and Black, 2000). Some magnetite grains from samples 11CC051
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11
12 643 and PC98102 show well-defined 120° triple junction (Fig. 3E, F), characteristic of
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14
15 644 mosaic texture. Mosaic textures are equilibrium textures that reflect the
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17
18 645 recrystallization of magnetite and annealing (Ciobanu and Cook, 2004; Nold et al.,
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20
21 646 2013). For example, mosaic textures in Chahgaz iron ore deposit (Bafq district, Iran)
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23
24 647 and Gol-Gohar deposit (southern Sanandaj-Sirjan belt, Iran) were interpreted to result
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26
27 648 from magmatic annealing (Foerster and Jafarzadeh, 1994; Mücke and Younessi,
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29
30 649 1994). However, similar magnetite fabrics in iron deposits within the Bafq district
31
32
33 650 were considered to be metasomatic replacement in origin (Daliran et al., 2010;
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35
36 651 Heidarian et al., 2016). High-temperature (~550°C) annealing and recrystallization of
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38
39 652 deformed and fractured magnetite was also used to explain the mosaic texture of
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41
42 653 magnetite in massive ores of skarn deposits (Ciobanu and Cook, 2004). However, Hu
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44
45 654 et al. (2015) considered that the mosaic texture in skarn magnetite was most likely the
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47
48 655 result of fluid-assisted recrystallization process. Magnetite in samples 11CC051 and
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51 656 PC98102 is composed of inclusion-rich core (Mag-1) and inclusion-poor rim (Mag-2)
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54 657 and lacks replacement textures that occur in other magnetite samples experienced
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57 658 CDR processes. Weakly compositional zoning in these samples is composed of Si-
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60 659 and Mg-rich core and rim depleted in these elements (Fig. 7B, C). The higher Si, Mg,
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63 660 and K contents in the magnetite core than rim (Fig. 9C, D) may result from

1 661 contamination of micrometer mineral inclusions in terms of heterogeneous
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3 662 distribution of these elements (Fig. 7B, C). But Si-Mg-K-rich cores also reflect fluids
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6 663 responsible for core formation are relatively rich in these elements because these
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9 664 elements can also occur as solid solution or nano-particles in magnetite (Xu et al.,
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11
12 665 2014; Deditius et al., 2018). No obvious differences in Ca, Al, Mn, Ti, Zn, V, Ni, Cr,
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15 666 and Fe contents are observed between Mag-1 and Mag-2 (Figs. 9C, D, 10), resulting
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17
18 667 in indistinguishable compositional fields in the plot of Fe versus total
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21 668 Si+K+Ca+Al+Mn+Mg contents (Fig. 12D). Therefore, we infer that the mosaic
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24 669 texture of magnetite from IOCG and IOA deposits results from simultaneous
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27 670 recrystallization and annealing of inclusion-rich magnetite (Fig. 11F).

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31 672 *Implication for the formation of IOCG and IOA deposits*

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34 673 IOCG deposits are considered to form in upper crustal environments from
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37 674 volatile-rich magmatic-hydrothermal fluids exsolved from high-temperature
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40 675 calc-alkaline melts variably contaminated by Fe-P-Si-rich crustal rocks and evolving
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43 676 to A-type granites (Hitzman et al., 1992; Pollard, 2000; Sillitoe, 2003; Corriveau et al.,
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45
46 677 2007; Groves et al., 2010; Tornos, 2011). But IOCG deposits lack clear spatial
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49 678 associations with igneous intrusions as, for instance, displayed by porphyry and skarn
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52 679 deposits (Williams et al., 2005). Non-magmatic fluids, particularly an evaporitic
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55 680 source, are also proposed as an important fluid source for IOCG deposits (Barton and
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58 681 Johnson, 1996, 2000). There are several examples supporting a mixed source of
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61 682 magmatic fluids, basinal brines, and/or meteoric water responsible for the formation

1 683 of IOCG deposits (Haynes et al., 1995; Kendrick et al., 2007; Baker et al., 2008;
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3 684 Kendrick et al., 2008; Zhao and Zhou, 2011; Chen, 2013; Huang et al., 2015b; Zhao
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5
6 685 et al., 2015). There are four main genetic models for the formation of IOA deposits: (1)
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8
9 686 crystallization from high-temperature, volatile-rich oxide melts, produced by magma
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11
12 687 immiscibility and segregated from a silicate liquid (Nyström and Henríquez, 1994;
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14 688 Frietsch and Perdahl, 1995; Henríquez and Nyström, 1998; Naslund et al., 2002;
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17 689 Henríquez et al., 2003; Tornos et al., 2016; Velasco et al., 2016); (2) replacement of
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20 690 the host rocks by iron-rich hydrothermal fluids (Hitzman et al., 1992; Rhodes et al.,
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22
23 691 1999; Hitzman, 2000; Sillitoe and Burrows, 2002; Edfelt et al., 2005; Valley et al.,
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25
26 692 2010; Dare et al., 2015; Broughm et al., 2017). The third model is evaporitic-source
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29 693 model that invokes thermal circulation of highly saline fluids originating from coeval
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32 694 or older sources (Barton and Johnson, 1996, 2004). Magmatism provides the
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35 695 necessary heat and igneous rocks also serve as the source and hosts for mineralization.
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37 696 Evaporitic sources provide the chloride for metal transport and the Na for
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39 697 hydrothermal alteration, and they drive fluids toward oxidized, relatively S-poor
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42 698 compositions. The fourth model for IOA deposits is a combination of the first two
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45 699 models that igneous magnetite crystallized from intermediate silicate melt overprinted
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47
48 700 by hydrothermal magnetite derived from magmatic-hydrothermal fluids (Knipping et
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50
51 701 al., 2015a, b; Simon et al., 2018).

52
53 702 Oxy-exsolution of ilmenite in magnetite from Cu-Au ores is rarely reported in
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55
56 703 IOCG and IOA deposits that are characterized by low-Ti magnetite and/or hematite
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59 704 (Williams et al., 2005). High-Ti magnetite with oxy-exsolution textures (Mag-1) in
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1 705 sample 080 from the Sossego IOCG deposit is magmatic in origin, whereas high-Ti
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3 706 magnetite with oscillatory zoning in sample 084 (Mag-1D and Mag-1L) is
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6 707 hydrothermal in origin, in spite of their similar Ti+V and Ca+Al+Mn contents (Fig.
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9 708 13A). The magmatic affinity of Mag-1 in sample 080 is confirmed by the granular
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11 709 ilmenite in equilibrium with ilmenite (Fig. 1B) and well-developed ilmenite
12
13 710 exsolution lamellae within magnetite (Fig. 2A, B), typical of Ti-rich magnetite or
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15 711 titanomagnetite in magmatic Fe-Ti oxide deposits and accessory Fe-Ti oxides in
16
17 712 igneous rocks (Buddington and Lindsley, 1964; Frost and Lindsley, 1991; Liu et al.,
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19
20 713 2015; Tan et al., 2016b). High-Ti magnetite with oscillatory zoning in sample 084
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22
23 714 cannot be explained as magmatic origin because it is commonly associated with
24
25
26 715 hydrothermal mineral actinolite and lack of regular exsolution lamellae of Fe-Ti
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29 716 oxides. Low-Ti magnetite from sample 080 (Mag-2) overgrowing on the Mag-1
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31
32 717 crystallized from a later moderate- to high-temperature magmatic-hydrothermal fluid
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35 718 (Fig. 13A). The decreasing Ti+V contents but constant V contents from Mag-1 in
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38 719 sample 080 and Mag-1D and Mag-1L in sample 084 to Mag-2 in samples 080 and
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41 720 084 (Figs. 9A-B, 13A) indicate decreased temperature (e.g., from >500°C to
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44 721 300-500°C) and relatively stable oxygen fugacity. This indicates that magnetite in
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46
47 722 some IOCG deposits has formed by both magmatic and magmatic-hydrothermal
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50 723 processes. This conclusion is supported by the features of two different orebodies in
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52
53 724 the Sossego deposit. The SPB orebodies in the deeper portion of the deposit are
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56 725 characterized by magnetite-(apatite) and albite-actinolite-rich zones, whereas the SC
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59 726 orebodies in shallower portion have predominant potassic and chlorite alteration
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1 727 typical of shallow crustal levels (Monteiro et al., 2008a). The temperatures for Na-Ca
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3 728 alteration and ore stage in SPB orebodies are >500°C and ~400°C, respectively,
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6 729 whereas those for K-Fe alteration and ore stage in SC orebodies are ~400°C and
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8
9 730 ~275°C, respectively (Moreto et al., 2015). The texture and chemical composition of
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11 731 magnetite in the SC orebodies thus record the evolution of fluids from higher
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13
14 732 temperature magmatic or to lower temperature magmatic-hydrothermal stages in the
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17 733 Sossego deposit.

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20 734 Magnetite from the El Romeral IOA deposit contains inclusion-rich cores (Mag-1)
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22 735 overgrown by inclusion-poor rims (Mag-2) which was further replaced by a trace
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25 736 element-rich magnetite (Mag-3). Mag-1 can be interpreted as igneous core observed
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27
28 737 in IOA magnetite from Missouri (Nold et al., 2014) and the Chilean Iron Belt
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31 738 (Knipping et al., 2015a, b; Rojas et al., 2018) because the regular distribution of Fe-Al
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34 739 oxides/Ti oxides and gangue minerals in the core (Figs. 3D, 7A) that indicates an
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37 740 exsolution process probably related to a magmatic event (Rojas et al., 2018). Both
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39
40 741 Mag-1 and Mag-2 have Ca+Al+Mn and Ti+V contents comparable with those from
41
42
43 742 Kiruna-type IOA deposits (Fig. 13B). The differences in composition between Mag-1
44
45
46 743 and Mag-2 may be due to changing composition in fluids (Fig. 13B) rather than
47
48
49 744 variations in temperature and oxygen fugacity in terms of similar Ti and V contents
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51
52 745 (Fig. 9B). Mag-3 has formed by replacement of Mag-2 via type 2 CDR process, the
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54
55 746 fluids responsible for Mag-3 are high-temperature magmatic-hydrothermal fluids
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57
58 747 similar in porphyry Cu deposits (Fig. 13B). Our magnetite generations and origins are
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60
61 748 consistent with the study of Rojas et al. (2018) where three generations of magnetite

1 749 were identified in El Romeral. Zoned magnetite grains with inclusion-rich cores and
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3 750 inclusion-poor rims (first and second generations) form the massive magnetite
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6 751 orebody, representing the main mineralization event. This main magnetite stage was
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9 752 followed by late hydrothermal events that are represented by magnetite veinlets (third
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11
12 753 generation) that crosscut the massive orebody. The first and second generations of
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14
15 754 magnetite were considered to be sourced from intermediate magmas, whereas the
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18 755 third generation of magnetite was formed by magmatic-hydrothermal fluids related to
19
20 756 post-ore dioritic dikes (Rojas et al., 2018).

