ZINCIAN SPINEL ASSOCIATED WITH METAMORPHOSED PROTEROZOIC BASE-METAL SULFIDE OCCURRENCES, COLORADO: A RE-EVALUATION OF GAHNITE COMPOSITION AS A GUIDE IN EXPLORATION

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Abstract

Zincian spinel [$(Zn,Fe,Mg)Al_2O_4$] is an accessory mineral in a variety of rock types, in particular, metamorphosed massive-sulfide deposits, pegmatites, aluminous metasedimentary rocks, skarns, marbles, and sulfide-bearing granulites. Textural and compositional studies of zincian spinel in thirteen Proterozoic sulfide deposits metamorphosed to the amphibolite and granulite facies in Colorado, many of which are spatially associated with Mg-rich alteration zones, shed new light on the use of zincian spinel composition as a guide to sulfide ores. Zincian spinel from the Independence, Bon Ton, and Sedalia deposits and some cases from the Green Mountain, Betty, Caprock, Cinderella, and Cotopaxi deposits show compositions that correspond to zincian spinel associated with metamorphosed massive-sulfide deposits hosted by hydrothermally altered Fe–Al-rich metasedimentary and metavolcanic rock units elsewhere in the world ($Gahnite_{44–90}Hercynite_{0–45}Spinel_{0–25}$). However, other compositions of zincian spinel from these last five deposits and from three locations in the Wet Mountains (Marion and Amethyst prospects and an unnamed prospect) are depleted in Zn and enriched in Mg and Fe. These examples of Mg-rich zincian spinel occur in rocks in or adjacent to metamorphosed massive sulfides dominated by Mg-rich minerals such as phlogopite, anthophyllite, gedrite, tremolite, forsterite, cummingtonite, sapphirine, cordierite, enstatite, and clinohumite. The composition of zincian spinel in and surrounding metamorphosed massive-sulfide deposits is influenced by reactions involving Zn and Fe sulfides, as well as by bulk-rock composition, which in the case of many metamorphosed massive-sulfide deposits in Mg-rich alteration zones in Colorado, causes a marked enrichment in the spinel component of zincian spinel, to $Gahnite_{0–65}Hercynite_{0–50}Spinel_{25–90}$. Knowledge of the geological setting must be considered when using zincian spinel as a guide to metamorphosed massive-sulfide deposits.

Keywords: gahnite, exploration guide, massive sulfides, magnesium enrichment, Colorado.

Sommaire

Le spinelle zincifère [$(Zn,Fe,Mg)Al_2O_4$] est un accessoire dans une grande variété de roches, mais en particulier dans les gisements de sulfures massifs métamorphisés, les pegmatites, les roches métasédimentaires alumineuses, les skarns, les marbres, et les granulites porteuses de sulfures. Les études texturales et compositionnelles du spinelle zincifère de treize gisements de sulfures protérozoïques au Colorado qui ont atteint le faciès amphibolite ou granulite, et dans plusieurs cas associés à des zones d'altération magnésiennes, révèlent de l'information nouvelle à propos de l'utilisation de la composition du spinelle zincifère comme indicateur de minéralisation. Le spinelle zincifère des gisements Independence, Bon Ton, et Sedalia, et certains échantillons des gisements de Green Mountain, Betty, Caprock, Cinderella, et Cotopaxi, ont des compositions qui correspondent au spinelle zincifère associé aux gisements de sulfures massifs métamorphisés et encaissés dans un hôte métasédimentaire et métavolcanique hydrothermalement altéré en roche riche en Fe et Al ailleurs ($Gahnite_{44–90}Hercynite_{0–45}Spinelle_{0–25}$). Toutefois, d'autres compositions de spinelle zincifère, provenant des cinq derniers gisements et de trois endroits dans la région des montagnes Wet (les indices Marion et Amethyst et un indice sans nom) sont pauvres en Zn et enrichis en Mg et Fe. Ces exemples de spinelle zincifère relativement magnésien se trouvent dans ou près de sulfures massifs métamorphisés, dans des asemblages à dominance de minéraux magnésiens, comme phlogopite, anthophyllite, gédrite, trémolite, forstérite, cummingtonite, sapphirine, cordiérite, enstatite, et clinohumite. La composition du spinelle zincifère dans et autour des gisements de sulfures massifs métamorphisés serait influencée par des réactions impliquant les sulfures de Zn et de Fe, de même que par la composition globale des roches. Dans ces cas au Colorado, le milieu magnésien a causé un enrichissement marqué en teneur de spinelle (*sensu stricto*) du spinelle

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zincifère: Gahnite$_{0-65}$Hercynite$_{0-50}$Spinelle$_{25-90}$. Il est donc clair qu'une connaissance du contexte géologique est essentielle dans l'utilisation de la composition du spinelle zincifère comme indicateur de minéralisation dans les gîtes de sulfures massifs métamorphisés.

(Traduit par la Rédaction)

Keywords: gahnite, guide en exploration minérale, sulfures massifs, enrichissement en magnésium, Colorado.

INTRODUCTION

Zincian spinel [(Zn,Fe,Mg)Al$_2$O$_4$] occurs in various geological settings and rock types, but is most common in and surrounding metamorphosed massive sulfide deposits; it is also known to occur in aluminous metasedimentary rocks and granitic pegmatites (Spry & Scott 1986a). Textural, experimental, and thermodynamic studies suggest that zincian spinel can form in multiple ways, including (1) metamorphism of Zn-oxide phases (Segnit 1961), (2) desulfidation of sphalerite during metamorphism (Spry & Scott 1986a, b, Spry 2000), (3) precipitation from a metamorphic-hydrothermal solution (Wall 1977), and (4) breakdown of zinc-bearing silicates such as staurolite (Stoddard 1979) and biotite (Atkin 1978) during metamorphism.

In view of the spatial relationship between zincian spinel and metamorphosed volcanogenic base-metal sulfide mineralization, and based on compositional considerations, zincian spinel has been proposed as a potential exploration guide in the search for ores of this type (Sandhaus & Craig 1982, Ririe & Foster 1984, Sheridan & Raymond 1984, Spry & Scott 1986a, b, Spry 2000, Spry *et al.* 2000, Walters 2001, Walters *et al.* 2002). The importance of this relationship is demonstrated by the spatial association of zincian spinel with some of the world's largest massive sulfide deposits, including Broken Hill and Cannington (Australia), and Aggeneys (Namaqualand, South Africa), as well as with many other smaller base-metal sulfide occurrences in, for example, the Appalachian and Scandinavian Caledonides (Spry & Scott 1986b), the Linda deposit, Canada (Zaleski *et al.* 1991), and the Mamandur deposit, India (Chattopadhyay 1999).

The present contribution, which involves a mineralogical and petrological study of zincian-spinel-bearing rocks in Colorado, was prompted by (1) the widespread distribution of zincian spinel in the Proterozoic terrane of central-northern Colorado, which is second in regional extent only to the well-known zincian spinel horizons in the Broken Hill Domain of the Curnamona Province, Australia (*e.g.,* Barnes *et al.* 1983, Plimer 1984), (2) the potential of zincian spinel as an exploration guide to massive sulfides, and (3) puzzling occurrences of zincian spinel from three massive sulfide occurrences in Colorado, the Cotopaxi and the Betty deposits (Salotti 1965, Spry & Scott 1986a) and an unnamed base-metal prospect near Round Mountain (Spry & Scott 1986a), enriched in Mg and outside the compositional field previously ascribed to zincian spinel spatially associated with metamorphosed massive sulfides by Spry & Scott (1986a).

The present study serves to complement the preliminary petrological studies of Sheridan & Raymond (1977, 1984) and the compositional data of Eckel *et al.* (1997), who analyzed zincian spinel from 22 locations in Colorado, by providing new petrological information and compositions of zincian spinel and coexisting minerals in twelve massive sulfide deposits and in gedrite–cordierite rocks near the town of Evergreen. The major objective of this contribution is to re-evaluate the use of major-element compositions (Zn, Fe, and Mg) of zincian spinel as an exploration guide to base-metal ore deposits in metamorphic terranes in the light of the composition of spinels obtained here from the thirteen sites in Colorado, the unusual compositions of zincian spinel in Colorado ores reported previously by Spry & Scott (1986a), and an updated review of the compositions of zincian spinel that have appeared in the literature since their study. To avoid confusion with terminology, the term "zincian spinel" is used here as a general term for aluminous spinels containing Zn, Fe, and Mg in the tetrahedral site, whereas *gahnite*, *hercynite*, and *spinel* refer to zinc-bearing spinels dominated by the ZnAl$_2$O$_4$, FeAl$_2$O$_4$, and MgAl$_2$O$_4$ components, respectively.

PREVIOUS STUDIES OF ZINCIAN SPINEL IN COLORADO

Studies of zincian spinel in Colorado are limited in number (Lindgren 1908, Salotti 1965, Boardman 1971, Sheridan & Raymond 1977, 1984, Raymond *et al.* 1980, Knight 1981, Ririe 1981, Eckel *et al.* 1997). Sheridan & Raymond (1977, 1984) determined the distribution, petrological setting, and bulk-rock composition of zincian-spinel-bearing rocks throughout Colorado. In a companion study, Raymond *et al.* (1980) described the rare association of zincian spinel with sapphirine and corundum in the Wet Mountains. Gahnite was reported in the Sedalia, Turret, Independence, and Ace High and Jackpot deposits by Boardman (1971), and in the Sedalia and Bon Ton deposits by Knight (1981), but no petrological or mineralogical studies were undertaken. However, Ririe (1981) described gahnite in the Green Mountain and Cotopaxi deposits and the Grape Creek district near Canyon City and noted the intimate association between gahnite and sphalerite and the possibility that gahnite formed by desulfidation of sphalerite. The remaining studies of zincian spinel in Colorado

have been restricted to reports of the compositions of zincian spinel at various locations. Salotti (1965) analyzed magnesian gahnite from the Cotopaxi deposit, whereas Ririe & Foster (1984) noted that the Zn:Fe ratio of gahnite in sillimanite-bearing gneisses increases with proximity to the Cotopaxi deposit and suggested that this ratio could be used as an exploration guide to ore elsewhere.

REGIONAL GEOLOGY

The regional geology of the Rocky Mountains in central and northern Colorado was described by Tweto & Sims (1963), Moench (1964), Hedge *et al.* (1967, 1968), Peterman *et al.* (1968), Hawley & Wobus (1977), and Tweto (1977); in addition, Karlstrom (1998b, 1999)

edited issues of *Rocky Mountain Geology* focused on the lithospheric structure and evolution of the Rocky Mountains, and Frost (1999, 2000) edited issues focused on Proterozoic magmatism of the Rocky Mountains and environs.

