Chapter H

ENVIRONMENTAL GEOCHEMISTRY OF SKARN AND POLYMETALLIC CARBONATE-REPLACEMENT DEPOSIT MODELS

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INTRODUCTION

Geoenvironmental models are compilations of geologic, geochemical, and hydrologic information that describe pre- and post-mining environmental signatures of mineral deposits. The environmental behavior of carbonate-hosted deposits varies according to deposit type. This discussion of the environmental geochemistry of carbonate-hosted sulfide deposits considers two major groups of deposits: (1) metallic ores deposited by low-temperature, basinal brines in platform carbonate host rocks, and (2) metallic ores deposited by the reaction of higher temperature fluids with carbonate host rocks. In part I, Foley and others address low-temperature platform-carbonate deposits of the Mississippi Valley type. In part II, we discuss high-temperature skarn and polymetallic carbonate-replacement deposits. General environmental considerations and characteristics of the deposits are discussed in part I.

Skarn and polymetallic carbonate-replacement deposits form by reaction of hydrothermal fluids ($>>250$ ^{o}C) generated in high-temperature igneous (e.g., porphyry) environments with carbonate-bearing country rocks. These fluids can be of low to high salinity and may contain CO_2 and other gaseous components. In contrast, the platform-carbonate deposits described in part I form by the interaction of low to moderate temperature (generally <200 ^{o}C), high salinity (10-30 equivalent weight percent NaCl) basinal brines or meteoric waters with carbonate-bearing sequences. The resulting ore and gangue mineralogies of these two deposit types reflect the ability of the two distinct fluid types to leach metals from the original source rocks and transport them to the depositional sites.

This paper presents a summary and some refinements of previous geoenvironmental models for high-temperature, carbonate-hosted deposits (du Bray, 1995, and references therein).

SKARN AND POLYMETALLIC CARBONATE-REPLACEMENT DEPOSITS

Skarn and polymetallic carbonate-replacement deposits are related genetically to magmas that intrude into sedimentary rocks (fig. 1). The deposits form when magmatic-hydrothermal fluids expelled from cooling magmas react chemically with carbonate-rich sedimentary rocks. Skarn and polymetallic carbonate-replacement deposits are associated with many other types of magmatic-hydrothermal deposits in mineral districts. In fact, distinction between skarn and other deposit types is not always easy. In many districts, skarns form an intermediate "zone" of deposits between porphyry deposits in the center of mining districts and outer zones of polymetallic vein and replacement, and distal-disseminated, deposits.

Carbonate-hosted mineral deposits generally are less likely than other deposit types to generate acid mine drainage because of the availability of acid- neutralizing minerals, such as carbonates and reactive silicates, the coarse mineral grain size, and the high metal to sulfur ratios of many sulfide minerals in skarns (Kwong, 1993). However, these deposits locally can include massive concentrations of sulfide minerals as well as potentially toxic elements that remain in solution at high pH (e.g., Zn, Mn) and therefore are difficult to remove in order to meet water-quality standards. We know of three cases where significant environmental problems associated with processed waste from carbonate-hosted mineral deposits led to U.S. Environmental Protection Agency (EPA) National Priority listing for site clean-up under the Superfund program. The Cleveland mill in Grant County, southwestern New Mexico (U.S. EPA, 2000a; Boulet and Larocque, 1997) processed ores from copper and zinc skarns. Mill tailings washed into a creek resulting in locally acidic surface waters (pH as low as 2.2) and elevated dissolved-metal concentrations (As, Pb, Cd, Zn, Be).   In western Colorado, a century of mining of polymetallic carbonate-replacement deposits in the Leadville and Gilman mining districts generated large volumes of mining wastes that impacted area soils and rivers. In the 1980s, ecological impacts and human health threats associated with mine waste led to Superfund site designations at California Gulch in the Leadville mining district, Colorado and at the Eagle mine in the historic Gilman mining district near Vail, Colorado (U.S. EPA 2000b, 2000c; Engineering Science, Inc., 1985).
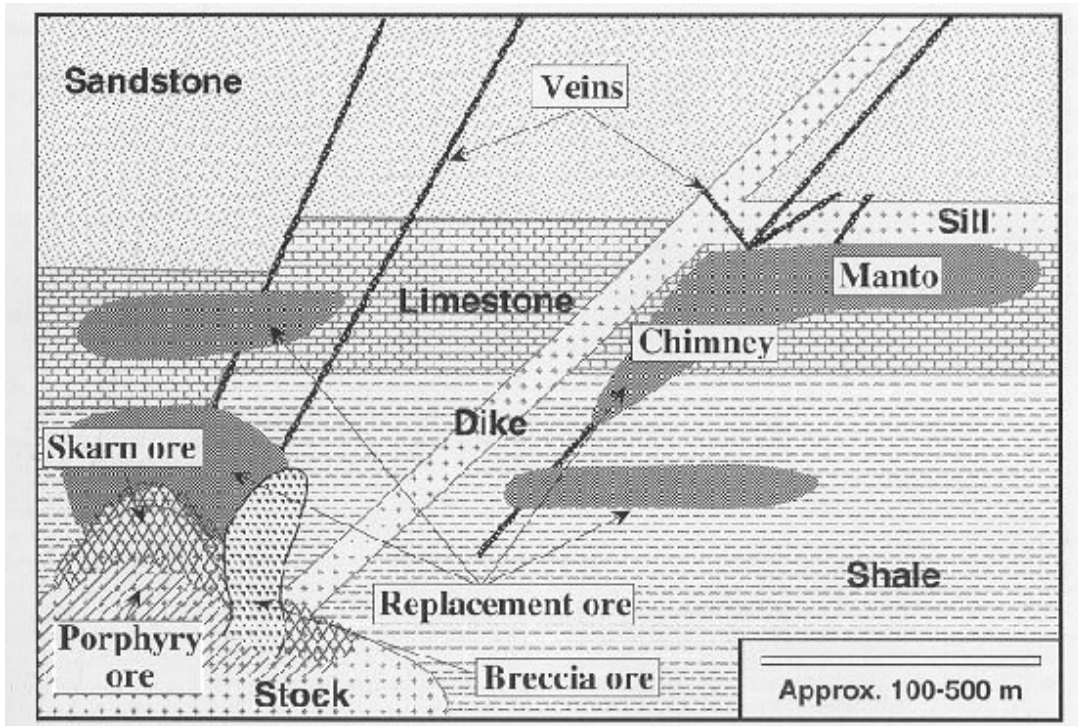
Figure 1. Generalized conceptual model for the geologic setting of high-temperature, carbonate-hosted and related deposits associated with igneous intrusions. (From Plumlee and others, 1999, figure 19.18)

Preliminary geoenvironmental models (duBray, 1995) were developed for skarns and polymetallic replacement deposits (Plumlee and others, 1995; Hammarstrom and others, 1995a, b, c). The most important geological characteristics shared by these types of deposits are listed in table 1. In the following discussion, we synthesize data included in the preliminary models, incorporate new data, and focus on salient differences between skarns and polymetallic carbonate-replacement deposits and differences among skarn types, with particular emphasis on differences that bear on their environmental signatures (table 1).

Table 1. Most important geological characteristics of skarn and polymetallic carbonate- replacement deposits (based largely on Meinert, 1998, 1992).

1.	Deposits are hosted by carbonate rocks (limestones, dololstones, calcareous clastic sediments).
2.	Deposits are epigenetic, formed at high temperature (>250 $^{\circ}$C), cut across host rocks, and have sharply discordant contacts with host rocks.
3.	Deposits are associated with igneous activity, typically with plutons or batholiths.
4.	Depth of formation varies from near-surface to about 10-12 km; depth of formation controls size, geometry, and type of alteration.
5.	Deposits cluster around igneous intrusions in mineralized districts that typically include other intrusion-related deposit types (e.g., porphyry deposits, polymetallic veins).
6.	Deposit types and metals are zoned spatially with respect to intrusions such that copper and gold are found proximal to intrusions; zinc and lead are distal to intrusions.
7.	Ore-mineral assemblages typically include pyrite or pyrrhotite, and other sulfide minerals, and calcsilicate and carbonate gangue minerals.
8.	Local concentrations of ore can consist of massive concentrations (>50%) of sulfide minerals.
9.	Deposits form in stages, which may overprint one another in time and space. Early hornfels metamorphism can reduce permeability but fracturing associated with igneous emplacement, and late-stage hydrofracturing increase permeability and provide pathways for fluid flow.
10.	Ore minerals typically are coarsely crystalline.
11.	Late-stage pyrite and other alteration minerals can be disseminated over a wide area.

<u>Deposit geology</u>
Skarns

Skarns (tactites) are coarsely-crystalline metamorphic rocks composed of calcium-iron-magnesium-manganese-aluminum silicate minerals (commonly referred to as "calcsilicate" minerals) that form by replacement mainly of carbonate-bearing rocks during contact or regional metamorphism and metasomatism. The majority of the world's major skarn deposits are thought to be related to hydrothermal systems (Einaudi and others, 1981). Skarns can be barren or may contain metals or other minerals with economic value. Skarn deposits are important sources of base and precious metals as well as tin, tungsten, and iron. Skarns are relatively high-temperature mineral deposits resulting from magmatic-hydrothermal activity associated with granitoid plutons in orogenic tectonic settings. Skarns generally form where a granitoid pluton has intruded sedimentary strata that include limestone or other carbonate-rich rocks. The processes that lead to formation of all types of skarn deposits include the following stages: (1) isochemical contact metamorphism during pluton emplacement, (2) prograde metasomatic skarn formation as the pluton cools and an ore fluid develops, and (3) retrograde alteration of earlier-formed mineral assemblages. Deposition of ore minerals accompanies stages 2 and 3. Skarn deposit mineralogy is spatially zoned with respect to pluton contacts, host rock lithology, and (or) fluid pathways. Later petrogenetic processes may partly or completely obliterate earlier stages of skarn development. Skarns are classified as calcic if the protolith was limestone, and as magnesian if the protolith was dolostone. Skarns also are classified by the most economically important metal present, including copper, iron, zinc-lead, gold, tin, tungsten, and molybdenum (table 2). In some cases, subdivisions also are made on the basis of oxidation state (oxidized versus reduced) as reflected by mineralogy. A variety of different skarn types can occur in a relatively small geographic area. In the Winnemucca area of north-central Nevada, for example, all skarn types except tin skarns are observed (fig. 2). In this part of Nevada, iron, tungsten, and base-metal skarns are associated with Jurassic and Cretaceous intrusions whereas gold skarns are associated with Tertiary intrusions.