21
22 757 A similar scenario is also proposed for the Los Colorados IOA deposit in the
23
24
25 758 Chilean iron belt where three generations of magnetite show chemical compositions
26
27
28 759 changing from purely magmatic to magmatic-hydrothermal (Knipping et al., 2015a, b;
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30
31 760 Simon et al., 2018). Based on trace element and Fe-O isotope compositions of
32
33
34 761 magnetite, Knipping et al. (2015a) proposed a model for IOA formation by flotation
35
36
37 762 of magmatic magnetite suspensions to explain the variation in chemical composition
38
39
40 763 of magnetite. Identification of igneous/magmatic magnetite in the Sossego IOCG
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43 764 deposit and El Romeral IOA deposit indicates that some IOCG deposits may have
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45
46 765 experienced similar process to IOA deposits where original Fe was derived from
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48
49 766 magmatic process, cf. either through magnetite flotation processes (Knipping et al.,
50
51
52 767 2015a, b) or crystallization from Fe-rich melt (25-32 wt% FeO; 38-42 wt% SiO₂)
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54
55 768 separated from Si-rich melt (60-70 wt% SiO₂) by liquid immiscibility (Roedder and
56
57
58 769 Weiblen, 1970; De, 1974; Dixon and Rutherford, 1979; Philpotts, 1982; Jakobsen et
59
60
61 770 al., 2005; Hou et al., 2018). There are other examples that support a magmatic source

1 771 for ore-forming fluids in IOCG and Kiruna-type IOA deposits from Missouri IOA
2
3 772 (USA), Kiruna IOA (Sweden), and Olympic Dam IOCG (Australia) districts (Simon
4
5
6 773 et al., 2018). For example, Hofstra et al. (2016) concluded that a
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8
9 774 magmatic-hydrothermal ore fluid evolved from a concealed mafic to
10
11 775 intermediate-composition magma was responsible for mineralization at the Pea Ridge
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13 776 IOA deposit in Missouri, based on mineral thermometry and fluid inclusion studies.
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15
16
17 777 Iron and oxygen stable isotope data of magnetite from the Pea Ridge and Pilot Knob
18
19
20 778 IOA deposits in Missouri further indicated that magnetite crystallized from a silicate
21
22
23 779 melt and grew in equilibrium with a magmatic-hydrothermal aqueous fluid (Childress
24
25
26 780 et al., 2016). Wawryk (2017) reported Fe isotope data for samples from the Olympic
27
28
29 781 Dam IOCG system that supports a magmatic source for Fe and, by inference, the
30
31 782 ore-forming fluid that transported Fe and other metals and S. Moreover, deep drill
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33
34 783 core (end at ~2,329 m) at Olympic Dam revealed the presence of abundant, early
35
36
37 784 magnetite and apatite at the deepest level of the mineralized system (Apukhtina et al.,
38
39 785 2017). The magnetite-fluorapatite mineralization, resembling those characteristic of
40
41
42 786 iron oxide-apatite deposits, extends more than 800 m (from 1,516 to 2,329 m) and
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44
45 787 likely continues beneath the bottom of the drill hole (Apukhtina et al., 2017).
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48 788 Therefore, we suggest that similar magmatic and magmatic-hydrothermal sources for
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51 789 ore-forming fluids link IOCG deposits with Kiruna-type IOA deposits.

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56 791 *Implication for deposit type discrimination diagrams*

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59 792 Different diagrams based on trace element composition of magnetite have been
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1 793 proposed to discriminate magnetite from different types of deposits. These
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3 794 discrimination diagrams are used here to illustrate the compositional modification of
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6 795 magnetite during reequilibration processes and their applicability for provenance
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9 796 studies.

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11 797 Dupuis and Beaudoin (2011) proposed the Ca+Al+Mn vs. Ti+V and Ni/(Cr+Mn)
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13
14 798 vs. Ti+V diagrams to discriminate IOCG and IOA deposits from Fe-Ti-V, porphyry,
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16
17 799 skarn deposits, and BIF. In these diagrams, iron oxides from IOCG deposits can be
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20 800 separated from those from IOA deposits due to lower total Ti and V contents. These
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23 801 diagrams were constructed based on a three-step discrimination process. The first step
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26 802 is to discriminate Ni-Cu-PGE deposits from other deposit types using Ni+Cr vs.
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29 803 Si+Mg diagram, whereas the second step is to discriminate VMS deposits from other
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32 804 deposit types using Al/(Zn+Ca) vs. Cu/(Si+Ca) diagram. The third step is to
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34
35 805 discriminate remaining deposit types such as IOCG, IOA, Fe-Ti-V, porphyry, skarn,
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37
38 806 and BIF. Moreover, these diagrams were based on the average magnetite composition
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40
41 807 of deposits and showed the compositional variety in a deposit. Because most
42
43
44 808 magnetite has Ni and Cr contents lower than their respective detection limits of 84
45
46
47 809 ppm and 47 ppm, the diagram of Ni/(Cr+Mn) vs. Ti+V was not evaluated. As shown
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49
50 810 in Fig. 13C, type 1 CDR process has resulted in lower Ca+Al+Mn contents in
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52
53 811 secondary magnetite than primary magnetite but Ti+V contents are relatively constant
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55
56 812 during this process. The primary magnetite (core) with skarn affinity in Igarapé Bahia
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59 813 and Candelaria IOCG deposits can be modified by type 1 CDR process to form
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61
62 814 secondary magnetite (rim) with IOCG affinity (Fig. 13C). Similarly, the primary

1 815 magnetite (core) with IOCG affinity in Alemao IOCG deposit can be modified to
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3 816 secondary magnetite (rim) with unknown origin (Fig. 13C). Type 2 CDR process is
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5
6 817 reverse to type 1 CDR process which results in increased Ca+Al+Mn contents (Fig.
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9 818 13A, B). Primary magnetite with unknown origin in the Sossego IOCG deposit can be
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11
12 819 changed to secondary magnetite with Kiruna, IOCG, and porphyry affinity by type 2
13
14 820 CDR process (Fig. 13A). Primary magnetite with Kiruna affinity in the El Romeral
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16
17 821 IOA deposit can be modified to secondary magnetite with porphyry affinity (Fig.
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19
20 822 13B). Hydrothermal-reequilibrated igneous magnetite in altered granitic plutons
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23 823 (Handan-Xingtai iron district, North China Craton) also shows a large compositional
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25 824 variation from magmatic Fe-Ti, V deposit to skarn, porphyry, and Kiruna deposits
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27
28 825 (Wen et al., 2017). Therefore, magnetite experienced CDR processes cannot be used
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30
31 826 to discriminate their origins in the Ca+Al+Mn vs. Ti+V diagram. The composition of
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34 827 magnetite is not obviously modified during recrystallization (Fig. 13D) and thus
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37 828 magnetite after recrystallization can be used provenance study.

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39 829 Loberg and Horndahl (1983) proposed V vs. Ti, V vs. Ni+Co, V vs. Ni, V/Ti vs.
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42 830 Ni/Ti, and V/Fe vs. Ti/Fe diagrams to discriminate IOA deposits from magmatic
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45 831 Fe-Ti deposits and BIF (Fig. 14). Although these diagrams are constructed by bulk
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48 832 composition of iron ores, they are considered to be reliable in discriminating
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50
51 833 magnetite from the studied deposit types (Heidarian et al., 2016; Broughm et al.,
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53
54 834 2017). Different generations of magnetite in the same sample have indistinguishable
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56
57 835 V and Ni contents (Fig. 14A), but have variable Ti contents and V/Ti, Ni/Ti, V/Fe,
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59
60 836 and Ti/Fe ratios (Fig. 14B-D). Magnetite from the IOCG and IOA deposits plots in

1 837 the field of magnetite-apatite and titaniferous iron ores in the V-Ni diagram (Fig.
2
3 838 14A), and the field of magnetite-apatite ores in the V/Ti-Ni/Ti and V-Ti diagrams (Fig.
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6 839 14B, C). Moreover, magnetite from the El Romeral IOA deposit plots in the field of
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9 840 Chadormalu IOA deposit (Central Iran) (Heidarian et al., 2016), but part of magnetite
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11 841 samples from the IOCG deposits overlap the field of Kiruna and Rektorn (Sweden),
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13 842 and El Laco (Chile) IOA deposits (Broughm et al., 2017) (Fig. 14A-C). Magnetite
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15 843 samples from El Romeral, Kiruna, Rektorn, and El Laco IOA deposits plot in the field
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17 844 of magnetite-apatite ores in the V/Fe vs. Ti/Fe diagram (Fig. 14D), whereas some
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19 845 magnetite samples from the IOCG deposits plot in the lower V/Fe values of BIF. This
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21 846 indicates that the above four discrimination diagrams are efficient in distinguishing
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23 847 IOA deposits from magmatic Fe-Ti deposits and BIF although magnetite has
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25 848 experienced reequilibration processes. But these diagrams fail to separate IOCG from
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27 849 IOA deposits and BIF.
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39 851 **Conclusions**

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42 852 Four types of textures have been identified in magnetite from IOCG and IOA deposits,
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44 853 including original oscillatory zoning and reequilibration textures such as extensive
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46 854 coupled dissolution and reprecipitation and less common oxy-exsolution and
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48 855 recrystallization. Single magnetite sample may have experienced one of these
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50 856 processes or all of them. The original oscillatory zoning was likely derived from the
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52 857 crystal growth during fluctuating fluid compositions rather than various temperature
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54 858 and oxygen fugacity. Two different types of CDR processes are identified according
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1 859 to textures and chemical compositions of different generations of magnetite. Type 1
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3 860 CDR process transforming Mag-1 to Mag-2 is extensive, whereas type 2 CDR process
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6 861 transforming Mag-2 to Mag-3 is local. During type 1 CDR process most minor and
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9 862 trace elements such as Si, K, Ca, Mg, Al, and Mn are expelled from magnetite while
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12 863 Fe contents increase, in contrast with type 2 CDR process. Type 1 CDR process is
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15 864 possibly induced by the changing fluid composition and/or decreasing temperature
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18 865 during progressive alteration and ore formation, whereas type 2 CDR process can be
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21 866 interpreted as post-ore replacement due to a new pulse of magmatic-hydrothermal
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24 867 fluids. Some magnetite grains in IOCG and IOA deposits may have formed by a
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27 868 similar process, i.e., transition from purely magmatic to magmatic-hydrothermal
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30 869 process. Magnetite in IOCG and IOA deposits is susceptible to textural and
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33 870 compositional reequilibration during high-temperature magmatic and
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36 871 magmatic-hydrothermal processes. The reequilibrated magnetite has textures and
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39 872 chemical compositions different from its precursor, complicating existing
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42 873 discrimination plots for genetic interpretation. This study highlights that
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45 874 understanding the ore genesis of IOCG and IOA deposits should combine magnetite
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48 875 chemistry with its textures.

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51 1383 871-884.
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58 1386 **Figure captions**

