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Secondary Enrichment of Copper at the Madison Gold Skarn Deposit, Silver Star District, Montana

Comments

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SECONDARY ENRICHMENT OF COPPER AT THE MADISON GOLD SKARN DEPOSIT, SILVER STAR DISTRICT, MONTANA

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Introduction

The Madison Gold skarn deposit is located near the southeastern margin of the Highland Mountains, near Silver Star, Montana. This deposit shares many similarities to other Au-Cu skarns in Montana and elsewhere in the world (Meinert et al., 2005), but is also unique in several aspects. Whereas previous workers (Foote, 1986) have examined the paragenesis and geochemistry of the primary skarn mineralization at Madison Gold, the current paper focuses on the chemical reactions responsible for secondary enrichment of copper. Secondary enrichment is a common phenomenon in copper deposits, including many skarns and porphyry deposits in the western

U.S. (e.g., Sillitoe, 2005). Such enrichment is usually the result of weathering processes in the near-surface environment, and is therefore referred to as “supergene”. At Madison Gold, we argue that most of the secondary Cu enrichment occurred during a late hydrothermal event that replaced the high temperature skarn mineral assemblage with hematitic jasperoid. Evidence favoring this “hypogene” Cu enrichment hypothesis is presented below, after a brief summary of the geology and mining history of the Silver Star district.

Local Geology

The Madison Gold deposit is a copper-gold skarn developed along the contact between the Cretaceous (80.4±1.2 Ma, Lund et al., 2002) Rader Creek granodiorite to the north and a NW-trending belt of folded and thrustured Paleozoic metasediments to the south (Fig. 1, modified from O'Neill et al., 1996). A major NW-trending reverse fault (termed the Green Campbell fault by early workers but renamed the Silver Star fault by O'Neill et al., 1996) separates the structural block of Paleozoic sediments from Precambrian basement to the southwest. The latter consists mainly of quartz-rich gneiss and amphibolite. According to the mapping of O'Neill et al. (1996), the outcrop pattern of the Paleozoic rocks at the

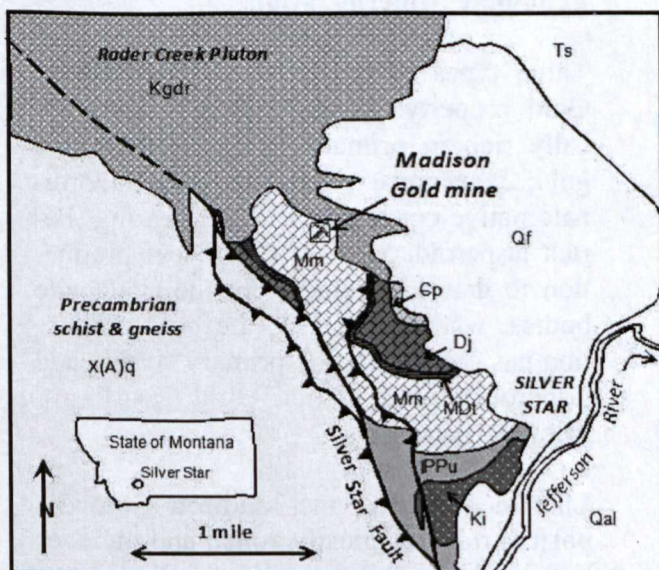


Fig. 1. Geology of the Silver Star area (modified from O'Neill et al., 2005). The geology of the Paleozoic block is simplified, as there are several faults and small intrusions not shown. Rock units: X(A)q = Precambrian quartzose schist and gneiss; Cp = Pilgrim Fm.; Dj = Jefferson Fm.; MDt = Three Forks Shale; Mm = Madison Limestone; PPu = Pennsylvanian and Permian, undivided; Ki = hypabyssal basalt and andesite; Kgdr = Rader Creek granodiorite; Ts = Tertiary sediments, undivided; Qf = alluvial fan; Qal = alluvium.

northern end of the Paleozoic structural block defines a synform, overturned to the west (Fig. 1). However, in detail the structure is more complicated than this, with some contacts being structural rather than stratigraphic. There has also been disagreement in the published literature regarding the identity of some of the sedimentary rocks (e.g., Amsden formation vs. Jefferson formation). Part of the confusion comes from the fact that the rocks are contact metamorphosed and therefore differ in color and texture from their unaltered appearance. However, all previous workers agree that the major skarn deposits in the district, including the Madison Gold deposit, are hosted by the Mississippian Madison Group limestone. The study area is sparsely vegetated with fair-to-good outcrop exposures, except in low-lying areas that are covered by alluvial fans.

