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Re-equilibration Processes of Magnetite from Iron Skarn Deposits

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Magnetite is widely present in a variety of iron ores including iron skarn, IOCG (iron oxide-copper-gold), Kiruna-type, BIF (banded iron formation), and magmatic Fe-Ti oxide deposits (Dupuis and Beaudoin, 2011). Magnetite typically hosts a large variety of trace elements that are largely dependent on its formation environments and thus can be used as an indicator for the genesis of this mineral and associated ore deposits (Dupuis and Beaudoin, 2011; Nadoll et al., 2014). However, recent studies have shown that magnetite could be re-equilibrated with subsequent hydrothermal fluids, forming secondary magnetite domains during the re-equilibration processes (Hu et al., 2014). Such processes would significantly modify the trace element composition of magnetite, making some of the existing trace-element discriminative diagrams (e.g., the Ti+V versus Ca+Al+Mn diagram; Dupuis and Beaudoin, 2011) problematic in deciphering the origin and formation environment of magnetite and associated ore deposits.

In this study, new textual and compositional data of magnetite from nine iron skarn deposits ranging in age from Mesoproterozoic to Mesozoic are presented to further document the re-equilibration reactions (dissolution-reprecipitation processes – DRP). A total of 11 samples were collected from 9 iron skarn deposits. Four samples were collected from the Iron Crown (GR-94-107-1 and GR-94-107-2), Merry Window (GR-94-115), and Paxton (GR-94-44) deposits from British Columbia, Canada. Another four samples were taken from the Grenville-age Forsyth (X-DL-1B and X-DL-1D) and Bristol (X-DL-2A) deposits from Quebec and the Marmora deposit (X-DL-3A) from Ontario. Sample OF-177 was selected from the Terezia Mica deposit, Romania. The remaining two samples were collected from the Daye (12-79) and Chengchao (CC100) iron deposits, eastern China. Magnetite is the dominant mineral (>80 vol. %) in most of the samples, coexisting variably with minor amounts of diopside, garnet, epidote, phlogopite, and chlorite. The sample CC100, which comes from a prograde skarn vein hosted within the ore-related granitic intrusion in the Chengchao iron deposit, contains much less magnetite (5%) that coexists with abundant diopside and garnet. The occurrence, morphology and paragenesis of magnetite within the samples were initially characterized optically. The morphological and textural features of magnetite were then investigated using a JEOL 6400 scanning electron microscope (SEM) equipped with an energy dispersive spectrometer. The electron probe microanalysis (EPMA) and elemental X-ray mapping were conducted using a JEOL JXA-733 Superprobe at the University of New Brunswick, Canada.

Both the oxy-exsolution and dissolution – reprecipitation textures have been recognized in magnetite from the studied samples. Exsolution lamellae of Fe-Al-Ti- oxides, including ulvospinel, hercynite, and corundum, were documented in samples DL-1D, GR-94-107-1, 12-79, CC100, and X-DL-3A. Within DL-1D, orientated exsolution lamellae of ulvospinel are widespread and closely related to corundum and hercynite. In contrast, magnetite from the rest iron deposits only contains ulvospinel as exsolution. In sample GR-94-107-1, magnetite grains exhibit distinct core-rim textures, with the core being rich in texturally equilibrated ulvospinel and the rim being free of ulvospinel. Similar textures have previously been observed in magnetite from magmatic Fe-Ti iron deposits (Dupuis and Beaudoin, 2011). Magnetite from the Marmoration Fe skarn deposit (Sample X-DL-3A) either exhibits a core-rim texture or is homogeneous with triple junction texture. Similarly, the core contains numerous ulvospinel inclusions, whereas the rims are homogeneous with no mineral inclusions.

The SEM-BSE images reveal that magnetite from the

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Iron Crown (GR-94-107-12), Merry Window (GR-94-115), and Paxton (GR-94-44) deposits exhibit textures indicative of dissolution and reprecipitation, forming multiple generations of this mineral. The first generation (Mag 1) is usually characterized by oscillatory zoning and partially replaced with the second generation (Mag 2) that lacks zonation. Notably, the early-stage magnetite grains from the Bristol and Forsyth deposits are marked by nicely developed triple junctions and are locally replaced by secondary magnetite domains (sample X-DL-2A) or cut by late magnetite veins (sample X-DL-1B). The Fe-Ti oxides bearing magnetite domains (Mag 1) from the Iron Crown deposit (GR-94-107-1) have also been partially replaced or overprinted by two successive generations, hereafter termed as Mag 3 and Mag 4, respectively. Magnetite with Fe-Ti oxides inclusions from the Daye and Marmora deposits has also been replaced with secondary domains comprising small magnetite grains with triple junction textures or occurring as overgrowths. Magnetite from the Terezia Mica deposit (sample OF-177) has particularly complex textures, commonly consisting of core (Mag1), mantle (Mag 2), and rims (Mag 3). The first generation (Mag 1) comprises alternative dark and light bands. The light bands are locally crosscut by secondary magnetite (Mag 1a) and contains wolframite inclusions, whereas the dark bands are partially replaced by light magnetite (Mag 1b). In addition, both Mag 2 (mantle) and Mag 3 (rim) are partly re-equilibrated with late stage hydrothermal fluids, forming Mag 2a and Mag 3a.

