

Magnetite chemistry in skarns of the Bohemian Massif: evaluating competing effects of protolith inheritance, crystal chemistry, fluid composition and pressure-temperature conditions

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Abstract. Magnetite-rich skarns in the Bohemian Massif (central Europe) frequently occur in supracrustal volcano-sedimentary sequences, metamorphosed up to greenschist, amphibolite or eclogite facies. Their magnetites are very pure (95.5-99.3 mol. % Fe_3O_4) and minor and trace element concentrations are very low, defined by hercynite and ulvöspinel substitution trends. These patterns are consistent with derivation of skarns by carbonate or calc-silicate replacement, and exclude their origin in other settings or by involvement exhalative or hydrogeneous components. Significant correlations at trace levels exist between ore-forming element pairs (e.g., Zn-Sn), various divalent pairs (e.g., Zn-Mn) as well as immobile couples (e.g., Al-Ti). Negatively correlated homovalent pairs (e.g., Mg- Fe^{2+} , Mn- Fe^{2+} , Al- V^{3+}) have the largest potential for reflecting the environmental conditions during magnetite crystallization, whereas the positively correlated Al-Ti pair reflects inheritance from the skarn precursor and element partitioning between coexisting phases. The $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratios in magnetites (5.4-11.6 by weight) are substantially lower than those in the bulk magnetite-rich skarns (18.3-22.6), which is due to aluminum partitioning into garnet and/or clinopyroxene. These observations suggest that trace elements in magnetites are subject to redistribution and re-equilibration during superimposed metamorphic or hydrothermal events, in addition to their solubilities in the spinel structure being temperature-dependent as well.

Keywords. magnetite, skarn, solubility, partitioning, protolith inheritance, metasomatism

1 Introduction

Magnetite, Fe_3O_4 , is the most common oxide in a number of ore deposit styles, ranging from Ni-PGE, Cu-sulfide or Fe-Ti-V mafic magmatic systems through hydrothermal iron oxide-copper-gold, or skarn deposits. Recent advances in microanalytical techniques prompted systematic studies of minor and trace element variations in magnetites from diverse geological settings (Dupuis and Beaudoin 2011, Dare et al. 2012). Incorporation of additional constituents into magnetite structure is controlled by competing effect of protolith bulk composition, fluid composition, crystalchemical constraints, and pressure-temperature conditions. In this contribution we present new analytical data from magnetites in calcic-iron skarns in the Bohemian Massif, central Europe in order to reconcile contributions from these individual factors.

2 Geological setting

Calcic and magnesian magnetite-rich skarns are a characteristic minor constituent in numerous volcanosedimentary metamorphic complexes in the Bohemian Massif (Fig. 1). They form lenses or discontinuous horizons up to 200 m thick surrounded by siliciclastic, calc-silicate metasediments, felsic or mafic meta-volcanics, or metagranitic gneisses.

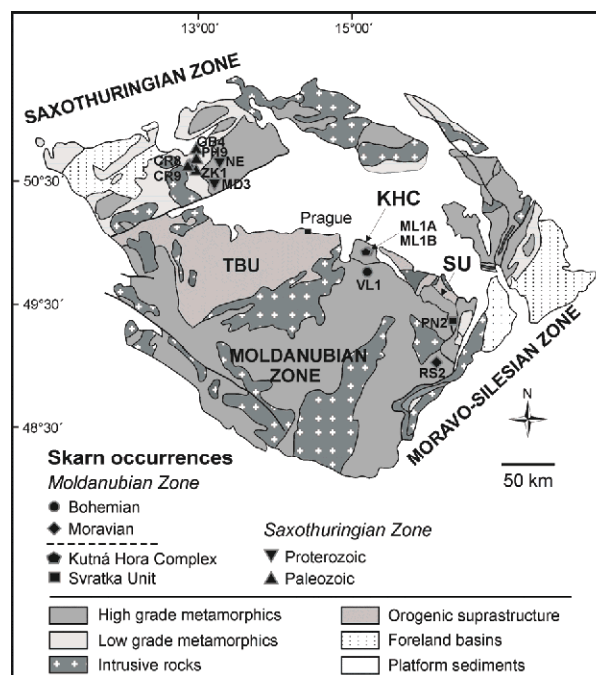


Figure 1. Geological map of the Bohemian Massif showing the main geological units and locations of individual magnetite skarn samples: VL1 – Vlastějovice, RS2 – Rešice, PN2 – Pernštejn, ML1A, ML1B – Malešov, MD3 – Měděnec, NE – Niederschmiedeberg, GB4 – Gelbe Birke (Beierfeld), PH9 – Pöhla, CR8, CR9 – St. Christoph (Breitenbrunn), and ZK1 – Zlatý kopec (Boží Dar).

