Gahnite composition as a means to fingerprint metamorphosed massive sulfide and non-sulfide zinc deposits

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ABSTRACT

Gahnite occurs in and around metamorphosed massive sulfide (e.g., Broken Hill-type Pb–Zn–Ag (BHT), volcanogenic massive sulfide Cu–Zn–Pb–Au–Ag (VMS), sedimentary exhalative Pb–Zn (SEDEX)), and non-sulfide zinc (NSZ) deposits. In addition to occurring in situ, gahnite occurs as a resistate indicator mineral in unconsolidated sediments (e.g., glacial till) surrounding such deposits. The spatial association between gahnite and metamorphosed ore deposits has resulted in its use as an empirical exploration guide to ore. Major and trace element compositions of gahnite from BHT, NSZ, SEDEX, and VMS deposits are used here to develop geochemical fingerprints for each deposit type.

A classification tree diagram, using a combination of six discrimination plots, is presented here to identify the provenance of detrital gahnite in greenfield and brownfield terranes, which can be used as an exploration guide to metamorphosed massive sulfide and non-sulfide zinc deposits. The composition of gahnite in BHT deposits is discriminated from gahnite in SEDEX and VMS deposits on the basis of plots of Mg versus V, and Co versus V. Gahnite in SEDEX deposits can be distinguished from that in VMS deposits using plots of Co versus V, Mn versus Ti, and Co versus Ti. In the Sterling Hill NSZ deposit, gahnite contains higher concentrations of Fe^{3+} and Cd, and lower amounts of Al, Mg, and Co than gahnite in BHT, SEDEX, and VMS deposits. Plots of Co versus Cd, and Al versus Mg distinguish gahnite in the Sterling Hill NSZ deposit from the other types of deposits.

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1. Introduction

Geochemical fingerprints of resistate indicator minerals allow explorationists to search for various types of commodities covered by recently deposited unconsolidated sediments (e.g., alluvium, colluvium, and glacial till). For example, detrital grains of gahnite have been used in the search for metamorphosed massive sulfide deposits concealed beneath glacial till (e.g., Hicken et al., 2013a,b; McClenaghan, 2005; McClenaghan et al., 2012; Morris et al., 1997). The dispersal of indicator mineral suites from various ore types is well documented for porphyry copper deposits (e.g., apatite, magnetite, rutile, tourmaline, zircon), Ni–Cu–PGE deposits (e.g., chromite, diopside, Cr-rich enstatite, forsterite), diamond-bearing kimberlites (e.g., chromite, entstatite, forsterite, garnets, Mg-ilmenite, omphacite), and metamorphosed massive sulfide deposits (e.g., gahnite, willemite, franklinite, zincian staurolite) (Averill, 2001, 2007, 2011; McClenaghan and Kjarsgaard, 2001). However, despite the use of these indicator minerals as empirical guides to mineralization, such minerals are also found in rocks unrelated to mineralization. This has led to the use of major and trace element compositions of

minerals to further refine their use as guides in exploration or in determining their provenance.

In particular, discrimination plots using major and trace element compositions have been used to infer the provenance of, for example, garnet (e.g., Aubrecht et al., 2009; Krippner et al., 2014), rutile (e.g., Scott and Radford, 2007), Cr-spinel (e.g., Aubrecht et al., 2009), magnetite (e.g., Dupuis and Beaudoin, 2011), and Zn-spinel (e.g., Heimann et al., 2005; Spry and Scott, 1986). In the case of garnet, the composition of the so-called "G-10" garnets, which are distinguished from other garnet compositions on the basis of a plot of wt.% Cr_2O_3 versus CaO, has been instrumental in exploring for diamonds (e.g., Gurney, 1984). Furthermore, using the trace element composition of magnetite, Dupuis and Beaudoin (2011) developed a series of discrimination diagrams to identify compositional differences for magnetite from various types of ore deposits.

Although the presence of gahnite (AB_2O_4), where $A = Zn^{2+}$, Fe^{2+}, Mg^{2+}, and lesser amounts of Mn^{2+}, where $Zn > (Fe + Mg + Mn)$, and $B = Al^{3+}$ and to a lesser extent Fe^{3+}, has long been used as an empirical exploration guide to ore (e.g., Sheridan and Raymond, 1984), it also occurs in a variety of sulfide-free rock types. Spry and Scott (1986), Heimann et al. (2005), and Spry and Teale (2009) used a ternary diagram, with Zn, Fe, and Mg as components, to identify

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compositional ranges for gahnite in: (1) marble, (2) granitic pegmatites, (3) metabauxites, (4) unaltered and hydrothermally altered Fe–Al-rich metasedimentary and metavolcanic rocks, (5) Al-rich granulites, and (6) metamorphosed massive sulfide deposits. Despite being able to distinguish gahnite compositions associated with sulfide-bearing deposits from those in other rock types, the use of major element composition of gahnite alone has its limitations as an exploration guide because the composition of gahnite in sulfide-rich rocks is indistinguishable from the composition of gahnite in sulfide-poor rocks (O'Brien et al., 2015a,b).