Each class of skarn deposit has a characteristic, though not necessarily unique, size, grade, tectonic setting, granitoid association, and mineralogy (Einaudi and Burt, 1982; Einaudi and others, 1981; Meinert, 1983; Ray and Webster, 1990). Not surprisingly, therefore, the various classes of skarn deposits have different geochemical signatures and oxidation-sulfidation states. Some skarn deposits are best described as polymetallic and are difficult to classify by existing schemes. The Nabesna Fe-Au skarn in Alaska, for example, has been classified as an iron skarn with by-product gold and as a gold-rich copper skarn by different workers (Eppinger and others, 2000, 1999, 1997). In addition, some skarns contain unusual concentrations of rare-earth minerals and uranium or platinum group elements (Meinert, 1998). Many skarns mined in the past for iron, copper, or tungsten have been reexamined and developed for gold in the past 30 years. The Bonfim W-Au deposit in northeastern Brazil , for example, has proven total reserves of 70 tons of scheelite, but discovery of gold in abandoned dumps in the 1990s led to further development and production of 100 kilos of gold (Souza Neto and others, 1998).

Most economic skarn ore is present as exoskarn, which forms in carbonate host rocks proximal to an intrusion. The parts of the intrusion that are altered and can host ore are referred to as endoskarn. Endoskarn is variably developed on the intrusion side of intrusion-wallrock contacts. Endoskarn may include high-grade ore zones or may be part of the waste rock. For a recent review of skarn classification, geology, mineralogy, genesis, exploration strategies, and case examples, see Meinert (1992).

Polymetallic carbonate-replacement deposits

Polymetallic carbonate- replacement deposits are massive lenses, pods, and (or) pipes (mantos or chimneys) of sulfide minerals that comprise Pb-Zn-Ag-Cu-Au ores hosted by, and replacing, limestone, dolostone, and other sedimentary rocks. Most massive replacement ores contain more than 50 percent sulfide minerals (Plumlee and others, 1995; Megaw, 1998). Some polymetallic carbonate-replacement deposits occur with, or grade into, skarn deposits at the contact between sediments and intrusion. In both polymetallic carbonate-replacement deposits and base-metal-rich skarn deposits, ore metals typically are zoned. Copper and gold are enriched proximal to the intrusion and lead-zinc-silver ores occur in distal parts of the mineralized system.

Examples of skarns and polymetallic carbonate-replacement deposits are listed in table 2, along with comments about associated igneous rocks and with references. Some types of igneous rocks potentially provide long-term acid-neutralizing capacity because mafic silicate minerals such as biotite, chlorite, pyroxene, and calcic plagioclase consume acid upon weathering. Many of these same minerals also are present in retrograde skarn mineral assemblages. Calcite (or dolomite) is ubiquitous in skarn and replacement deposits. Calcite in ores, along with carbonate host rocks, typically provides enough neutralization capacity to mitigate any acid generated by weathering of iron sulfide minerals. Endoskarn minerals or altered igneous rocks may neutralize acid, albeit at a much slower rate than the highly reactive carbonate minerals.

Table 2. Classification of skarn and polymetallic carbonate-replacement deposits. [Mt, million tonnes. Examples include individual deposits well as mining districts; for U.S. deposits, state abbreviations are listed]

| Metal Suite	Deposit type	Subtype and Size	Examples	Comments	References
Fe (Cu,Co,Ni, Au)	Fe skarn	Calcic *Size: 5 to 200 Mt* *Grade: 50% Fe*	Hancock, NV Jumbo, MT Shinyama, Japan Daquiri, Cuba Empire, Canada	Form large skarn deposits. Mined primarily for iron. Intrude limestones and volcanics. Igneous rocks are Fe-rich and altered (feldspars, scapolite).	Meinert, 1998a Einaudi and others, 1981 Sangster, 1969 Cox, 1986 Mosier and Menzie, 1986
		Magnesian *Size: 5 to100 Mt* *Grade: 50% Fe*	Fierro-Hanover, NM Cornwall, PA Eagle Mountain, CA Janggun, Korea	Dolomitic wallrocks. Skarn minerals are Mg-rich silicates (Fe forms magnetite).	Meinert, 1998a Hall and others, 1988 Lapham, 1968
		Scapolite-albite *Size: 5 to100 Mt* *Grade: 40% Fe*	West Humboldt, NV Kachar, Sarbay, USSR	Very large tonnage deposits. Albite and scapolite in addition to garnet and pyroxene. Form in volcanic-sedimentary basins so host rocks include volcanics as well as carbonates. Some deposits are enriched in cadmium.	Zitzmann, 1977 Einaudi and others, 1981 Sokolov and Grigorev, 1977
Au	Au skarn	Calcic Reduced *Size: 0.2 Mt* *Grade: 9 g/t Au, 5 g/t Ag*	Fortitude, NV Crown Jewel, WA Elkhorn, Beal MT Junction Reefs, Australia Itajubatiba, Brazil Nickel Plate, British Columbia, Canada	Mined for gold. Associated with reduced, ilmenite-bearing diorite-granodiorite plutons. Form in clastic-rich protoliths rather than pure limestones. Wide (100's of meters) hornfels halos. Distinctive Au-Bi-Te-As geochemical signature. Low garnet:pyroxene ratios. Abundant sulfides (pyrrhotite, arsenopyrite). Pyrrhotite>pyrite.	Meinert, 1998a,b Meinert, 1989 Theodore and others, 1991 Souza Neto and others, 1998 Souza Neto, 1999 Ettlinger and Ray, 1989

Metal Suite	Deposit type	Subtype and Size	Examples	Comments	References
		Calcic Oxidized Size: 0.4 Mt Grade: 4 g/t Au	McCoy, NV Nambija, Ecuador	Low total sulfides (minor but ubiquitous chalcopyrite, sphalerite, galena). Pyrite>pyrrhotite. High garnet:pyroxene ratios. Gold associated with K-feldspar and quartz as part of late retrograde alteration.	Meinert, 1998a,b Brooks and others, 1991 Theodore and others, 1991
		Magnesian	Butte Highlands, MT Cable, MT	Dolomitic protolith. Magnetite rich (strong magnetic signature). Mg-rich silicate minerals.	Meinert, 1998a,b Ettlinger and others, 1996
Cu (Au)	Cu skarn	None Size: 0.6 Mt Grade: 2% Cu, <1 g/t Au, 10 g/t Ag	Carr Fork, UT Cyprus-Pinos Altos, NM Cananea, Mexico Meme, Haiti	Most abundant skarn type Associated with I-type, calcalkaline magnetite-series porphyritic plutons. Largest are associated with porphyry copper deposits. Garnet>pyroxene. Zoned: pyrite and chalcopyrite proximal to pluton, bornite in distal zones. Intense retrograde alteration (sericite, K-feldspar).	Einaudi and others, 1981 Einaudi, 1982 Meinert, 1998a,b Cox and Theodore, 1986 Jones and Menzie, 1986 Boulet and Larocque, 1997 Theodore & Blake, 1975
	Cu-Au skarn	None Size: 37.4 Mt Grade: 2.7% Cu, 1 g/t Au, 16 g/t Ag	Big Gossan, Ertsberg, Indonesia	Gold is a by-product of copper mining. Sulfide-rich (chalcopyrite, pyrite dominant). Locally, massive orebodies of sulfides .	Meinert, 1998a Meinert and others, 1997
W (Cu) (Mo)	W skarn	Reduced Size: 0.1 to 5 Mt Grade: 0.8% WO_3	Fairbanks, AK MacTung, Canada Salau, France Sandong, Korea	Associated with granites. Pyroxene>garnet. Scheelite is main ore mineral, with pyrrhotite, chalcopyrite, sphalerite.	Newberry, 1998 Menzie and others, 1992
		Oxidized Size: 0.1 to 5 Mt Grade: 0.7% WO_3	Pine Creek, CA Mill City, NV Brown's Lake, MT King Island, Australia	Associated with granites and granodiorites. Garnet>pyroxene. Scheelite is main ore mineral, with pyrite, chalcopyrite, magnetite.	Newberry, 1998

Metal Suite	Deposit type	Subtype and Size	Examples	Comments	References
W-F (Be) (Bi) (Mo)	W-F skarn	Mo-poor *Size: 0.1 to 1 Mt* *Grade: 0.2% WO₃*	McCullogh Butte, NV Upper Salcha, AK	Associated with S-type peraluminous granites. Garnet, pyroxene, scapolite. Ore includes fluorite and scheelite, Be minerals, sphalerite, and pyrite.	Newberry, 1998
	W-F skarn	Mo-rich *Size: >9 Mt* *Grade: 0.2% WO₃, 0.05% MoS₂*	Blue Ribbon, NV Shizhuyuan, China Mt. Reed, Canada Logtung, Canada	Associated with granite Alteration includes greisen, quartz-molybdenite-wolframite stockworks. Garnet>pyroxene, vesuvianite. Ore includes Mo-rich scheelite, fluorite, pyrite, molybdenite, cassiterite, and wolframite.	Newberry, 1998 Kwak, 1987 Einaudi and others, 1981 Zhao, 1989 Meinert, 1995a,b Elliott, 1988
Sn	Sn skarn	Skarn sensu stricto *Size: 0.1 to 5 Mt* *Grade: 0.25% Sn*	Lost River, AK Moina, Australia	Associated with S-type, ilmenite series granite. Ore includes cassiterite, stannite, arsenopyrite, pyrrhotite, and wolframite. Greisen can be minor to extensive. Garnet, pyroxene, vesuvianite.	Newberry, 1998 Ray and Webster, 1997 Kwak, 1987 Meinert, 1995a,b Zhao, 1989 Reed and Cox, 1986 Menzie & Reed, 1986a
		Sn replacement *Size: 1 to 5 Mt* *Grade: 0.7% Sn*	Geiju district, China Renison Bell, Mt. Bishoff, and Cleveland, Australia	Associated with A-, S-type, ilmenite-series granite. Ore includes pyrrhotite, arsenopyrite, cassiterite, sphalerite, and galena. Extensive greisen development. Prograde calcsilicate minerals absent.	Newberry, 1998 Kwak, 1987 Einaudi and others, 1981 Zhao, 1989 Menzie & Reed, 1986b Reed, 1986