All occurrences underwent regional metamorphism during Variscan orogeny (360-320 Ma) and were overprinted under greenschist, amphibole or eclogite facies conditions. The skarns are homogeneous or modally banded, consisting of clinopyroxene, garnet and magnetite-rich varieties. The magnetite content increases up to 80-90 vol. %, forming characteristic granoblastic texture with clinopyroxene, rare calcic garnet, secondary calcic amphibole, oxide or sulfide ore minerals such as cassiterite, sphalerite or chalcocopyrite (Fig. 2a). The skarns were interpreted as products of

metasomatic replacement of carbonate precursors (Němec 1991) or as syndimentary exhalative deposits (Pertoldová et al. 2009); their origin thus remains unresolved.

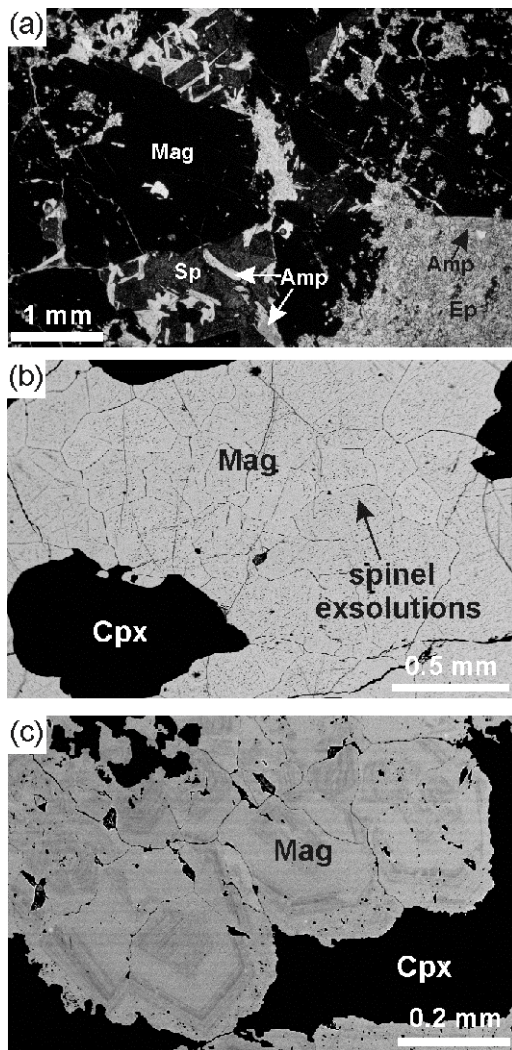


Figure 2. Optical and backscattered electron photomicrographs of magnetite-rich skarns: (a) amphibole-magnetite skarn with sphalerite mineralization, CR9; (b) clinopyroxene-magnetite skarn with exsolution lamellae of Mg- and Ti-rich spinel, RS2; (c) clinopyroxene-magnetite skarn showing compositional growth zoning of magnetite, ZK1.

3 Methodology

Twelve samples of magnetite-rich skarns were analyzed using the Cameca SX100 electron microprobe at the Institute of Geological Sciences, Masaryk University in Brno. Measurements were conducted with accelerating voltage of 15 kV and a beam diameter of 3.5 μm . The beam current was varied between 40 nA for iron and minor elements (Al, Ca, Cr, Mg, Mn, and Ti) and 100 nA for trace elements (Co, Cu, Ni, Pb, Si, Sn, Ta, V, and Zn). Natural and synthetic solid phases were used for calibration. The detection limits varied between 70-100 ppm (Ti, Si, V), 100-150 ppm (Al, Mg, Ca, Co, Cr, Ni, Sn), and 170-500 ppm (Mn, Cu, Zn, Ta, Pb). We analyzed 18 elements in total and the concentrations of Al, Fe, Mg, Mn, Si, Sn, Ti and Zn commonly exceed the respective detection limits (Fig. 3).