1 1387 Fig. 1. Photomicrographs of ores from selected IOCG and IOA deposits showing
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3 1388 mineral association and magnetite textures. All images are acquired by back-scattered
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6 1389 electron (BSE) imaging except those in (E) and (H) by reflected light. (A) Sample 080
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9 1390 from the Sossego IOCG deposit composed of euhedral to subhedral magnetite and
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11 1391 apatite and minor chalcopyrite cut by a quartz and calcite assemblage. (B) Sample 080
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13 1392 from the Sossego IOCG deposit consisting of magnetite, apatite, chlorite, and talc.
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15 1393 Magnetite has exsolution lamellae of ilmenite and contains calcite, chalcopyrite, and
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17 1394 chlorite microinclusions. Granular ilmenite is also associated with magnetite. The
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19 1395 inset at upper right is enlargement of the area marked by yellow rectangle. (C) Sample
20
21 1396 084 from the Sossego IOCG deposit composed of magnetite and apatite cut by quartz
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23 1397 and chalcopyrite veins. (D) Sample F392 from the Igarapé Bahia IOCG deposit has a
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25 1398 mineral association of magnetite, chlorite, siderite, and chalcopyrite. (E) Sample
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27 1399 Alemao from the Alemao IOCG deposit composed of magnetite and apatite cut by
28
29 1400 calcite and quartz. Magnetite shows core-rim texture with inclusion-rich core and
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31 1401 inclusion-free rim. (F) Ore from the Alemao IOCG deposit consisting of subhedral
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33 1402 magnetite and accessory apatite replaced by quartz, chlorite, and minor chalcopyrite.
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35 1403 (G) Sample SAL2 from the Salobo IOCG deposit composed of magnetite and
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37 1404 chalcopyrite, and minor quartz and grunerite. (H) Sample 11CC051 from the Salobo
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39 1405 IOCG deposit comprising subhedral magnetite replaced by chlorite, chalcopyrite and
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41 1406 quartz. Magnetite shows foam-like texture. (I) Sample 367A from the Candelaria
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43 1407 IOCG deposit composed of magnetite, K-feldspar, actinolite, and minor albite and
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45 1408 biotite. (J) Sample PC98102 from the Candelaria IOCG deposit consisting of
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1 1409 magnetite and chalcopyrite, and minor chlorite, biotite, and monazite. (K) Sample
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3 1410 PC1492 from the Candelaria IOCG deposit composed of magnetite, chalcopyrite,
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6 1411 K-feldspar, and actinolite. Magnetite is commonly cut by chlorite veins. (L) Sample
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8
9 1412 El Romeral from the El Romeral IOA deposit consisting of magnetite and actinolite,
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11 1413 and minor biotite and chlorite. Abbreviations: Act = actinolite, Ab = Albite, Ap =
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13 1414 apatite, Bt = biotite, Cal = calcite, Ccp = chalcopyrite, Chl = chlorite, Gru = grunerite,
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15 1415 Kfs = K-feldspar, Mag = magnetite, Mnz = monazite, Qz = quartz, Sd = siderite, Tlc =
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17 1416 talc.
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25 1418 Fig. 2. BSE images showing textures of magnetite from the Sossego, Igarapé Bahia
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27 1419 and Alemao IOCG deposits. (A) Three generations of magnetite identified in sample
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29 1420 080 from the Sossego IOCG deposit. The first generation of magnetite (Mag-1) with
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31 1421 exsolution lamellae of ilmenite was overgrown by smooth, light gray magnetite
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33 1422 (Mag-2). Mag-2 was further replaced by dark gray magnetite (Mag-3) along the
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35 1423 fracture. Amphibole inclusions are mainly distributed along the boundary between
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37 1424 Mag-1 and Mag-2, whereas rutile inclusions are mainly within Mag-1. (B) Two
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39 1425 generations of magnetite in sample 080 from the Sossego IOCG deposit displaying
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41 1426 different textures. The first magnetite with exsolution lamellae of ilmenite in the core
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43 1427 (Mag-1) was replaced by dark gray, inclusion-rich magnetite (Mag-3). Inclusions in
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45 1428 Mag-3 are mainly quartz and rutile. (C) Two generations of magnetite in sample 084
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47 1429 from the Sossego IOCG deposit. The first generation of magnetite contains ilmenite
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49 1430 and hercynite inclusions, and shows oscillatory zoning composed of dark gray
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1 1431 (Mag-1D) and light gray (Mag-1L) zones. The second generation of magnetite
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3 1432 (Mag-2) crosscut both Mag-1D and Mag-1L and contains silicate inclusions. (D)
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6 1433 Magnetite grain in sample 084 from the Sossego IOCG deposit characterized by
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8
9 1434 oscillatory zoning composed of dark gray (Mag-1D) and light gray (Mag-1L) zones.
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11 1435 Ilmenite, hercynite, and actinolite are mainly inclusions in magnetite. (E) Magnetite in
12
13 1436 sample F392 from the Igarapé Bahia IOCG deposit composed of inclusion-rich
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15 1437 (Mag-1) and inclusion-poor (Mag-2) domains. The inclusions in Mag-1 are mainly
16
17 1438 siderite and chalcopyrite. (F) Magnetite in Alemao IOCG deposit consisting of
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19 1439 inclusion-rich core (Mag-1) and inclusion-poor rim (Mag-2). Both Mag-1 and Mag-2
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21 1440 are crosscut by later calcite veins. The inclusions in Mag-1 are mainly quartz, chlorite,
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23 1441 and chalcopyrite. Abbreviations: Act = actinolite, Amp = amphibole, Cal = calcite,
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25 1442 Ccp = chalcopyrite, Chl = chlorite, Hc = hercynite, Ilm = ilmenite, Mag = magnetite,
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27 1443 Qz = quartz, Rt = rutile, Sd = siderite.
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39 1444
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41 1445 Fig. 3. BSE images showing textures of magnetite from the Candelaria and Salobo
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43 1446 IOCG and El Romeral IOA deposits. (A) Sample 367A from the Candelaria IOCG
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45 1447 deposit showing two generations of magnetite. The first generation of magnetite
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47 1448 (Mag-1) is dark gray and inclusion-rich, which was replaced by smooth,
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49 1449 inclusion-poor magnetite (Mag-2). Some grains also show triple junction textures
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51 1450 (yellow lines). Titanite and quartz are main inclusions in Mag-1. (B) Sample PC1492
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53 1451 from the Candelaria IOCG deposit comprising dark gray, inclusion-rich (Mag-1) and
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55 1452 light gray, inclusion-poor magnetite (Mag-2). Inclusions in Mag-1 are mainly biotite
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1 1453 and albite. (C) Magnetite in sample SAL2 from the Salobo IOCG deposit composed
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3 1454 of dark gray (Mag-1) and light gray (Mag-2) domains. (D) Three generations of
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6 1455 magnetite in El Romeral IOA deposit showing different textures. The primary
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9 1456 magnetite (Mag-1) is inclusion-rich and replaced by secondary magnetite (Mag-2).
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11 1457 Mag-2 is further replaced by dark gray magnetite (Mag-3) along the grain boundary
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14 1458 or fractures. (E-F) Magnetite in sample 11CC051 from the Salobo IOCG deposit and
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17 1459 sample PC98102 from the Candelaria IOCG deposit composed of inclusion-rich
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20 1460 (Mag-1) and inclusion-poor (Mag-2) domains. Chlorite and quartz are the main
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23 1461 inclusions in Mag-1. Yellow lines indicate triple junction textures. Abbreviations: Act
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25 1462 = actinolite, Ab = albite, Bt = biotite, Ccp = chalcopyrite, Chl = chlorite, Mag =
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28 1463 magnetite, Qz = quartz, Rt = rutile.

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34 1465 Fig. 4. BSE images and chemical X-ray maps of sample 080 from the Sossego IOCG
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36 1466 deposit. Magnetite generations in A and B correspond to A and B in Fig. 2,
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39 1467 respectively. The scales of X-ray maps are the same as that of corresponded BSE
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42 1468 images. (A) Three generations of magnetite showing different Ti, Al, Si, Ca, Mg, and
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45 1469 Mn contents. Mag-1 has the highest Ti contents due to the exsolution of ilmenite,
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47
48 1470 whereas Mag-2 and Mag-3 have the lower but relatively homogeneous Ti contents.
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51 1471 Silicon, Ca, and Mg contents increase from Mag-2, Mag-1, to Mag-3. Mag-1 and
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53 1472 Mag-3 have similar Al and Mn contents that are higher than Mag-2. Iron contents
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56 1473 between different generations of magnetite are indistinguishable in terms of available
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59 1474 resolution. (B) Two generations of magnetite showing different Ti, Al, Si, Ca, and Mn

1 1475 contents. Mag-1 contains exsolution lamellae of ilmenite indicated by anomalously
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3 1476 high Ti contents. Mag-3 has higher Si and Ca but lower Al, Ti and Mn contents than
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6 1477 Mag-1. Iron and Mg contents in two generations of magnetite are indistinguishable.
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11 1479 Fig. 5. BSE images and chemical X-ray maps of sample 084 from the Sossego IOCG
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14 1480 deposit. Magnetite generations in A and B correspond to C and D in Fig. 2,
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17 1481 respectively. (A) The first generation of magnetite composed of Mag-1D and Mag-1L
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20 1482 and containing ilmenite and hercynite inclusions indicated by characteristic
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23 1483 distribution of Ti and Al contents. The first generation of magnetite shows Al, Si, Ca,
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26 1484 and Mg chemical zoning. Both Mag-1D and Mag-1L were replaced by Mag-2. Mag-1
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28 1485 has higher Ti, Al, Si, Ca, and Mg contents than Mag-2. (B) Magnetite with oscillatory
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31 1486 zoning composed of dark gray (Mag-1D) and light gray (Mag-1L) domains. The
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34 1487 oscillatory zoning shows consistent changes in Al, Si, Ca, and Mg contents. No
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37 1488 systematic variations in Fe and Ti contents between Mag-1D and Mag-1L are
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39 1489 observed, but the whole magnetite grain shows heterogeneous Ti contents.
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45 1491 Fig. 6. BSE images and X-ray maps of selected elements in magnetite. Magnetite
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48 1492 generations in (A) and (B) correspond to (E) and (F) in Fig. 2, respectively, whereas
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51 1493 magnetite generations in (C) and (D) correspond to (A) and (B) in Fig. 3, respectively.
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53 1494 (A) Dark gray, inclusion-rich magnetite (Mag-1) in sample F392 from the Igarapé
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56 1495 Bahia IOCG deposit containing more Si and Mg and less Fe than light, inclusion-poor
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59 1496 magnetite (Mag-2). No obvious variation in Ti contents is observed between two
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1 1497 generations of magnetite. (B) Dark gray, inclusion-rich cores (Mag-1) in magnetite
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3 1498 from the Alemao IOCG deposit having higher Si and Mg, but lower Fe contents than
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6 1499 light gray, inclusion-poor rims (Mag-2). Titanium, Al, and Ca contents are
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9 1500 indistinguishable between two generations of magnetite under available resolution.
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11 1501 (C-D) Dark gray, inclusion-rich magnetite domains (Mag-1) in samples 367A and
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13 1502 PC1492 from the Candelaria IOCG deposit having higher Si and Mg contents but
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16 1503 lower Fe contents than light gray, smooth magnetite domains (Mag-2). Titanium
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19 1504 contents are similar in both generations of magnetite.
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25 1506 Fig. 7. BSE images and chemical X-ray maps of samples, El Romeral (A), 11CC051
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27 1507 (B), and PC98102 (C), from the El Romeral IOA, Salobo and Candelaria IOCG
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29
30 1508 deposits, respectively. Magnetite generations in (A), (B), and (C) correspond to (D),
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33 1509 (E), and (F) in Fig. 3, respectively. (A) Three generations of magnetite showing
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36 1510 different chemical compositions. Mag-1 and Mag-3 have lower Fe but higher Mg
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39 1511 contents than Mag-2. Silicon, Ca and Al contents increase from Mag-2, Mag-1, to
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42 1512 Mag-3. Moreover, Si, Ca and Al contents are not homogeneous in Mag-3. No obvious
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45 1513 differences in Ti contents between different generations of magnetite. The inclusions
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48 1514 in Mag-1 are mainly silicate minerals characterized by higher Si, Mg, Al and/or Ca
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51 1515 contents. (B-C) Inclusion-rich magnetite domains (Mag-1) showing higher Si, Mg and
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53 1516 Mn contents than inclusion-poor magnetite domains (Mag-2).

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58 1518 Fig. 8. Multi-element box and whisker plots for EPMA minor and trace element data
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1 1519 showing the compositional differences between different magnetite generations.
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3 1520 Boxes outline the 25th to 75th percentiles and whiskers extend to the minimum and
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6 1521 maximum values. Short line within the box represents the median value, whereas
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9 1522 circle filled by white on the whisker represents the average value. Trace element
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12 1523 contents below the limit of detection were excluded in the box and whisker plots.

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17 1525 Fig. 9. Multi-element box and whisker plots for EPMA minor and trace element data
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20 1526 showing the compositional differences between different magnetite generations. The
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23 1527 meaning of box is the same as in [Fig. 8](#).

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28 1529 Fig. 10. Box and whisker plot for Fe contents in different generations of magnetite.
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31 1530 The meaning of box is the same as in [Fig. 8](#).

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36 1532 Fig. 11. Schematic illustrations showing different chemical or physical processes
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38
39 1533 responsible for the formation of multiple generations of magnetite in IOCG and IOA
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42 1534 deposits. These processes include oxy-exsolution (OE), coupled dissolution
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45 1535 reprecipitation (CDR), and recrystallization (RC). Fragmentation (FR) and
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48 1536 overgrowth (OG) is also involved in some magnetite. (A) High-Ti magnetite (Mag-1)
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51 1537 from the Sossego IOCG deposit (sample 084) shows oscillatory zoning with dark gray,
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53 1538 Si-rich (Mag-1D) and light gray, Si-poor zones (Mag-1L). High-Ti magnetite was
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56 1539 further replaced by secondary magnetite (Mag-2) via type 1 CDR process. Ilmenite
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59 1540 and hercynite formed as inclusions in Mag-1 because of Ti-Al-rich fluids. Both first

1 1541 and second magnetite has experienced fragmentation. (B) High-Ti magnetite (Mag-1)
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3 1542 from the Sossego IOCG deposit (sample 080) experienced widespread oxy-exsolution
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6 1543 of ilmenite. Mag-2 may have formed by overgrowth, whereas Mag-3 formed by type
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9 1544 2 CDR process. (C) Low-Ti magnetite in the Alemao IOCG deposit with abundant
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11 1545 inclusions of siderite, quartz, chlorite, or chalcopyrite experienced type 1 CDR
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13 1546 process to form inclusion-rich core (Mag-1) and inclusion-poor rim (Mag-2). Some of
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15 1547 the cores evolved to inclusion-absent with the progressive type 1 CDR process.
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18 1548 Fragmentation is also common due to volume change during mineral growth. (D)
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20 1549 Low-Ti magnetite with silicate inclusions in samples F392 and PC1492 from the
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23 1550 Igarapé Bahia and Candelaria IOCG deposits, respectively experienced one or
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25
26 1551 multiple type 1 CDR processes, forming the secondary magnetite as stockworks. (E)
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29 1552 Si-rich magnetite from the Salobo IOCG deposit (SAL2) suffered from type 1 CDR
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32 1553 process, resulting in the formation of Si-poor magnetite. Quartz formed along the
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35 1554 boundary between Mag-1 and Mag-2. (F) Low-Ti magnetite from the Candelaria
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38 1555 IOCG (samples 367A and PC98102), Salobo IOCG (sample 11CC051), and El
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41 1556 Romeral IOA (sample El Romeral) deposits experienced types 1 and 2 CDR processes
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43
44 1557 and recrystallization, forming two or three generations of magnetite. See text for
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46
47 1558 detail. Abbreviations: Act = actinolite, Amp = amphibole, Ccp = chalcopyrite, Chl =
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50 1559 chlorite, Hc = hercynite, Ilm = ilmenite, Mag = magnetite, Qz = quartz, Rt = rutile, Sd
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53 1560 = siderite, Ttn = titanite.