Most of the samples analyzed contain variable amounts of Si, Mg, Ca+Al+Mn, V, and Ti. Chromium and Ni are generally below the EPMA detection limit. Based on the chemical composition, two types of magnetite are recognized, each consisting of multiple generations due to the re-equilibration processes. Type 1 magnetite contains elevated Ti with abundant Fe-Al-Ti oxide inclusions, including samples X-DL-1D, GR-94-107-1, CC100, 12-79, X-DL-3A and X-DL-3A. Type 2 magnetite, which is the dominant magnetite type in the deposits under investigation, is Ti depleted and lacks oxy-exsolution textures.

Type 1 magnetite (i.e., sample X-DL-1D) contains moderately high, but variable Al_2O_3 (0.54-0.87 wt.%), TiO_2 (0.37-1.27 wt.%), V_2O_3 (0.05-0.09 wt.%), and has low MgO (<0.02 wt.%), SiO_2 (0.08-0.15 wt.%), CaO (<0.01 wt.%), and MnO (0.03-0.14 wt.%). The Fe-Ti-Al oxide exsolution within the magnetite consists mainly of hercynite (55.45-55.48 wt.% Al_2O_3) and corundum (76.18-77.17 wt.% Al_2O_3). The first generation of type 2 magnetite from samples GR-94-44, GR94-115, and GR-94-107-2 is notable for its high concentrations of SiO_2 (1.0-3.96 wt.%) and highly variable Al_2O_3 (0.06-2.32 wt.%), CaO (0.11-1.15 wt.%), and MgO (0.04-1.46 wt.%). These elements are much lower in the second generation of magnetite (0.05-1.11 wt.% SiO_2, 0.02-0.53 wt.% Al_2O_3, 0.01-0.42 wt.% CaO, ≤0.53 wt.% MgO). In addition, the first generation contains low 0.01-0.08 wt.% TiO_2, 0.01-0.04 wt.% V_2O_3, and 0.03-0.37 wt.% MnO. These oxides do not show obvious variations in the secondary magnetite, being 0.11 wt.% (on average), ≤0.08 wt.%, and ≤0.27 wt.%, respectively. Sample OF-177 of the Terezia Mica skarn deposit is marked by a sharp decrease in SiO_2 content at the boundary between Mag 1 and Mag 2, and then a tremendous increase at the margin between Mag 2 and Mag 3, reaching 4.62 wt.% in Mag 3. Overprints of those magnetite, however, are poor in SiO_2, with an exception for Mag 1b in which SiO_2 is up to 2.85 wt.%. Other elements do not show obvious variations in the different generations of magnetite in this deposit.

The DRP is particularly common and have been widely recognized in most of the deposits under investigation, whereas the oxy-exsolution occurs only in the high Ti magnetite containing Fe-Ti oxide inclusions in this study. Some of the high Ti magnetite grains have also been re-equilibrated by multiple DRP subsequent to oxy-exsolution. In addition, magnetite grains from some samples have the triple junction texture, indicating recrystallization and complete replacement by late hydrothermal fluid. The textural evidence demonstrates that magnetite grains from many iron skarn deposits represent the final product of mineralization, with the precursor phase or domains having been completely obscured during the re-equilibration processes. The EPMA results show that DRP have significantly modified the minor and trace element compositions of magnetite, particularly Si, Mg, Ca, Al, Mn, and Ti. The oxy-exsolution process is notably effective in decreasing the Ti content of the high Ti magnetite. Some analyses of the magnetite grains from the skarn deposits variably fall into the BIF, IOCG, or porphyry fields in the Ti+V vs. Ca+Al+Mn diagram, suggesting that texturally complicated magnetite cannot be simply used as a genetic indicator. Mixing of the ore fluids with external saline components, an increase in the temperature and local decrease in pressure, and fO_2 are considered as the most important mechanisms causing the DRP or oxy-exsolution of magnetite. Results presented here demonstrate that textural characterization must be conducted before *in situ* compositional analysis of magnetite grains. An additional implication is that the application and reliability of the widely used trace-element discriminative plots (e.g., the Ti+V vs. Ca+Al+Mn diagram) of magnetite should be reevaluated, particularly for mineral grains that have subjected to extensive re-equilibration.

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