Mining History

The Silver Star area is one of the oldest lode-gold mining districts in Montana. Two types of gold deposits are present: 1) fissure veins cutting Precambrian schist and gneiss; and 2) gold-rich skarns. Examples of the former include the Green Campbell and Iron Rod mines (Sahinen, 1939). Most of the gold production from the district has come from skarns developed along the contact between the Madison Group and the Rader Creek pluton. The Broadway (also known as Victoria) was the largest of several historic mines exploiting this skarn zone. An estimated 450,000 tons of ore was mined from the Broadway between 1870 and 1942, at an average grade of around 0.32 ounces per ton (144,000 oz Au) (Price, 2005). The Broadway mine has several thousand feet of horizontal workings extending to a maximum of 650 feet below surface. Three small open pits (American, Victoria, and Black) are located a short distance to the NW of the main Broadway mine.

Prior to 1900, ore from the Broadway mine was hauled to the towns of Silver Star and Iron Rod for milling. A 100-ton mill and cyanide plant was later built on the property, and gold bars were poured on site and shipped directly to the U.S. mint (Price, 2005). The mine shut down in 1942 owing to the general ban on gold mining during WWII. The Broadway-Victoria property has changed owners several times in recent decades, with sporadic exploration drilling. The property was renamed the "Madison Gold" mine in 1986. The current owners, Coronado Resources, are advancing an elliptical decline to explore the down-dip extension of copper and gold-rich skarn below the Black and Victoria pits. At the time of this writing, the decline has been driven over 1420 feet and locally to a depth of 265 feet below surface. Many of the observations and ideas that follow have come from underground mapping and examination of rock samples collected from this active underground operation.

Economic Mineralization

Three types of ore exist at the Madison Gold property: 1) unweathered skarn, locally rich in primary Fe-Cu sulfides and gold; 2) secondary chalcocite with subordinate native copper; and 3) Au-bearing, Fe-rich jasperoid. Most of the copper production to date has come from the chalcocite bodies, whereas most of the gold production has come from the primary sulfide and jasperoid zones.

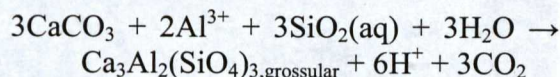
Primary Skarn

Like most skarns, the Madison Gold deposit is mineralogically zoned and includes both *endoskarn* (i.e., metasomatized intrusive rock) and *exoskarn* (metasomatized country rock). Foote (1986) described the mineralogy and geochemistry of the Madison Gold skarn in detail. A simplified summary is included here.

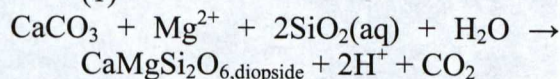
The Rader Creek pluton is a medium-grained, non-porphyrific granitoid with a slabby outcrop pattern defined by low-angle joint sets. Near its contact with the Madison limestone, the pluton is altered to a light-green color with abundant epidote veins and replacements. A thin band of black Mn-oxide often occurs near the boundary between the epidote alteration and fresh granodiorite. Although disseminated sulfides are present, the endoskarn has generally low Cu and Au grades. The exoskarn which developed within the Madison limestone has a gangue mineralogy dominated by grossular-garnet + diopside closest to the intrusive contact grading to massive hedenbergite skarn and calcitic marble with greater distance from the intrusion. The garnet-diopside skarn has a mottled, green- to light-brown color and is disappointingly fine-grained with few collectable mineral specimens. In contrast, the hedenbergite skarn is very coarse-grained, with radiating clusters of dark-green to jet-black pyroxene crystals up to 5 cm long. The outer contact of the hedenbergite zone is very abrupt, with black pyroxene on one side and white calcitic marble on the other (Fig. 2). Primary sulfide minerals, including pyrite, pyrrhotite, chalcopyrite, and bornite, are present throughout the entire exoskarn, but are especially abundant in the garnet-diopside zone, locally forming pods or bands of nearly 100% sulfide. In sulfide-rich zones, the primary anhydrous skarn assemblage has been retrograde-metamorphosed to hydrous minerals, including Fe-rich amphibole, chlorite, and epidote (Foote, 1986). These sulfide-rich zones are oxidized to hematite/limonite near the surface, and at depth where they are cut by jasperoid (see below).

