

Major and trace element chemistry of gahnite in metamorphosed massive sulphide deposits: discrimination diagrams to determine provenance

Joshua J. O'Brien^{1*}, Paul G. Spry¹, Graham S. Teale², Simon Jackson³ & Dean Rogers⁴

¹Department of Geological and Atmospheric Sciences, 253 Science I, Iowa State University, Ames, Iowa, USA 50011-3212

²Teale and Associates, P.O. Box 740, North Adelaide, South Australia 5006, Australia

³Natural Resources Canada, Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario, Canada K1A 0E8

⁴Perilya Limited, P.O. Box 5001, Broken Hill, New South Wales 2880, Australia

(*e-mail: jjobrien@iastate.edu)

Zincian spinel, or gahnite (ZnAl_2O_4), occurs in and around a variety of metamorphosed massive sulphide deposits, including Broken Hill-type (BHT) Pb-Zn-Ag, volcanogenic massive sulphide (VMS) Cu-Zn-Pb, and sedimentary exhalative (Sedex) Pb-Zn deposits. The empirical association of gahnite-rich rocks with ores of this type has been recognized as a potential exploration guide by several workers (e.g. Sheridan & Raymond 1984), and has previously led mining companies to target gahnite-rich rocks with expensive drilling programs, which have led to mixed success in ore discoveries. Efforts to distinguish gahnite in prospective or sulphide-rich rocks, from comparatively sulphide-poor ones, have focused on evaluating the major element chemistry of gahnite as a targeted exploration guide (e.g. Spry & Scott 1986; Heimann *et al.* 2005; Spry & Teale 2009). However, O'Brien *et al.* (2012) conducted the first trace element study of gahnite (measured using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS)), and proposed that the major-trace element chemistry of gahnite constitutes an exploration guide to high-grade Broken Hill-type Pb-Zn-Ag mineralization, in the Broken Hill domain, Australia. Although great attention had been paid to determining the variability of gahnite chemistry within a single ore field (i.e. the Broken Hill domain), little has been done to characterize the trace element chemistry of gahnite from various types of ore deposits.

The composition of gahnite from various ore fields and deposit types will provide insight into the natural range of gahnite chemistry. Within the past decade, advances in analytical equipment have improved the ability of geoscientists to measure in situ concentrations of trace elements. Studies requiring high-precision, in situ measurements of trace elements have benefitted from wider availability and increased use of LA-ICP-MS and electron probe microanalyzers (EPMA). Laser ablation-ICP-MS facilitates the measurement of many elements (e.g. concentrations of 52 elements were measured in gahnite by O'Brien *et al.* (2012)) at low concentrations (i.e. parts per billion) (e.g. Jackson *et al.* 1992).

Using trace element compositions of magnetite, Dupuis & Beaudoin (2011) developed a series of discrimination diagrams to identify compositional differences among magnetite originating from various types of ore deposits. Like magnetite, gahnite is an indicator mineral that is resistant to erosion and weathering due to its physicochemical properties (McClenaghan 2005). Therefore, detrital gahnite can be transported, and has been found to persist in a variety of unconsolidated sediments, which include glacial till (e.g. Morris *et al.* 1997), beach sands (e.g. Kaye & Mrose 1965), soil (e.g.

Nachtegaal *et al.* 2005), and stream sediments (e.g. Crabtree 2003). Using previously developed discrimination plots, the major-trace element chemistry of detrital gahnite may be used by explorationists conducting restite mineral studies to determine its provenance, deposit type, and aid in the location and discovery of metamorphosed massive sulphide deposits in greenfield and brownfield terranes.