Metal Suite	Deposit type	Subtype and Size	Examples	Comments	References
Zn-Pb-Ag	Zn-Pb skarn	None *Size: 1.4 Mt Grade: 5.9% Zn, 2.8% Pb, 0.5% Cu, 0.5 g/t Au, 100 g/t Ag*	Groundhog, NM Cleveland, NM Kelly, NM Bismark, Mexico	Most are distal to, or not obviously associated with, intrusive rocks. Distinctive manganese-rich skarn mineralogy. Pyroxene, garnet, pyroxenoid. Zoned from proximal silicates to distal sulfide replacement bodies (mantos, chimneys). Ore includes sphalerite, galena, pyrrhotite, pyrite, magnetite, chalcopyrite, arsenopyrite.	Einaudi and Burt, 1982 Mosier, 1986 Cox, 1986c Boulet and Larocque, 1998 Larocque and others, 1995
Pb-Zn-Ag	Polymetallic carbonate replacement	None *Size: 1.8 Mt Grade: 5.2% Pb, 3.9% Zn, 0.3% Cu, 2 g/t Au, 150 g/t Ag*	Leadville, Gilman, Breckenridge, CO Eureka, NV Magdalena, NM Tintic, Park City, UT Nakatatsu, Japan Naica, Mexico Drina, Yugoslovia	Wide spectrum of deposits that grade from skarn to massive sulfide chimneys and mantos. Generally in thick carbonate sequences; host rock can include limestone, dolostone, and other calcareous sedimentary rocks. Calcsilicate (skarn) minerals may or may not be present. Simple ore assemblages of galena, sphalerite, chalcopyrite, arsenopyrite, pyrite, and pyrrhotite. Carbonate, sulfate, and quartz gangue minerals.	Megaw, 1998 Vikre, 1998 Plumlee and others, 1995 Mosier and others, 1986 Morris, 1986 Wallace, 1993 Titley, 1993

Related Deposit Types

    A variety of other types of mineral deposits associated with igneous rocks can be spatially or genetically related to skarns and polymetallic carbonate-replacement deposits (fig. 1). Related deposit types vary as a function of igneous rock composition. Deposit types (models of Cox and Singer, 1986) related to tin and tungsten skarns include other deposit types related to relatively evolved (silica-rich) granites; examples are tin greisens (Model 15c) and tin or tungsten veins and stockworks (Model 15b). On a regional or district scale, copper, gold, iron and zinc-lead skarns and polymetallic carbonate-hosted replacement deposits are associated with porphyry copper (Model 17), polymetallic vein (Model 22c) and replacement (Model 19a), placer gold (Model 39a), and distal disseminated silver-gold (Model 19c; Cox, 1992) deposits, and with each other. Some deposits contain local concentrations of a metal that is atypical of the principal commodities for the deposit type. Therefore, many skarn and replacement deposits are classified as different deposit types by different investigators. For example, magnetite-rich ore is mined as a by-product at some of the tin skarns in Malaysia, and at many copper skarns. Recently, gold skarns have been recognized as a discrete type of skarn deposit (Meinert, 1989). Before the 1970s, most gold from skarns was mined as a by-product of mining for copper, iron, or zinc and lead (Meinert, 1998b).
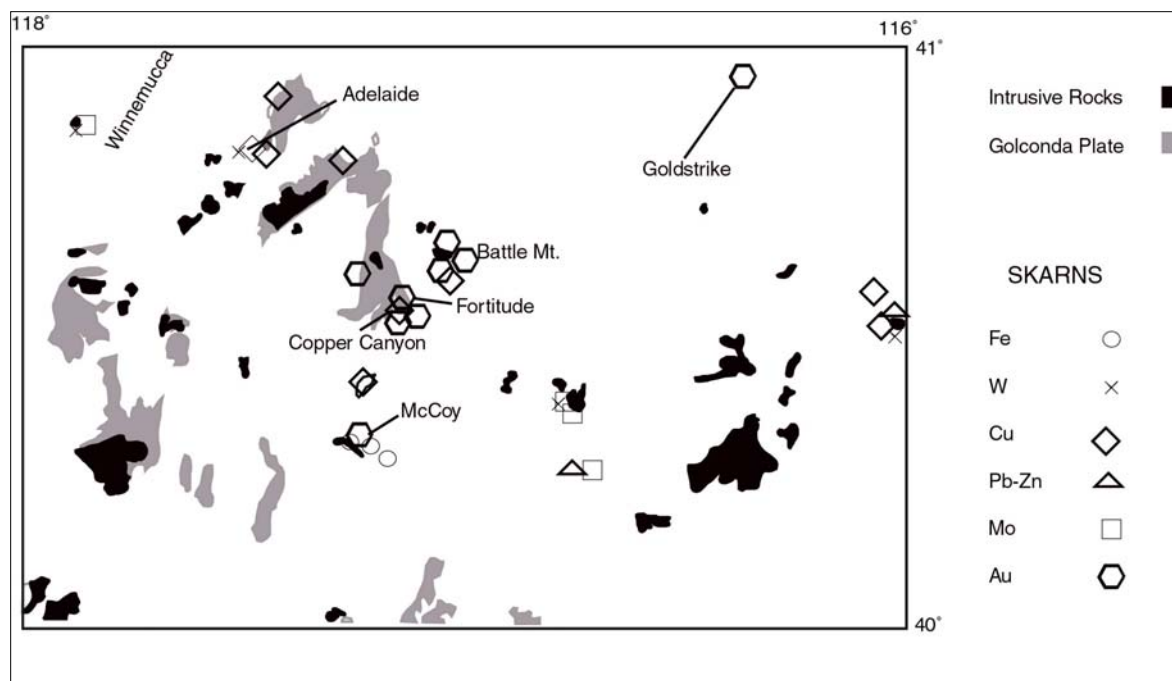
Figure 2. Distribution of skarn types in the Winnemucca 1° x 2° quadrangle, north-central Nevada. The Fortitude deposit is an example of a calcic, reduced gold skarn; McCoy is a calcic, oxidized gold skarn (table 2). At McCoy, calcic Fe skarn formed at the contact between Jurassic diorite and dolostone whereas the Au skarn formed along the contact of a Tertiary granodiorite stock. Intrusive rocks are shown in black; thick sequences of predominantly carbonate-rich Paleozoic sedimentary rocks crop out in the Golconda thrust plate (gray) in the western half of the quadrangle.

Deposit Size

    The largest deposits are the iron skarns, which can approach 200 million tonnes or ore (table 2). Median or typical tonnages and grades for different deposit types and subtypes are listed in table 2. Tin and tungsten skarns tend to be larger than base metal-skarns. Polymetallic carbonate-replacment deposits range from quite small (10,000 tonnes) to as much as 30 to 40 million tones, but average about 1.8 million tonnes. Relative to porphyry deposits and Carlin-type gold deposits, for example, skarns and polymetallic carbonate-replacement deposits are small and high-grade. The environmental implication of deposit size relates to the amount of land disturbed by the mining, the mining methods used to extract ores, and the amount of iron sulfide minerals available to generate acid waters.

Host rocks

    Host rocks include limestone, dolostone, marble, and other calcareous sedimentary rocks such as pelite, argillite, shale, greywacke, and other clastic rocks. Host rocks are highly calcareous sedimentary or metamorphosed calcareous sedimentary rocks (type IV of Glass and others, 1982) that have extensive acid-neutralizing capacity. Reduced gold skarns tend to occur in rocks with a significant clastic component, rather than in pure limestones (Meinert, 1998b).

Geologic Setting

    Skarns and polymetallic carbonate-replacement deposits are associated with batholiths and their sedimentary wallrocks. Associated volcanic rocks may or may not be present. Skarn can form in roof pendants within batholiths as well as along contacts. Skarn can underlie intrusive rocks, such as along the basal margins of laccoliths. Most base-metal skarns are associated with magmatic arcs related to subduction zones and form in tectonic settings that also host porphyry copper deposits. Tin and some tungsten deposits are more typical of anorogenic or continental settings.

Wall-Rock Alteration

Wall-rock alteration styles vary with deposit type. Extensive development of greisen and sericitic and silicic alteration are hallmarks of Sn-W deposits. Copper and some gold skarns associated with plutons that host porphyry deposits develop alteration zones that correlate with hydrothermal events in the pluton (Einaudi, 1982). Wall-rock can be altered to hornfels over areas as large as 15 to 20 km^2. Marbles, bleached zones, and skarn mineral assemblages can form in wall rocks. Potassic, sericitic, argillic, and propylitic alteration assemblages are variably developed and endoskarn may form within plutons. Silica and marble "fronts" may be present. In polymetallic carbonate-replacement deposits, calcsilicate minerals may or may not form. Host rocks typically are recrystallized, dolomitized, bleached, and (or) sanded (carbonate cement removed). Alteration of host rocks to jasperoid occurs in some deposits.

Nature of Ore

In gold and base-metal skarns, ore minerals may be present in massive, stratiform, vein, and (or) disseminated forms; crystal size is highly variable and ranges from fine to very coarse. Ore may be present in sulfide mineral zones, oxide zones, and in supergene, clay-rich oxidized zones. Sulfide minerals and gold generally are deposited during late, retrograde alteration within zones of hydrous calcsilicate minerals. Retrograde alteration may be best developed along faults cutting paragenetically earlier assemblages. Gold commonly is associated with a late pyrite + quartz assemblage. Total sulfide mineral content at the McCoy, Nevada calcic oxidized gold skarn (table 2) is low (<2 volume percent) and many sulfide minerals are oxidized. In contrast, at the Fortitude, Nevada calcic reduced gold skarn (table 5, fig. 2b) about 30 km to the north, high- grade ore is pyrrhotite-rich, with smaller amounts of chalcopyrite, pyrite, arsenopyrite, and native bismuth.