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58 1562 Fig. 12. Binary plots showing compositional variations during different reequilibrium
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1 1563 processes. (A) Plot of V versus Ti showing decreased Ti and increased V contents in
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3 1564 magnetite during oxy-exsolution. Chemical composition of magnetite before
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6 1565 exsolution is the average LA-ICP-MS data of Huang et al. (2019). (B) Plot of Fe
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9 1566 versus Si+K+Ca+Al+Mn+Mg showing decreased contents of minor and trace
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12 1567 elements and increased Fe contents during type 1 CDR process. (C) Plot of Fe versus
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14 1568 Si+K+Ca+Al+Mn+Mg showing increased contents of minor and trace elements
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17 1569 during type 2 CDR process. (D) Plot of Fe versus Si+K+Ca+Al+Mn+Mg showing
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20 1570 indistinguishable variations in trace element and Fe contents during recrystallization.
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25 1572 Fig. 13. Plot of EPMA data of IOCG and IOA deposits in the Ti+V vs. Ca+Al+Mn
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28 1573 diagram. (A) Compositional variations between different generations of magnetite
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31 1574 from the Sossego IOCG deposit. The decreased Ti+V and Ca+Al+Mn contents of
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34 1575 Mag-1 in samples 080 and 084 (Mag-1D and Mag-1L) to Mag-2 are due to decreasing
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36 1576 temperature and changing melt/fluid composition. During type 2 CDR process,
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39 1577 Ca+Al+Mn contents in magnetite increase but Ti+V contents are relatively stable. (B)
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41
42 1578 Compositional variations between different generations of magnetite from the El
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45 1579 Romeral IOA deposit, induced by various fluid compositions or type 2 CDR process.
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47
48 1580 (C) Compositional variations in magnetite during type 1 CDR process. During this
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51 1581 process, Ca+Al+Mn contents decrease to various degrees but Ti+V contents keep
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53 1582 constant. (D) No obvious compositional differences between primary magnetite
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56 1583 (Mag-1) and recrystallized magnetite (Mag-2). EPMA data of sample Chadormalu in
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59 1584 (D) are individual analyses from Chadormalu IOA deposit (Heidarian et al., 2016),
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1 1585 whereas data of CIB are average values from Chilean iron belt (Nyström and
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3 1586 Henríquez, 1994). The fields for different deposit types are based on Dupuis and
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6 1587 Beaudoin (2011). If the content of one of the elements Ti, V, Ca, Al, and Mn is lower
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9 1588 than the detection limit, data are plotted as hollow symbol. The temperatures near the
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12 1589 top abscissa are from Nadoll et al. (2014) where temperatures of magnetite
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15 1590 crystallization in a variety of ore deposits were compiled. Deposit type abbreviations:
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17 1591 Skarn = Fe-Cu skarn deposits, IOCG = iron oxide–copper–gold deposits, Porphyry =
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20 1592 porphyry Cu deposits; Kiruna = Kiruna-type magnetite-apatite deposits.
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23 1593

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25 1594 Fig. 14. Plot of EPMA data of IOCG and IOA deposits in the magnetite discrimination
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28 1595 diagrams used to distinguish magnetite from magnetite-apatite ores, titaniferous iron
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30
31 1596 ores, and BIF (Loberg and Horndahl, 1983). (A) Plot of V vs. Ni. (B) Plot of V/Ti vs.
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33
34 1597 Ni/Ti. (C) Plot of V vs. Ti. (D) V/Fe (ppm/wt%) vs. Ti/Fe (ppm/wt%). Data below
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37 1598 detection limits are removed from these plots. Pink circle with dotted line represents
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40 1599 the field of Chadormalu IOA deposit (Bafq district of Central Iran) (Heidarian et al.,
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42 1600 2016), whereas orange circle with dotted line represents the field of Kiruna and
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45 1601 Rektorn (Norrbotten region of Sweden), and El Laco (Chile) IOA deposits (Broughm
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48 1602 et al., 2017). Gray area represents the composition range of magnetite from El
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51 1603 Romeral IOA deposit.
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54 55 1605 **Tables**

56
57
58 1606 Table 1. Summary of Information on Samples from the Studied IOCG and IOA
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1	1607	Deposits
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6	1609	Table A1. Chemical Composition of Magnetite (in wt%) from the IOCG and IOA
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9	1610	Deposits
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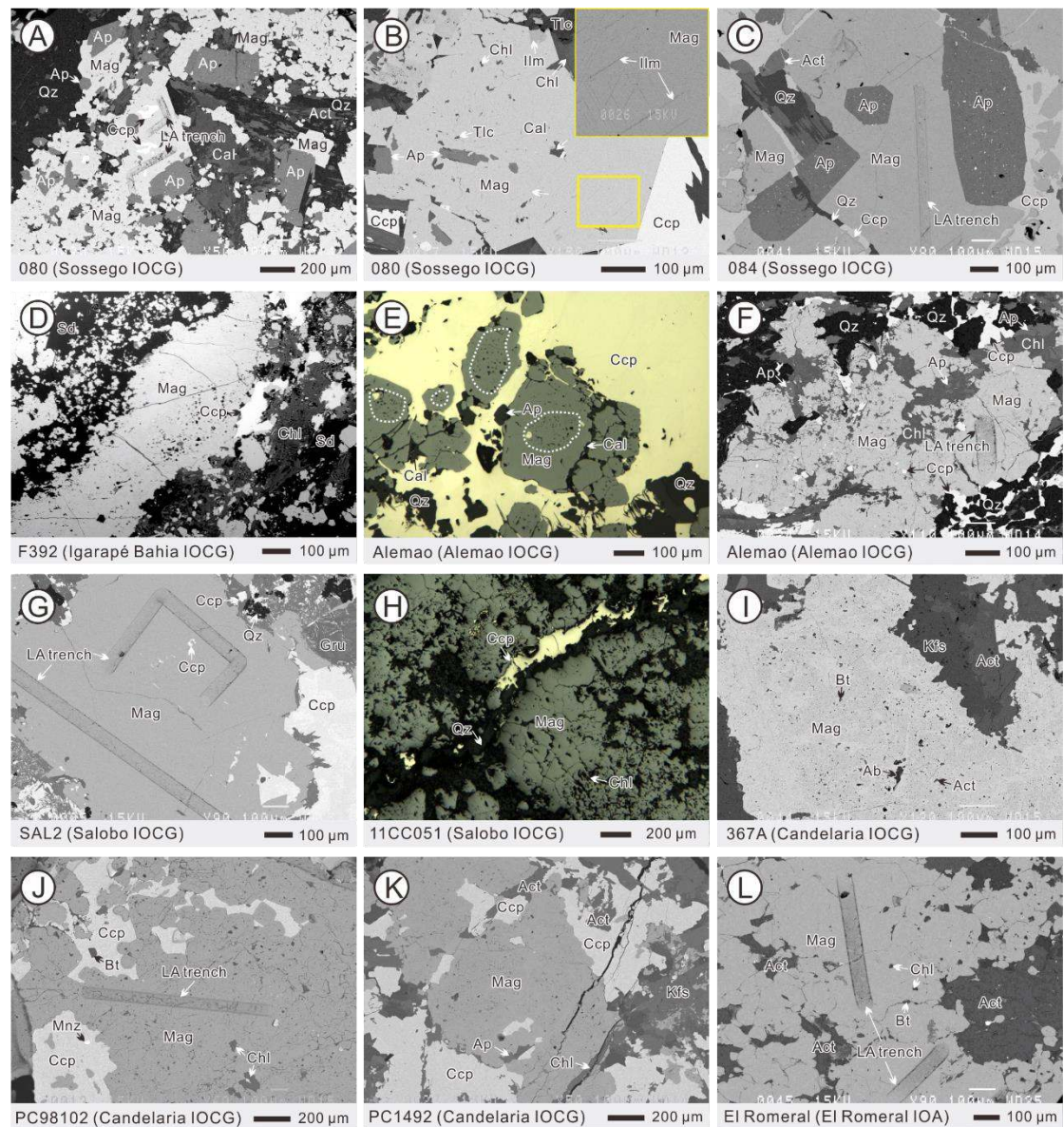