The major-trace element chemistry of gahnite in Broken Hill-type deposits (i.e. Broken Hill, Australia; Broken Hill, South Africa; Melbourne Rockwell, Australia; and Mutooroo, Australia), volcanogenic massive sulphide deposits (i.e. Bleikvassli, Norway; Mamandur, India; Moskosel, Stollberg, Sweden; several small Proterozoic Cu-Zn deposits, Colorado (i.e. Bon Ton, Caprock, Cotopaxi, Independence, and Sedalia)), and sedimentary exhalative deposits (i.e. Angas, Australia; Foster River, Saskatchewan) is used to determine the range in trace element compositions of gahnite in metamorphosed ore deposits and to develop a series of discrimination diagrams that can be used to distinguish among gahnite in BHT, Sedex, and VMS deposits.

METHODS

Major element compositions of gahnite (MgO , Al_2O_3 , SiO_2 , TiO_2 , MnO , FeO , ZnO) were measured using EPMA at the University of Minnesota, operated with an accelerating voltage of 15 kV, a beam current of 20 nA, and a spot size of 1–2 μm , and using a range of mineral standards including gahnite (Zn, Al), pyrope (Si, Mg), hornblende (Ti), ilmenite (Fe), and spessartine (Mn). The beam time for background and peaks were 10 seconds each.

Concentrations of 52 elements were measured at the Geological Survey of Canada using a LA-ICP-MS, with a Photon Machines "Analyte 193" excimer (Ar-F) laser that has a UV wavelength of 193 nm, which undergoes a high degree of absorption by most minerals. This instrument was connected to an Agilent 7700 Series ICP-MS with a second rotary pump that doubles instrument sensitivity. Data reduction was performed using the computer program GLITTER!, which allowed for the integration of inclusion-free analyses through visual recognition of anomalous peaks from time resolved graphical profiles of the data (Van Achterberg 2001).

GAHNITE CHEMISTRY

Major element compositions of gahnite. The major element chemistry of gahnite (AB_2O_4) comprises varying proportions