Iron skarn ore consists of massive magnetite layers or lenses. Orebodies are associated spatially with garnet zones or form in limestone outward beyond calc-silicate skarn zones. Calcic magnetite skarns and scapolite-(albite) iron skarns may be present within mafic stocks as replacements of gabbro and diorite, or of limestone xenoliths (Einaudi and others, 1981). Stockwork veins may be present in mafic volcanic rocks overlying altered gabbro. Orebodies may be lenticular, lensoid, tabular, contact-controlled deposits extending hundreds of meters to 4 km or more along strike and having thicknesses of tens to hundreds of meters. The deposits also occur as irregular and pipelike replacements of mafic intrusions and as stockworks. Ore may be present in nearly monomineralic veins, pods, layers, or lenses of magnetite, or may consist of magnetite-rich lamina or layers alternating with, or intergrown with, gangue minerals. Ore mineral associations in the Cornwall, Pennsylvania iron skarn include magnetite-chalcopyrite-pyrite, magnetite-pyrite-actinolite, magnetite-chlorite, magnetite-hematite-calcite, and magnetite alone. Magnetite varies from anhedral and granular to euhedral, and forms platy pseudomorphs after hematite (Lapham, 1968).

Tungsten skarn orebodies are stratiform deposits that can extend for hundreds of meters along lithologic contacts. Stockwork and local crosscutting veins are common. The crystal size and molybdenum content of scheelite in tungsten skarns varies. Paragenetically early, anhydrous skarn generally contains finely-crystalline, high-molybdenum scheelite, whereas retrograde skarn contains medium to coarsely crystalline, low-molybdenum scheelite. Coarsely crystalline, vuggy skarn with uneven ore grades forms from impure marble. More finely crystalline, compact skarns with evenly distributed ore grades tend to form from pure marbles (Einaudi and others, 1981).

Tin skarn orebodies may develop at intrusive contacts with carbonate rocks, or along intrusion-related fractures and veins at distances up to 300 m from the intrusion (Reed and Cox, 1986). Tin occurs in very finely crystalline cassiterite, and in some deposits, in silicate minerals, including garnet and hornblende (Eadington, 1983). Tin in silicate minerals poses metallurgical problems. Therefore, most of the deposits that have been economic to mine are those that contain cassiterite as the primary tin ore mineral (Newberry, 1998). Other tin skarn ore minerals include stannite, arsenopyrite, pyrrhotite, and wolframite. Magnetite and fluorite are common tin skarns minerals and may form alternating light and dark lamellae.

In polymetallic carbonate-replacement deposits, ore is present in massive lenses (mantos), pipes (chimneys), and veins of iron, lead, zinc, and copper sulfide minerals. Massive ore contains >50 percent sulfide minerals. A specific district or mine may contain a single massive orebody or a series of orebodies aligned along structural features. Ore controls include fractures, joints, fold limbs, karst openings, or lithologic discontinuities that control fluid movement (fig. 2). Manto and chimney ore is compact and can be relatively impermeable. Some ore replaces carbonate clasts in karst breccias and may fill interstices between clasts.

Mining and Ore-Processing Methods

Base-metal skarns and polymetallic carbonate-replacement deposits have been developed as underground mines and as open pit mines. At many small historic mines, ores were sorted by hand and transported to smelters; metal- and sulfide-rich ore piles remain at many abandoned mine sites. By about 1900, the development of efficient flotation processes allowed on-site milling to produce zinc-, lead-, and (or) copper-rich concentrates that were subsequently smelted. Modern processing typically involves milling followed by concentrate smelting. Mine stopes are backfilled with coarse tailings. Fine-grained tailings are stored in surface impoundments. Copper-gold ore is milled primarily by gravity and flotation methods. Copper is usually recovered by flotation. Gold is recovered by cyanide leaching of crushed ore or by a modern pyrite flotation process that substitutes for cyanide processing of pyrite-rich gold ore. Some copper-mining operations use sulfuric acid heap leach, followed by solvent extraction-electrowinnowing, to extract copper. The primary drawback of the acid-leach method for copper recovery is generation of potentially large volumes of acidic, iron- and aluminum-rich wastewater that must be treated. Differential flotation and separation processes are used to produce metals concentrates from complex polymetallic ores such as the ores at the Minera Bismark lead-zinc skarn in Mexico (Mining Magazine, 1994). Gravity separation was used on high-grade zinc ores at the Hanover, New Mexico, lead-zinc skarn (Walder and Chavez, 1995) when mining began. Subsequently, a froth flotation process was used. The additional crushing necessitated by the flotation process resulted in finer-grained tailings, which potentially are more reactive due to increased surface area and are more susceptible to wind erosion.

The mining method used for tungsten skarns generally depends on the grade and shape of the deposit; high average ore grades (0.7 weight percent WO_3 or more) generally are required to support the high costs of underground mining. Underground methods include room-and-pillar (Cantung, British Columbia; King Island, Australia), cut-and-fill, stoping (Pine Creek, California) or combinations of these methods (Anstett and others, 1985). Gravity, flotation, and chemical methods are used to produce natural and artificial scheelite, and ammonium paratungstate (APT) (Smith, 1994). Scheelite concentrate was produced in Nevada in the past using gravity, flotation, and magnetic separation techniques (Stager and Tingley, 1988). After crushing and grinding, sulfide minerals and scheelite were separated by flotation, and the sulfide slimes were removed to tailings piles. Molybdenum was removed via a precipitation process and an organic solvent extraction technique is used to produce crystalline APT.

Modern mining of the large tin replacement deposit at Renison Bell, Tasmania, is accomplished by cut-and-fill stoping methods. Sulfide-mineral-rich and sulfide-mineral-poor ore are stockpiled selectively on the surface. Blended ore is fed into a three-stage open crushing circuit that reduces ore from 750 mm to 15 mm. The ore is processed by flotation to remove sulfide minerals prior to gravity concentration of cassiterite (Morland, 1986). Staged grinding is used to liberate fine-grained cassiterite. Residual sulfide minerals in the gravity concentrate are removed by flotation. Cassiterite concentrates are leached with sulfuric acid to remove siderite. Magnetic material is removed using magnetic separators. The refined concentrates are shipped to smelters. Tailings are combined with lime to adjust pH to 8.5 before being pumped to impoundments.

Ores may need to be very finely ground for efficient flotation, depending on the ore textures. Grinding increases mineral surface area. Grinding also liberates fast-weathering ore minerals from enclosing silicate minerals that may protect against oxidative weathering. Pressures and stresses of milling increase the rate and susceptibility of pyrrhotite and magnetite to oxidative weathering (Pratt and others, 1996). Iron sulfide minerals are abundant in all of the mineral deposit types considered here (table 2) and end up in sulfide-rich mill tailings, where they are susceptible to oxidation that can produce acid-mine drainage. Because of the water requirements of milling, most mills are located along or near creeks. Early miners discharged mill tailings directly into creeks, or dammed tailings in holding ponds near creeks. Modern mining operations discharge mill tailings to lined surface tailings ponds, or dispose of tailings by backfilling and cementing mined stopes. Pyrite-rich tailings produced as a milling by-product have high potential for generation of highly acidic, metal-bearing water, especially if the water is evaporatively concentrated. Spring snowmelt or storm flushing of soluble secondary salts from mill tailings surfaces can degrade downstream surface water quality.

Deposit Trace Element Geochemistry

Minor- and trace- element geochemical signatures typical of each deposit type are listed in table 3a. Trace element signatures can be diagnostic of some deposit types. Calcic reduced gold skarns, for example, typically contain arsenic, bismuth, or tellurium. Zinc-lead skarns contain distinctive manganese minerals and manganese-enriched garnet and pyroxene. Trace amounts of cadmium, lead, arsenic are characteristic of the scapolite-albite iron skarn subtype, but not of other iron skarns. Copper skarns are enriched in copper, gold, and silver in proximal zones; in lead, zinc, and silver in distal zones (Cox and Theodore, 1986). Cobalt, arsenic, antimony, bismuth and molybdenum are enriched in some copper skarns. The geochemical signature of zinc-lead skarns includes a wide

variety of metals (table 3a). Meinert and others (1997) documented vertical zonation of metals at the Big Gossan Cu-Au skarn, Irian Jaya . Analysis of assay data showed that copper, gold, silver, lead, and zinc increased upwards in the system and molybdenum increased with depth. Kotlyar and others (1998) used drill-hole sample geochemistry to document 3-dimensional district- and deposit-scale metal zonation at the Fortitude gold skarn at Copper Canyon in north central Nevada. In the highly mineralized porphyry and skarn system at Copper Canyon, gold and copper are concentrated in proximal parts of the porphyry system. An unexpected result of the study was the identification of a mercury anomaly on the fringes of some gold and copper skarn orebodies; highest mercury concentrations coincided with polymetallic veins peripheral to the skarns. Thus, the trace element signature and zoning patterns around the skarns are affected by other mineral deposit types in the mining district.

Polymetallic carbonate-replacement deposits are characterized by elevated abundances of gold, molybdenum, arsenic, bismuth, and (or) antimony. In some districts, ore proximal to igneous intrusions is copper- and gold-rich, and grades laterally and sometimes vertically into lead-zinc-silver-rich ore. A distal, manganese-enriched zone is present in some districts.

Primary Mineralogy and Zonation
Primary ore and gangue minerals are tabulated by deposit type and by mineral groups (table 3) to facilitate comparisons of expected environmental signatures. Weathering of iron sulfide minerals is the leading cause of acid mine drainage. Although pyrrhotite oxidizes more rapidly than pyrite, it produces less acid, or, in some cases, consumes acid depending on reaction pathways. For skarn deposit types that can be subdivided into oxidized and reduced variants, the oxidized type contains pyrite in excess of pyrrhotite and greater variety in base-metal sulfide minerals (table 3a). Pyrrhotite typically alters to marcasite, and subsequently can generate significant amounts of acid in reactions with oxygen and water. Many of the other sulfide minerals in skarn ores have metal/sulfur ratios <1, such as sphalerite, galena, and chalcopyrite. These minerals are strongly oxidized by aqueous ferric iron, but typically do not produce acid when oxygen is the oxidant (Plumlee, 1998). Some deposit types rich in zinc and manganese may not contribute much acid to ground and surface waters, yet may contribute metals that are transported readily as dissolved species at near-neutral pH and are difficult to remove. High dissolved zinc concentrations in surface waters may be less of a problem in carbonate-hosted deposits than in other types of zinc deposits because zinc tends to be redeposited as the secondary carbonate mineral smithsonite (Walder and Chavez, 1995).