The area that contains the zincian-spinel-bearing metamorphosed massive sulfides occurs in a sequence of Proterozoic metasedimentary and metavolcanic rocks that extends from the Wet Mountains, in the south, to the Independence Mountains, near the Colorado–Wyoming border (Fig. 1). Several geochronological techniques applied to these rocks (Shaw & Karlstrom 1999) yielded ages of formation of ~1.8 Ga (Tweto 1980), whereas the main period of deformation and metamorphism occurred at ~1,775 to 1,700 Ma (Hedge *et al.* 1967, 1968). This initial phase of deformation in the
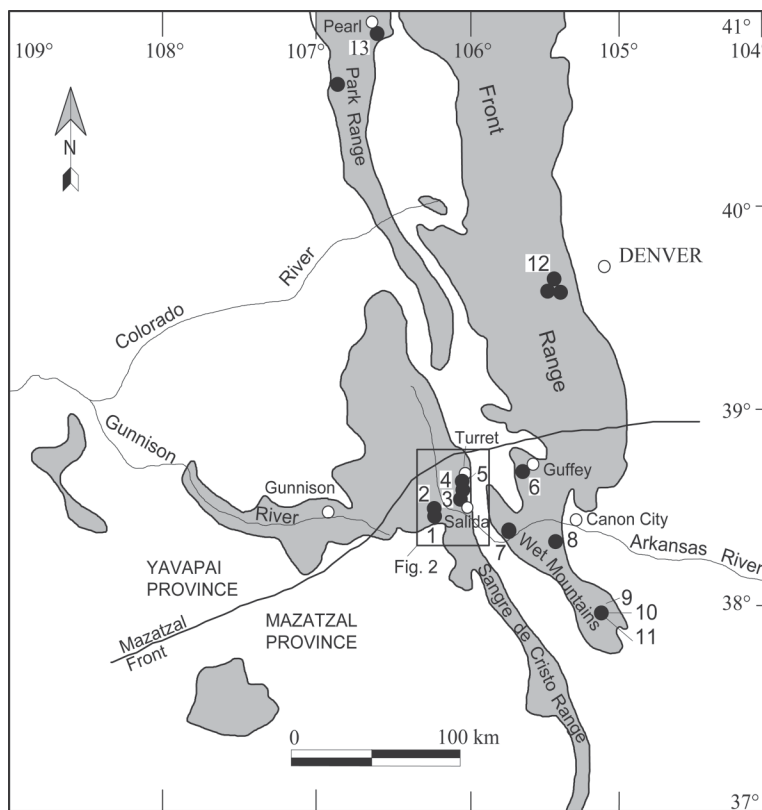

FIG. 1.   General map of western Colorado showing the extent of Proterozoic rocks (grey shaded pattern; after Sheridan & Raymond 1984), terrane boundaries (after Shaw & Karlstrom 1999), and the zincian spinel localities. 1: Bon Ton deposit, 2: Cinderella deposit, 3: Sedalia deposit, 4: Ace High – Jackpot deposit, 5: Independence deposit, 6: Betty (Lone Chimney) deposit, 7: Green Mountain deposit, 8: Cotopaxi deposit, 9: Marion deposit, 10: Amethyst prospect, 11: Unnamed prospect, 12: Evergreen zone of hydrothermal alteration, 13: Caprock deposit. MF: Mazatzal Deformation Front (Shaw & Karlstrom 1999). The area covered by Figure 2 is shown as an inset.

southern part of the study area is characterized by iso-clinal folds, whereas the second and third episodes of deformation are characterized by the development of large open folds. The major structures developed during the Proterozoic are northwest- to north-trending.

Recent tectonic studies by Shaw & Karlstrom (1999) of the southern Rocky Mountains suggest that the study area lies near the boundary of two northeast-oriented Proterozoic tectonic provinces: the Yavapai Province composed of 1.7–1.8 Ga juvenile volcanic-arc crust in the north, and the Mazatzal Province, consisting of 1.7–1.6 Ga crust to the south (Condie 1982, Benett & DePaolo 1987, Karlstrom 1998a, b, Karlstrom & Humphreys 1998). The boundary between the two provinces consists of a zone ~300 km wide oriented northeast, although there is considerable uncertainty concerning the exact location of this zone (Shaw & Karlstrom 1999, Karlstrom 1998a, b, Karlstrom & Humphreys 1998). If we accept the approximate location of the Yavapai–Mazatal crustal boundary of Shaw & Karlstrom (1999), the Caprock deposit and the Evergreen hydrothermal zone are located in the Yavapai Province, whereas all the other deposits occur in the transition zone close to the northern limit of the boundary zone (Fig. 1).

A considerable volume of granitic rocks was emplaced in the study area from 1.75 Ga to 1.00 Ga during three episodes. Syntectonic magmatism is represented by SHRIMP U–Pb zircon ages of 1714 ± 5 Ma for the Boulder Creek intrusion (Premo & Fanning 2000), whereas two later episodes of magmatism are associated with the Silver Plume and related intrusions (1.45 Ga; Peterman *et al.* 1968) and the Pikes Peak intrusion (1.0 Ga; Hedge 1970).

GEOLOGY OF ZINCIAN SPINEL LOCATIONS AND THE ORIGIN OF MASSIVE SULFIDE DEPOSITS IN COLORADO

Zincian spinel occurs in and adjacent to more than twenty occurrences of Proterozoic Cu–Zn sulfides in central and northern Colorado (Figs. 1, 2). Although most of the sulfide deposits were mined between 1880 and 1900, the Betty (Lone Chimney) deposit was mined during the 1950s. All sulfide deposits are considered small, with the largest being the Sedalia mine, which contained about 1.2 million tonnes of ore at 3.25% Cu, 5.6% Zn, 23 g/t Ag, and 0.3 g/t Au (Heinrich 1981). Metallic minerals in these deposits are dominated by pyrite, pyrrhotite, chalcopyrite, sphalerite, and galena, with subordinate amounts of zincian spinel, magnetite, ilmenite, hematite, and rutile. Molybdenite and scheelite are locally abundant. Most of the deposits occur in rocks metamorphosed to the upper amphibolite facies (sillimanite zone), although those in the Wet Mountains (Amethyst, Marion, and unnamed prospect) reached the lower granulite facies (Sheridan & Raymond 1984). Host rocks to the sulfide deposits consist mainly of sil-

limanite–biotite gneiss, amphibolite, calc-silicate rock, biotite–muscovite schist, and nodular sillimanite rock. The most common mineralized rock-types are garnet – biotite – muscovite schists, garnet gneisses, chlorite schists, nodular sillimanite rocks, calc-silicate rocks, iron formation, quartz garnetite, and rocks consisting almost entirely of zincian spinel, amphiboles (actinolite, anthophyllite, gedrite), or chlorite. Zincian spinel is found in most of these rocks. We summarize details of the grades, ore production, ore minerals, metamorphic grade, structure, host rocks, and the mineralized rock-types for the thirteen zincian-spinel-bearing locations studied here [Bon Ton, Cinderella, Sedalia, Ace High – Jackpot, Independence, Betty (Lone Chimney), Green Mountain, Cotopaxi, Marion, Amethyst, an unnamed prospect near Amethyst, Evergreen, and Caprock] in Table 1. Additional details are given in Heinrich (1981) and Sheridan & Raymond (1984).

Lindgren (1908), Boyd (1934), and Lovering & Goddard (1950) proposed that the Proterozoic sulfide deposits of central Colorado are magmatic-hydrothermal in origin. However, Sheridan & Raymond (1977, 1984) suggested that the deposits formed on the ocean floor by volcanic-exhalative processes and were subsequently metamorphosed. In contrast to this model, Heinrich (1981) considered the Cu–Zn deposits to be skarns, in large part on the basis of "skarn-like" assemblages of minerals and the presence of tungsten skarns in central Colorado. Previously, Salotti (1965) considered the Cotopaxi Cu–Zn deposit to be a skarn. However, there are several reasons to suggest that the Cu–Zn deposits are metamorphosed volcanogenic deposits rather than skarns: (1) Cu–Zn deposits in the Gunnison belt (Vulcan, Headlight, Anaconda) occur in volcanic rocks metamorphosed to the greenschist to lower amphibolite facies, and are devoid of typical skarn minerals (Sheridan & Raymond 1984). Instead, banded and massive pyrite and sphalerite of the Vulcan deposit, for example, the largest in the Gunnison area, are hosted by a fragmental quartz–chlorite schist that resembles a typical assemblage of alteration minerals associated with Archean volcanic-rock-hosted massive sulfide deposits in the Canadian Shield (Franklin 1993). (2) According to Einaudi & Burt (1982, p. 745), skarns are a coarse-grained, generally iron-rich mixture of Ca–Mg–Fe–Al silicates. However, silicates associated with Cu–Zn deposits in central and northern Colorado are dominated by Mg–Fe silicates (*e.g.,* anthophyllite, almandine, enstatite, phlogopite, cordierite, sapphirine) and minor Mg–Ca silicates (*e.g.,* diopside, actinolite). (3) Meta-exhalites are associated with several deposits. For example, banded iron-formation occurs adjacent to Cu–Zn sulfides near the Cinderella and Bon Ton deposits, and a gahnite-bearing schist crops out intermittently for 240 m along strike from the Sedalia deposit (Sheridan & Raymond 1984). (4) Nodular sillimanite "pod" rocks, which bear considerable resemblance to nodular sillimanite rocks in and adjacent to the Montauban Cu–Zn

deposit, Quebec (Bernier 1992), the Geco Cu–Zn deposit, Ontario (Zaleski & Peterson 1995), the Don Mario Cu–Au deposit, Bolivia (Brazell *et al.* 1997), and the Bathurst–Norsemines Cu–Zn deposit, Northwest Territories, Canada (Casselman & Mioduszewska 1982), occur in and adjacent to most Cu–Zn deposits in central and northern Colorado. These are excellent stratigraphic marker horizons in central Colorado and likely represent zones of stratabound alteration (Ray *et al.* 1993, Shallow & Alers 1996). In the Cinderella – Bon Ton area, a nodular sillimanite horizon extends intermittently for over 8 km and is up to 400 m wide (Fig. 3a). (5)

Trace- and major-element studies of rocks in and adjacent to Cu–Zn deposits in central and northern Colorado by Ray *et al.* (1993), Alers & Shallow (1996), and Shallow & Alers (1996) have shown that the deposits are hosted in bimodal felsic to mafic volcano-plutonic successions akin to those associated with Kuroko- and Noranda-type volcanic-rock-hosted massive sulfide deposits. (6) The Mg-rich assemblages in and adjacent to Cu–Zn deposits in Colorado resemble those spatially associated with metamorphosed volcanogenic Cu–Pb–Zn deposits in granulites in the Arunta Block, Australia (Warren & Shaw 1985).
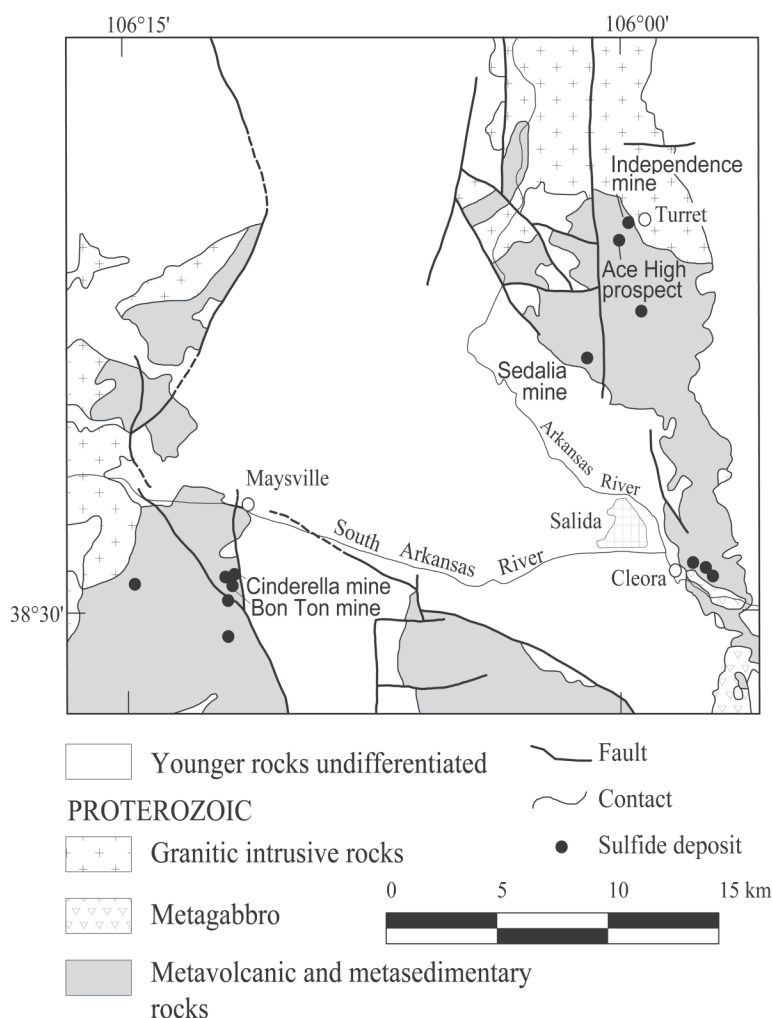

FIG. 2. General Proterozoic geology and location of massive sulfide deposits in the Salida area, Colorado (modified from Sheridan & Raymond 1984). The area covered is shown as an inset on Figure 1.