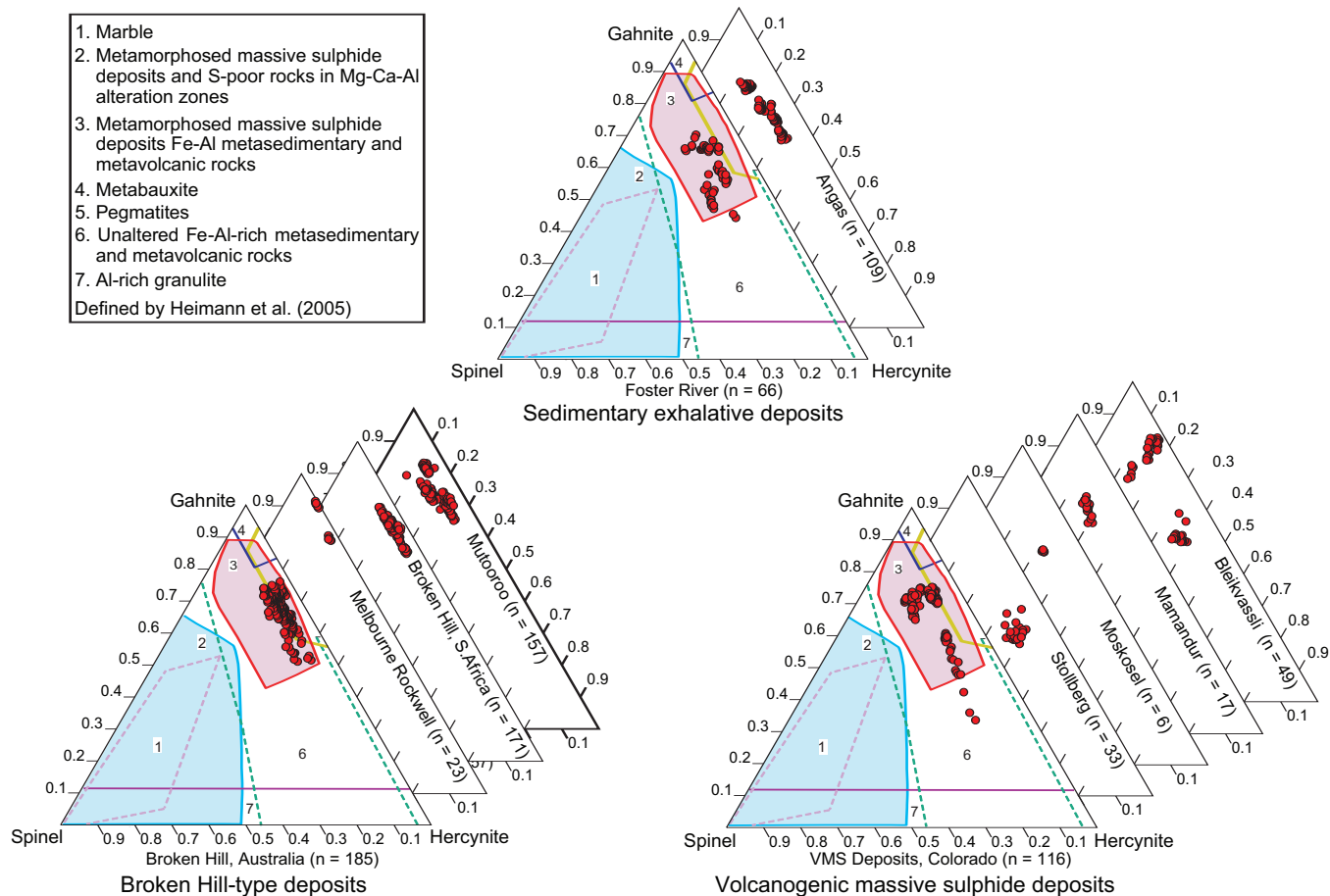


Fig. 1. Ternary plots of gahnite compositions from various ore fields grouped by deposit type, in terms of the gahnite(Zn)-hercynite(Fe)-spinel sensu stricto (Mg) spinel end members. Numbers correspond to compositional ranges of gahnite from different geological settings defined by Heimann *et al.* (2005). The number of analyses obtained from each location is given in brackets.

of Zn^{2+} , Fe^{2+} , Mg^{2+} and lesser amounts of Mn^{2+} in the tetrahedral site (A) with Al^{3+} and to a lesser extent Fe^{3+} in the octahedral site (B). Using the same components as Spry & Scott (1986) and Heimann *et al.* (2005) (i.e. gahnite ($ZnAl_2O_4$), hercynite ($FeAl_2O_4$), and spinel sensu stricto ($MgAl_2O_4$)), relative proportions of Zn, Fe, and Mg for each analysis are presented here in a series of ternary plots (Fig. 1). For the purposes of comparison, separate plots were created for each deposit type and overlain by compositional fields of gahnite from different geological settings (identified by Heimann *et al.* 2005). Gahnite mostly plots within the field for metamorphosed massive sulphide deposits hosted by hydrothermally altered Fe–Al-rich metasedimentary and metavolcanic rocks (gahnite_{45–85}hercynite_{15–45}spinel_{0–20}). However, some gahnite from the Foster River and Colorado Cu–Zn deposits contain a higher proportion of Fe, and plot within the field of unaltered Fe–Al-rich metasedimentary and metavolcanic rocks. Gahnite in VMS deposits and Sedex deposits mostly contains a higher Mg content than gahnite from BHT deposits.

Different physicochemical conditions (e.g. fO_2 , fS_2 , temperature, pressure, and host rock composition) affect the major element chemistry of gahnite in sulphide-bearing rocks (e.g. Spry *et al.* 1986; Heimann *et al.* 2005). Experiments by Spry *et al.* (1986) showed that the composition of zincian spinel in the gahnite–hercynite solid solution is strongly dependent upon fS_2 and fO_2 , which is dictated by the a_{FeS} content of Fe-bearing sulphides (i.e. sphalerite, pyrite, and pyrrhotite) that coexist

with gahnite. For the broad range of metamorphic conditions (the upper greenschist to the granulite facies) at which gahnite is stable, the composition of gahnite in the gahnite–hercynite solid solution is buffered and fixed (i.e. ~65–85 mole % $ZnAl_2O_4$) by coexisting Fe-bearing sulphides (Spry & Scott, 1986).