In skarn deposits, early, prograde zones are characterized by high temperature, anhydrous minerals, especially garnet and pyroxene. Subsequent lower-temperature retrograde skarn zones are marked by hydrous minerals that can overprint, crosscut, or completely replace prograde assemblages. Retrograde minerals include amphibole, chlorite, epidote as well as variety of other minerals that comprise gangue (table 3b). The relative reactivity of skarn calc-silicate minerals in acid solutions is not well understood. Kwong (1993) and Sverdup (1990) ranked garnet, pyroxene, and wollastonite as fast-weathering minerals that could contribute to acid neutralization. Based on the observation that low pH waters drain some skarn deposits (Plumlee and others, 1999) that contain these minerals in abundance, Plumlee (1999) concluded that they do not readily react with acid waters. He included garnet, pyroxene, and wollastonite as an intermediate-weathering mineral group, along with retrograde minerals.

Ores typically are associated with later stages of skarn evolution. Mineral assemblages and mineral compositions vary among skarns of different types and subtypes (table 3). For detailed information on skarn zone mineralogy and mineral chemistry for the various skarn subtypes, see Hammarstrom and others (1995a, b, and c) and the references in table 2. Examples of some of the distinguishing mineralogical characteristics of various deposit types are discussed below.

The primary ore minerals vary among the different skarn deposit types. The type of primary ore mineral (e.g., oxide, sulfide, or tungstate) and the abundance of iron sulfide minerals in ore mineral assemblages will affect the weathering behavior and acid generation potential of mine waste and mill tailings. Magnetite is the principal ore mineral in all iron skarn subtypes (table 3). However, the mineralogy of the prograde, retrograde, and ore zones of iron skarn subtypes are distinct (table 4). Sulfide mineral contents in iron skarns generally are low, but can be quite variable. Reported magnetite:pyrite ratios range from 100:1 to 3: 1 for the Larap calcic iron skarn in the Phillipines (Einaudi and others, 1981). In addition to magnetite, the magnesian iron skarn at Cornwall, Pennsylvania, produced copper, gold, and silver from chalcopyrite and cobalt from pyrite. In gold skarns, gold may be present in sulfide-mineral-rich, massive lenses or pods, or it may be disseminated. At the Nickel Plate calcic reduced gold skarn deposit in Canada, <25-micron-diameter grains of native gold associated with hedleyite are adjacent to arsenopyrite and gersdorffite. In other parts of the same deposit, electrum is concentrated in microfractures in and around chalcopyrite, pyrrhotite, sphalerite, and bismuth (Ettlinger and Ray, 1989). In contrast, gold at the McCoy, Nevada calcic oxidized gold skarn deposit (Brooks and others, 1991) is spatially and

paragenetically associated with late-stage pyrite. Gold grains bordering pyrite cubes are 20- to 100-microns in diameter. Mineral characteristics in skarns are likely to vary considerably within a single deposit because of the zoned nature of skarns and the replacement of early-formed minerals by later mineral assemblages. Manganese-rich silicate and carbonate minerals are a distinctive characteristic of prograde and retrograde mineral zones in zinc-lead skarn deposits. In zinc-lead skarns, ore commonly forms massive pods of pyrrhotite, sphalerite, galena, and chalcopyrite in pyroxene zones. The oxidation state of tungsten skarns is reflected in the mineralogy. In reduced tungsten skarns, pyroxene is more abundant than garnet in prograde mineral assemblages. Pyroxene is iron-rich hedenbergite and garnet is iron-poor (Newberry, 1998). Retrograde zones contain iron-rich amphibole and chlorite, and ores include molybdenum-poor scheelite, gold, pyrrhotite, chalcopyrite, sphalerite. In oxidized tungsten skarns, garnet is more abundant than pyroxene. Garnet is iron-rich andradite and pyroxene is intermediate in composition. Epidote is present in retrograde zones, and ores contain molybdenum-rich scheelite, pyrite, chalcopyrite, and magnetite. In tungsten skarns, scheelite is deposited near the marble front during early prograde metasomatism but generally is remobilized and redeposited in coarse-grained, high-grade masses with sulfide minerals in zones of hydrous alteration. In all of the W-F and Sn skarns deposit subtypes, garnet is more abundant than pyroxene in prograde zones and white mica and fluorite are present as retrograde minerals. In tin-bearing Mo-rich W-F skarns (table 2), tungsten is concentrated proximal to intrusive rock whereas tin is concentrated in more distal parts of skarns (for example, Shizhuyuan, China). Tin replacement deposits (table 2) are grouped with tin skarns sensu stricto because they appear to form a continuum with classic skarn deposits. Although they lack prograde calcsilicate mineral assemblages, the tin carbonate replacement deposits are spatially associated with plutons and exhibit mineral and metal zoning (Newberry, 1998). Extensive greisen alteration is present, and ore minerals include cassiterite, pyrrhotite, arsenopyrite, sphalerite, and galena.

   Most polymetallic carbonate-replacement deposits are pyrite-rich; however, a few (rare?) deposits are pyrite-poor and are dominated by sphalerite and galena. The following list of minerals in polymetallic carbonate-replacement ores is based on Plumlee and others (1995). Minerals are listed in approximate decreasing order of abundance. Potentially acid-generating minerals are underlined and minerals that are acid-generating when oxidized by aqueous ferric iron are denoted by *: Pyrite, sphalerite*, galena*, siderite, quartz, marcasite, rhodochrosite, dolomite, chalcopyrite, pyrrhotite, tetrahedrite, digenite*, argentite, electrum, ± enargite, ± bornite, ± arsenopyrite, ±Bi-Te-Hg-Au-Ag minerals (hessite, petzite, pyrargyrite, etc.), ± barite, ± fluorite. In many deposits, ore grades from copper-mineral-rich (chalcopyrite, enargite, bornite) within and near igneous intrusions, to sphalerite- and galena-rich away from intrusions, to sphalerite- and manganese carbonate-bearing distal ore.

Secondary Mineralogy
   Secondary minerals form by weathering in the oxidized parts of mineral deposits. Secondary minerals can form in-situ on exposed ore bodies, or on mine waste dumps and tailings. In-situ weathering promotes gossan development over sulfide-mineral- rich parts of skarn deposits; supergene alteration enhances ore metal grades in parts of some skarn deposits.   Secondary minerals reported in skarns and polymetallic carbonate-replacement deposits are listed by mineral group in table 5. Notably absent from the list are the halotrichite-pickeringite group minerals common in massive sulfide deposits. These minerals may be under reported in skarns, or may not form because of the low availabilty of dissolved aluminum. Reports of aluminum oxyhydroxides or hydroxysulfate minerals also are notably absent. Examples of secondary mineral assemblages for different deposit types are described in the following discussion.
   Supergene alteration leads to formation of clays, hematite and goethite (after pyrite and other sulfide minerals), and secondary copper minerals (after chalcopyrite). The calcic oxidized gold skarn deposit at McCoy, Nevada, is highly oxidized and argillized to as much as 245 m below the present surface (Brooks and others, 1991). Minerals in these argillized zones include a variety of clays (montmorillonite, nontronite, and illite), manganese oxide minerals, supergene copper oxide minerals, claudetite (As_2O_3), willemite (Zn_2SiO_4), marcasite, and hydrated iron oxide minerals. At the Red Dome Au skarn deposit in North Queensland, Australia, high-grade gold ore is concentrated in highly oxidized karst-collapse breccia that formed during post-mineralization uplift and erosion; oxidation of primary tellurium-rich hypogene sulfide ore enhanced karst formation and concentration of free gold (Torrey and others, 1986). Minerals and mineral zoning that develops during supergene alteration of zinc-lead-silver sulfide ore in carbonate rocks depends on local Eh and pH conditions, permeability, and the relative activities of carbonate species and sulfate ions in leaching ground water (Sangameshwar and Barnes, 1983). For example, cerussite is the first lead mineral to precipitate where dissolved carbonate is more abundant than sulfate, but anglesite precipitates if the situation is reversed. Supergene minerals associated with base- and precious metal skarns include azurite, malachite, smithsonite, and cerargyrite, as well as cerussite, anglesite, manganese minerals (pyrolusite, groutite), and goethite.   Manganese-rich gossans are associated with zinc-lead

Table 3. Mineralogical and metal associations of skarn and polymetallic carbonate-replacement deposits.
   A. Primary ore minerals. [XX, most common iron sulfide mineral. See references in table 2 for data sources]

Deposit Type	Fe skarn			Au skarn			Cu skarn	
Subtype	Calcic	Magnesian	Scapolite-albite	Calcic reduced	Calcic	Magnesian	Copper	Copper-gold
Major metals	Fe	Fe	Fe	Au	Au	Au	Cu	Cu Au
Minor and trace metals	Cu Co Au Ni	Cu Zn As	Cu Zn Pb As Cd	Ag Cu As Pb Zn Bi Co Sb Te Se Cd	Ag Cu Pb Zn As	Ag Cu Pb Zn	Au Ag Pb Zn Fe As Mo Co Sb Bi	Ag Pb Zn As Mo Co
Ore minerals								
Iron sulfide minerals								
Marcasite			X	X				
Pyrite		X	X	X	XX		XX	XX
Pyrrhotite	X	X	X	XX	X	XX	X	X
Other sulfide minerals								
Arsenopyrite		X	X	X	X			
Bismuthinite				X			X	
Bornite					X		X	X
Cobaltite	X						X	
Chalcopyrite	X	X	X	X	X		X	X
Galena				X	X		X	X
Molybdenite					X		X	
Sphalerite		X	X	X	X		X	X
Non-sulfide ore minerals								
Cassiterite	X(rare)							
Gold/electrum				X	X	X	X	X
Hematite			X		X		X	
Magnetite	X	X	X		X	X	X	
Scheelite								
Other ore minerals (minor or less common)				Bi°, maldonite, loellingite, hedleyite,pearcite, stannite,hessite, and gersdorffite	Bi° , hedleyite, and hessite		Cosalite, enargite, tennantite, tetrahedrite,and loellingite	

Table 3a. Continued.