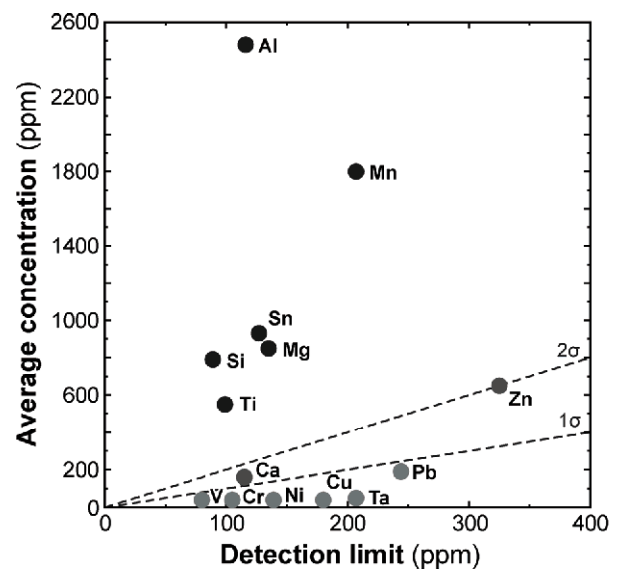


Figure 3. Detection limits and average concentrations of minor and trace elements in magnetite.

4 Results

Magnetites are compositionally homogeneous, with the exception of the sample ZK1 (Zlatý kopec) where a conspicuous hydrothermal growth zoning is preserved (Fig. 2c). Electron microprobe analyses were recalculated to formula units using 3 cations and 4 oxygen equivalents by adjusting the ferrous and ferric iron proportions (Fig. 4).

All skarn magnetites are nearly pure (95.5-99.3 mol. % Fe_3O_4) when compared to those from other hydrothermal or magmatic settings (Dupuis and Beaudoin 2011, Barnes and Roeder 2001). They contain 0.04-0.81 wt. % MnO, 0.01-0.63 wt. % MgO, 0.01-1.50 wt. % Al_2O_3 , and up to 0.20 wt. % TiO_2 , and these variations correspond to magnetite-hercynite and magnetite-ulvöspinel substitutions as well as homovalent M^{2+} mixing in the B site.

The data set reveals several regional trends: (i) magnetites from the Moldanubian skarns show the lowest manganese and silicon concentrations (0.06-0.13 wt. % MnO; 0.08-0.12 wt. % SiO_2), (ii) magnetites from the Kutná Hora-Svratka skarns are extremely depleted in magnesium (0.003-0.011 wt. % MgO), (iii) the titanium concentrations in magnetites are high in the Moldanubian skarns (0.06-0.21 wt. % TiO_2), decrease in the Saxothuringian Neoproterozoic skarns (0.03-0.07 wt. % TiO_2), and become irregularly scattered and high in the Saxothuringian Paleozoic occurrences (0.06-0.28 wt. % TiO_2), (iv) each locality has a well-defined, narrow range in MgO, MnO and TiO_2 concentrations.

Pearson correlation coefficients (r) were calculated for all element pairs in the entire data set and they reveal significant positive correlation between Al_2O_3 and TiO_2 ($r = 0.70$), MnO and ZnO ($r = 0.68$), ZnO and SnO_2 ($r = 0.75$), and negative correlation between FeO and MnO ($r = -0.74$). Negative correlations between homovalent elements indicate ionic substitutions, whereas positive correlations appear among both the ore-forming and immobile constituents. For instance, the ZnO- SnO_2 correlation mainly results from elevated concentrations

in the Saxothuringian Paleozoic skarns that were metasomatized by fluids derived from peraluminous collisional granitic magmas.