Because the gahnite:hercynite ratio is buffered by the presence of these sulphides, the major element chemistry of gahnite can be used to determine whether or not sulphides were present during gahnite formation. The abundance of pyrrhotite, sphalerite, and pyrite must comprise more than ~1 volume % for the composition of gahnite to be buffered by Fe-sulphides in the host rock (Spry & Teale 2009) and produce a characteristic major element composition (i.e. gahnite_{45–85}hercynite_{15–45}spinel_{0–20}) for gahnite in sulphide-bearing assemblages, which may contain as little as 1 to 3 volume % sulphides. Therefore, major element chemistry may serve as a first-order indicator of whether or not detrital gahnite originally coexisted with sulphides. However, this diagnostic compositional range is not indicative of the modal percentage of sulphides present and is, therefore, incapable of distinguishing sulphide-poor from sulphide-rich rocks.

Trace element chemistry of gahnite

Like other members of the spinel group (e.g. magnetite and chromite), the trace element chemistry of gahnite is dominated

Table 1. Compositions of gahnite from different types of metamorphosed ore deposits measured by LA-ICP-MS.

Trace Elements (ppm)		Ti	V	Cr	Mn	Co	Ni	Ga	Cd	
Sedimentary Exhalative Deposits	Angas n = 10	Min.	1	58	30	1841	8	1	62	2
		Max.	4	114	464	3067	17	3	173	5
		Med.	2	87	253	2268	9	1	92	3
		Mean	2	84	219	2346	11	2	108	3
	Foster River n = 53	Min.	3	27	2	3124	19	1	94	1
		Max.	29	131	692	12276	130	17	571	6
		Med.	10	57	25	4776	42	3	188	3
		Mean	12	65	70	5675	55	4	255	3
Broken Hill-type Deposits	Broken Hill Australia n = 95	Min.	1	15	1	481	12	0	111	1
		Max.	161	706	403	3119	145	30	425	13
		Med.	56	160	55	1001	57	4	247	4
		Mean	60	173	107	1199	59	7	252	4
	Broken Hill S. Africa n = 56	Min.	6	10	0	3429	19	2	76	1
		Max.	52	378	741	6106	112	11	244	6
		Med.	14	62	11	4122	61	4	135	3
		Mean	18	109	124	4437	59	4	137	3
	Melbourne Rockwell n = 19	Min.	9	149	40	1518	45	25	62	3
		Max.	47	195	186	2486	73	48	105	16
		Med.	18	176	117	2072	67	30	80	7
		Mean	22	177	110	2049	64	34	85	8
Mutooroo n = 54	Min.	1	45	1	370	39	1	84	2	
	Max.	43	194	490	1687	109	28	167	12	
	Med.	3	133	7	840	65	7	109	5	
	Mean	11	118	65	928	64	11	113	5	
Volcanogenic Massive Sulphide Deposits	Bleikvassli n = 19	Min.	1	3	1	558	1	0	94	2
		Max.	17	9	23	1621	20	3	168	10
		Med.	5	6	3	1074	8	1	108	4
		Mean	6	5	6	1107	8	1	113	5
	Colorado Cu-Zn Deposits n = 72	Min.	1	1	0	318	7	0	109	1
		Max.	102	144	257	6749	114	10	1275	11
		Med.	9	38	4	2045	31	4	182	5
		Mean	17	51	35	2651	33	5	316	5
	Mamandur n = 34	Min.	15	15	1	1800	14	42	124	2
		Max.	77	112	31	3745	22	62	249	11
		Med.	26	28	3	2464	17	53	141	3
		Mean	31	43	5	2639	17	51	174	4
Moskosel n = 3	Min.	2	0	0	391	2	1	292	4	
	Max.	1	1	0	462	3	1	441	5	
	Med.	2	1	0	431	2	1	419	5	
	Mean	2	1	0	428	2	1	384	5	
Stollberg n = 10	Min.	8	1	2	779	2	1	114	1	
	Max.	15	3	6	1243	3	1	169	2	
	Med.	9	1	4	1028	2	1	144	1	
	Mean	10	2	4	1022	2	1	144	1	