Deposit Type	W skarn		W-F skarn		Sn skarn		Zn-Pb skarn	Polymetallic carbonate-replacement
Subtype	Reduced	Oxidized	Mo-poor	Mo-rich	Skarn	Sn replacement		
Major metals	W Cu	W Mo	W F Be	W Mo Bi F	Sn W F As	Sn F As Bi	Zn Pb Ag	Pb Zn Ag Cu
Minor and trace metals	Bi Au	Cu Zn Ag Bi	Zn Sn	Be Sn Ag Zn	Be Bi	Zn Ag Pb	Mn Cu Cu Au As W F Sn W Be	Au Mo As Bi Sb Mn
Ore minerals								
Iron sulfide minerals								
Marcasite								X
Pyrite		X	X	X	X	X	X	XX
Pyrrhotite	X				XX	XX	X	X
Other sulfide minerals								
Arsenopyrite					X	X	X	X
Bismuthinite								X
Bornite								X
Cobaltite								
Chalcopyrite	X	X			X	X	X	X
Galena						X	X	X
Molybdenite				X				
Sphalerite	X		X		X	X	X	X
Non-sulfide ore minerals								
Cassiterite				X	X	X		
Gold/electrum	X							X
Hematite								
Magnetite		X					X	X
Scheelite	X	X	X	X	X			
Other ore minerals (minor or less common)			Fluorite, Be silicates	Fluorite, wolframite	Stannite, wolframite	Ilmenite		Digenite, enargite, argenite, tetrahedrite, Bi-Te-Hg minerals such as hessite, petzite, and pyrargyrite

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Table 3. Mineralogical and metal associations of skarn and polymetallic carbonate-replacement deposits.
B. Gangue minerals. [In addition to the minerals listed, quartz is ubiquitous. See references in table 2 for data sources]

Deposit Type	Fe skarn			Au skarn			Cu skarn	
Subtype	Calcic	Magnesian	Scapolite-albite	Calcic reduced	Calcic	Magnesian	Copper	Copper-gold
Gangue minerals (**Carbonates in bold**)								
Albite			X					
Amphibole	X	X	X	X		X	X	
Anhydrite								X
Barite								
Biotite		X			X	X	X	
Calcite	X	X	X	X	X	X	X	X
Chlorite	X	X	X	X	X	X	X	
Epidote	X		X	X	X		X	
Fluorite								
Forsterite		X				X		
Garnet	X		X	X	X		X	X
K-feldspar				X	X	X	X	
Muscovite/sericite								
Pyroxene	X	X	X	X	X	X	X	X
Scapolite			X	X				
Serpentine		X				X		
Siderite				X				
Talc		X						
Vesuvianite				X		X	X	
Wollastonite				X			X	
Zeolites								
Other gangue minerals	Ilvaite	Spinel, apatite, ludwigite, humite, clinohumite, chondrodite, **magnesite**, and periclase	Zeolites, apatite, prehnite, and titanite	Clays, boron minerals, and prehnite	Clay	Zoisite, prehnite, and spinel		

Table 3b. Continued.

Deposit type	W skarn			W-F skarn	Sn skarn and replacement		Zn-Pb skarn	Polymetallic carbonate-replacement
Subtype	Reduced	Oxidized	Mo-poor	Mo-rich	Skarn	Sn replacement		
Gangue minerals (Carbonates in bold)								
Albite								
Amphibole	X	X	X	X	X		X	
Anhydrite								
Barite								X
Biotite	X	X		X				
Calcite	X	X	X	X	X	X	X	X
Chlorite	X	X	X		X	X	X	
Epidote		X	X		X		X	
Fluorite			X	X	X	X		X
Forsterite								
Garnet	X	X	X	X	X		X	
K-feldspar								
Muscovite/sericite	X		X	X	X	X		
Pyroxene	X	X	X	X	X		X	
Scapolite			X					
Serpentine						X		
Siderite								X
Talc								
Vesuvianite				X				
Wollastonite		X			X			
Zeolites								
Other gangue minerals					Malayite, danburite, datolite, Be silicates, and tourmaline		Bustamite, rhodonite, ilvaite, dannemorite, and **rhodochrosite** Skarn silicates are distinctly Mn-rich.	**Dolomite, rhodochrosite**

Table 4. Mineralogy of skarn stages for iron skarn subtypes.

Iron skarn subtype	Calcic	Magnesian	Scapolite- albite
Prograde minerals	Garnet (grossular-andradite), pyroxene (ferrosalite).	Forsterite, calcite, spinel, diopside, magnetite, apatite, and ludwigite-group minerals.	Garnet, pyroxene.
Retrograde minerals	Amphibole, chlorite, and epidote.	Amphibole, humite, serpentine, phlogopite, talc, chlorite, chondrodite, magnesite, and clinohumite.	Scapolite, albite, chlorite, calcite, zeolites, actinolite, epidote, apatite, quartz, prehnite, and sphene.
Ore minerals	Magnetite, chalcopyrite, cobaltite, and pyrrhotite.	Magnetite, pyrite, chalcopyrite, sphalerite, pyrrhotite, and arsenopyrite**.	Magnetite, hematite, pyrite, marcasite, chalcopyrite, sphalerite, pyrrhotite, and arsenopyrite.

skarn deposits; iron-rich gossans develop over copper skarns. In iron skarns, magnetite may alter to hematite, maghemite, goethite, limonite, or lepidocrocite during oxidation and weathering.

Secondary minerals formed by weathering prior to mining in polymetallic carbonate-replacement deposits (Plumlee and others, 1995) include relatively insoluble minerals indicative of deposition from relatively high-pH water: anglesite, cerussite, smithsonite, hemimorphite, hydrozincite, manganese oxide minerals (psilomelane, pyrolusite, and braunite), iron oxide minerals (limonite), cerargyrite, and jarosite. In contrast, secondary minerals formed by recent weathering after the onset of mining are primarily soluble sulfate minerals indicative of deposition from locally acidic water. Examples are zinc sulfate minerals, including goslarite, which grades to magnesium-rich epsomite and iron sulfate minerals such as copiapite, coquimbite, melanterite, szomolnokite, fibroferrite, and roemerite. Chalcanthite is the dominant copper sulfate mineral although others also may be present.

Soil, Sediment, and Tailings Signatures
Geochemical data for soils and sediments acquired during mineral exploration can be used to establish pre-mining baseline conditions. Knowledge of the pre-mining soil and sediment signatures for specific deposit types in specific climates can help land managers set realistic post-mining remediation goals. These data also provide analogues for areas where historic mining has obliterated pre-existing baseline conditions (du Bray, 1995). In disturbed areas, stream sediment sampling upstream and downstream from mine sites provides a measure of the changes due to mining. Geochemical and mineralogical data for tailings, especially when paired with leaching studies, indicate the potential for metal mobility and acid generation. Examples of data for pre-mining soils and post-mining tailings for a number of deposit types are discussed in the following section.

Pre-mining
Soil sampling has been a useful exploration tool for finding gold skarns. Hastings and Harrold (1988, fig. 7) showed that ranges for selected trace elements in rocks and soil at the Beal calcic reduced gold-skarn deposit generally overlap. Arithmetic means for most trace element concentrations in soils over this deposit are similar to concentrations in rock samples, with the exception of gold (0.05 ppm in soil, 1 ppm in rock). Mean values for arsenic, copper, and zinc for both soil and rock at the Beal deposit are between 10 and 100 ppm, and soil appears to be slightly enriched in arsenic and zinc relative to rocks.
Soils associated with similar deposits in similar climates can have distinctly different soil geochemical signatures. A number of gold skarns and gold-bearing copper skarns are associated with 39 Ma granitoid intrusions in north-central Nevada (fig. 2). This region has an arid climate (Bailey and others, 1994); precipitation averages 100 to 300 mm and elevations range from 1,200 to 3,000 m. In the general area of the McCoy, Nevada, calcic oxidized gold skarn deposit (fig. 2), soil contains as much as 15 to 20 ppm arsenic and as much as 200 to 300 ppm copper. Prior to large-scale mining at McCoy, an area as much as 750 m wide contained soil with more than 5 ppm arsenic. In contrast, soils associated with gold-rich copper skarn at the West orebody, a few miles north of McCoy at Copper Canyon, Nevada (fig. 2) are much more arsenic-rich. Analyses of the minus-80-mesh fraction of 140 soil samples in the general area of the West orebody, indicated alkaline soils (pH typically 9.0 to 9.6). Calcite was

present in about one-third of the samples (Theodore and Blake, 1978). Contents of silver, arsenic, gold, copper, lead, and mercury in soil above the West orebody skarn are generally anomalous. Arsenic is >160 ppm in some soil samples. Median values are: 3 ppm silver, 0.15 ppm gold, 150 ppm copper, 50 ppm lead, and 0.7 ppm mercury. Mercury contents in the soil appear to be higher along some traverses just outside or beyond the surface projection of underlying ore. These are natural concentrations, uncontaminated by mining activities.

The buried, carbonate-hosted Rubiales zinc-lead skarn deposit in the Lugo province, northwestern Spain, was discovered by a soil survey that detected soil metal anomalies generated by weathering of sphalerite, galena, and chalcopyrite in the silicified alteration halo around the deposit (Arias, 1996). The deposit was not detected by a stream sediment survey. The zinc soil anomaly was more extensive than the lead or copper anomalies, reflecting the greater mobility of zinc in the surface environment. The copper anomaly was highest over feeder zones where highest grade ores subsequently were discovered.

Post-mining

The mineralogy and geochemistry of mine waste and tailings, and the waters in contact with them, vary widely among skarn types and subtypes, and in response to climatic variables. For example, calcic iron skarn ore at Cornwall, Pennsylvania, has a grade of 40-42 percent iron. Mining of this ore produces typical final tailings containing 7.7 weight percent iron, 0.61 weight percent sulfur, and 0.04 weight percent copper (Lapham, 1968). These tailings are similar to typical iron ore tailings, which contain 7 to 9 weight percent iron as reported by Andrews (1975). Weathering of these tailings yields insoluble iron hydroxides.