TABLE 1. SUMMARY OF GEOLOGICAL CHARACTERISTICS OF ZINCIAN SPINEL-BEARING SULFIDE LOCALITIES
IN COLORADO

Deposit	Grades, reserves, past production, metallic minerals	Metamorphic grade, structure	Country rocks	Mineralized rocks	References
Ace High – Jackpot	Unknown grade, best sample from dump: >10 % Cu, 0.4% Zn, 198 g/t Ag, cp, sp, mgt	Upper amphibolite, NE-trending isoclinal folds	Bt-qtz gneiss, amphibolite, bt schist, nodular sil schist	Nodular sil-grt schist, ghn-phl-ms-chl gneiss, grt-bt-py gneiss, mgt-hbl gneiss, ath-ghn schist, crd-ath-ghn-ms rock	Van Alstine (1969) Boardman (1971)
Amethyst	Unknown production, sp, cp, gn, py, and po	Upper amphibolite-granulite	Amp-bt gneiss, granite	Spr-amp rock, spl-amp rock, spr-spl-bt-crn rock, spr-crd-pl-spl rock, spr-crd-spl-bt rock	Raymond *et al.* (1980)
Betty (Lone Chimney)	Past production: 3,900 kg Cu, 1,680 kg Pb, 1,680 kg Zn, 4.76 kg Ag, 312 g Au, py, cp, sp, gn, po, py, bn, cv, ilm, mgt, hem	Upper amphibolite, shear and fault have disrupted the orebody	Bt gneiss, qtz-ms schist, qtz-crd-sil gneiss, amphibolite	Qtz-crd-sil gneiss, nodular sil gneiss, calc-silicate gneiss, crd-ath rock, ghn rock, act-bt rock, ath rock, qtz-crd rock	Heinrich (1981)
Bon Ton	Unknown grade, best sample from dump: 1.9% Cu, 6.4% Zn, 47 g/t Ag, sp, py, cp, po	Upper amphibolite, complex folds, three events of deformation	Fsp-bt-qtz-ep gneiss, amphibolite, feldspathic quartzite, qtz-fsp-ms-sil gneiss, bt-qtz-fsp-hbl gneiss, qtz-fsp-bt gneiss	Nodular sil gneiss, iron formation, bt-grt schist, quartzite, ms schist	Knight (1981)
Caprock	0.9 Mt of 8% (Zn+Pb) projected reserves; sp, gn, py, po	Upper amphibolite, three events of folding NE-trending thrust faults	Qtz-fsp-sil-grt-bt gneiss, nodular bt-sil-qtz-gneiss	Spl-alm-bt gneiss, nodular sil-ms rock, spl rock	Klipfel (1992)
Cinderella	Unknown grade, best sample from dump: 1.9% Cu, 6.4% Zn, 47 g/t Ag, sp, cp, gn, py	Upper amphibolite, complex folds, three events of deformation	Sil-qtz-ms-mc gneiss, qtz-bt-ep gneiss, amphibolite, grt gneiss	Calc-silicate rock, nodular sil gneiss, bt-grt schist, bt gneiss, ms schist, ath rock, quartzite	Heinrich (1981)
Cotopaxi	Past production: 0.01 Mt, with at least 1,337 tonnes Zn, 83 tonnes Cu, 71 tonnes Pb, 301 kg Ag, 4.5 kg Au, sp, cp, gn, po, py, mrc, rt, ilm, mlb, cv, mgt	Upper amphibolite, orebody hosted in monocline	Qtz-bt-fsp-sil gneiss, nodular sil schist, hbl gneiss, bt schist, calc-silicate gneiss, granite gneiss, pegmatite	Ghn-ath rock, nodular sil-bt schist, ath-bt gneiss, ghn-qtz-grt rock, pegmatitic ghn-bt rock, chl schist, qtz-bt garnetite	Lindgren (1908) Heinrich & Salotti (1959) Salotti (1965) Ririe (1981) Ririe & Foster (1984)
Evergreen	No production, cp, sp, po	Upper amphibolite	Sil-ms-qtz-alm gneiss, ged-alm-crd gneiss, amphibolite, calc-silicate rock	Ged-alm-crd gneiss, nodular sil-ms rock	Gable & Sims (1969) Heimann *et al.* (2002)
Independence	Unknown grade but best sample from dump: 3.3% Cu, 1.3% Zn, 1.8 g/t Ag, cp, sp, po, py, cv, mlb, ilm, mgt	Upper amphibolite, NE-trending isoclinal folds	Bt-qtz gneiss, granite, amphibolite, pegmatite, bt-ms schist	Ghn-ath rock, marble, nodular sil-ms-qtz gneiss	Lindgren (1908) Boardman (1971) Heinrich (1981)

Green Mountain	Best drill-hole intersection: 18.1% Cu and 4.3% Zn over 1.5 m, cp, py, sp, gn, mo, po, ilm, hem, rt	Upper amphibolite, broad NE–SW-trending folds	Qtz-fsp gneiss, qtz-crd-bt gneiss, migmatite, ath-crd rock, sil gneiss, hbl-bt-crd gneiss, amphibolite	Nodular sil-crd-grt rock, qtz-grt gneiss, ath-ghn rock, grt amphibolite, grt-sil gneiss, qtz garnetite, qtz-bt gneiss, grt-bearing pegmatite	Ririe (1981)
Marion	Unknown production; sp, cp, gn, apy, po, py, mrc, mlb, bo, mgt, rt	Upper amphibolite-granulite	Amp-bearing gneiss, calc-silicate gneiss, impure marble, granite, migmatized gneiss	Spr-amp-spl-bt rock	Boyer (1963) Heinrich (1981) Raymond *et al.* (1980)
Sedalia	1.2 Mt @ 3.2% Cu, 5.6% Zn, 23 g/t Ag, 0.28 g/t Au, sp, cp, gn, cv, py, mrc, po, mgt, ghn, ilm, native gold, native silver	Middle amphibolite, shallow to moderately plunging anticline	Feldspathic gneiss, bt-ms schist, amphibolite, grt-crd amphibole gneiss, grt-bt schist, pegmatite	Crd-ath-sil-grt gneiss, minor calc-silicate rocks, nodular sil-and schist, mgt-chl-alm rocks, hbl-ep-qtz-sil-pl rock, act rock, tr-pl rock, tr-chl rock	Lindgren (1908) Boardman (1971) Heinrich (1981) Knight (1981)
Unnamed prospect	Unknown production: sp, cp, gn, py, po, cv, ilm, mgt, rt	Upper amphibolite to granulite	Amp-opx gneiss, calc-silicate gneiss, marble	Spr-amp-opx rock, spr-opx-spl-bt rock, spr-amp-crd rock, spr-amp-spl rock	Raymond *et al.* (1980)

Mineral symbols after Kretz (1983), except for amp: amphibole, fsp: feldspar, ghn: gahnite, mrc: marcasite.
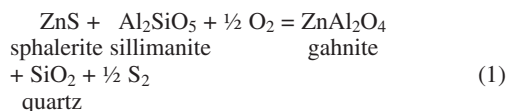
Sampling and Analytical Procedure

Although some zincian-spinel-bearing rocks were collected from outcrop, many were derived from dump samples near mine portals. Access to diamond drill-core and underground workings was not possible. Samples were studied petrographically, and the compositions of silicates and oxides were obtained using an ARL–SEMQ electron microprobe in the Department of Geological and Atmospheric Sciences at Iowa State University. The instrument was operated at an accelerating voltage of 15 kV and beam current of 20 nA. Natural and synthetic silicates and oxides were used as standards. Three hundred and ninety-eight analyses of zincian spinel were obtained, along with >1,100 compositions of silicates and oxides in 114 zincian-spinel-bearing rocks. All data are listed in Heimann (2002), whereas representative compositions of spinel-group minerals and coexisting minerals are given in Tables 2 and 3, respectively. Compositional ranges for spinel-group minerals are given in the text using the following format. For example, $Gah_{8-32}Spl_{9-33}Hc_{59-64}$ shows a range in the gahnite (Gah), spinel (Spl), and hercynite (Hc) components of 8 to 32 mole %, 9 to 33 mole %, and 59 to 64 mole %, respectively. Figure 4 is a plot of spinel compositions from the thirteen locations studied here in terms of gahnite, hercynite, and spinel components. Note that the galaxite ($MnAl_2O_4$), magnetite (Fe_3O_4), franklinite ($ZnFe_2O_4$), and chromite ($FeCr_2O_4$) components of all spinels analyzed here were found to be less than 1% and have not been included in Figure 4.
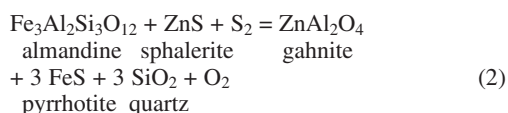
Petrography and Mineral Compositions

A brief summary of zincian spinel-bearing assemblages from occurrences in Colorado is provided here, but detailed descriptions of assemblages from each of the thirteen locations studied are given in Heimann (2002). A list of representative zincian-spinel-bearing assemblages for all thirteen locations is given in Table 4.

Zincian spinel has been known in Colorado for over 100 years, ever since Genth (1882) described gahnite porphyroblasts associated with sulfides from the Cotopaxi deposit. It occurs in massive sulfides and associated Fe–Al-rich rocks in the Bon Ton, Independence, and Sedalia deposits and Mg–Ca–Al-rich rocks in the Ace High, Amethyst, and Marion deposits. It also occurs in deposits where both Fe–Al-rich and Mg–Ca–Al-rich rocks are present (Cotopaxi, Cinderella, Caprock and Betty). In Fe–Al-rich rocks, zincian spinel occurs in contact with a variety of minerals, including sillimanite (Fig. 3b), zincian staurolite, with up to 2.4 wt. % ZnO (Fig. 3c), biotite (Fig. 3d), garnet (Fig. 3e), and sphalerite (Fig. 3f). The gahnite component of zincian spinel in parts of the Bon Ton, Green Mountain, Cotopaxi, and Caprock deposits was likely a product of sulfidation–oxidation reactions of the type (Spry & Scott 1986a, Spry 2000):

$$ZnS + Al_2SiO_5 + \tfrac{1}{2} O_2 = ZnAl_2O_4$$
sphalerite sillimanite   gahnite
$$+ SiO_2 + \tfrac{1}{2} S_2 \tag{1}$$
   quartz

and

$$Fe_3Al_2Si_3O_{12} + ZnS + S_2 = ZnAl_2O_4$$
  almandine   sphalerite   gahnite
$$+ 3\, FeS + 3\, SiO_2 + O_2 \tag{2}$$
   pyrrhotite   quartz

However, gahnite-forming reactions unrelated to sulfidation and oxidation are also likely to have occurred in other parts of these deposits. For example, in the Caprock deposit, gahnite was a product of the retrograde breakdown of zincian biotite (up to 0.4 wt.% ZnO) (Fig. 3d), and pegmatitic veins and metamorphic segregations composed of gahnite – quartz – feldspar – biotite ± sillimanite are relatively common at the Cotopaxi deposit (Heimann 2002).