by the first series transition metals (i.e. Ti, V, Cr, Mn, Co, Ni), Ga, and Cd (Pagé & Barnes 2009; Nehring *et al.* 2010; Dupuis & Beaudoin 2011; Nadoll *et al.* 2012). Unlike major element chemistry, little is known about the factors controlling the trace element chemistry of gahnite. However, concentrations of trace elements in gahnite likely depend upon several factors, which include bulk rock chemistry, the partitioning of elements between gahnite and other minerals in the matrix, temperature, pressure, fO_2 , fS_2 , fH_2O , crystal-chemical controls (i.e. the major element chemistry), and the composition of precursor minerals (e.g. sphalerite, garnet, pyrrhotite).

The minimum, maximum, median, and mean trace element compositions of gahnite from each deposit are reported in Table 1, which allows for comparison among deposits within

each deposit type. Compositions of gahnite in Sedex deposits contain similar concentrations of V, Ni, and Cd. Gahnite in the Foster River Zn deposit contain more Ti, Co, Ga, Mn, and lesser amounts of Cr than gahnite in the Angas Zn-Pb-Ag deposit, which are among the most Cr-rich in this study.

Gahnite in different BHT Pb-Zn-Ag deposits contain similar concentrations of V, Cr, Co, and Cd. Concentrations of Ga and Ti are higher in gahnite from Broken Hill (Australia), than in gahnite from Broken Hill (South Africa), Melbourne Rockwell, and Mutooroo; whereas elevated Ni content distinguishes gahnite from Melbourne Rockwell from the other three deposits. Gahnite in the Broken Hill deposit (South Africa) contains the highest concentration of Mn for gahnite in BHT deposits.

Gahnite in different VMS deposits contains similar amounts of Cd, but the concentrations of other trace elements are variable and not as uniform as those in Sedex and BHT deposits. With the exception of gahnite in the Independence Cu-Zn deposit in Colorado, which contains 2 to 257 ppm Cr, the Cr content of gahnite in VMS deposits is generally less than 30 ppm. Vanadium, Co, and, to a lesser extent, Mn occur in comparatively lower concentrations (less than 3 ppm, 20 ppm, and 1621 ppm, respectively) in gahnite in the Bleikvassli, Moskosel, and Stollberg deposits than in gahnite from the Mamandur deposit and some Cu-Zn deposits in Colorado. Gahnite from the Mamandur deposit contains the highest Ti content among VMS deposits, and the highest amount of Ni in gahnite measured in this study. With exception of this deposit, gahnite in other VMS deposits contains comparable concentrations of Ni and Ti. The Ga content of gahnite in the Moskosel deposit is among the highest measured in this study.

Gahnite in BHT deposits generally contains similar amounts of Mn and Cd, more Ti, V, Co, Ga, Ni, and less Cr than gahnite in Sedex deposits, and similar amounts of Ni and Cd, more Ti (with the exception of some Colorado Cu-Zn deposits and Mamandur), V, Cr, Co, and less Mn, and Ga than gahnite in VMS deposits. Gahnite in Sedex deposits generally contains similar quantities of Cd, less Mn, Ni, and Ga, and more Ti, V, Cr, and Co (with the exception of Mamandur and some Cu-Zn deposits in Colorado) than gahnite in VMS deposits.