Boulet and Larocque (1998) conducted a comparative mineralogical and geochemical study of sulfide-rich mine tailings at two sites in New Mexico. The copper skarn at the Cyprus-Pinos Altos mine, New Mexico, which closed in 1995, and the Cleveland zinc-lead skarn deposit, which closed in 1950, are similar in mineralogy, geochemistry, geology and climactic setting. The impounded copper skarn tailings from Pinos Altos mostly are water-saturated with no secondary phases developed and no evidence of dissolution of primary minerals. Tailings pond pH's are 7 to 8.3. In contrast, the older zinc skarn tailings at the Cleveland deposit, which are in a valley at the headwaters of an ephemeral stream, are oxidized, cemented, and dominated by the secondary minerals jarosite, goethite, hematite, and Fe-oxyhydroxides. A cemented hardpan layer at 46 cm depth in the Cleveland tailings sequesters a number of potentially toxic metals within the tailings pile. This study also demonstrated that although lead in the tailings was present at much greater concentrations than cadmium, the reverse is observed in the stream where mobile zinc and cadmium are enriched relative to lead. The result of this paired study of the solids and waters showed that zinc and cadmium mobility from tailings is of greater concern than lead mobility.

The Hillsboro mining district of New Mexico includes two types of polymetallic carbonate-replacement deposits: lead-zinc deposits and silver-manganese deposits. Munroe and others (1999) characterized waste rock piles at abandoned mines in the Hillsboro district. The study showed that: (1) a homogeneous composite of 15 to 30 samples was sufficient to adequately characterize the waste rock piles, which is similar to the USGS method developed by Smith and others (2000), (2) chemical analysis of six different size fractions showed that the less-than-0.25-mm-grain-size fraction contained the highest metal concentrations, (3) metal concentrations in the carbonate-hosted lead-zinc waste rock pile, though somewhat variable by grain size, are $Zn \geq Pb$ (1,000 to 10,000 ppm) > Cu (100 ppm) > As (20 to 100 ppm), and (4) metal concentrations in the carbonate-hosted Ag-Mn waste rock pile are $Zn \geq Pb$ (1,500 to 2,000 ppm) > Cu (100 ppm) > As (<10 ppm).

In the semi-arid climate of the San Luis Potosi area of Mexico, mine waste from 200 years of mining and processing active Cu-Au skarn (Cobriza and Dolores mines) and inactive Ag-Pb-Zn (Santa Maria de La Paz) vein deposits is dispersed from uncovered dumps by strong winds and washed out during seasonally heavy rains. This dispersal affects an area of 100 km^2 (Castro-Larragoita and others, 1997). Most of this environmental effect is attributed to the oxidized La Paz tailings, which are composed of calcite, quartz, pyrite, arsenopyrite, sphalerite, galena, chalcopyrite, and bornite. Arsenic is released as dissolved arsenate from the base of the dumps where secondary iron sulfate salts contain up to 10% arsenic. Windblown tailings contaminate soils over distances of more than 5 kilometers. Contamination by waterborn material from tailings extends up to 10 kilometers from the site. Mine waters are near-neutral and some are used for irrigation. However, plants irrigated with this water and used for animal fodder contain elevated concentrations of lead and cadmium. The Cobriza skarn tailings consist of quartz, pyroxene, wollastonite, calcite, and relatively unoxidized sulfide minerals.

Table 5.   Secondary minerals associated with skarn and polymetallic carbonate-replacement deposits. [Secondary minerals formed by weathering prior to mining or by weathering after the onset of mining (includes outcrops, mine waste, and tailings). Secondary minerals are not widely reported for these deposit types, so this list should be considered preliminary. No data are available to distinguish secondary mineral assemblages among the deposit subtypes described in tables 2 and 3. Clays are ubiquitous as gangue minerals associated with retrograde alteration and as secondary minerals formed by weathering.]

Deposit type	Fe skarn	Au skarn	Cu skarn	W skarn	Sn skarn	Zn-Pb skarn	Polymetallic carbonate-replacement
Fe and Mn oxide, oxyhydroxide, and hydroxysulfate minerals							
Goethite	X	X	X	X		X	X
Hematite	X	X	X				X
Jarosite (K, Na, H_3O^+)		X				X	X
Lepidocrocite						X	
Schwertmannite						X	
Mn –oxide minerals (pyrolusite, etc.)		X	X	X		X	X
Secondary carbonate minerals							
Azurite		X	X				
Malachite		X	X				
Cerussite						X	X
Smithsonite						X	X
Secondary sulfate minerals (*, highly soluble)							
Anglesite						X	X
Butlerite*							
Chalcanthite*							X
Copiapite*							X
Coqiumbite*							X
Epsomite*							X
Fibroferrite		X					X
Goslarite*							X
Gypsum						X	
Hexahydrite*						X	X
Melanterite*						X	X
Penetahydrite*						X	
Rozenite*						X	
Starkeyite*		X				X	

Deposit type	Fe skarn	Au skarn	Cu skarn	W skarn	Sn skarn	Zn-Pb skarn	Polymetallic carbonate-replacement
Other minerals		Chrysocolla Nabesna Fe-Au skarn, AK: cacoxenite, kalinite, rostite, carbonate hydroxylapatite, aplowite, and ferrian sepiolite McCoy calcic, oxidized Au skarn: claudetite, and willemite	Chrysocolla		varlamoffite	Hemimorphite, halite, S^o	Chrysocolla , hydrozincite, cerargyrite, szomolnokite, and roemerite
References	Hammarstrom and others, 1995a	Eppinger and others, 1997 Brooks and others, 1991	Hammarstrom and others, 1995c	Hammarstrom and others, 1995b	Hammarstrom and others, 1995b	Walder and Chavez, 1995; Boulet and Larocque, 1997	Plumlee and others, 1995 Desborough and others, 1999 Wallace, 1993

Topography and Physiography

Skarn deposits in the western conterminous United States typically are present in mountain ranges, but also are known in a variety of other settings. Some skarn deposits are buried in fault blocks under Tertiary or Quaternary basin fill.

Hydrology

In some deposits, shear zones and faults are important structural controls for channeling hydrothermal and mineralizing fluids. In other deposits, lithologic contacts serve as fluid conduits. Post-mineralization faults also may channel subsequent fluids. At Minera Bismark, a zinc-lead skarn deposit in northern Mexico, water flows continuously along a major post-mineralization fault, as well as along other faults and fractures in the granitic rocks. A pumping system is required to dewater the orebody during mining (Mining Magazine, 1994). Surface ferricrete deposits represent iron remobilized from weathered sulfide minerals by surface and subsurface water and indicate locations of former springs or drainage seepages (Plumlee, 1998). Mapping of ferricrete deposits may provide clues to pre-mining discharge points that could be reactivated if the groundwater flow is perturbed by adit plugging, for example. Manganese or iron bog deposits provide similar clues to paleohydrology.   Faults at Copper Canyon, Nevada, are known to have channeled ground water for several kilometers during periods of high ground-water availability. Natural ground water flow in the vicinity of polymetallic carbonate-replacement deposits dominantly is along fractures and faults or through karst systems in carbonate rocks. Mine workings also substantially enhance ground-water permeability. Karst, where present, can impose significant control on the local hydrologic regime because of its ability to channel ground water for long distances from mine sites. Some flow also may occur in sedimentary rock aquifers, including sandstone and fractured carbonate rocks.

Drainage Signatures

Relatively few data are available for skarn and polymetallic carbonate-replacement drainage signatures relative to the data available for other deposit types. In general, acid mine drainage is not a significant problem in most carbonate-hosted deposits. Plumlee and others (1999) and Ficklin and others (1992) showed that drainage water compositions from skarn and polymetallic carbonate-replacement deposits are variable. Water draining carbonate-poor copper skarn ores at New World, Montana, present an unusual case because the waters are relatively acidic and copper rich (see case study by Kirk and Kirk, this volume). Mine-drainage associated with most polymetallic carbonate-replacement deposits is near-neutral because of the acid-neutralizing capacity of the carbonate host rocks. However, waters draining pyrite-rich deposits may contain elevated concentrations of dissolved zinc (up to tens of mg/L Zn) and copper (up to several mg/L Cu), especially where low dissolved oxygen concentration inhibits ochre precipitation and therefore limits metal removal by sorption (Plumlee and others, 1999).

Oxidation of galena produced cerussite at the polymetallic carbonate-replacement deposit at Leadville, Colorado. Cerussite is very insoluble under oxidizing conditions and effectively immobilizes lead (Wallace, 1993). Although the ores at Leadville replaced part or all of some carbonate units including the Leadville dolomite, adjacent igneous rocks essentially were unaltered. Surface and groundwater contamination from mining at Leadville and Gilman, Colorado, along with heavy metal concentration in soils and mine tailings, resulted in both of these areas being remediated under Superfund, including the California Gulch and Eagle mine sites. Jerz (1998) conducted leach studies on fluvial tailings in the Arkansas River south of Leadville and showed that the soluble efflorescent sulfate minerals, especially copiapite that forms during wetting-drying cycles, affect the leaching behavior of the tailings and account for the very low pH (<2.0) and high metals in leachates.

Case studies illustrate the range of drainage signatures associated with some skarn and polymetallic carbonate-replacement deposits. Some case studies that describe drainage geochemistry include reports on (1) the Thompson Creek tungsten skarn in central Idaho (Van Gosen and others, 2000), (2) the Nabesna, Alaska, gold-bearing iron skarn (Eppinger and others, 1999; Eppinger and others, 2000), and (3) the Clayton silver mine, a polymetallic carbonate-replacement deposit in central Idaho (Hammarstrom and others, 2001).