Mg–Ca-rich rocks that contain zincian spinel are generally diagnostic of Mg-rich alteration zones and calc-silicate rocks. Mg-rich minerals such as cummingtonite (Fig. 5a), enstatite (Fig. 5a), phlogopite (Fig. 5b), anthophyllite (Fig. 5c), chlorite (Figs. 5b, c) and gedrite are commonly associated with zincian spinel (Table 4). The zincian-spinel-bearing assemblages ob-served in these rocks are complex, and the nature of the zincian-spinel-forming reactions is unclear. Assemblages containing zincian spinel and minerals in contact with zincian spinel generally contain a large number of major and minor (Mg, Fe, Ca, Al, K, Mn, Ti, F, Na, Zn, Cu, Pb, Si, S, O, H) elements, which makes it difficult to apply the phase rule and to establish equilibrium or disequilibrium conditions among minerals. Precursor phases and many assemblages reflect the open chemical system related to metasomatic processes prior to metamorphism, and diffusion of components during metamorphism is limited in scale. Furthermore, the coarse grain-size of minerals, up to 20 cm in some instances, almost certainly required reactants in some spinel-forming reactions to have been millimeters to decimeters away from the spinel.

Zincian spinel coexisting with sapphirine was described by Raymond *et al.* (1980) and Eckel *et al.* (1997) from several locations (Isabel, Marion, and Cisneros Trail mines, the Amethyst and Dewey prospects, and an unnamed prospect just west of Amethyst) in the Wet Mountains. At the Marion mine, the largest Cu–Zn deposit in the Wet Mountains, zinc-bearing spinel occurs in several assemblages (Table 4), some of which contain sapphirine and corundum. In places, dark green spinel *sensu stricto* forms a corona around subhedral to anhedral crystals of corundum and associated corroded inclusions of sapphirine (Fig. 5d). Surrounding this co-

TABLE 2. REPRESENTATIVE COMPOSITIONS OF ZINCIAN SPINEL FROM COLORADO

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
SiO_2 wt.%	0.31	0.14	0.08	0.00	0.13	0.35	0.18	0.06	0.31	0.22	0.29	0.03	0.00	0.23	0.25	0.28
Al_2O_3	55.65	60.12	57.41	56.38	58.62	56.67	55.31	61.31	58.47	59.22	56.24	60.80	56.89	59.96	63.12	63.45
FeO	13.58	5.74	7.08	21.28	6.09	21.09	6.58	27.03	9.79	30.56	11.62	5.27	6.22	21.40	19.77	18.63
MnO	0.00	0.28	0.78	0.08	0.11	0.14	0.18	0.11	0.12	0.06	0.10	0.45	0.50	0.53	0.10	0.02
MgO	1.29	13.22	3.06	3.72	7.30	2.65	2.92	7.66	1.99	8.88	2.44	13.09	2.28	17.31	15.19	13.83
ZnO	29.53	19.70	31.68	18.27	28.68	18.88	35.60	4.29	28.63	0.08	29.89	19.59	34.81	0.62	0.64	4.51
Total	100.36	99.20	100.09	99.73	100.93	99.78	100.77	100.46	99.31	99.02	100.58	99.23	100.70	100.05	99.07	100.72
Si *apfu*	0.009	0.004	0.003	0.000	0.004	0.010	0.005	0.002	0.009	0.006	0.009	0.001	0.000	0.006	0.007	0.007
Al	1.956	1.943	1.988	1.946	1.958	1.956	1.939	1.982	2.015	1.938	1.956	1.957	1.981	1.870	1.960	1.964
Fe^{2+}	0.304	0.079	0.165	0.467	0.106	0.483	0.108	0.604	0.239	0.654	0.252	0.078	0.135	0.350	0.402	0.380
Fe^{3+}	0.035	0.053	0.009	0.054	0.038	0.034	0.056	0.016	0.000	0.056	0.035	0.042	0.019	0.124	0.033	0.029
Mn	0.000	0.007	0.019	0.002	0.003	0.004	0.005	0.002	0.003	0.001	0.002	0.010	0.012	0.012	0.002	0.000
Mg	0.057	0.540	0.134	0.162	0.308	0.116	0.130	0.313	0.087	0.367	0.107	0.533	0.101	0.683	0.596	0.542
Zn	0.650	0.399	0.687	0.395	0.600	0.408	0.782	0.087	0.618	0.002	0.651	0.395	0.760	0.012	0.012	0.088
Total	3.011	3.025	3.005	3.026	3.017	3.011	3.025	3.006	2.971	3.024	3.012	3.016	3.008	3.057	3.012	3.010

1. Gahnite, Bon Ton; 2. Spinel, Cinderella; 3. Gahnite, Cinderella; 4. Hercynite, Sedalia; 5. Gahnite, Ace High; 6. Hercynite, Independence; 7. Gahnite, Independence; 8. Hercynite, Betty (Lone Chimney); 9. Gahnite, Betty (Lone Chimney); 10. Hercynite, Green Mountain; 11. Gahnite, Green Mountain; 12. Spinel, Cotopaxi; 13. Gahnite, Cotopaxi; 14. Spinel, Marion; 15. Spinel, Amethyst; 16. Spinel, Unnamed prospect (west of Amethyst). Cation proportions are quoted in *apfu*, atoms per formula unit based on four atoms of oxygen. Fe^{3+} content based on deficiency of cations in the octahedral site assuming $Al^{3+} + Si^{4+} + Fe^{3+} = 2$. Ti, Cr, Ca, Na, and K were also sought, but are below detection limits.
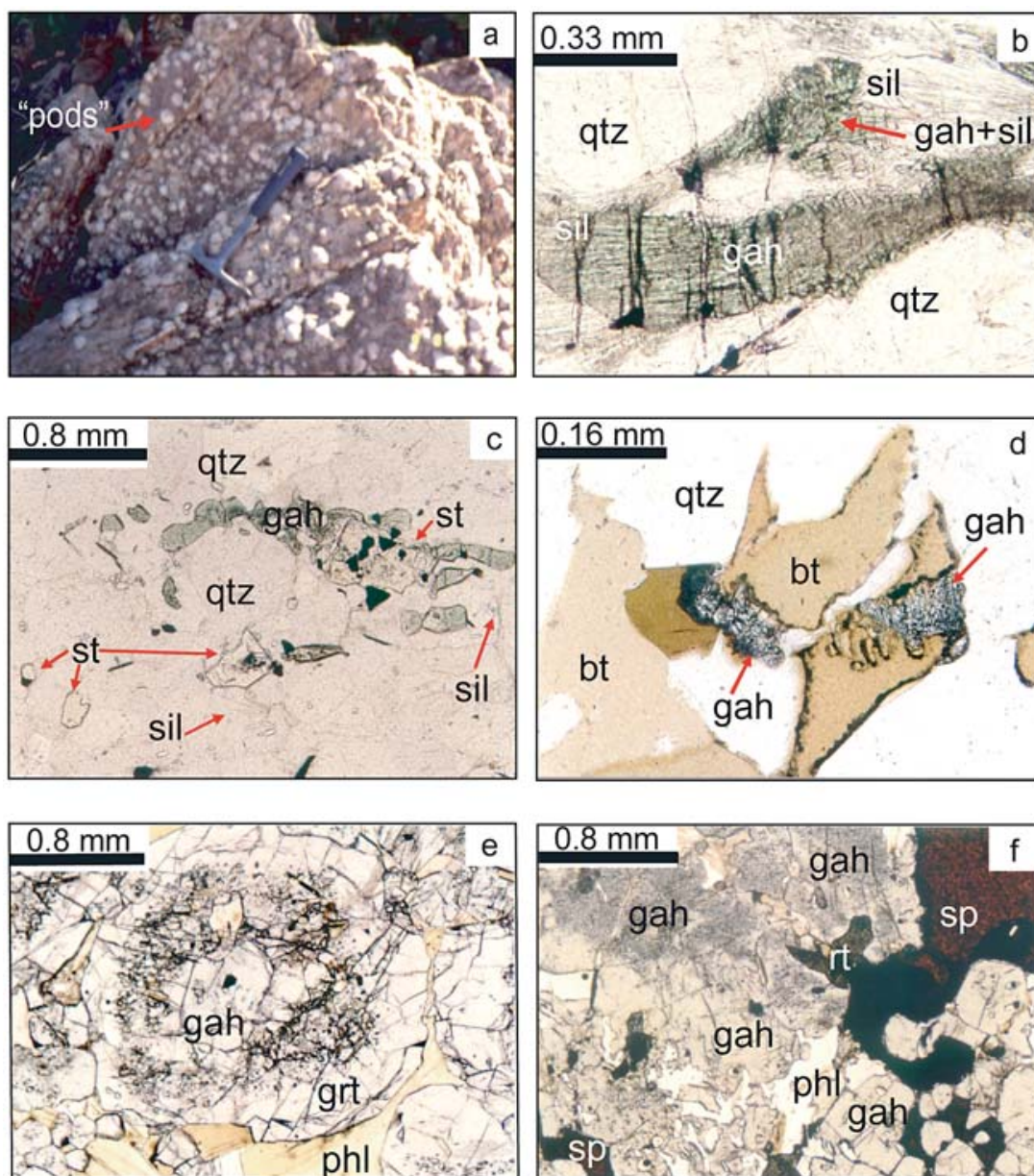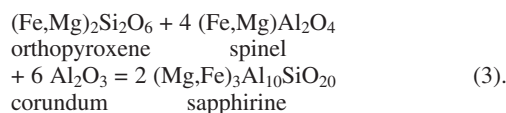
FIG. 3. Plane-polarized transmitted light photomicrographs and field photographs from metamorphosed massive-sulfide deposits from Colorado. a. Nodular sillimanite "pod rock" composed of sillimanite, quartz, muscovite, feldspar, and gahnite adjacent to the Cinderella deposit. b. Gahnite (gah) after sillimanite (sil) in contact with quartz (qtz) from the Bon Ton deposit. c. Coexisting quartz, gahnite, zincian staurolite (st), and sillimanite from the Independence deposit. d. Biotite–quartz rock showing gahnite after biotite (bt) from the Green Mountain deposit. e. Gahnite core surrounded by almandine-rich garnet (grt). Phlogopite (phl) occurs on the margins of garnet porphyroblasts from the Caprock deposit. f. Inclusion-free and inclusion-rich gahnite partially surrounded by sphalerite (sp) and in contact with phlogopite and rutile (rt) from the Cotopaxi deposit.