The primary gangue mineral zonation described above for Silver Star is typical of many skarns (e.g., see Meinert et al., 2005), and can be explained by differences in the

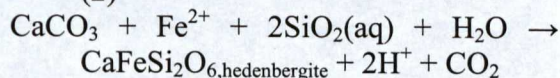
hydrothermal mobility of Al, Mg, Si, and Fe (Fig. 3). Because Al and Mg are relatively immobile, garnet and diopside are found closest to the intrusive contact. Fe and Si are more soluble, resulting in the formation of hedenbergite at the outer margins of the exoskarn. Simplified reactions can be written as follows:



(1)



(2)



(3)

Beyond the furthest extent of metasomatism (i.e., hydrothermal mass transfer), dissipation of heat from the intrusion causes recrystallization of micritic limestone to coarse-grained marble. At Silver Star, the marble is creamy-white to bluish-gray, with large crystals that sparkle in the sun, in contrast to the unaltered Madison limestone that has a dull gray luster.

Jasperoid and Secondary Copper Enrichment

Three of the features of the Madison Gold deposit that set it apart from typical Cu-Au skarns are: 1) the presence of gold-bearing, Fe-rich jasperoid cut by calcite veins; 2) the presence of small but very high-grade bodies of chalcocite ore; and 3) the presence of unusual concentrations of native copper. The remainder of this article will attempt to show how these observations might be linked.

Jasperoid and jasperoid breccia crop out in the vicinity of the Victoria and American pits. This material locally carries good gold grades (> 0.1 opt), and obviously was mined for gold in the early days. The deep orange-



Fig. 2. Black, hedenbergite skarn (left) in near-vertical contact with light-colored marble (right). Tree for scale. Photo taken from the north rim of the Black Pit, looking south.