DISCRIMINATION DIAGRAMS

A series of discrimination plots were created to demonstrate variability in gahnite chemistry for the three types of metamorphosed massive sulphide deposits, to identify specific combinations of elements that can be used as discriminators to these ore types, and to compositionally fingerprint detrital gahnite (Fig. 2).

A scatter plot of Mg (ppm) versus V (ppm) shows that gahnite in BHT deposits contain less Mg and comparable to slightly higher V contents than that in VMS and Sedex deposits (Fig. 2). Because the spinel *sensu stricto* component does not take part in gahnite-forming desulphidation reactions, its MgO content is generally related to the bulk MgO composition of the host rocks (i.e. Sedex and VMS host rocks are generally more MgO-rich relative to the host rocks of BHT deposits; Heimann *et al.* 2005).

A bivariate plot of Co (ppm) versus V (ppm) shows that the composition of gahnite in BHT and Sedex deposits can be distinguished from the composition of gahnite in VMS deposits,

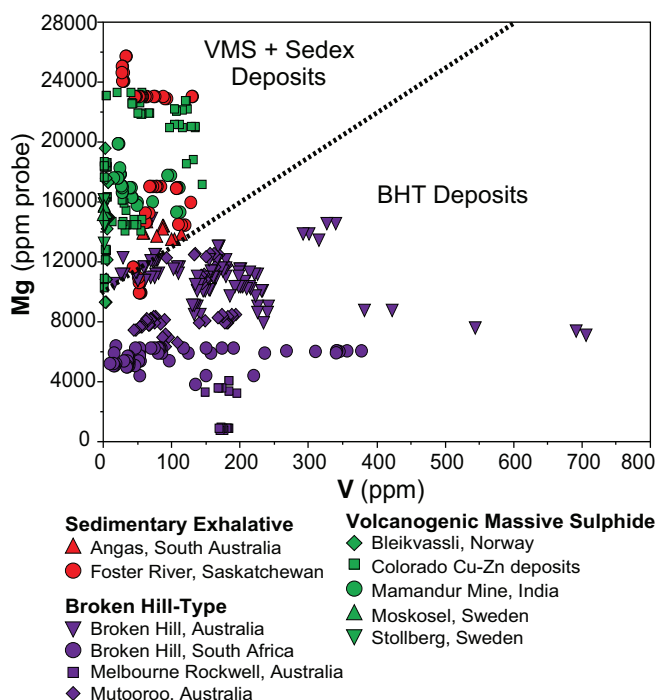


Fig. 2. Bivariate plot of Mg versus V for gahnite from different deposit types, which include sedimentary exhalative (Sedex) Pb-Zn-Ag deposits (Angas, South Australia; Foster River, Saskatchewan), volcanogenic massive sulphide (VMS) Cu-Zn-Pb deposits (Cotopaxi, Sedalia, Cinderella, Bon Ton, and Independence, Colorado; Bleikvassli, Norway; Mamandur, India; Moskosel and Stollberg, Sweden), and Broken Hill-type deposits (BHT) (Broken Hill, Australia; Broken Hill, South Africa; Mutooroo and Melbourne Rockwell, Australia). Note that gahnite from BHT deposits can be distinguished from those in Sedex and VMS deposits, which mostly overlap.

which mostly contain less than 30 ppm Co and 140 ppm V (Fig. 3). Exceptions include Co- and V-rich gahnite from some Colorado Cu-Zn deposits (i.e. Bonton, Cotopaxi, Independence, and Sedalia). The compositions of some gahnite from the Angas and Foster River deposits overlap the compositional field identified for gahnite in VMS deposits in Figure 3.