The Thompson Creek tungsten skarn (Van Gosen and others, 2000) is an abandoned mine that was worked briefly in the 1950s. The mine produced 493 tons of ore containing an average grade of 0.77% WO_3 (Cook, 1956). The ore is composed of scheelite, powellite, pyrite, and pyrrhotite in a gangue of garnet, quartz, and calcite. The deposit formed in argillaceous limestone adjacent to granite. Waste piles from the underground and open-pit mining line the floodplain of a creek that drains into the Salmon River. A small pool 30 meters below the collapsed mine adit appears to be adit drainage. This mine effluent and creek waters have pH 5.5 to 5.8. Geochemical analysis of mine waste shows that Cu>Zn>Pb. Mine waste leachate (Hageman and Briggs, 2000) had a pH of 3.1; in leachates, Zn>Cu>Pb. Dissolved tungsten concentrations were less than 0.5 ppb in all water samples.

The environmental geochemistry of the Nabesna iron skarn and other mineral deposits in Wrangell-St. Elias National Park, Alaska, was studied by Eppinger and others (2000). Nabesna ore is composed of pyrite, pyrrhotite, magnetite, and chalcopyrite with minor amounts of galena, sphalerite, arsenopyrite, and stibnite. Gold ore mainly occurs in pyrite-quartz veins that crosscut limestone and silica-sulfide-rich skarn; some gold was produced from massive pyrrhotite and magnetite orebodies. Gangue minerals include garnet, wollastonite, vesuvianite, epidote, amphibole, chlorite, scapolite, serpentine, and quartz. Mill tailings form a thin cover (<1 m thick) over an area of several thousand square meters. A variety of soluble secondary sulfate salts were observed on tailings, mine waste, and outcrops (see table 4). Eppinger and others (2000) sampled surface waters over three field seasons that included dry summer periods, intermittent and extended rain events, and spring melt. Total dissolved solids and alkalinities varied over more than two orders of magnitude and pH ranged from 2.2 to 8.6. Maximum permissible contaminant levels were exceeded for a number of elements during spring melt and summer rain events. Although carbonate host rocks maintain near-neutral surface waters in the mine area and reduce downstream effects of seasonal discharges of acidic waters from fine-grained mill tailings, the study demonstrated that season and surface flow conditions are important controls on the major- and trace-element compositions of surface waters. We know of no other water data for iron skarn deposits. However, chemical analyses of water from iron-ore mines and milling operations in Canada (Ripley and others, 1995) probably are reasonable indicators of mine water discharge characteristics of iron skarns. Like the iron skarn deposits, Canadian iron ore has a low sulfide-mineral content and is dominated by magnetite, hematite, and siderite. Mine water and direct-discharge tailings effluent from these Canadian deposits have pH of 6.4 to 9 and relatively low dissolved metal contents, including: 0.01 to 0.4 mg/L copper, 0.05 to 1.3 mg/L iron, <1 mg/L lead, and 0.01 to 0.15 mg/L zinc. Much higher dissolved-metal concentrations, including >40 mg/L copper and >6,000 mg/L iron, were reported for marine-discharge tailings effluent from these deposits. Although iron is an essential nutrient for plants and animals, extreme iron concentrations downstream from historic, large-scale iron-ore operations can harm salmon and benthic organisms. However, residual materials from iron ore mining generally are considered to have only minor toxicity.

Stream pH associated with Cyprus-Pinos Altos copper skarn tailings is as low as 2.2, and maximum dissolved-metal concentrations are: 5,305 ppm Zn, 454 ppm Cu, 1.16 ppm Pb, 17.5 ppm Cd. 1.2 ppm As, and 0.01 ppm Hg (Boulet and Larocque, 1998). Low dissolved-lead concentrations are attributed to precipitation of plumbojarosite. Metal concentrations decrease downstream from the tailings because of dilution by a neutral seep and co-precipitation and sorption of metals by secondary ochre minerals in the streambed (Boulet and Larocque, 1998).

Drainage waters from polymetallic carbonate-replacement deposits typically are near-neutral and low in total dissolved-metal concentrations. However, pyrite-rich deposits, such as those at Leadville, Colorado, can be near-neutral yet carry elevated or extreme (>100,000 ppb) dissolved base-metal concentrations (Plumlee and others, 1999). The Clayton lead-zinc-silver deposit in Idaho is hosted by dolostone (Hammarstrom and others, 2001). Ore is composed of galena, sphalerite, tetrahedrite, and chalcopyrite. Gangue minerals included dolomite, quartz, barite, calcite, fluorite, pyrite, chlorite, siderite, goethite, and garnet. Mining ceased in 1986. An on-site flotation mill produced a lead concentrate. Mill tailings were placed as terraces along steep slopes along a narrow stream valley. Wind and water erosion of a 15-acre pile of fine-grained flotation mill tailings threaten aquatic life in the stream. The U.S. Environmental Protection Agency (2000) stabilized mill tailings and is working with other agencies to develop a long-term site remediation plan. Hammarstrom and others (2001) sampled adit drainage, a stream draining mine tailings, and mine waste for leaching in 1999, prior to tailings stabilization. Results show that all waters associated with the site plot in the near-neutral, low-metal field on a Ficklin diagram (fig. 3).

Climatic Effects

Acidity and total-metal concentrations in mine drainage in arid environments are several orders of magnitude greater than in more temperate climates because of the concentrating effects of mine effluent evaporation and the resulting "storage" of metals and acidity in highly soluble metal-sulfate minerals. In a 1995 report, the Nevada Bureau of Mines and Geology estimated that fewer than 100 of an estimated 200,000 or more inactive and abandoned mines in the state pose acid-mine drainage concerns. The low number of sites likely to produce acid drainage reflects the extremely arid climate of most of Nevada, where only 10% of about 15,000 mile of rivers and streams flow year round. The Nevada report included an examination of 72 mines in the state, which were classified by deposit types and included a number of skarn deposits and polymetallic carbonate-replacement deposits. Most of the carbonate-hosted deposits were dry when visited in August of 1995; shaft and adit waters at abandoned mines at two base-metal replacement deposits were near-neutral. Minimal surface water flow in arid areas inhibits generation of significant volumes of highly acidic, metal-enriched drainage. However, concentrated release of these stored contaminants into local watersheds may be initiated by precipitation from brief thunderstorms following a dry spell, or by spring runoff of snow melt. In areas where precipitation exceeds evaporation, metals and acidity can be

recycled through secondary minerals on a regular basis and soluble secondary minerals can form locally in sheltered areas. Climate influences the extent of pre-mining oxidation and leaching of the upper parts of orebodies to form gossans.
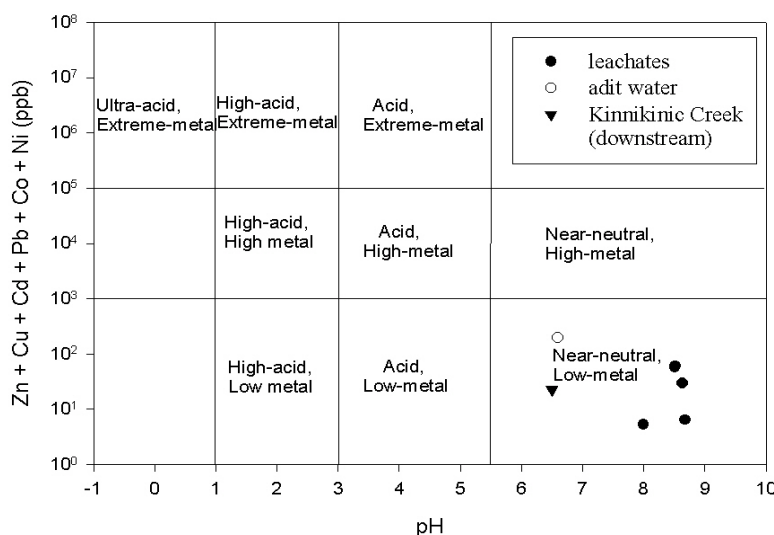
Figure 3. Ficklin diagram showing the sum of selected dissolved metal concentrations in waters associated with the Clayton mine, a polymetallic carbonate-replacement deposit in Custer County, Idaho (Hammarstrom and others, 2001). Water draining from the main adit, water in the creek that drains the mine workings, and leachates from mill tailings and mine waste plot in the near-neutral, low-metal field. Dissolved metal concentrations were below detection limits in creek waters upstream of the mine site.

Potential Environmental Concerns

(1) Differences in ore mineralogy among subtypes of skarns and polymetallic carbonate-replacement deposits indicate different potentials for acid mine drainage and differences in geoavailability of potentially toxic substances. For example, the principal ore minerals in base- and precious-metal skarns and polymetallic carbonate-replacement deposits are sulfide minerals. The principal ore minerals in tin and iron skarns are the oxide minerals cassiterite and magnetite, respectively. Pyrite is ubiquitous in copper, gold, and zinc-lead skarns and in polymetallic carbonate-replacement deposits and pyrite is reported from all other skarn types. Thus, the potential is present for acid-mine drainage to develop at least locally depending on the distribution of pyrite in mine waste and tailings, the exposure of pyritic waste to oxidative weathering, and the availability of acid-neutralizing minerals.

(2) Carbonate-rich host rocks consume acid, generally inhibit transport of most metals, and produce high alkalinity in surface waters that flow over and through them. Effluent waters from underground mines, and surface runoff from sulfide-rich tailings, can be acidic on a year-round or seasonal basis depending on climate. Maximum permissible contaminant levels in these effluents may be exceeded for dissolved concentrations of Fe, Al, Mn, As, Pb, Zn, Cd, F, and sulfate. Some of these potentially toxic metals may be sequestered effectively in hardpan layers in tailings, or in iron ochre precipitating in streams.

(3) Mine waste and mill tailings typically are situated in stream floodplains. During natural floods and(or) impoundment failures, influxes of fine-grained sediments can rapidly degrade downstream aquatic ecosystems, especially fish habitat, both physically and, in some cases, chemically.

(4) Smelter slag may contain elevated Cu, Pb, Zn, and other metals. Metal mobility from slag depends on the processing method: metals in slag cooled by air frothing tend to be more easily mobilized than metals in slag cooled by pouring the molten slag on the ground (Plumlee and others, 1995). Soils downwind from smelters can contain elevated concentrations of Pb, Zn, Cu, As, Sb, Mo, Hg, and Au.

(5) Mercury typically is <u>not</u> associated with any of the skarn deposit types or with polymetallic carbonate-

replacement deposits. However, mercury may be present at inactive or abandoned mines that exploited these deposits types, especially where historic placer mining occurred or where gold was produced as a by-product.

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