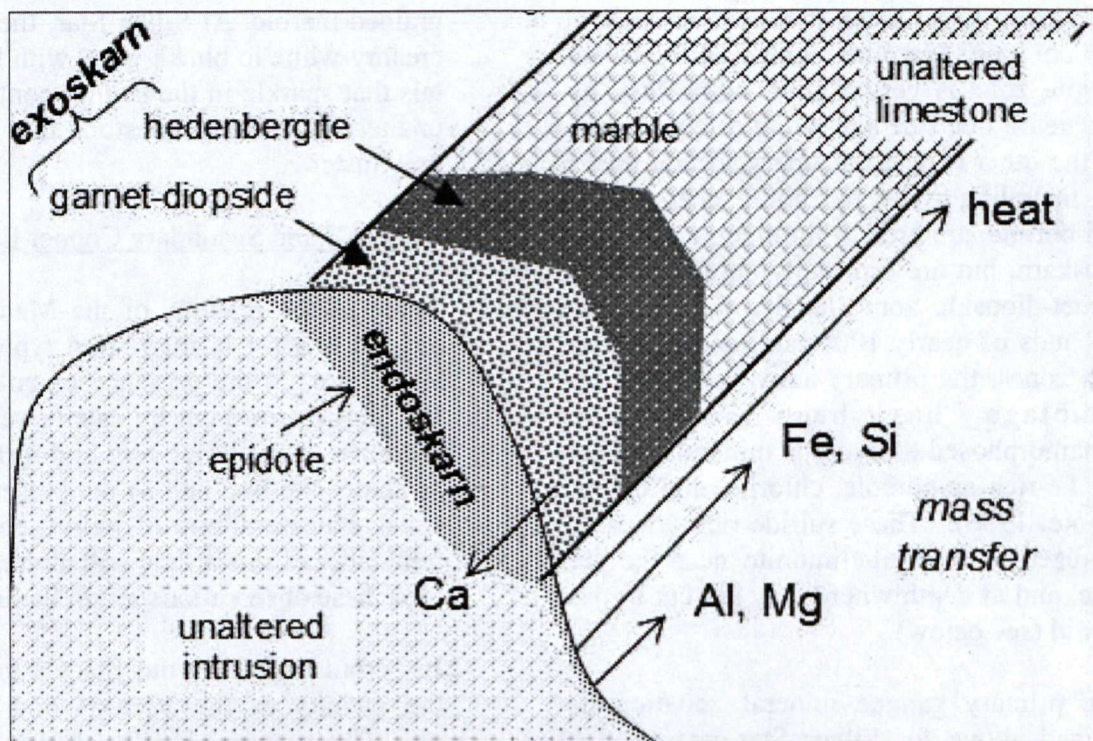


Fig. 3. Schematic diagram showing how differences in the hydrothermal mobility of different elements can explain the observed zonation of primary skarn minerals at Madison Gold.