TABLE 3. REPRESENTATIVE COMPOSITIONS OF SILICATES AND ILMENITE COEXISTING WITH ZINCIAN SPINEL
FROM COLORADO

Mineral	Chm 1	Ann 2	Phl 3	Chl 4	St 5	Ilm 6	Phl 7	Chu 8	Spr 9	En 10	Chu 11	Alm 12	Ath 13	Fo 14
SiO$_2$ wt.%	22.93	35.20	39.35	28.10	26.73	0.11	35.90	39.34	13.67	51.80	34.34	38.36	57.41	39.43
TiO$_2$	0.02	0.71	0.69	0.08	0.24	50.72	1.99	1.45	0.04	0.12	1.79	0.03	0.03	0.00
Al$_2$O$_3$	25.19	19.85	17.47	23.55	55.30	0.12	17.74	0.01	62.08	5.51	0.10	21.18	0.75	0.00
FeO	30.28	20.88	6.32	5.73	11.97	38.62	16.88	4.23	6.31	9.66	6.03	20.21	6.82	13.71
MnO	0.75	0.26	0.06	0.05	0.30	5.36	0.04	0.30	0.06	0.19	0.14	12.94	4.58	4.04
ZnO	0.44	0.38	0.50	0.89	2.52	4.84	0.35	0.02	0.00	0.00	0.17	0.00	0.19	0.19
MgO	9.03	8.73	22.43	28.70	1.58	0.15	12.63	54.56	17.46	31.48	53.13	5.47	25.90	43.23
CaO	0.09	0.08	0.03	0.03	0.02	0.01	0.03	0.14	0.04	0.08	0.00	2.12	1.09	0.00
Na$_2$O	0.01	0.26	0.73	0.00	0.00	0.00	0.48	0.00	0.03	0.05	0.00	0.00	0.10	0.00
K$_2$O	0.01	8.76	7.87	0.03	0.00	0.02	9.52	0.00	0.02	0.00	0.00	0.00	0.00	0.00
F	0.00	0.53	0.76	0.00	0.34	0.00	0.47	2.73	0.61	0.26	6.24	0.00	0.68	0.00
Cl	0.13	0.05	0.08	0.01	0.02	0.06	0.11	0.05	0.03	0.03	0.06	0.05	0.04	0.05
Total	88.87	95.67	96.29	87.17	99.02	100.00	96.14	102.83	100.35	99.17	102.01	100.36	97.59	100.65
Oxygen atoms	14	22	22	14	48	3	22	14	20	6	14	24	23	4
Si *apfu*	2.464	5.398	5.566	2.688	7.724	0.003	5.407	3.314	1.622	1.841	3.080	6.037	7.965	0.996
Ti	0.002	0.082	0.073	0.007	0.052	0.974	0.225	0.092	0.003	0.003	0.121	0.004	0.003	0.000
Al	3.190	3.588	2.912	2.657	18.835	0.004	3.150	0.001	8.680	0.231	0.011	3.928	0.122	0.000
Fe	2.721	2.678	0.748	0.459	2.893	0.825	2.127	0.298	0.626	0.287	0.452	2.660	0.791	0.29
Mn	0.068	0.033	0.008	0.004	0.074	0.116	0.005	0.021	0.006	0.006	0.011	1.725	0.538	0.087
Zn	0.035	0.043	0.052	0.063	0.537	0.091	0.039	0.001	0.000	0.000	0.011	0.000	0.020	0.004
Mg	1.447	1.996	4.730	4.095	0.681	0.006	2.837	6.853	3.088	1.667	7.105	1.284	5.357	1.628
Ca	0.010	0.013	0.004	0.004	0.007	0.000	0.005	0.013	0.005	0.003	0.000	0.357	0.162	0.000
Na	0.003	0.076	0.201	0.000	0.003	0.000	0.141	0.000	0.007	0.003	0.000	0.000	0.027	0.000
K	0.002	1.713	1.421	0.004	0.002	0.001	1.829	0.000	0.003	0.000	0.000	0.001	0.000	0.000
F + Cl	0.023	0.268	0.361	0.000	0.321	0.003	0.252	0.735	0.235	0.031	1.781	0.013	0.307	0.002
Total	9.965	15.888	16.076	9.979	31.129	2.023	16.017	11.328	14.275	4.072	12.572	16.009	15.292	3.007

Abbreviations after Kretz (1983). 1, 2. Bon Ton; 3, 4. Ace High; 5, 6. Independence; 7. Green Mountain; 8. Marion; 9. Amethyst; 10, 11. Unnamed prospect (west of Amethyst); 12, 13, 14. Caprock.

rona is a moat of cordierite that locally contains anorthite. Sapphirine is more abundant at the Amethyst mine than at the Marion mine; it occurs there in several spinel-bearing assemblages that contain varying proportions of gedrite, anorthite, cordierite, phlogopite, corundum, and forsterite (Fig. 5e, Table 4). Zinc-bearing spinel occurs in sapphirine-bearing assemblages similar to those observed in the Amethyst prospect and in an unnamed prospect 150 m to the west of Amethyst. Enstatite is also commonly observed in these assemblages (Table 4). In places, spinel has replaced corundum and sapphirine, and retains the lamellar structure of multiple twins found in corundum and sapphirine (Fig. 5f). The presence of a sapphirine rim around spinel and of spinel inclusions in sapphirine spatially associated with orthopyroxene indicates that sapphirine probably formed by a reaction of the type (Kriegsman & Schumacher 1999):

$$(Fe,Mg)_2Si_2O_6 + 4\ (Fe,Mg)Al_2O_4$$
orthopyroxene   spinel
$$+\ 6\ Al_2O_3 = 2\ (Mg,Fe)_3Al_{10}SiO_{20} \tag{3}$$
corundum   sapphirine

Compositional zoning observed in spinel grains from the Ace High – Jackpot, Independence, Betty, and Green Mountain deposits shows weak to moderate enrichment of the gahnite component and a corresponding depletion in spinel and hercynite components from the center to the edge of grains. This is the most common pattern of compositional zoning observed in zincian spinel, and is consistent with growth during a period of retrogression (Spry 1987a). It indicates that gahnite formed during the protracted metamorphic history.

DISCUSSION

*Use of zincian spinel composition
as a guide in exploration*

During the early 1980s, BHP Limited undertook a proprietary study to evaluate zincian spinel as a potential indicator to Broken-Hill-type massive sulfide deposits. That study involved the collection of data from known ore districts worldwide and resulted in a database with >3,000 compositions of zincian spinel (Walters *et al.* 2002). These authors developed empirical discriminants using major-element (Fe, Mg, Mn, Zn, and Al) signatures to distinguish among barren regional zincian spinel horizons, small prospects, and economic deposits. At about the same time, Spry & Scott (1986a) independently derived a triangular plot of spinel compositions in terms of Zn, Fe, and Mg from 106 sulfide-free and sulfide-bearing locations, in an attempt to distinguish zinc-bearing spinel associated with metamorphosed massive sulfide deposits from that found in marbles, granitic pegmatites, and aluminous metasedimentary rocks (Fig. 6). Using the data from Spry & Scott (1986a), Spry (2000) proposed that zincian spinel

associated with metamorphosed massive sulfide deposits contains 55–90 mole % $ZnAl_2O_4$, 10–40 mole % $FeAl_2O_4$, and 5–20 mole % $MgAl_2O_4$.

Since the study of Spry & Scott (1986a), a considerable number of data from metamorphosed massive sulfide deposits, hydrothermally altered metasedimentary and metavolcanic rocks (some of which are associated with known occurrences of massive sulfides), aluminous granulites, aluminous metasedimentary units (metabauxites and metapelites), granitic pegmatites, and iron formations have been published in the literature (Fig. 6). In most cases, the zincian spinel in or associated with these metamorphosed massive sulfide occurrences and aluminous metasediments show compositions within the fields defined by Spry & Scott (1986a). Some compositions fall outside these fields, however; for example, several compositions of zincian spinel from the Mamandur Zn–Pb–Cu deposit in India (Chattopadhyay 1999) are relatively depleted in the gahnite component ($Gah_{50-63}Spl_{20-33}Hc_{11-20}$) compared to gahnite associated with metamorphosed massive sulfide deposits elsewhere in the world. Furthermore, green zincian spinel that coexists with minor galena and chalcopyrite in metapelites and quartzites subjected to the granulite fa-
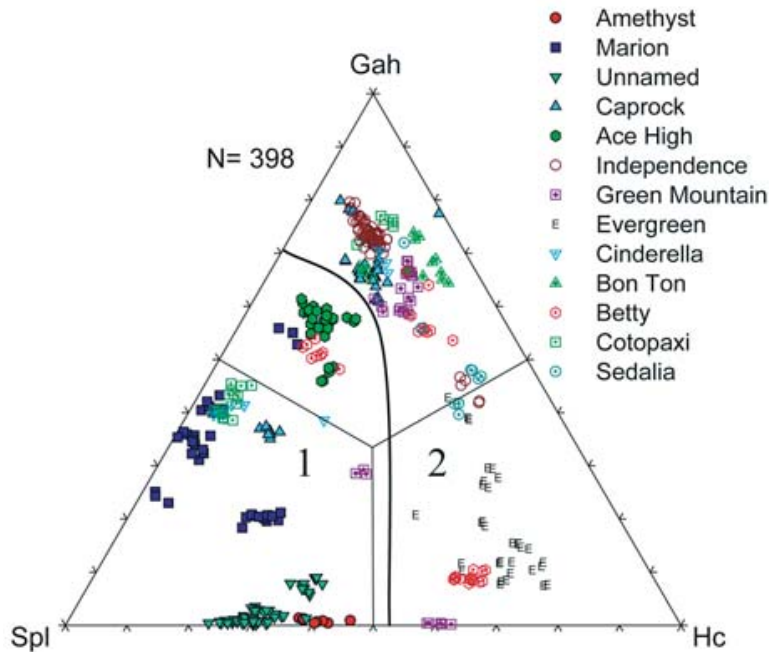