Fig. 1

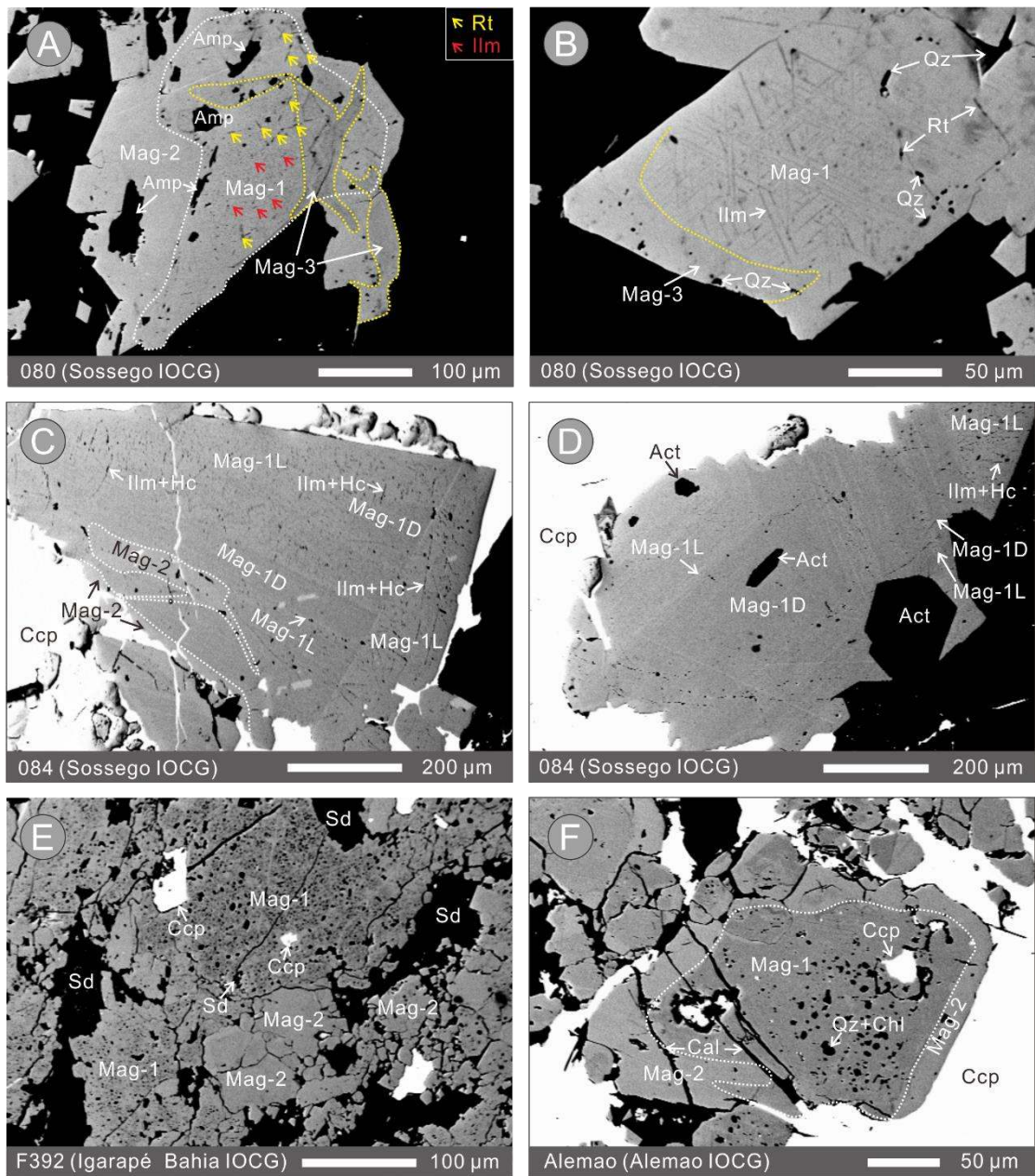


Fig. 2

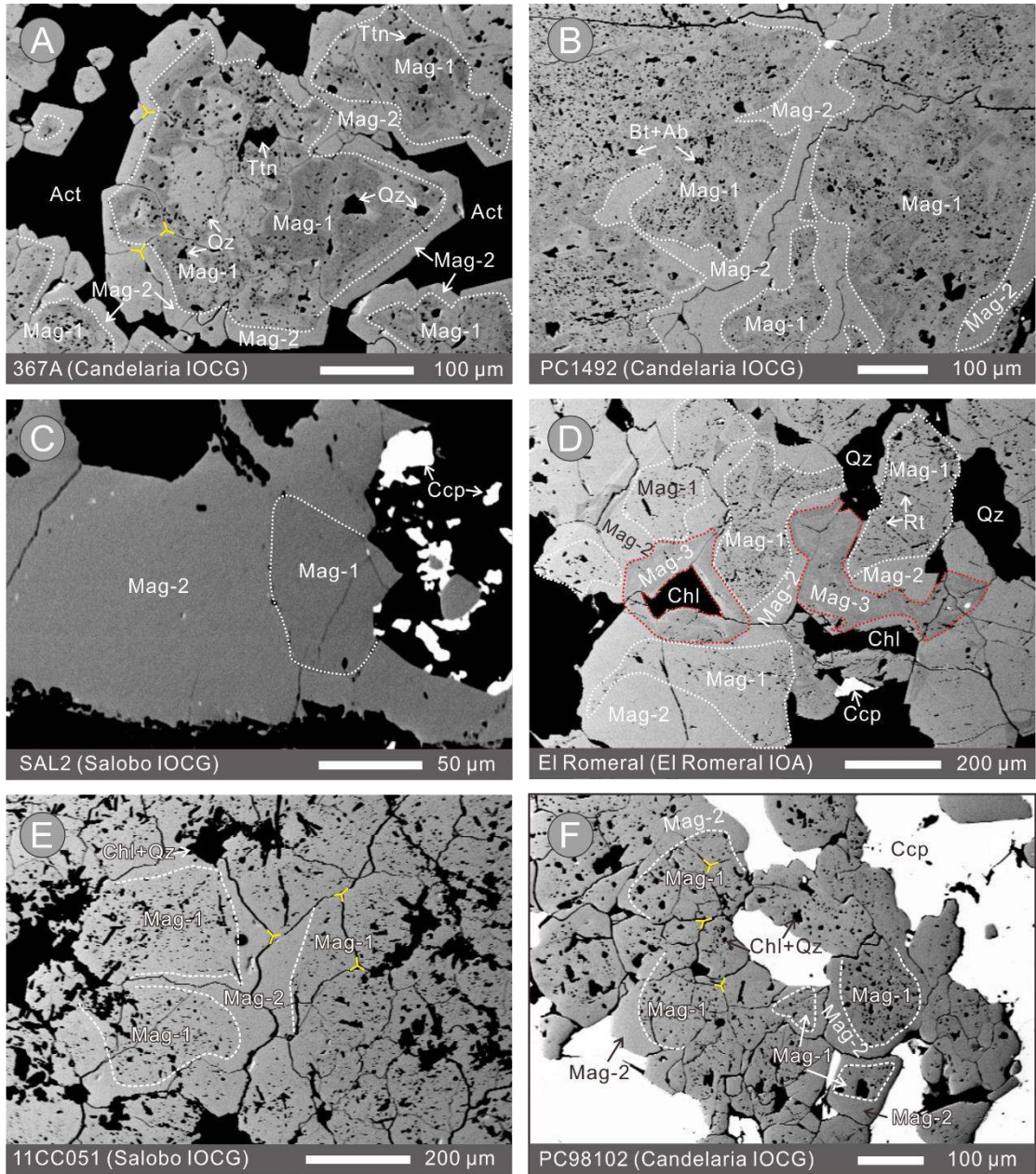


Fig. 3

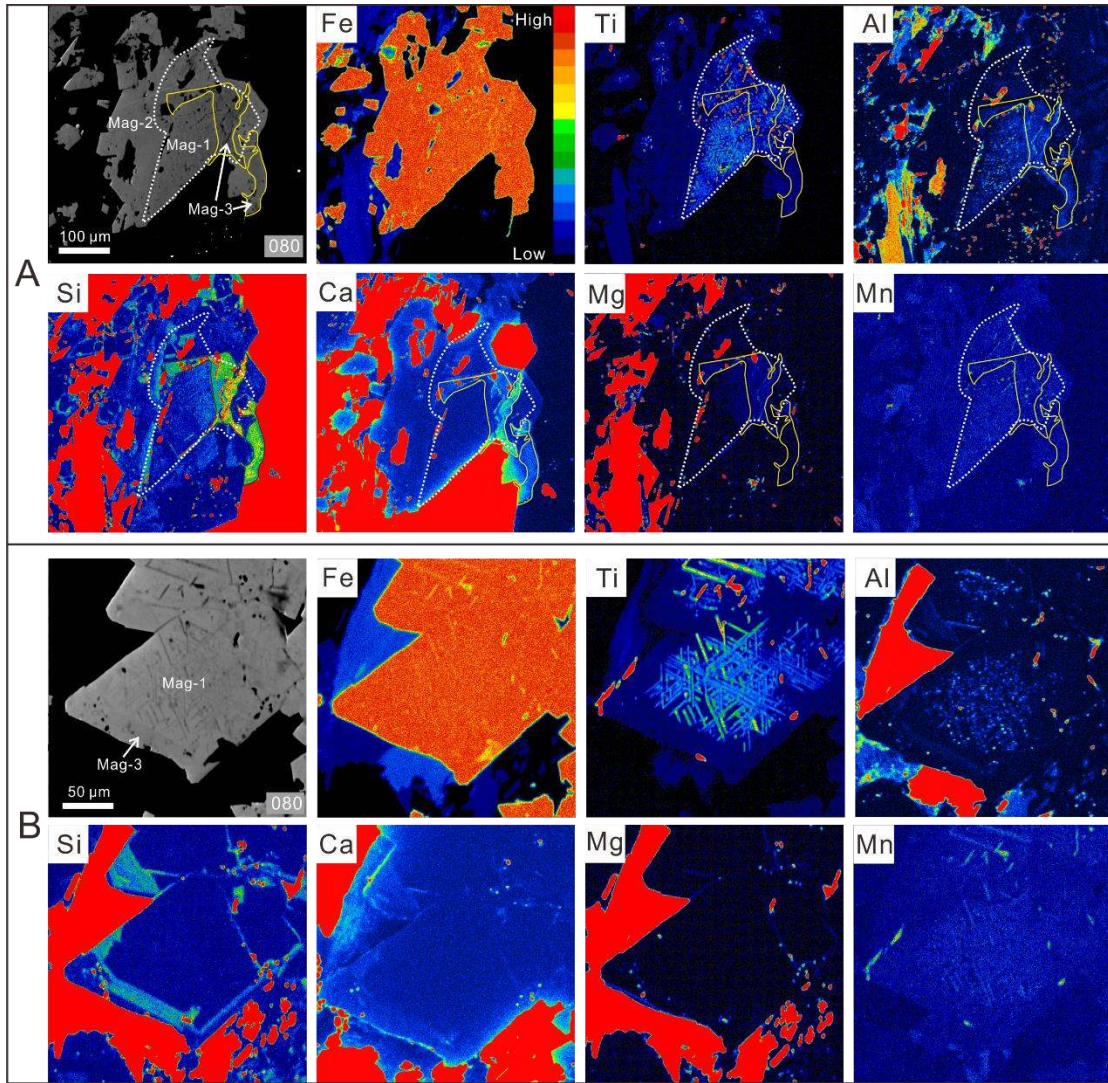


Fig. 4

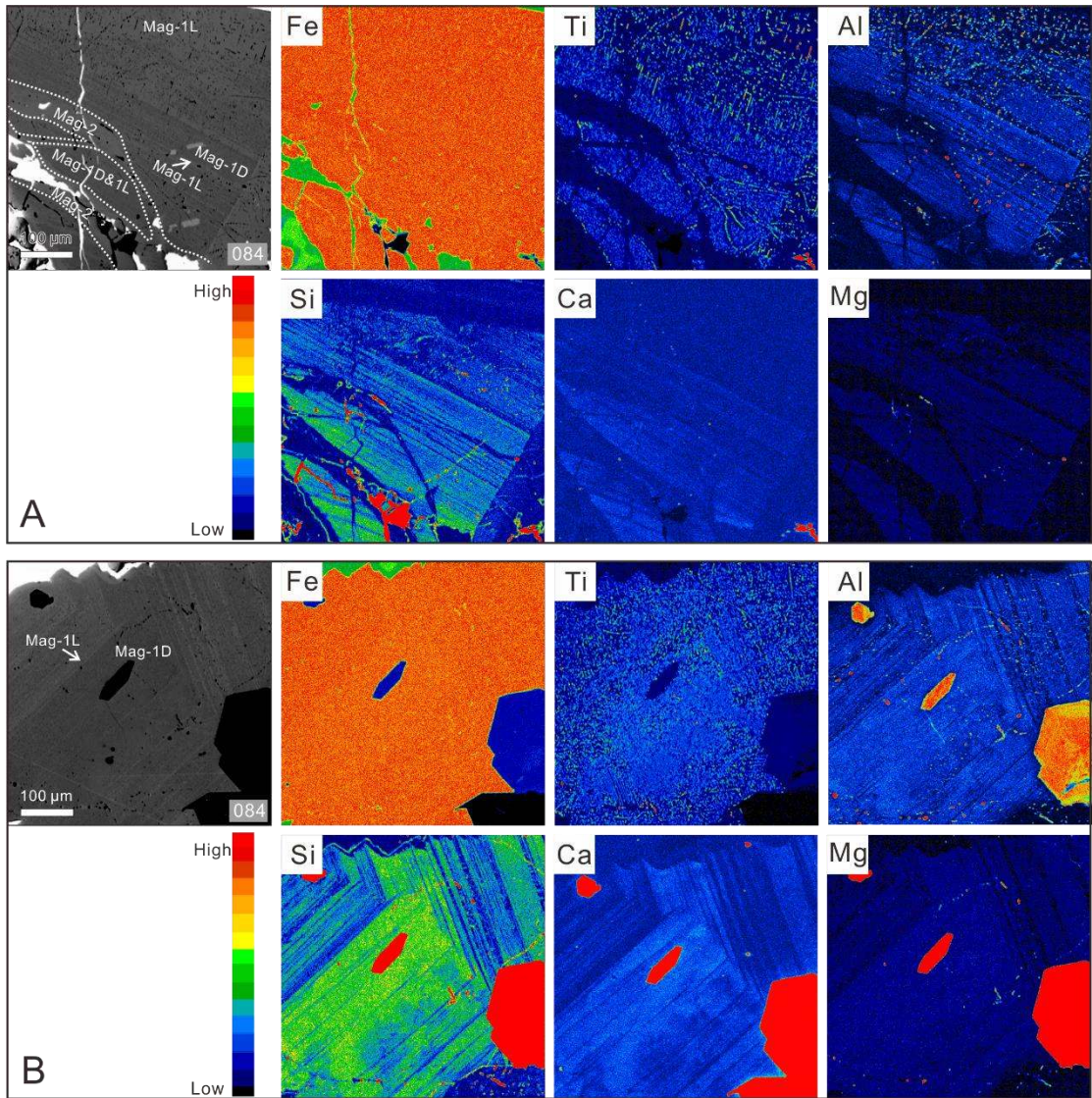


Fig. 5

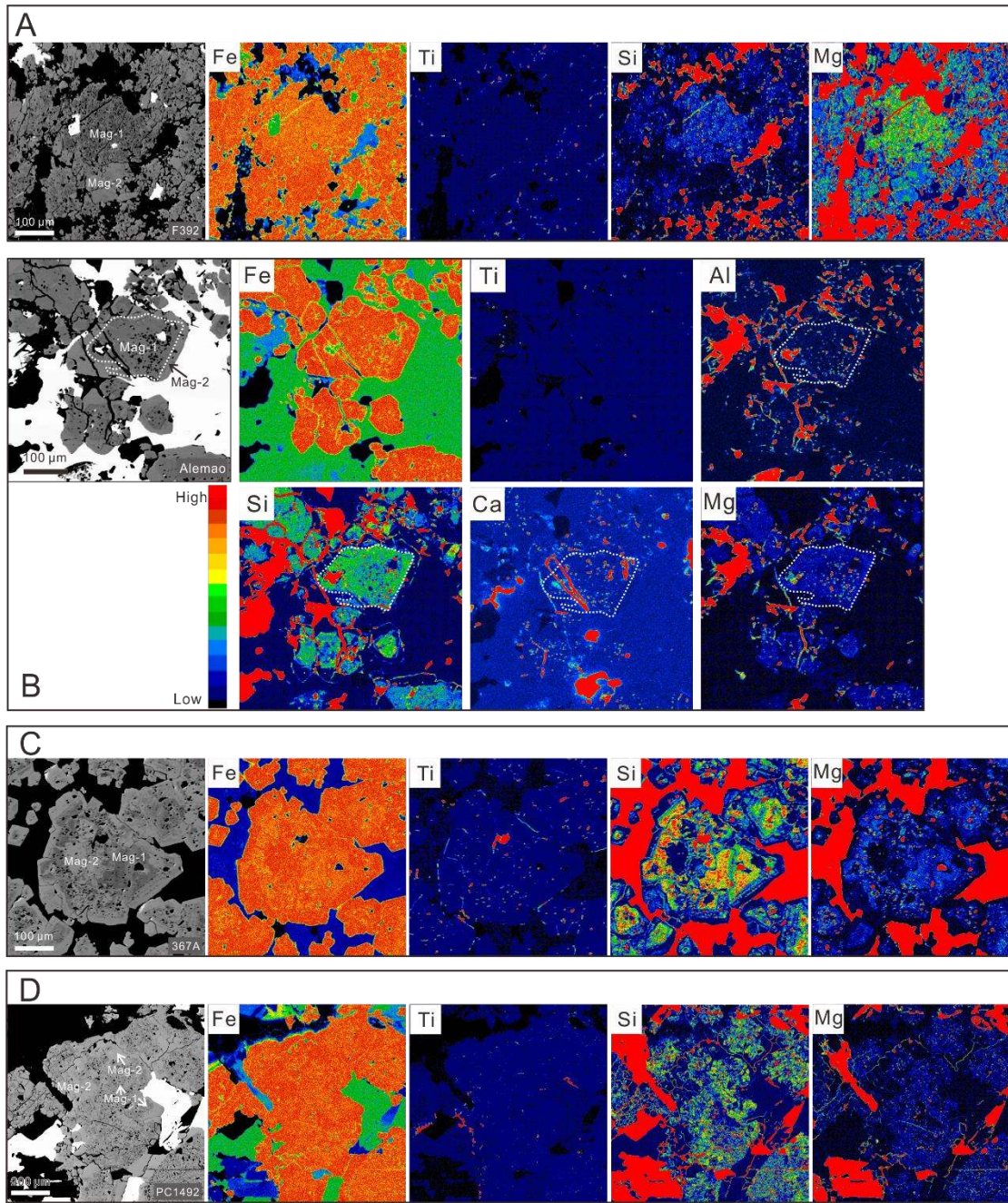


Fig. 6

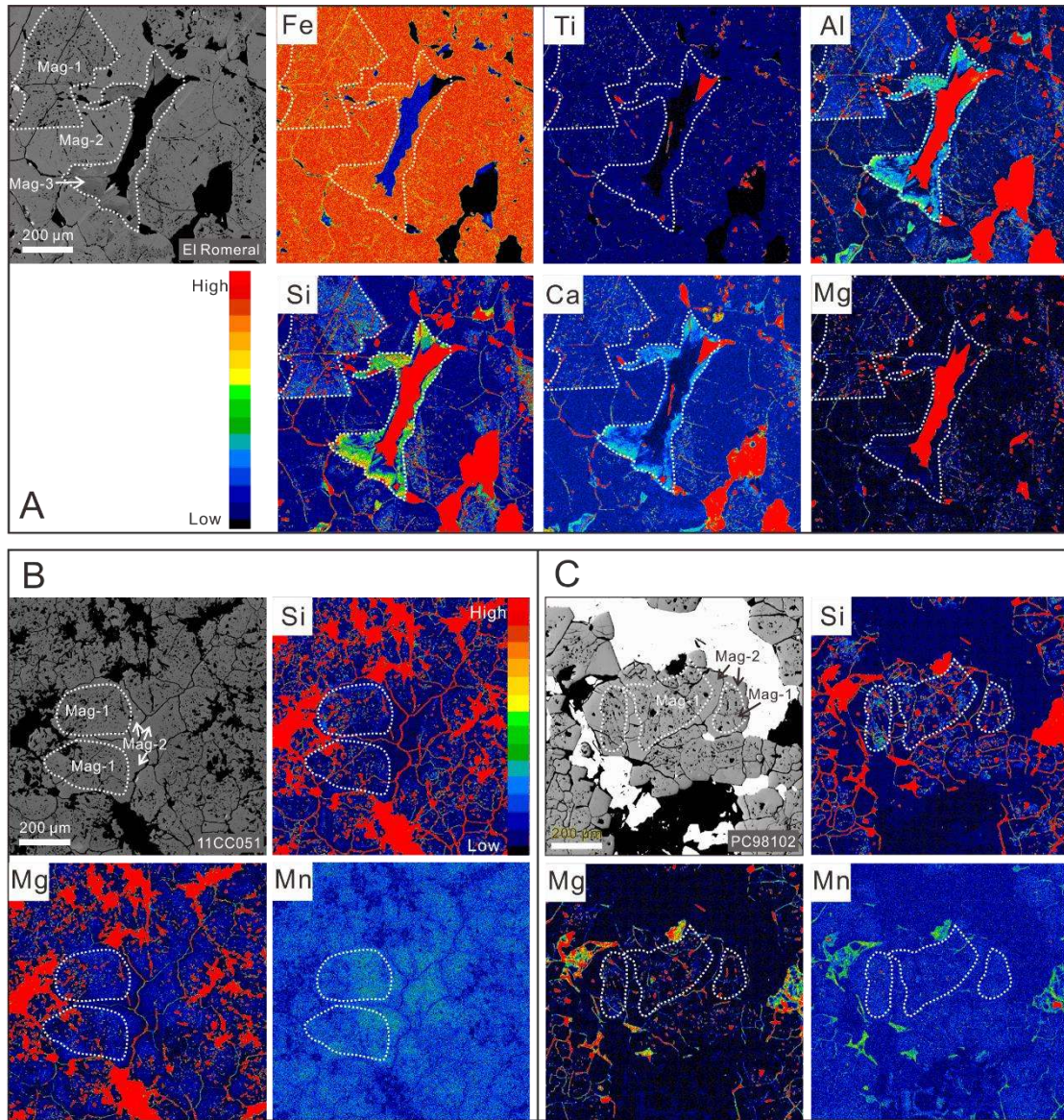


Fig. 7

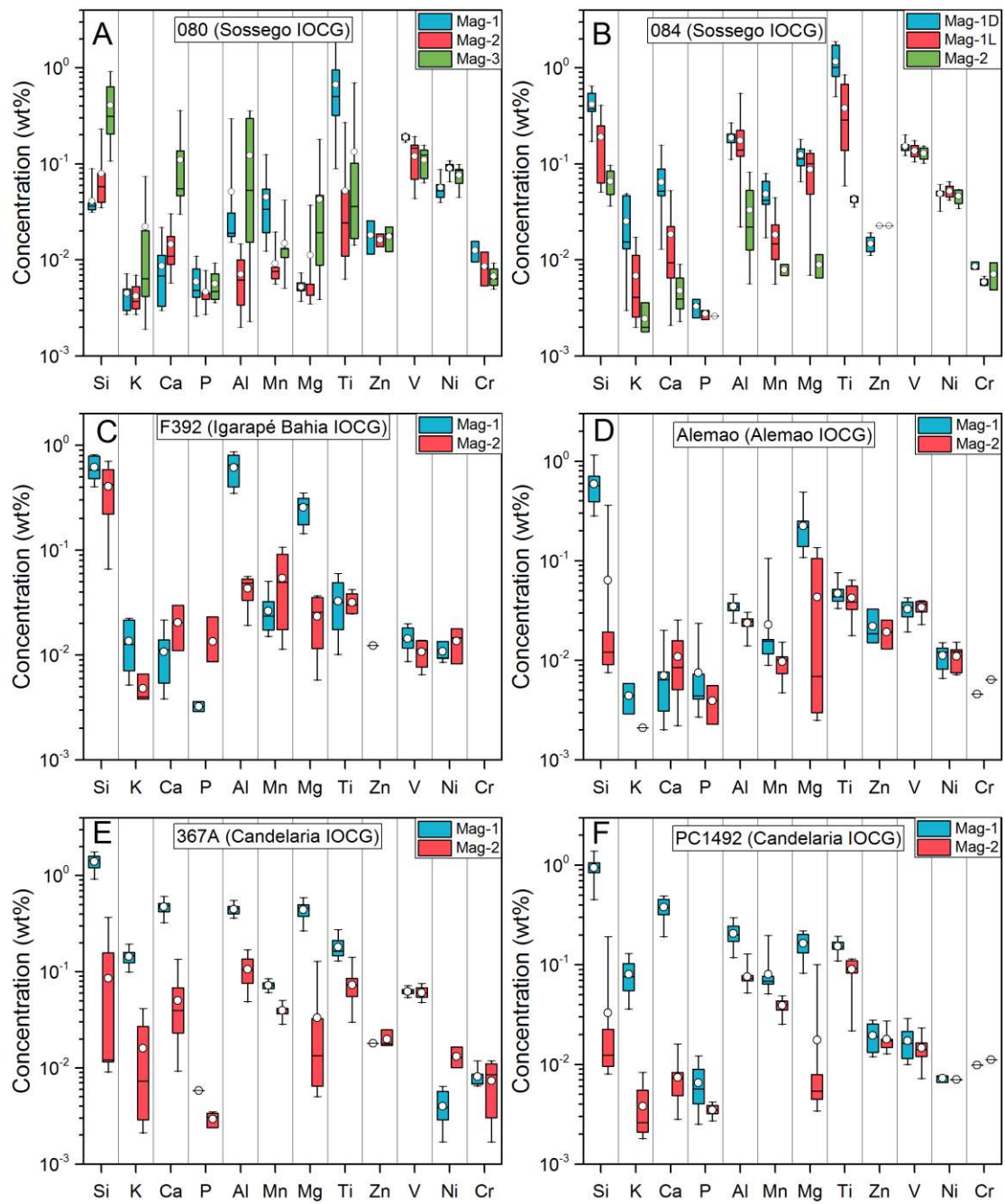


Fig. 8

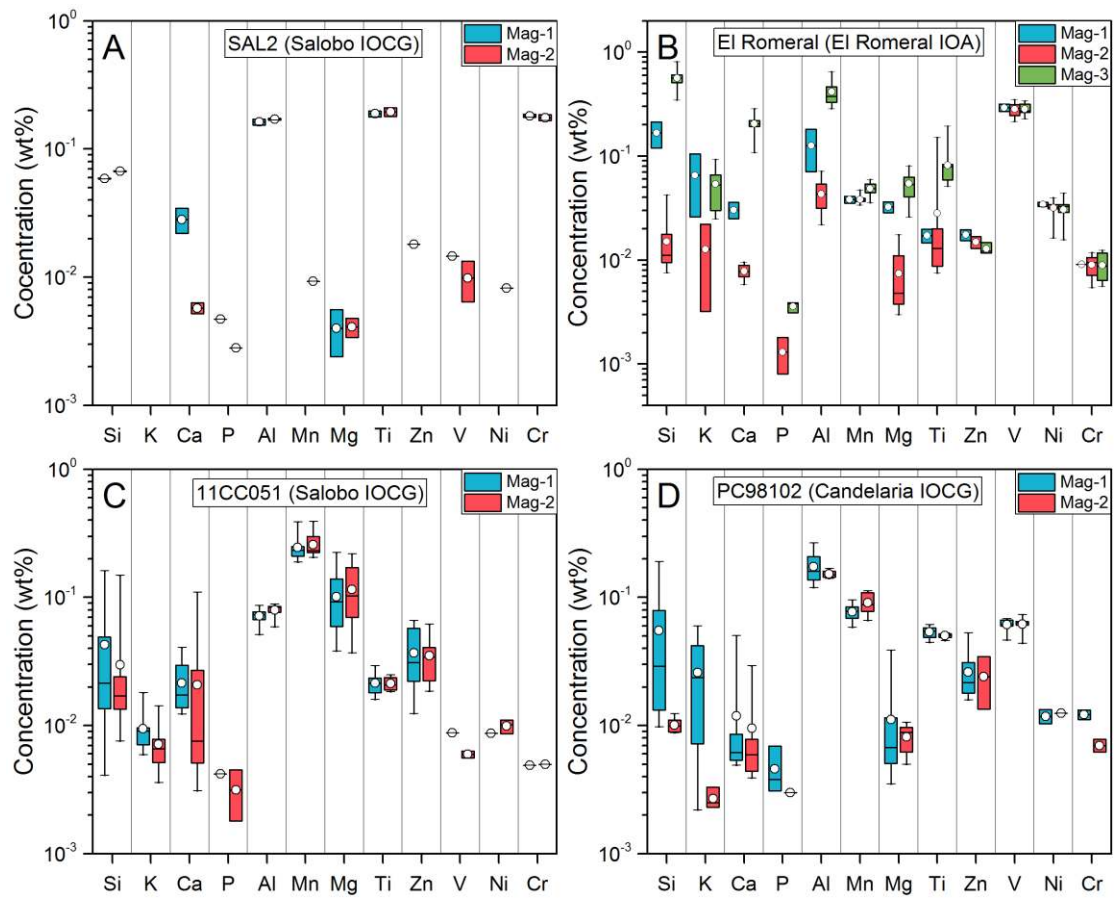


Fig. 9

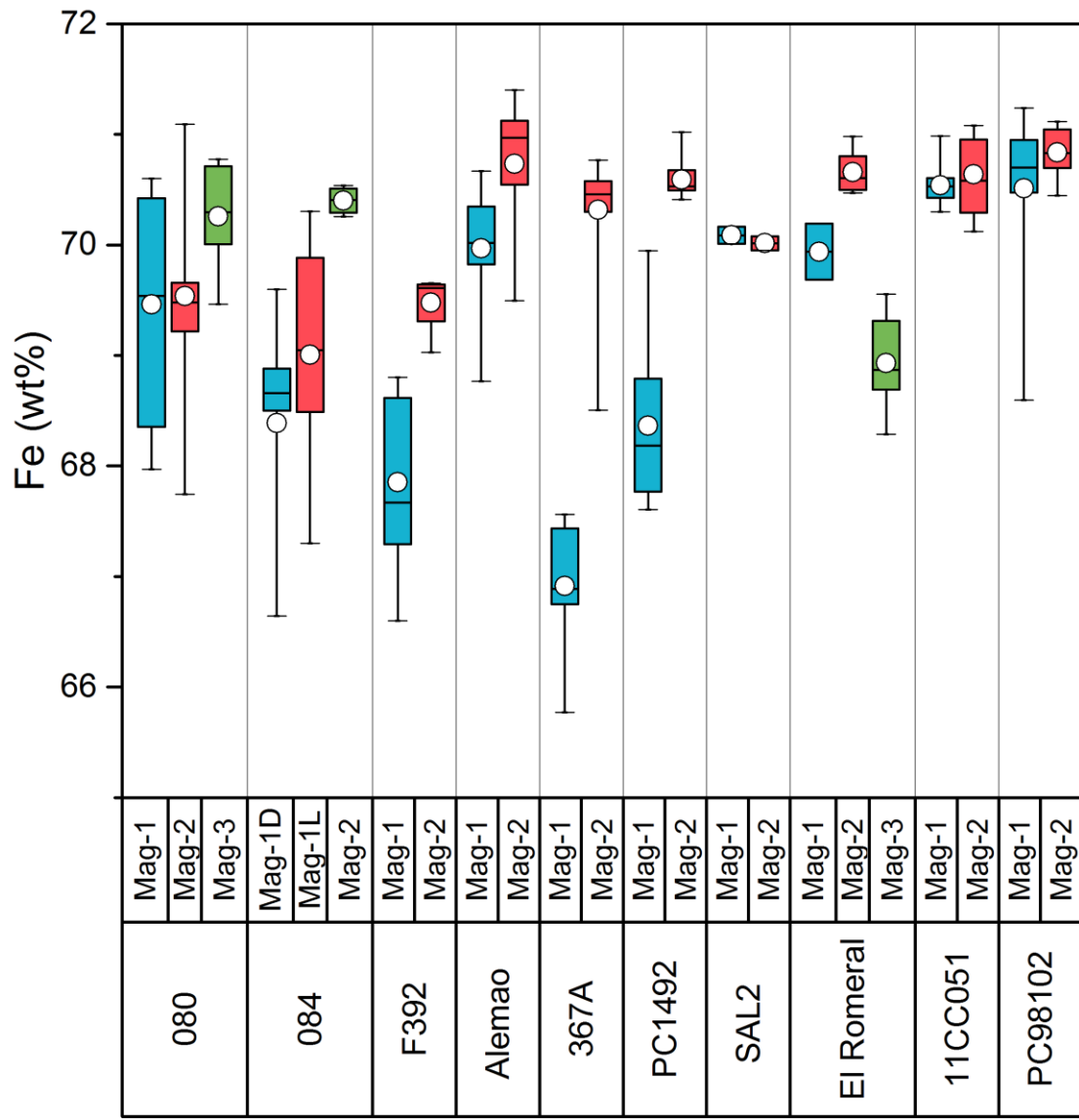


Fig. 10

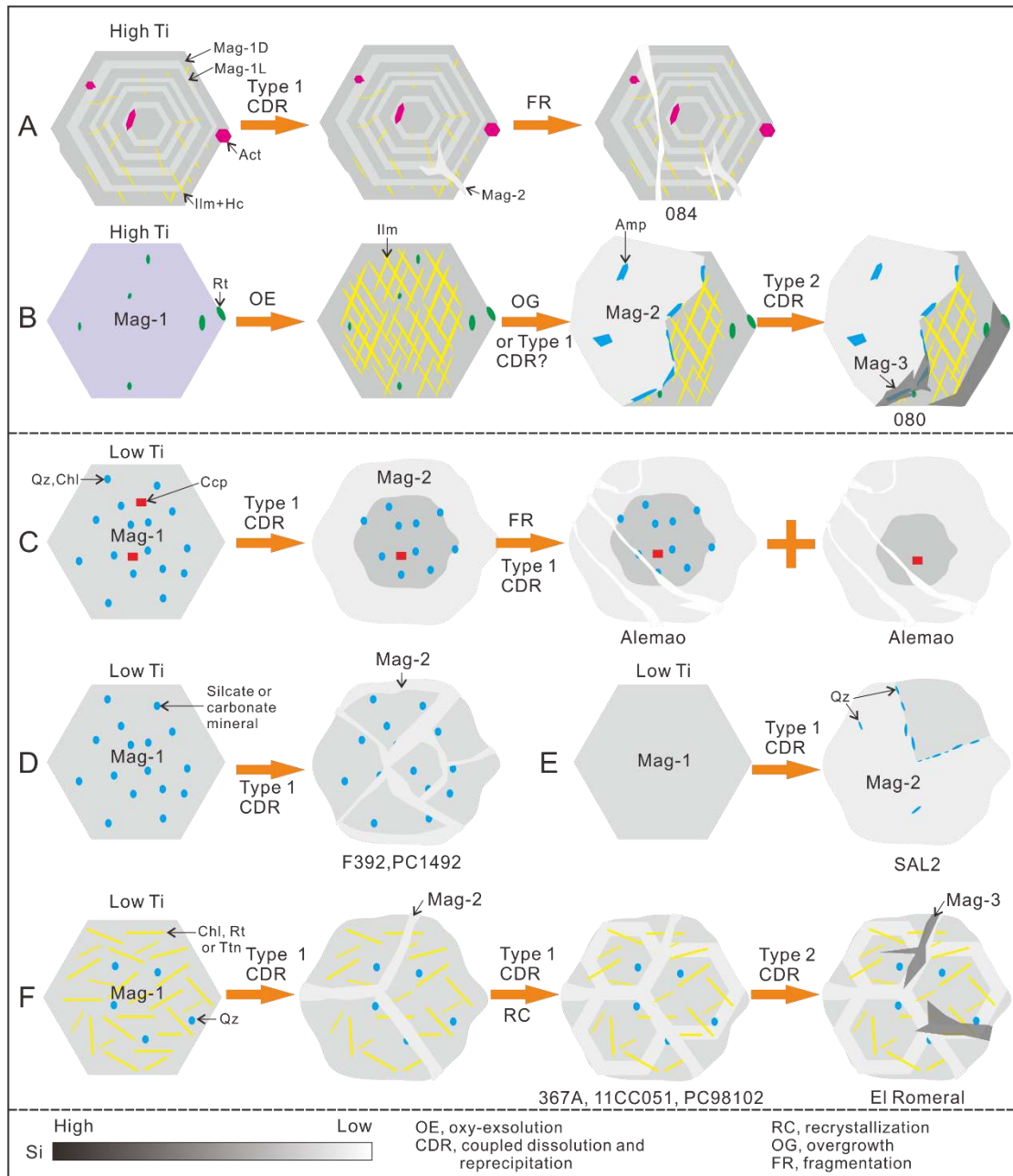


Fig. 11

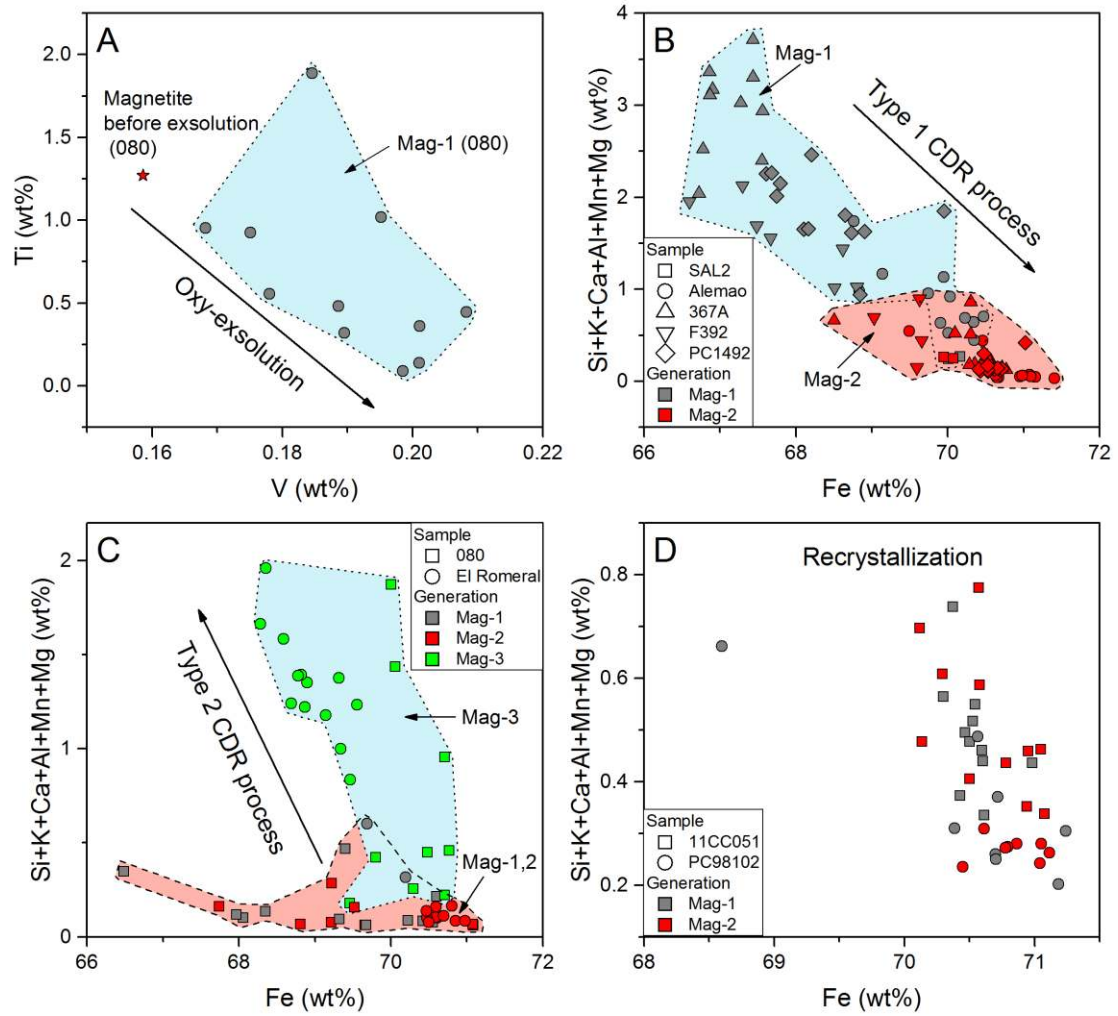


Fig. 12

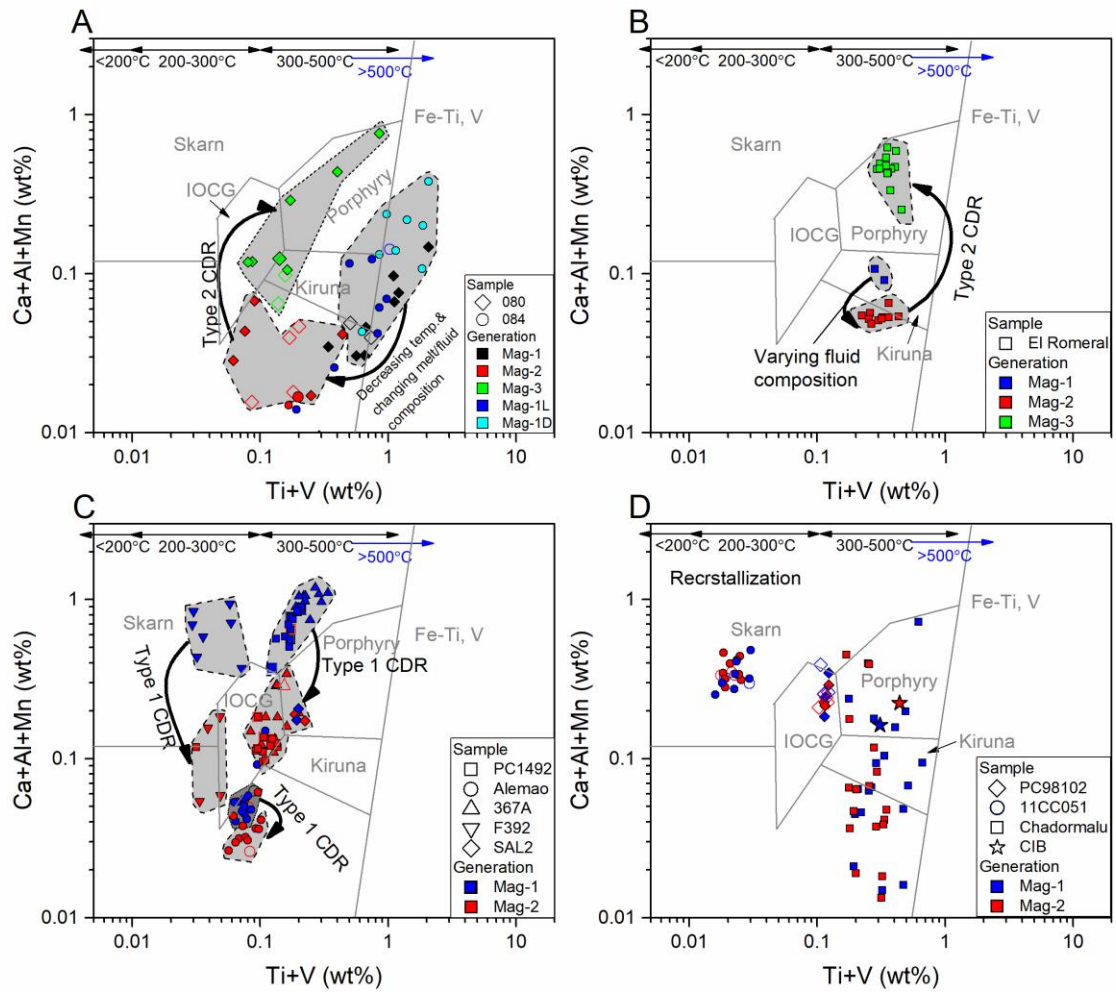


Fig. 13

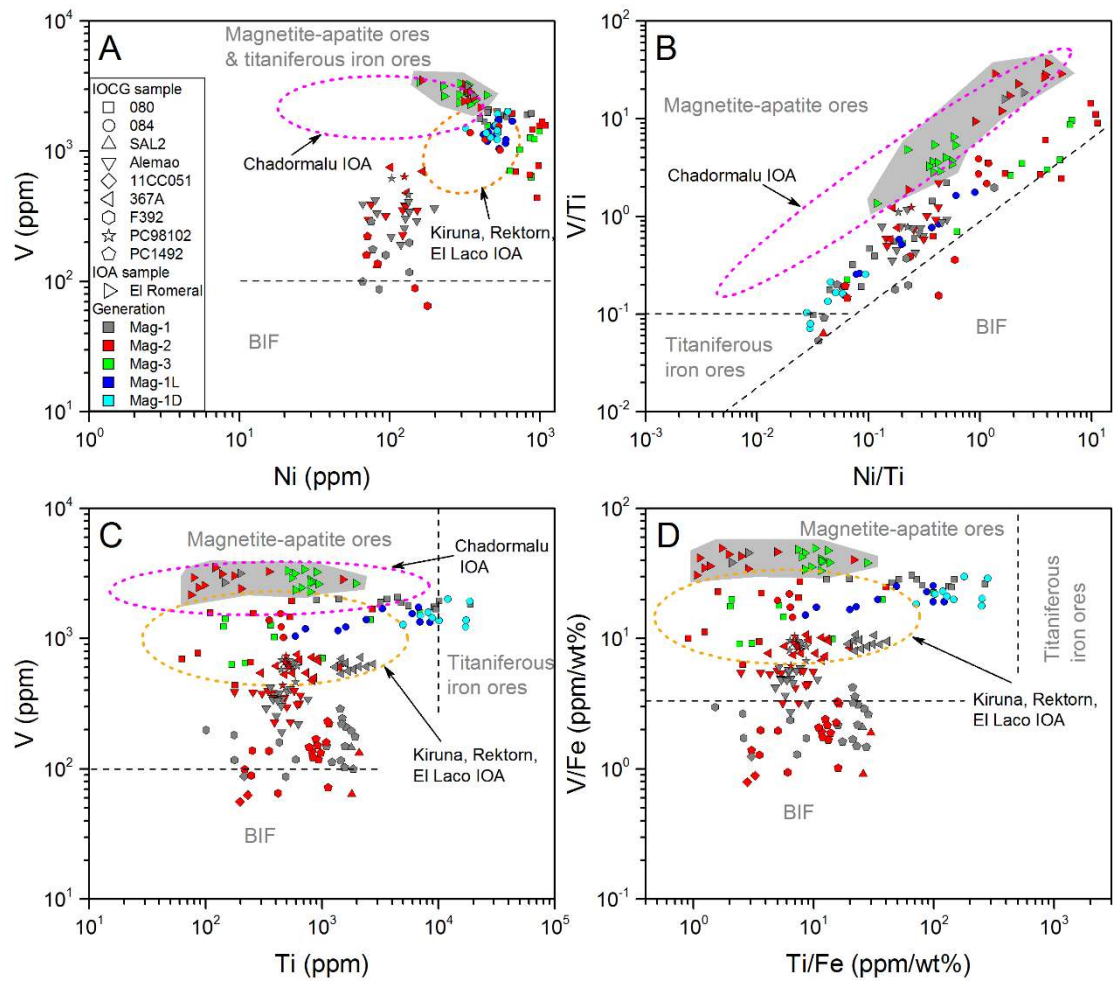


Fig. 14

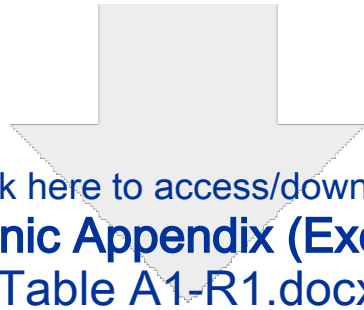