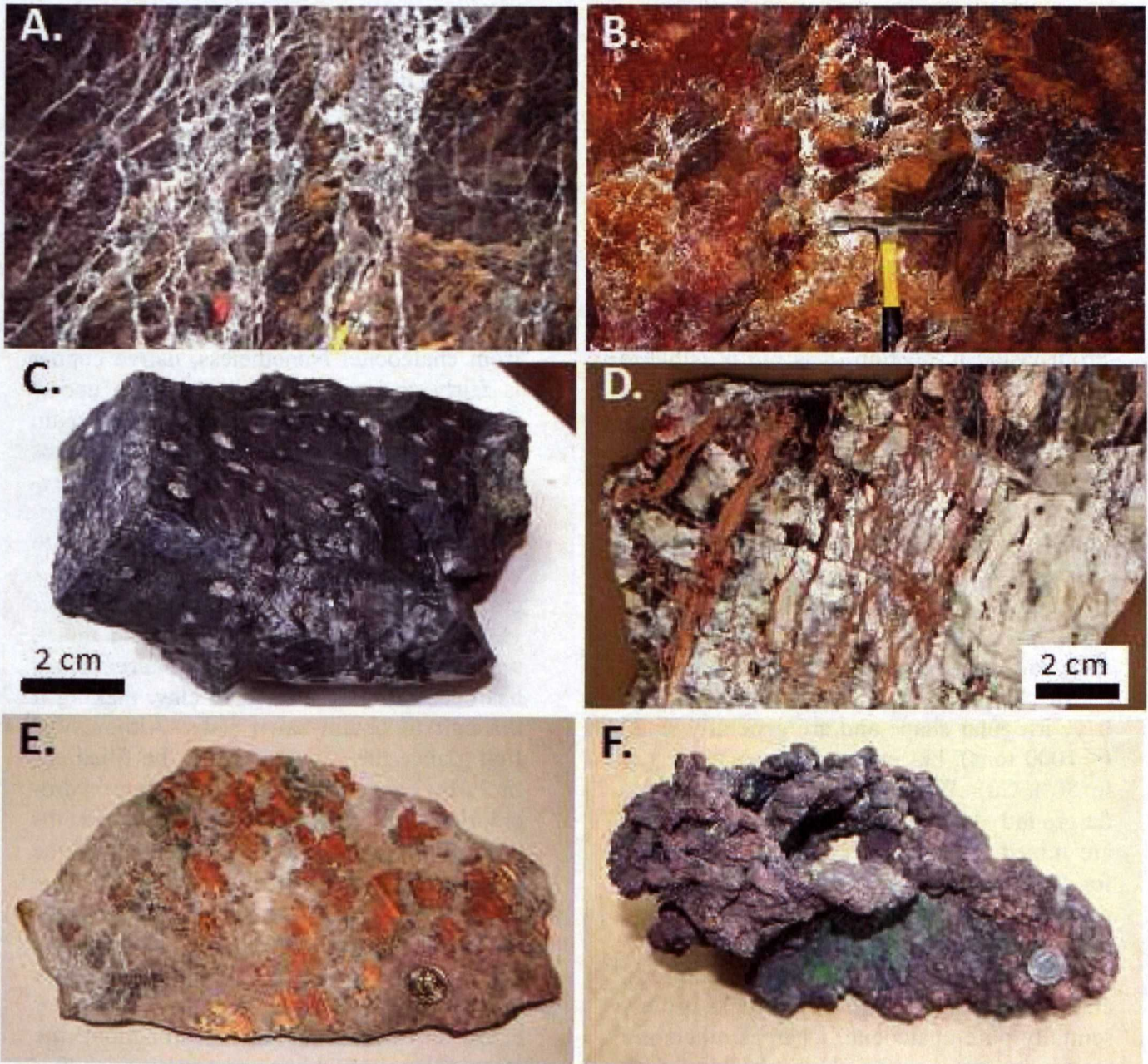


Fig. 4. Photographs of hydrothermally-altered skarn and secondary copper minerals. A) Fe-rich jasperoid with stockwork of white calcite veins. The field of view is roughly 3 m across; B) Jasperoid with bright red pods of pure hematite, most likely replacing primary sulfide minerals: white veins are calcite; C) Massive chalcocite (dark gray) replacing pyrite. Small remnants of pyrite appear as light spots. D) Native copper stockwork in bleached skarn; E) Podiform native copper in garnet-diopside skarn: white is calcite (quarter for scale); F) Large native copper nugget (weight 47 lbs!) with malachite stains (quarter for scale).

brown to red color attests to its high Fe-oxide content, which is confirmed by chemical assay. Exposures of the same jasperoid body in the Madison Gold decline show that it is cut by a stockwork of anastomosing calcite veins (Fig. 4A). Quartz is comparatively rare, with the exception of the siliceous jasperoid itself. Jasperoid is commonly resistant to the strike of a rock hammer but locally contains soft patches of bright red hematite (Fig. 4B). Gold grades in the jasperoid body are locally good, but also unpredictable. From visual inspection, it is not possible to discern ore from waste. The jasperoid body is not restricted to the near-surface environment, and extends to deep levels of the mine. In certain areas, the jasperoid is located along the boundary between the aforementioned garnet-diopside and hedenbergite skarns, although elsewhere it is in direct contact with the Rader Creek pluton.

Adjacent to the jasperoid are localized pockets of chalcocite ore. The chalcocite bodies have irregular shape and are generally small (< 1000 tons), but extremely high-grade (25 to 50% Cu). When encountered during underground drilling, these chalcocite bodies are mined out and stockpiled at the surface for direct shipment to a smelter; no milling is necessary. Examination of hand samples and polished thin-sections shows that the chalcocite has replaced pre-existing sulfides, chiefly pyrite (Fig. 4C). Some rocks are essentially pure chalcocite, whereas others are mainly pyrite, with chalcocite invading along grain boundaries and cracks. Although chalcocite is a very common secondary mineral in weathered, hydrothermal copper deposits, the chalcocite bodies at Silver Star are unusually high-grade, due to whole-scale replacement of massive pyrite by secondary Cu-sulfide. For comparison, supergene-enriched copper ore at the Berkeley Pit of Butte, Montana, typically graded < 1% Cu, but was nonetheless significantly richer than

the deeper ore that had not seen secondary enrichment (< 0.5% Cu) (McClave, 1973).