FIG. 4. Triangular plot in terms of gahnite, hercynite, and spinel components showing samples of zincian spinel spatially associated with metamorphosed massive-sulfide deposits or hydrothermal alteration zones in Colorado. Fields 1 and 2 refer to zincian spinel associated with Mg–Al–Ca-rich rocks and Fe–Al-rich rocks in Figure 7, respectively.
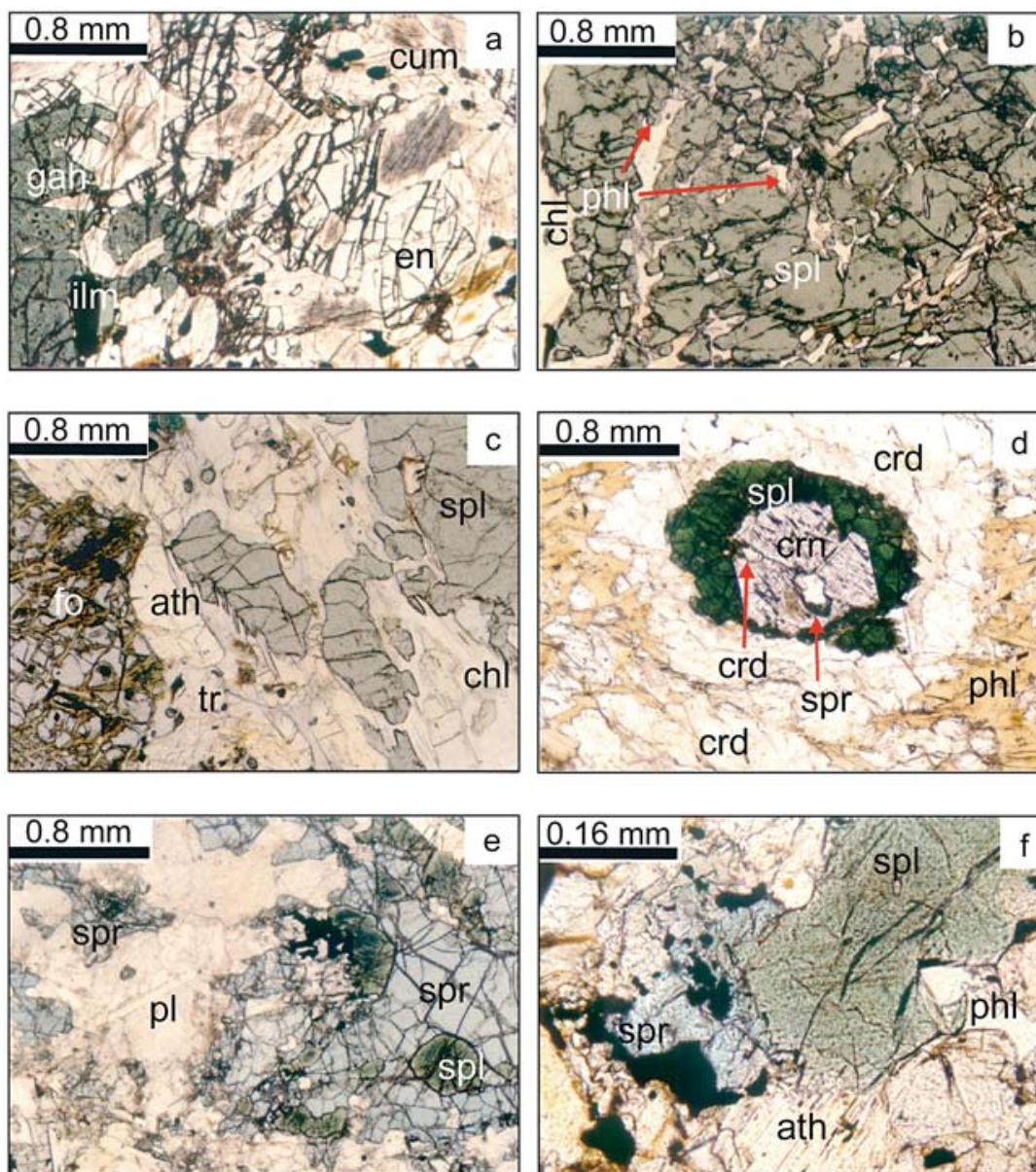
Fig. 5. Plane-polarized transmitted-light photomicrographs of textural relationships involving zincian spinel from Colorado. a. Gahnite (gah) – cummingtonite (cum) – enstatite (en) – zincian ilmenite (ilm) rock (Green Mountain). b. Phlogopite (phl) and chlorite (chl) on the margins of and as inclusions in zincian spinel (spl) (Cotopaxi). c. Zincian spinel – anthophyllite (ath) – forsterite (fo) – tremolite (tr) assemblage in contact with retrograde chlorite (Caprock). d. Corundum (crn) with sapphirine (spr) and cordierite (crd) inclusions mantled by spinel and surrounded by cordierite and phlogopite (Marion). e. Spinel – sapphirine – plagioclase (pl) assemblage (Amethyst). Note the spinel inclusion in sapphirine. f. Sapphirine surrounding spinel next to anthophyllite and phlogopite (Unnamed prospect).

cies at Orangefontein, South Africa (Hicks *et al.* 1985) is highly enriched in the spinel component, whereas blue zincian spinel in the same rocks, but associated with a retrograde greenschist-facies event, is enriched in the gahnite component. These examples demonstrate the dependence of zincian spinel compositions on temperature. Hercynite in equilibrium with quartz is stable at granulite-facies conditions (Shulters & Bohlen 1989) and is only stabilized to amphibolite- and greenschist-facies conditions by the addition of other components, such as Zn. This finding accounts for the relatively low proportion of the gahnite component of some examples

of zincian spinel from Mamandur, which formed during granulite-facies conditions, compared to the more Zn-rich gahnite in rocks metamorphosed to greenschist-facies conditions at Orangefontein. Other samples of zincian spinel that fall outside of the field for massive sulfide deposits defined by Spry & Scott (1986a) include those at Kinniwabi Lake area, Ontario (Morris *et al.* 1997), Palmeiropolis Zn–Cu deposit, Brazil (Araujo *et al.* 1995), and the Isua greenstone belt, Greenland (Appel 2000). By combining data from the present study with those listed in Spry & Scott (1986a) and those published since their study, spinel-group minerals in
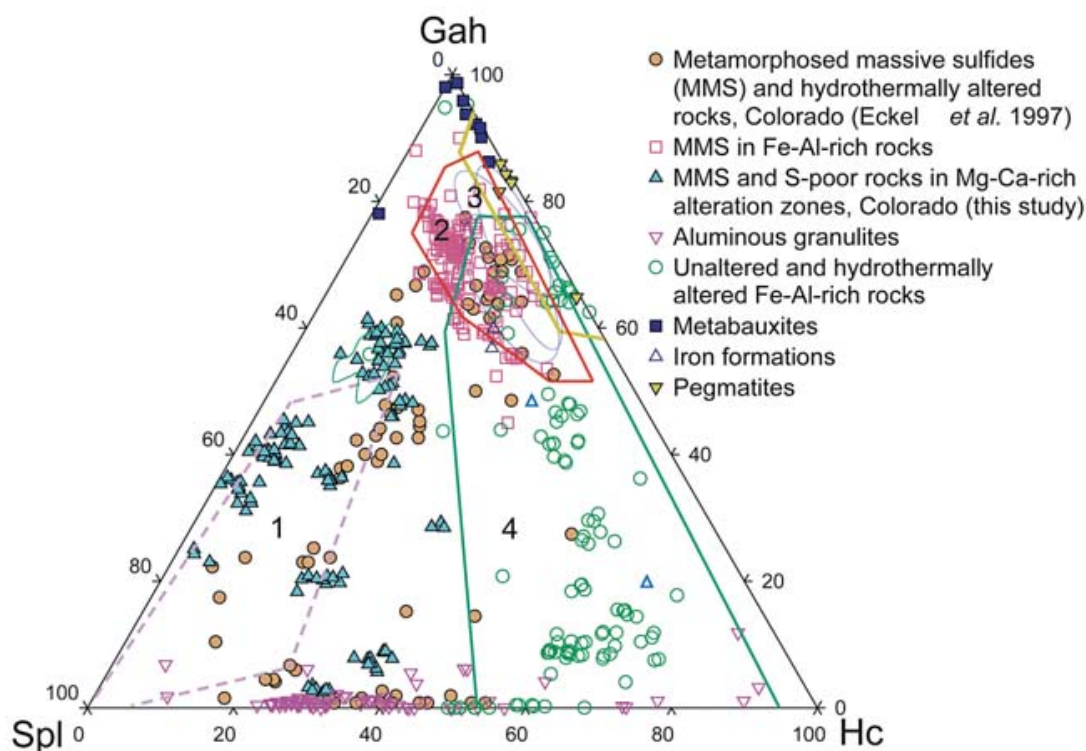

Fig. 6. Compositional fields of zincian spinel from (1) marbles, (2) metamorphosed massive-sulfide deposits, (3) granitic pegmatites, and (4) aluminous metasedimentary rocks (after Spry & Scott 1986a). Individual data-points pertain to zincian spinel compositions derived from this study and worldwide localities, that have appeared in the literature since Spry & Scott (1986a): metamorphosed massive-sulfide deposits from Colorado (Eckel *et al.* 1997), metamorphosed massive-sulfide deposits in Fe–Al-rich aluminous metasedimentary and metavolcanic units (Hicks *et al.* 1985, Appel 1986, 2000, Spry 1987b, Spry *et al.* 1988, Froese *et al.* 1989, Petersen *et al.* 1989, Zaleski *et al.* 1991, Parr 1992, Araujo *et al.* 1995, Höller & Gandhi 1997, Morris *et al.* 1997, Chattopadhyay 1999, Jain 1999, Toteff 1999, Rosenberg *et al.* 2000, Schwartz & Melcher 2003), unaltered and hydrothermally altered Fe–Al-rich rocks (Hicks *et al.* 1985, Spry 1987b, Schumacher & Robinson 1987, Damman 1989, Moore & Reid 1989, Spry & Petersen 1989, Petersen *et al.* 1989, Schneiderman & Tracy 1991, Parr 1992, Soto & Azañón 1993, Pedrick *et al.* 1998, Dasgupta *et al.* 1999, Sawaki *et al.* 2001), aluminous granulites (Sengupta *et al.* 1991, Visser *et al.* 1992, Ouzegane *et al.* 1996, Carson *et al.* 1997, Dawson *et al.* 1997, Raith *et al.* 1997, Osanai *et al.* 1998, Dasgupta *et al.* 1999, Dunkley *et al.* 1999, Kriegsman & Schumacher 1999, Pitra & De Waal 2001, Scrimgeour & Raith 2002), metabauxites (Yalçin *et al.* 1993, Henry & Dutrow 2001), pegmatites (Eckel *et al.* 1997, Morris *et al.* 1997), and iron formations (Appel 1986, Spry 1987b).

metamorphosed massive sulfide deposits hosted by hydrothermally altered aluminous metasedimentary and metavolcanic units exhibit the following compositional range: $Gah_{45-90}Hc_{0-45}Spl_{0-25}$. This range of zincian spinel compositions is considered to be useful as a guide to ores in Fe–Al-rich rocks.

The relationship between bulk-rock composition and the composition of zincian spinel

Spry & Scott (1986a) pointed out that spinel-group minerals from the Betty and Cotopaxi deposits, as well as from an unnamed prospect near Round Mountain (Colorado), possess compositions that fall outside the field they ascribed to metamorphosed massive sulfide deposits because of an enrichment in the spinel component. These compositions, when combined with spinel compositions obtained by Eckel *et al.* (1997) and those determined in the present study from metamorphosed massive sulfide deposits in Colorado, exhibit the broadest variation in gahnite, hercynite, and spinel components of any known ore-district (Fig. 6). Spinel-group minerals from the Bon Ton, Sedalia, Independence, and Caprock deposits, most from Green Mountain deposit, and some from the Betty, Cinderella, and Cotopaxi deposits, are within the range given above for zincian spinel in metamorphosed massive sulfide deposits hosted by hydrothermally altered Fe–Al-rich metasedimentary and metavolcanic units. However, where the grains occur with sulfides in Mg-rich or Mg–Ca-rich zones of pre-metamorphic alteration in Colorado, they are enriched in the spinel component (Cotopaxi, Marion). In these deposits, Mg-rich assemblages contain one or more of the following minerals: enstatite, anthophyllite, gedrite or cummingtonite, forsterite, phlogopite, and clinohumite, whereas Mg–Ca-rich assemblages contain diopside, actinolite, tremolite, hornblende, anorthite, and apatite (Table 4). Zincian spinel grains from the Marion and Amethyst deposits, and the unnamed prospect near Amethyst, are depleted in the gahnite component and contain the highest spinel component of any known Zn-bearing sulfide deposit. These spinels occur in rare sapphirine-, enstatite-, and forsterite-bearing rocks (Table 4).
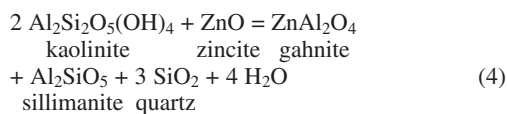
In order to evaluate the dependence of zincian spinel compositions on bulk-rock compositions, in the absence of bulk-rock analyses, the composition of silicates coexisting with zincian spinel in Colorado is plotted in terms of the molar proportions of MgO, Al_2O_3 and FeO (Fig. 7) from the two fields designated in Figure 4. These two fields were chosen to essentially distinguish spinel grains with a high content of spinel component (field 1) from those enriched in the gahnite or hercynite component (field 2). Samples of zincian spinel in field 2 also fall in the compositional field of zincian spinel associated with metamorphosed massive sulfide deposits of Spry & Scott (1986a). Figure 7a shows that

samples of zincian spinel enriched in the spinel component (*i.e.*, field 1) coexist with silicates with compositions that fall close to the MgO–Al_2O_3 join (*e.g.*, forsterite, clinohumite, enstatite, sapphirine, phlogopite, gedrite, anthophyllite, cordierite, dravite, tremolite, hornblende, and diopside). Alternatively, those enriched in the gahnite or hercynite components (or both; *i.e.*, field 2, Fig. 7b) generally coexist with silicates less enriched in Mg and more enriched in Fe (*e.g.*, almandine, staurolite, annite, sekaninaite, ferrogedrite, ferroanthophyllite, grunerite, ferrohornblende). Zincian spinel compositions in field 1 occur in Mg- and Mg–Ca-rich rocks from the Cotopaxi, Marion, Amethyst and Caprock deposits, whereas spinel compositions in field 2 occur in Fe–Al-rich rocks in the Bon Ton, Betty, Sedalia, Green Mountain, and Independence deposits, as well as some rocks from the Cotopaxi and Caprock deposits. Note that sphalerite is not present in all zincian-spinel-bearing assemblages shown in Figure 7 (Table 4).