Gahnite in BHT deposits are excluded from Figures 4 (Mn versus Ti) and 5 (Co versus Ti) for two reasons: (1) because the composition of gahnite in BHT deposits are easily distinguished from gahnite in the other two classes of metamorphosed sulphide deposits using Figure 2; and (2) to highlight compositional differences between gahnite in Sedex and VMS deposits. Gahnite in Sedex deposits generally contains more Mn, but less Ti than most gahnite in VMS deposits (Fig. 4). However, gahnite in some Colorado Cu-Zn deposits plot within the Sedex field; moreover, the Mn content of gahnite in the Angas deposit and in some gahnite from the Foster River deposit overlaps with gahnite in VMS deposits. The Co content of gahnite in Sedex deposits is higher than that for gahnite in VMS deposits, which, when plotted against Ti, allows them to be distinguished from each other (Fig. 5).

CONCLUSIONS

- 1) The trace element chemistry of gahnite in VMS, Sedex, and BHT deposits is dominated by Ti, V, Cr, Mn, Co, Ni, Ga, and Cd.

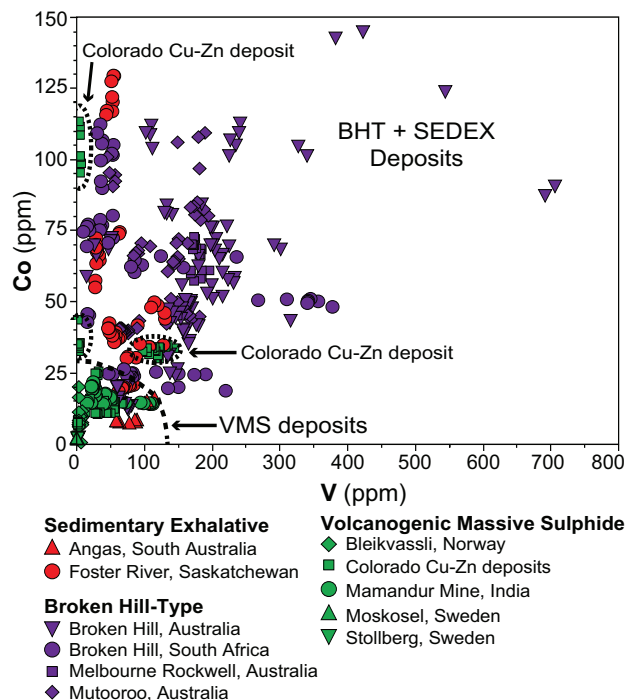


Fig. 3. Bivariate plot (Co versus V) of gahnite from BHT, VMS, and Sedex deposits. Note gahnite from the Stollberg, Bleikvassli, Moskosel, and Mamandur deposits mostly contain less than 30 ppm Co and 140 ppm V, where as those from the Colorado Cu-Zn deposits are comparatively enriched in these elements and overlap with gahnite from BHT and Sedex deposits.

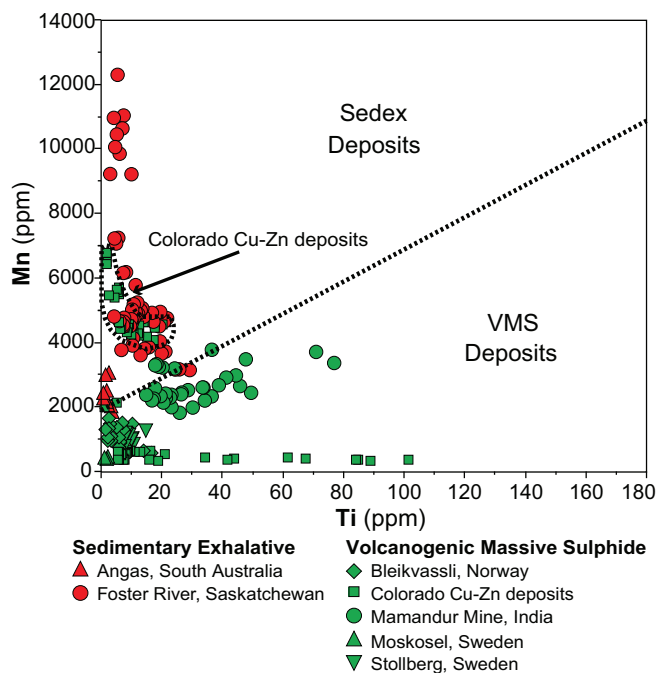


Fig. 4. Bivariate plot (Mn versus Ti) of gahnite from Sedex and BHT deposits. Compositional fields identified for gahnite in Sedex deposits and gahnite in VMS deposits are denoted by a dashed line. Note gahnite in Sedex deposits mostly contains higher Mn and lower Ti contents than gahnite in VMS deposits. Compositions of gahnite in Sedex deposits are overlapped by gahnite in the Colorado Cu-Zn deposits.