>From a mineralogical standpoint, the most fascinating aspect of the ore being mined at Madison Gold is the localized occurrence of native copper pods and veins. Native copper is definitely subordinate to chalcocite in terms of abundance; an estimated 350 lbs of copper nuggets have been hand-picked during the current mining operation, compared to an estimated 1 million lbs of Cu mined from chalcocite. Nonetheless, native copper is fairly common, even in the deep underground workings. Copper occurs in two main forms: stockworks of anastomosing veins (Fig. 4D), and pods or irregular masses several cm in diameter (Figs. 4E, 4F). The copper stockworks are particularly striking, with cross-cutting veins of native copper up to 1 cm in thickness. In some samples, the copper veins cut skarn that is still hard and intact, whereas in other samples the skarn matrix has been severely altered to clay, making it difficult to obtain sawn slabs. Although at first glance the veins appear to be filled entirely by copper, reaction with dilute hydrochloric acid shows that many of the veins have thin selvages of calcite, which is a clue to their origin. Another clue is that the overall geometry of the copper veins resembles that of the calcite stockworks that cut the nearby Fe-rich jasperoid bodies (compare Figs. 4A and 4D). Although native copper exists in minor quantities throughout the mine, some of the richest native copper zones were found adjacent to the aforementioned chalcocite bodies. At the boundary between the two mineral zones, arborescent masses of native copper have been found encasing marble-to golf-ball-sized pods of chalcocite.