The compositions observed here suggest that in most cases, zincian spinel in and adjacent to metamorphosed massive sulfide deposits in Colorado reflect the bulk composition of the host rock. Zincian spinel from the Independence, Caprock, Cotopaxi, and Betty deposits exhibit at least two markedly different ranges of compositions. For example, two groups of zincian spinel from the Independence deposit, one of gahnite and the other one of hercynite, are associated with anthophyllite – phlogopite – gahnite ± chalcopyrite ± pyrrhotite ± sphalerite ± ilmenite ± rutile, and cordierite – almandine – quartz – sillimanite – zincian staurolite – hercynite ± biotite ± magnetite ± ilmenite ± pyrite ± chalcopyrite assemblages, respectively. However, we stress here that grains of zincian spinel from the Independence deposit are not found in massive sulfides but in the sulfide-poor alteration zone adjacent to the massive sulfides.

Zincian-spinel-forming reactions

The presence of stable equilibrium assemblages and the absence of reaction textures between the zincian spinel and sulfides in most of the metamorphosed massive sulfide deposits in Colorado does not allow for the unequivocal identification of balanced desulfidation reactions of the type identified by Spry & Scott (1986a), Zaleski *et al.* (1991), and Rosenberg *et al.* (2000). However, the replacement of sillimanite by gahnite from the Bon Ton deposit (Fig. 3b) is supportive of a desulfidation mechanism (reaction 1), although a sulfur-free reaction of the type (Segnit 1961):

$$2\ Al_2Si_2O_5(OH)_4 + ZnO = ZnAl_2O_4$$
$$\text{kaolinite} \qquad \text{zincite} \quad \text{gahnite}$$
$$+ Al_2SiO_5 + 3\ SiO_2 + 4\ H_2O \qquad\qquad (4)$$
$$\text{sillimanite} \quad \text{quartz}$$

may have also been responsible for the formation of coexisting gahnite and sillimanite in sulfide-free rocks, such as sillimanite-pod rocks, where minor amounts of gahnite occur in sillimanite crystals. Although the adsorption of zincite on kaolinite has not been recognized in natural settings, Rivière *et al.* (1985) reported a spatial association between aluminous clays and $Zn(OH)_2$. Further support for the participation of desulfidation mechanisms involving sphalerite in the formation of zincian spinel in Colorado comes from the mantling of gahnite by sphalerite and the presence of a fine dusting of sphalerite inclusions in gahnite at Cotopaxi (Fig. 3f) and possibly in the unnamed prospect in the Wet Mountains (Fig. 5f). Although it is likely that the desulfidation of sphalerite was responsible for the formation of zincian spinel in some locations, it is also likely that other zincian-spinel-forming reactions occurred in and adjacent to each of the sulfide deposits. These reactions could involve (1) the breakdown of Zn-bearing biotite at the Green Mountain deposit (Fig. 3d), (2) the breakdown of zincian staurolite at the Independence deposit (Fig. 3c), and (3) the precipitation from a metamorphic-hydrothermal solution in pegmatitic veins and metamorphic segregations in the Cotopaxi deposit. Textural evidence and mass-balance considerations indicate that hercynite from Evergreen, which occurs in corona and symplectite textures along with cordierite, corundum, staurolite, ilmenite and högbomite, was derived from a reaction between gedrite and sillimanite (Heimann *et al.* 2002). Elsewhere, textural relations suggest that spinel in sulfide-absent rocks from the Marion deposit and the unnamed prospect in the Wet Mountains was derived from reactions involving corundum and sapphirine.

Studies here show that grains of zincian spinel in Mg-rich alteration zones of Proterozoic metamorphosed massive sulfide deposits in Colorado contain a much higher proportion of the spinel component than those shown by Spry (2000) because in most cases the zincian spinel did not form by the desulfidation of sphalerite (Fig. 8a). Most metamorphosed massive-sulfide deposits that contain gahnite and sphalerite also contain pyrite and pyrrhotite, or S-rich pyrrhotite compositions near the pyrrhotite–pyrite equilibrium boundary. These assemblages buffer the sulfur fugacity at or near the pyrite–pyrrhotite boundary, which in turn buffers the sphalerite composition and the gahnite-to-hercynite ratio of the zincian spinel. This is the main reason why gahnite compositions usually have a restricted Zn-to-Fe ratio in a given deposit (Fig. 8b). The restricted Zn-to-Fe ratio of zincian spinel found in massive sulfide occurrences was verified by the experiments and thermodynamic calculations of Spry & Scott (1986a). It is noted here that for sulfidation reactions involving Fe-silicates, such as almandine in reaction 2, the activity of iron in the sphalerite and pyrrhotite will dictate the activity of Fe in the Fe-silicate. Details concerning the method of calculation, the chemical potential of species

in the gahnite-forming reaction, and anticipated compositions of zincian spinel at given P–T conditions are discussed by Spry (2000). However, with few exceptions (*e.g.,* Green Mountain and some samples in Cotopaxi), grains of zincian spinel in metamorphosed massive-sulfide deposits in Colorado are not found in the sphalerite – pyrrhotite – pyrite-rich ore, but coexist with disseminated sulfides, and most of these samples contain <1 vol.% sphalerite, pyrrhotite, and pyrite (some up to approximately 5 vol.%). In samples from the Green Mountain, Cotopaxi and Bon Ton deposits, which are not enriched in Mg-bearing minerals, minor amounts of sphalerite, pyrrhotite, and pyrite (traces to 5 vol.%) seem to be sufficient to buffer $f(S_2)$ and to generally fix

TABLE 4. REPRESENTATIVE ZINCIAN-SPINEL-BEARING ASSEMBLAGES, COLORADO DEPOSITS

Deposit	Sample	Assemblage
Ace High	AHCO–112	Phl–ghn–qtz–sil–rt–aln–zrn–ap–cp*
	AHCO–113	Phl–ghn–ged–rt–aln–tur–zrn
	AHCO–120	Phl–ghn–ath–ap–rt–chu–zrn
Amethyst	AHCO–56	Crd–ged–spl–phl–spr–an–py*–cp*–po*–sp*–zrn
	AHCO–58	Ol–sp–cp–spl–mag*–po*–gn*
Betty	99CO–86	Cum–sp–ghn–cp*–po*–py*–gn*
	99CO–87	Ged–alm–hc–phl–cum–hbl–st–crn–aln–zrn–cp*–po*
	99CO–89	Ath–ghn–rt
	99CO–94	Qtz–crd–ghn–sil–pl–phl–mnz–zrn
	G9914A1A	Qtz–grt–crd–phl–ghn–sil–mnz–zrn–cp*
Bon Ton	99CO–22	Alm–bt–qtz–sil–and–ghn–ms–py*–cp*–sp*
	99CO–23	Phl–qtz–alm–ghn–pl–chu–py*–cp*–sp*
Caprock	AHCO–151	Ghn–alm–phl–oli–zrn–py*–cp*
	AHCO–158	Fo–spl–cum–act–zrn–mgt*
Cinderella	99CO–2	Tr–spl–phl–sp*
	99CO–3	Spl–ath–phl–sil–py*
	99CO–4	Phl–qtz–grt–ghn–aln–zrn–py*
	99CO–5	Qtz–phl–ghn–pl–kfs–grt–sil
	99CO–8	Ath–spl–tr–phl–ol–chu
	99CO–9	Act–phl–grt–ghn–sil
Cotopaxi	99CO–12	Ghn–phl–ath–rt*
	99CO–70	Fo–spl–act–phl–chu–mgt*–ilm*–cp*–gn*–sp*
	99CO–72	Qtz–ghn–sp–gn–phl–spn–rt–mgt*–cp*–po*–mlb*
Evergreen	99CO–64B	Ged–crd–alm–hc–sil–crn–st–hög–qtz–pl–phl–ilm
Green	AHCO–11	Ged–hc–phl–mgt–zrn–aln–rt–hem*–ilm*–cp*–po*
Mountain	AHCO–18A	Hbl–ghn–pl–cp–sp–cum–bt–mgt*–py*–po*
	AHCO–26A	Cum–ghn–en–ilm–cp*–mgt*–po*–sp*
	AHCO–33	Ged–ghn–phl–pl–zrn–ilm*–cp*–po*
	AHCO–34	Qtz–bt–alm–ghn–zrn–py*–cp*–sp*
Independence	AHCO–128	Ath–phl–ghn–rt*–ilm*–zrn*
	AHCO–129	Ath–phl–ghn–cp–sp–zrn–aln–ilm*–po*–mlb*
	AHCO–133	Hbl–ghn–cum–phl–aln–zrn–ilm*–sp*–cp*
	AHCO–134	Qtz–crd–alm–pl–sil–st–ghn–bt–mgt–ilm*–py*–cp*
Marion	AHCO–87	Spl–phl–crd–an–crn–aln–spr–rt–zrn
	AHCO–88	Spl–phl–cum–hbl–an–aln–sil–rt–zrn–ap–mgt*–py*–cp*–po*–gn*
	AHCO–91A	Act–pl–qtz–sp–ghn–phl–zrn–po*–cp*–py*–gn*
	AHCO–94	Di–sp–po–spl–cp*–mgt*–py*
	AHCO–101	Fo–spl–chu–sp–cp*–po*
Sedalia	99CO–38	Ged–hc–mgt*–ilm*–py*–sp*–gn*
	99CO–39	Cum–ghn–ilm*–cp*–sp*
	99CO–42	Cum–qtz–crd–grt–hc–st–zrn–mgt*–ilm*–po*
Unnamed	AHCO–77	Spl–en–ged–crd–spr–an–phl–sil–chu–ilm*–py*–cp*
	AHCO–78	Spl–ath–en–phl–crd–sil–chu–mgt*–ilm*–py*–cp*
	AHCO–80	Spl–crd–ged–phl–en–pl–sil–mgt*–ilm*–sp*–py*–cp*–po*