Table 1. Summary of Information on Samples from the Studied IOCG and IOA Deposits

Deposit name	Deposit type	Sample no.	Host rock	Age (Ga)	Metallic mineral	Gangue mineral	Mineral inclusion in magnetite	Magnetite generations	Magnetite textures	References
Igarapé Bahia, Brazil	IOCG	F392	Archean volcano-sedimentary rocks	2.57	Mag, Ccp, Py	Sd, Cal	Sd	Mag-1, 2	CDR	Tallarico et al. (2005)
Alemao, Brazil	IOCG	Alemao	Archean volcano-sedimentary rocks	2.57	Mag, Hem, Ccp, Py	Ap, Bt, Chl, Cal, Qz	Qz, Cal, Chl	Mag-1, 2	CDR	Ronzê et al. (2000)
Sossego, Brazil	IOCG	080	Archean volcano-sedimentary rocks	1.90-1.88	Mag, Ilm, Ccp, Po, Py	Ap, Amp, Act, Qz, Cal, Chl	Amp, Ap, Act, Chl	Mag-1, 2, 3	OE, CDR	Monteiro et al. (2008a, b);
		084			Mag, Ilm, Ccp, Po, Py	Ap, Act, Qz, Cal, Chl	Ap, Act	Mag-1D, 1L, 2	OZ, CDR	Moreto et al. (2015)