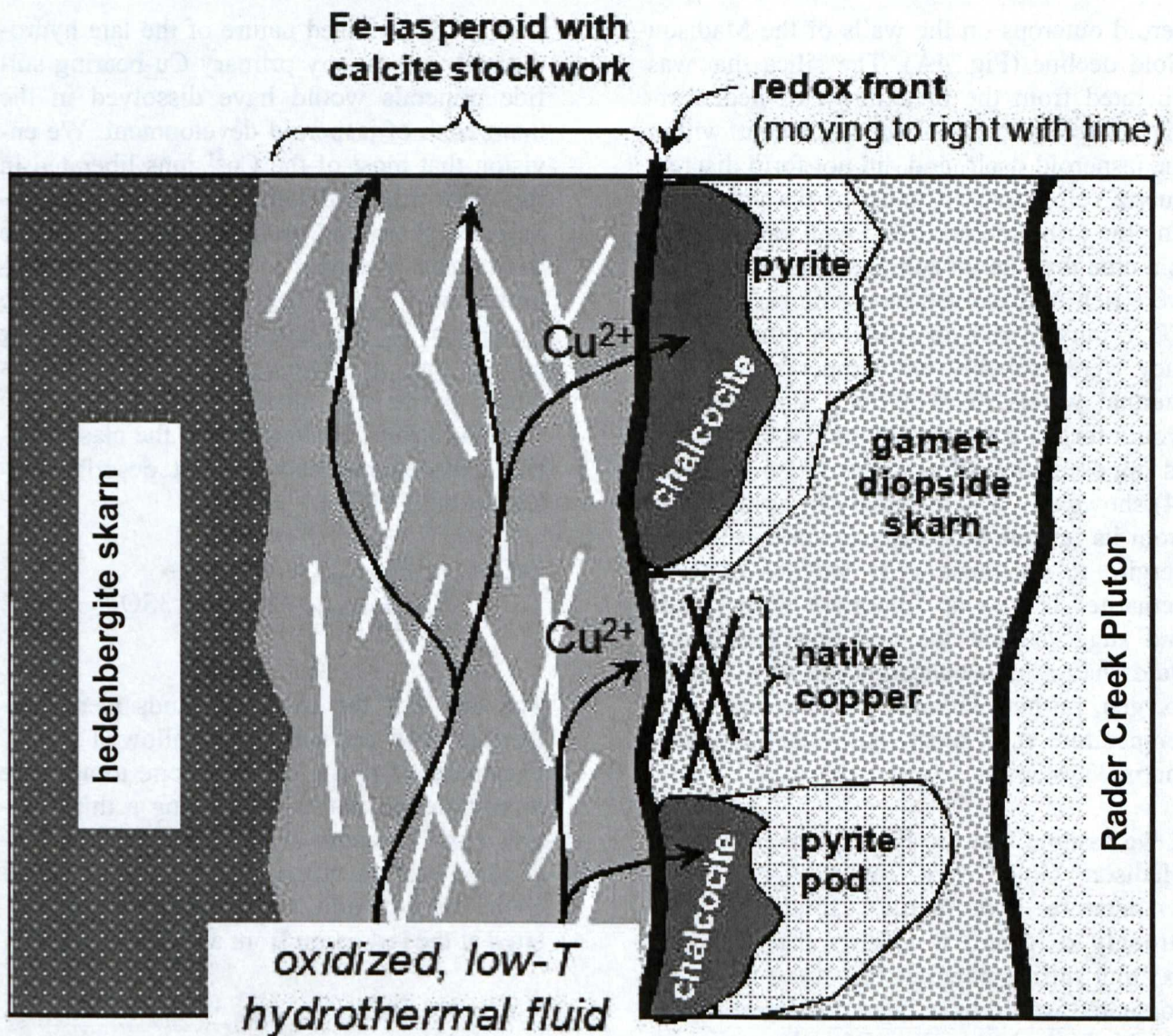


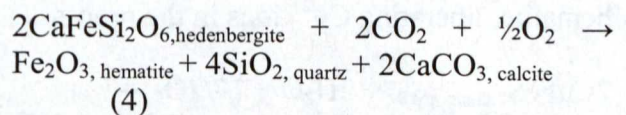
Fig. 5. Conceptual model of low-temperature hydrothermal alteration of the Madison Gold skarn. Oxidized geothermal waters infiltrate through the prograde skarn, converting hedenbergite to hematite + amorphous silica (Fe-jasperoid). Copper is leached out of the skarn protore and is re-deposited at an advancing redox front as either chalcocite (where pre-existing pyrite is present) or native copper (where no sulfides are present).

Genetic Model

The following is a preliminary geochemical model that attempts to link together the spatial association of Fe-rich jasperoid, chalcocite bodies, and native copper at the Madison Gold deposit. A cartoon of the overall process is shown in Fig. 5.

To begin with, the occurrence of Fe-rich jasperoid cut by calcite veins can be explained by interaction of a lower-temperature geo-

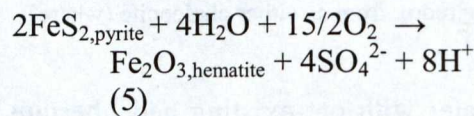
thermal water with pre-existing hedenbergite skarn, as shown by the following simplified reaction:



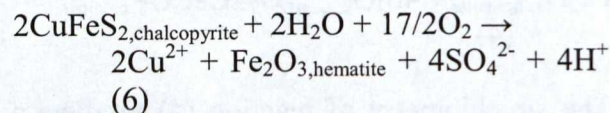
The stoichiometry of reaction (4) predicts a molar ratio of 1:4:2 for hematite:quartz:calcite, which is in qualitative agreement with visual inspection of the jas-

peroid outcrops on the walls of the Madison Gold decline (Fig. 4A). The silica that was liberated from the breakdown of hedenbergite now exists as siliceous cement within the jasperoid itself, and did not form discrete quartz veins. Instead, most of the veins cutting the jasperoid are filled with calcite. This is a clue that the invading geothermal waters were rich in dissolved inorganic carbon (i.e., CO₂), but not rich in silica. In other words, they were probably low-temperature hydrothermal waters (T < 200°C), the type that would form a travertine mound at the surface as opposed to a silica sinter. Also, reaction (4) shows that it is necessary to oxidize iron from its ferrous (+2) valence state in hedenbergite to its ferric (+3) valence state in hematite. This is an important observation, and suggests that the invading geothermal fluids had a high concentration of dissolved oxygen, further evidence that this was a low temperature (and most likely shallow) geothermal system.