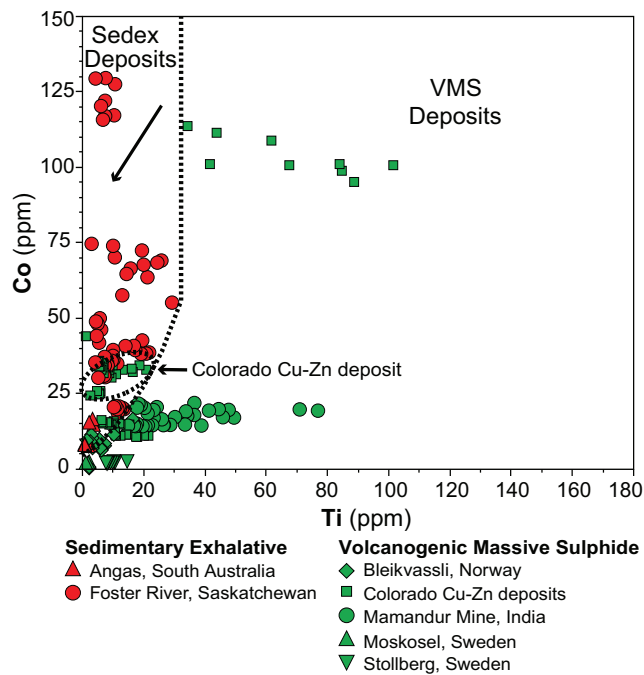


Fig. 5. Bivariate plot (Co versus Ti) of gahnite from Sedex and BHT deposits. Compositional fields identified for gahnite in Sedex deposits and gahnite in VMS deposits are denoted by a dashed line. Note gahnite in Sedex deposits mostly contains higher Co and lower Ti contents than gahnite in VMS deposits. Compositions of gahnite in Sedex deposits are overlapped by gahnite from the Colorado Cu-Zn deposits.

- 2) Gahnite in BHT deposits contains similar amounts of Mn and Cd, higher Ti, V, Co, Ni, and Ga content, and less Cr than gahnite in Sedex deposits, and similar amounts of Ni and Cd, more V, Cr, Co, and less Mn and Ga than gahnite in VMS deposits.
- 3) Gahnite grains in Sedex deposits contain similar amounts of Cd, less Mn, Ni, and Ga, and more V, Cr, and Co than gahnite in VMS deposits.
- 4) Trace element compositions of gahnite in VMS deposits are variable. Gahnite from Bleikvassli, Moskosel, and Stollberg contains lower V, Co, and Mn contents than that from the Mamandur deposit and some of the Colorado Cu-Zn deposits and gahnite in Sedex and BHT deposits; whereas, the compositions of gahnite in Mamandur and some of the Colorado Cu-Zn deposits partially overlap the other two deposit types (BHT and Sedex). Gahnite in BHT deposits can be distinguished from that in Sedex and VMS deposits based on a plot of Mg (ppm) versus V (ppm); whereas, the composition of gahnite in Sedex deposits is distinct from that in VMS deposits on the basis of plots of

Co versus V, Mn versus Ti, and Co versus Ti.

- 5) The major and trace element composition of gahnite can be used as an exploration guide to metamorphosed massive sulphide deposits in productive ore camps and in greenfield terranes where it occurs as a resistate mineral in unconsolidated sediments.

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