Minerals are listed in approximate order of abundance; *: less than 1% is present. The symbols are those of Kretz (1983), except for cp: chalcopyrite, ghn: gahnite, hög: högbomite, oli: oligoclase.
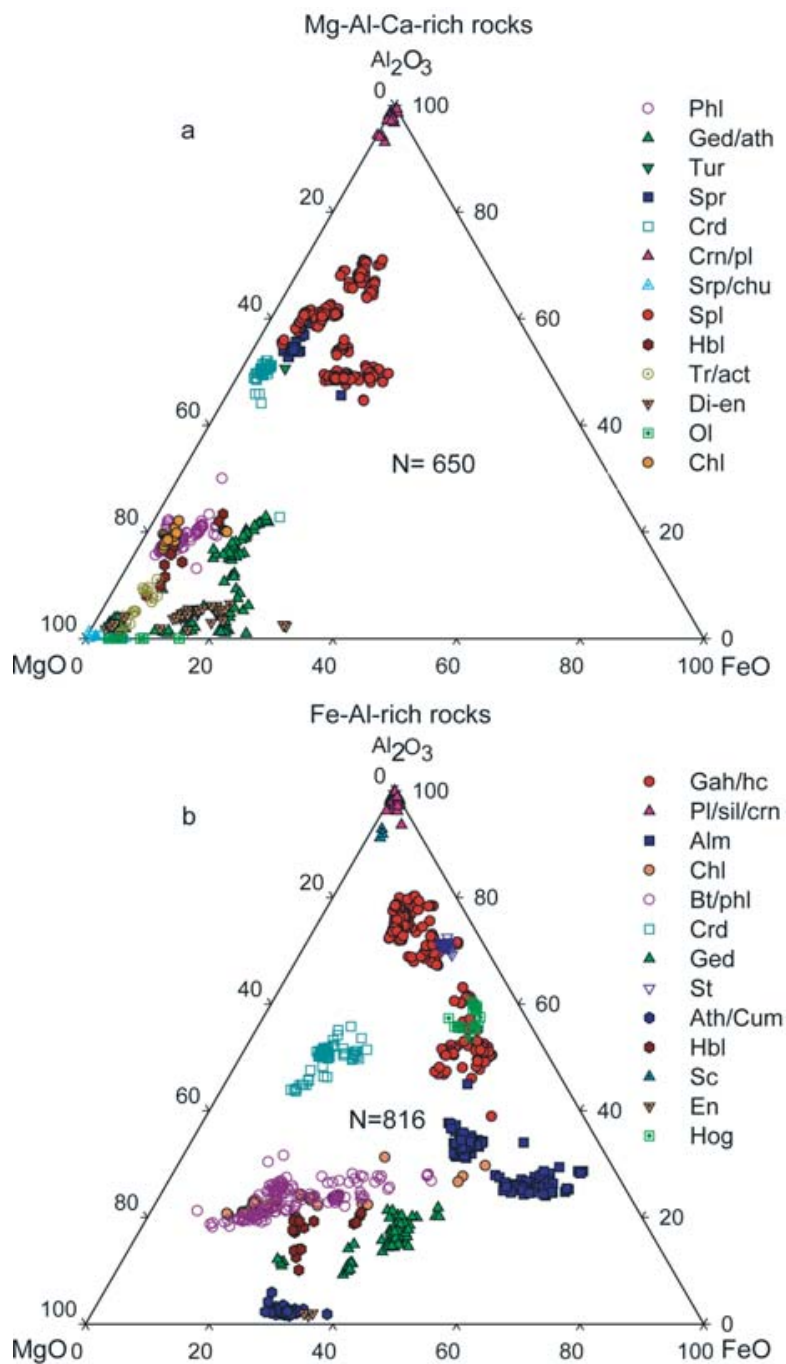
Fig. 7. Triangular diagram in terms of molar proportions of Al₂O₃, MgO and FeO showing the chemical variations of silicates associated with zincian spinel in metamorphosed massive-sulfide deposits and zones of hydrothermal alteration from Colorado in a) Mg–Ca-rich rocks (field 1) and b) Fe–Al-rich rocks (field 2) in Figure 4. For abbreviations, see Kretz (1983) and the footnote to Table 4.
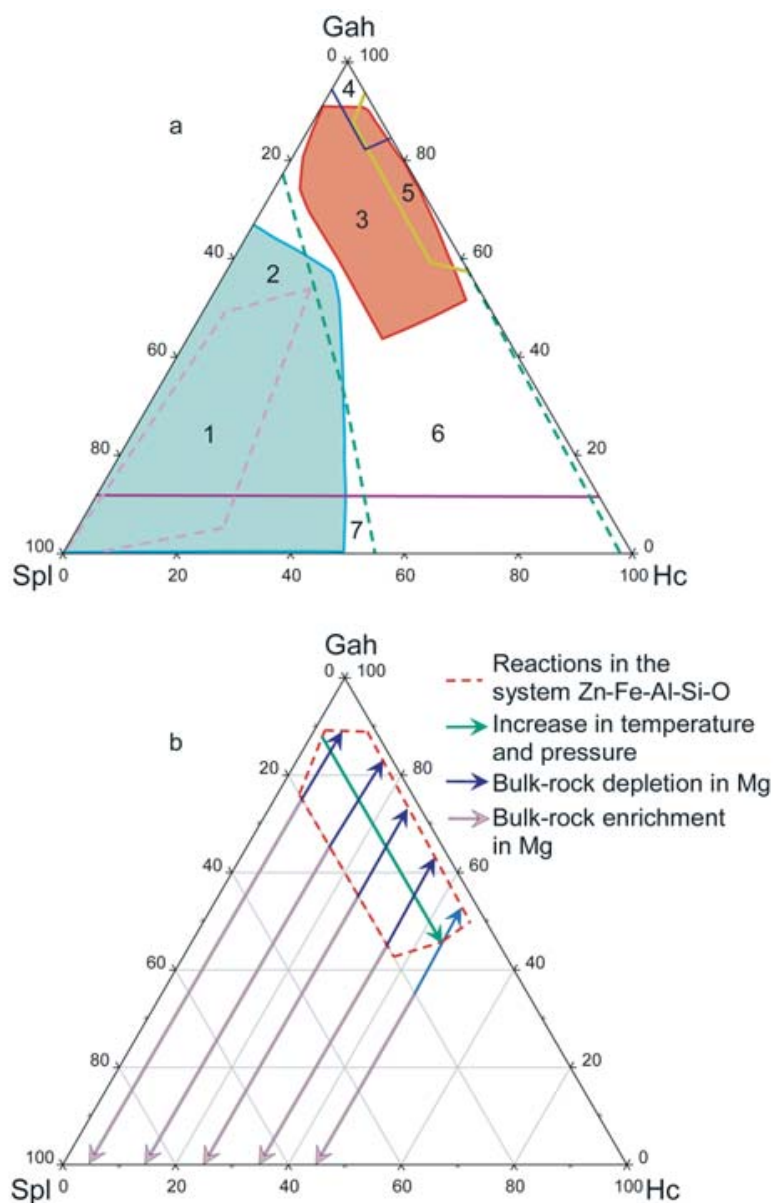
FIG. 8.   a. Triangular plot of zincian spinel compositions in terms of gahnite, hercynite and spinel components from worldwide localities in (1) marbles, (2) metamorphosed massive sulfide deposits and S-poor rocks in Mg–Ca–Al alteration zones, (3) metamorphosed massive sulfide deposits in Fe–Al metasedimentary and metavolcanic rocks, (4) metabauxites, (5) granitic pegmatites, (6) unaltered and hydrothermally altered Fe–Al-rich metasedimentary and metavolcanic rocks, and (7) Al-rich granulites (that area below the red line where the gahnite component is less than 12 %). The data used in this plot are from Spry & Scott (1986a) and Figures 4 and 6. b. Schematic triangular diagram showing the gahnite, hercynite, and spinel content of zincian spinel in metamorphosed massive-sulfide deposits. Samples of zincian spinel in metamorphosed massive-sulfide deposits in Fe–Al rich rocks typically form an area containing 10 ± 9 mole % $MgAl_2O_4$ and between 50 and 90 mole % $ZnAl_2O_4$ (dashed line). The Mg content of the spinel is low owing to the low Mg-to-Fe ratio of the ore and host rocks, whereas the Zn-to-Fe ratio of the zincian spinel is buffered by $f(S_2)$, which is dictated by the composition of sulfides in the system Zn–Fe–S. The Zn:Fe ratio of the zincian spinel will decrease with increasing T and, to a lesser extent, P. In Mg-rich rocks, compositions of the zincian spinel shift toward the Mg apex. These competing physical and chemical parameters allow for a complete range of compositions of spinel in metamorphosed massive-sulfide deposits, from $MgAl_2O_4$-rich to $MgAl_2O_4$-poor with $ZnAl_2O_4$ contents > 50 mole %.

the Zn:Fe ratio of the zincian spinel. Such compositions overlap those of zincian spinel spatially associated with metamorphosed massive-sulfide deposits elsewhere in the world. However, in other deposits, such as Marion and Amethyst, which contain between a trace and 10 vol.% sphalerite, pyrrhotite, and pyrite, the high Mg content of the host rocks will dictate that the spinel is Mg-rich. Note that whereas the gahnite:hercynite ratio may be fixed by the presence of sphalerite, pyrite, and pyrrhotite, the (gahnite + hercynite) : (gahnite + hercynite + spinel) ratio will be small if the zincian-spinel-bearing rocks are Mg-rich since the Mg component does not take part in the desulfidation reaction. This concept is schematically illustrated in Figure 8b.

CONCLUSIONS

1. The composition of zincian spinel in rocks is controlled by a variety of physical and chemical parameters including $f(O_2)$, $f(S_2)$, pressure, temperature, the composition of the host rocks, and the ability of minerals in the host rock, other than spinels and sulfides, to incorporate Zn in their structures. The gahnite-to-hercynite ratio of zincian spinel is higher at low metamorphic grades (*e.g.*, upper greenschist facies) than at high metamorphic grades (*e.g.*, granulite facies), and at high $f(O_2)$ and $f(S_2)$ conditions. Although the gahnite: hercynite ratio of the spinel will be dictated by the buffering capacity of associated sphalerite, pyrite, and pyrrhotite, an elevated content of the spinel component is to be expected in Mg-rich sulfide-bearing rocks. In zincian-spinel-bearing rocks with less than a few percent Zn–Fe sulfides, the buffering capacity of the rock may not have been reached. In this situation, the composition of the zincian spinel will be dictated by bulk-rock composition. For most gahnite-forming reactions, unless sphalerite is in equilibrium with the zincian spinel, the zincian spinel contains all of the Zn rather than the coexisting silicates, with staurolite and, less commonly, biotite, being the major exceptions.

2. The composition of zincian spinel can be used as an exploration guide to metamorphosed massive-sulfide deposits, as previously proposed by Spry & Scott (1986a), but the preferred range of compositions has been modified to incorporate new data published in the literature since 1986, data from granulites that were not included originally, and new data obtained here (Fig. 6). Nearly all occurrences of zincian spinel in and adjacent to metamorphosed massive-sulfide deposits are hosted by hydrothermally altered aluminous metasedimentary and metavolcanic rocks and have the following compositional range: $\text{Gahnite}_{45–90}\text{Hercynite}_{0–45}\text{Spinel}_{0–25}$. However, zincian spinel in zones of unusually Mg-rich (and Ca-rich) alteration spatially associated with metamorphosed massive-sulfide deposits, as observed for example in Colorado, are more enriched in the spinel component and show a markedly different composi-

tional range: $\text{Gahnite}_{0–65}\text{Hercynite}_{0–50}\text{Spinel}_{25–90}$. The choice of spinel compositions to be used as an exploration guide will be dictated by a preliminary assessment of the host rocks and alteration types observed in a given terrane. This study serves to stress the importance of bulk-rock composition in affecting the composition of zincian spinel, particularly where the rocks are Mg-rich.

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