If we assume that the Fe-jasperoid bodies at Madison Gold were caused by a low-temperature hydrothermal fluid that was strongly oxidized, it follows that any pre-existing sulfide minerals that these fluids encountered would have been destroyed. Pyrite would have been altered to hematite, as shown by the following reaction:

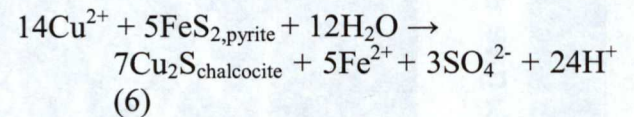


Primary Cu-bearing sulfides such as chalcopyrite would also have been converted to hematite, liberating Cu²⁺ ions in the process:

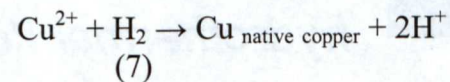


The soft “pods” of hematite in the otherwise hard jasperoid bodies (Fig. 4B) most likely owe their origin to replacement of pre-existing sulfides, e.g., via reactions (5) or (6).

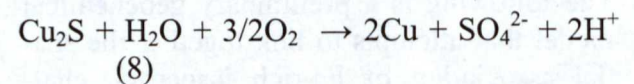
Due to the oxidized nature of the late hydrothermal waters, any primary Cu-bearing sulfide minerals would have dissolved in the main zone of jasperoid development. We envision that most of the Cu²⁺ ions liberated in this way migrated laterally into the garnet-diopside skarn and precipitated as chalcocite and/or native copper at an advancing reduction front (Fig. 5). This is the key step in the formation of the unusually rich secondary copper ores at Madison Gold. In instances where pyrite was already present, the Cu²⁺ reacted to form chalcocite, via the classic pyrite replacement reaction first described by Zies et al. (1916):



The fact that the oxidized fluids were geothermal (and not supergene) allowed the replacement of pyrite by chalcocite to advance to completion, rather than being a thin reaction rim. In areas of the skarn where pre-existing sulfide minerals were absent, chalcocite did not form, and instead Cu²⁺ precipitated at the reduction front as native copper:



This could explain the existence of cm-wide veins of nearly pure copper cutting bleached and clay-altered skarn. It is also possible to form native copper by oxidation of chalcocite:



Reaction (8) could explain the localized intergrowths of native copper nuggets and chalcocite.

Unlike copper, gold is immobile in low temperature, oxidized environments (Gammons and Williams-Jones, 1997). Much of the gold from the historic Broadway mine was recov-

ered from a single drift of oxidized skarn ore, located within 200 feet of surface (Price, 2005). The grade of gold in this oxide ore was probably close to what it would have been in the primary skarn ore, on average ~ 0.3 opt. Preliminary examination of polished sections of primary, sulfide-rich skarn from the Madison Gold mine has revealed the rare presence of micron-sized inclusions of gold within other sulfides, including pyrite and chalcopyrite. Gold has also been identified as micron-sized inclusions within jasperoid. Our current hypothesis, which agrees with the conclusions of Foote (1986), is that most of the gold in the Madison Gold deposit was introduced, along with Fe-Cu-sulfides, during the late stages of the main skarn event. The lower-temperature hydrothermal system responsible for jasperoid development and calcite veining was incapable of remobilizing gold, due to its inferred oxidized character. Thus, oxidation and silicification of the skarn protore resulted in the complete remobilization of copper to form chalcocite and native copper along the margins of the jasperoid, whereas gold remained in place.

Concluding Statements

The above model for hypogene secondary enrichment of copper at the Madison Gold deposit should be considered preliminary. The authors are still at an early stage in their study, and have quite a bit of mineralogy and geothermometry work yet to accomplish. Nonetheless, the general model appears robust in the sense that it explains many of the mineralogical observations at the deposit, while at the same time being geochemically and geologically plausible. If correct, one of the more significant implications of the hypogene enrichment model is that zones of high-grade chalcocite ore may persist to even greater depth than currently seen in the Silver Star district. This is opposed to conventional wisdom which would predict that this type of

secondary copper mineralization would only be present near surface, e.g., at or near the present-day water table. Another important idea to keep in mind is that the late geothermal fluids, if oxidized, could not have introduced any new gold into the deposit. Thus, the grades and distribution of gold within the jasperoid most likely reflect the grades and distribution of gold within the skarn protore.

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