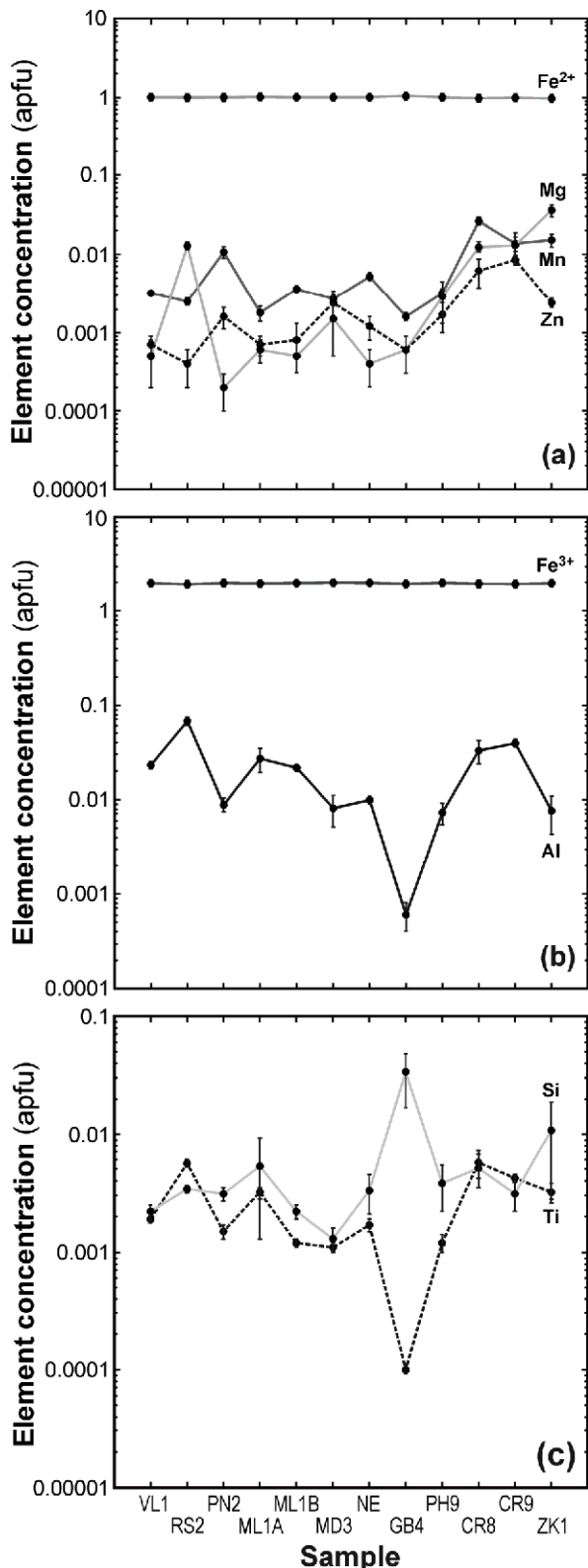


Figure 4. Minor and trace element concentrations in magnetites, expressed in atoms per formula unit (apfu).

5 Discussion and implications

We interpret our analytical dataset by addressing the following open questions:

(1) Are the observed trace element patterns consistent with skarn origin by epigenetic metasomatic replacement or by involvement of synsedimentary exhalative or hydrogeneous components? The concentrations of Al₂O₃, TiO₂ and MnO are very low, and NiO, CoO and V₂O₃ abundances appear to be lower than their detection limits (~ 140 ppm). The depletion in Mn and Ni excludes formation of magnetite by metamorphism of exhalative or hydrogeneous components, and the low Ti and V abundances do not support origin in hydrothermal systems similar to porphyry, iron oxide-copper-gold or Kiruna-type settings (Fig. 5). In addition, the depletion in Ti and V is probably limited by their decreasing solubility in the spinel structure at low hydrothermal temperatures. Subject to this restriction, we suggest that these elements were largely immobile in aqueous fluid during magnetite formation.

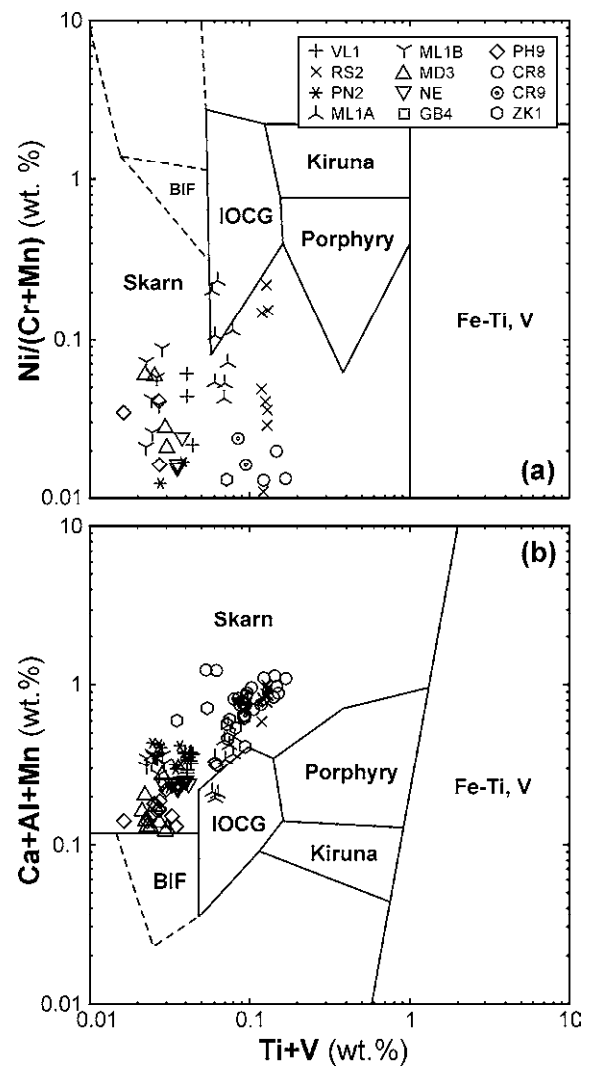


Figure 5. Discrimination diagrams for magnetites from various geological settings (Dupuis and Beaudoin 2011).