In addition to gahnite occurring in situ in a variety of host rocks, it also occurs in unconsolidated sediments, including beach sands (e.g., Kaye and Mrose, 1965), glacial till (e.g., Morris et al., 1997), soil (e.g., Nachtegaal et al., 2005), and stream sediments (e.g., Crabtree, 2003). Identification of gahnite in the heavy mineral fraction separates of glacial till is facilitated by its green–blue color, high specific gravity (G = 4.55), hardness (8 on Moh's hardness scale), and chemical stability under oxidizing conditions (Hicken et al., 2013b; Morris et al., 1997). Morris et al. (1997) reported gahnite in glacial sediments in northwestern Ontario, where gahnite also occurs in situ in volcanogenic massive sulfide (VMS) (i.e., Mattabi and Geco) and sedimentary exhalative (SEDEX) (i.e., Hurdman Township) deposits, peraluminous granites, and granitic pegmatites. Using major element chemistry, Morris et al. (1997) attempted to determine the provenance of gahnite recovered from glacial sediments. However, gahnite compositions plot within the metamorphosed massive sulfide field of Spry and Scott (1986) in a Zn–Fe–Mg ternary diagram, and are unable to distinguish detrital gahnite derived from VMS deposits from those spatially associated with SEDEX deposits (Morris et al., 1997).

Recent studies by O'Brien et al. (2013, 2015a,b) utilized the trace element composition of gahnite (in conjunction with major elements), measured using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS), as a potential exploration guide to Broken Hill-type (BHT) Pb–Zn–Ag deposits in the Broken Hill domain, Australia. They noted that variability in the trace element composition of gahnite was a function of different physicochemical conditions during gahnite growth, whole-rock geochemistry, pre-metamorphic alteration, and the chemistry of precursor minerals. Like other members of the spinel group (e.g., magnetite and chromite), the trace element chemistry of gahnite is dominated by the first series transition metals (i.e., Ti, V, Cr, Mn, Co, Ni), Ga, and Cd (Dupuis and Beaudoin, 2011; Nadoll et al., 2012; Nehring et al., 2010; Pagé and Barnes, 2009). No trace element compositions of gahnite from other metamorphosed massive sulfide deposits (e.g., SEDEX, VMS, and non-sulfide zinc (NSZ) deposits) have previously been obtained.

The primary objective of this study is to show how a series of compositional discrimination plots, presented as a tree diagram, can be used to distinguish the composition of gahnite among the following deposit types: BHT (i.e., Broken Hill, Australia; Broken Hill, South Africa; Melbourne Rockwell, Australia; and Mutooroo, Australia), VMS (i.e., Mamandur, India; Kvänberget, Sweden; several small Proterozoic Cu–Zn deposits, Colorado (i.e., Bon Ton, Caprock, Cotopaxi, Independence, and Sedalia)), SEDEX (i.e., Angas, Australia; Foster River, Saskatchewan), and NSZ (Sterling Hill, New Jersey) (Fig. 1). We also analyzed gahnite from the Bleikvassli Zn–Pb-(Cu) deposit, Norway, and the Stollberg Zn–Pb–Ag + magnetite deposits, Sweden. It is noted here that some researchers consider Bleikvassli to be a SEDEX deposit (Cook et al., 1998; Lockington et al., 2014; Skauli, 1992, 1993). However, studies by Larsen et al. (1997) and Bjerkgård (1999) suggest the prominent microcline gneiss stratigraphically below the deposit is an alkali syenite, and that Bleikvassli is of the VMS-type. The Stollberg deposits formed as sub-sea floor replacement deposits in volcanic rocks spatially associated with carbonate rocks, and appear to have affinities with VMS deposits (Jansson et al., 2013). The origin of BHT deposits is controversial and several different genetic models have been proposed (see Greenfield, 2003). It has been suggested in the past that they are, for example, metamorphosed SEDEX deposits (e.g., Gustafson and Williams, 1981), but we consider them to be a separate class of deposit based on the classification schemes of Walters (1998), Greenfield (2003), Leach et al. (2005), and Spry et al. (2009). Utilization of the tree diagram developed here can be applied to the composition of detrital gahnite to determine their provenance, or the type of ore deposit from which they were derived. These geochemical fingerprints and the tree diagram will aid in the search for metamorphosed massive sulfide deposits in greenfield and brownfield terranes.

2. Sampling and analytical methods

Samples of gahnite from the Broken Hill (Australia) and Melbourne Rockwell (O'Brien et al., 2015b; Spry, 1978; Spry et al., 2010), Mutooroo

Fig. 1. Global map showing the location of gahnite-bearing deposits examined in this study: 1. Foster River, Saskatchewan; 2. several small Proterozoic Cu–Zn deposits, Colorado (i.e., Bon Ton, Caprock, Cotopaxi, Independence, and Sedalia); 3. Sterling Hill, New Jersey; 4. Bleikvassli, Norway; 5. Stollberg, Sweden; 6. Kvänberget, Sweden; 7. Broken Hill, South Africa; 8. Mamandur, India; 9. Mutooroo, Australia; 10. Angas, Australia; 11. Broken Hill, Australia; 12. Melbourne Rockwell, Australia.