Salobo, Brazil	IOCG	SAL2	Archean volcano-sedimentary rocks	2.58	Mag, Ccp, Cct, Bn, Py	Bt, Fa, Fl, Gru, Qz, Tur, Chl	Ccp, Bt, Chl	Mag-1, 2	CDR	Requia and Fontboté (2000)
		11CC051			Mag, Ccp, Py	Bt, Grt, Chl, Qz	Chl, Qz	Mag-1, 2	RC	
Candelaria, Chile	IOCG	367A	Early Cretaceous volcanic rocks	0.12	Mag, Ccp, Py	Bt, Amp, Ap, Act, Ttn, Chl, Ep	Chl, Ttn, Bt, Act	Mag-1, 2	CDR, RC	Marschik and Fontboté (2001);
		PC98102			Mag,	Bt, Chl,	Chl, Qz	Mag-1, 2	RC	Mathur et al.

							Ccp, Py	Cal, Qz					(2002)
			PC1492				Mag,	Kfs, Bt, Ab,	Bt, Ab, Kfs	Mag-1, 2	CDR		
							Ccp, Py	Ap, Ttn					
El	Romeral,	IOA	El	Cretaceous volcanic	0.13-0.10	Mag	Act,	Ab,	Ab, Chl	Mag-1, 2, 3	CDR, RC		Bookstorm,
Chile			Romeral	rocks			Chl						1977;
													Alva-Valdivia
													et al. (2003)

Notes: Samples 080 and 084 are from Sossego–Curral orebodies of the Sossego deposit. OE = oxy-exsolution; OZ = oscillatory zoning; CDR = coupled dissolution and reprecipitation; RC = recrystallization

Mineral abbreviations: Ab = albite, Act = actinolite, Amp = amphibole, Ap = apatite, Bn = bornite, Bt = biotite, Cal = calcite, Ccp = chalcopryrite, Cct = chalcocite, Chl = chlorite, Fa = fayalite, Fl = fluorite, Grt = garnet, Gru = grunerite, Hem = hematite, Ilm = ilmenite, Kfs = K-feldspar, Mag = magnetite, Po = pyrrhotite, Py = pyrite, Qz = quartz, Sd = siderite, Ttn = titanite



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Table A1-R1.docx