(2) Are the immobile elements (Al, Ti) in magnetite reflecting inheritance from the skarn precursor? Fig. 5b shows a broad linear trend due to the correlation between Al and Ti ($r = 0.70$). In several occurrences, field and petrographic evidence suggests that skarns formed by replacement of calcitic or dolomitic

precursors as well as their siliciclastic wall rocks (phyllites, mica schists), preserved as incompletely metasomatized relics. The $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratios in magnetites are, however, generally lower than those found in volcanic rocks or average sediments (Fig. 6). Whole rock analyses of magnetite skarns (Vlastějovice, Malešov) reveal the ratio of $\text{Al}_2\text{O}_3/\text{TiO}_2 = 18.3\text{--}22.6$, whereas electron microprobe analyses of individual magnetite grains yield $\text{Al}_2\text{O}_3/\text{TiO}_2 = 5.4\text{--}11.6$. This departure is related to partitioning of available Al between magnetite, garnet and/or clinopyroxene in the skarns, whereas Ti is almost exclusively hosted by magnetite. Therefore, the Al and Ti enrichments in magnetite seem to generally indicate increasing proportion of detrital component in the skarn precursor but in detail their proportions may be affected by partitioning to other skarn-forming silicates.

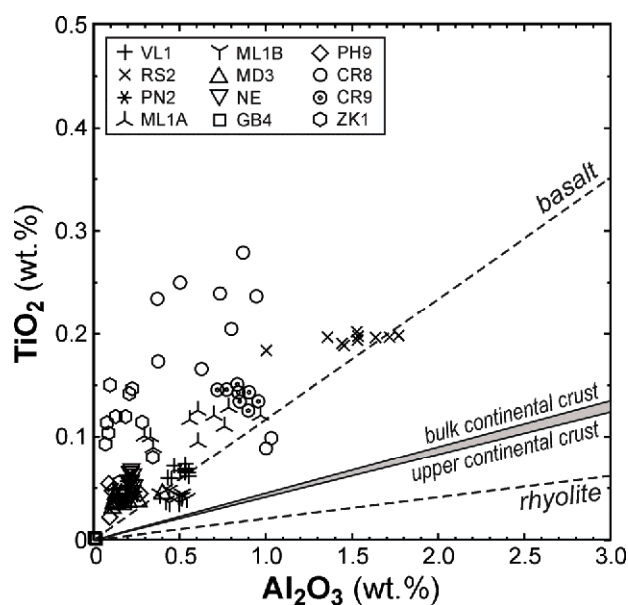


Figure 6. Al_2O_3 vs. TiO_2 concentrations in magnetites illustrating the systematic difference from the $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratios in volcanic or sedimentary precursors (represented by the continental crust).

(3) Is the incorporation of Al and Ti in magnetite influenced by subsequent metamorphic events? In general, minor elements such as Ti, Al, Cr and Ni provide useful geochemical discriminators because their incorporation (solubility) in magnetite is expected to be temperature- and pressure-dependent as their ionic radii or partial molar volumes differ. In our data set, the maximum Al_2O_3 solubility limit in magnetite has been exceeded in one sample (Rešice, RS2) and this has led to exsolution of Mg-Ti-rich spinel during post-metamorphic cooling (Fig. 2b). The corresponding Al_2O_3 content in magnetite, the largest in the entire data set, is 1.50 ± 0.15 wt. %.

The TiO_2 concentrations in magnetites increase up to 0.28 wt. % but are generally lower than 0.15 wt. %. Because the Ti incorporation in magnetite is controlled by the ulvöspinel substitution and the Fe^{3+} content becomes non-stoichiometric, the activities of FeO and Fe_2O_3 in magnetite solid solution provide means for calculating oxygen fugacity during its crystallization. In

our study, the low-Ti magnetites from Měděnec, Niederschmiedeberg and Pöhla formed at more oxidizing conditions than their high-Ti counterparts at St. Christoph near Breitenbrunn or Zlatý kopec.

We conclude that magnetites in calcic and magnesian iron-rich skarns in central Europe are very pure and their Al, Ti, Mn, Mg, V, Zn and Sn concentrations are very low but comparable to replacement skarns worldwide. This behavior results from their low-temperature origin as well as im/mobility of these elements in aqueous fluids. At trace levels, positive correlations between immobile elements, Al and Ti, suggest that they are inherited from impure carbonate protolith but subject to local redistribution and reequilibration during subsequent metamorphic or hydrothermal events.

Acknowledgements

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