ABSTRACT

The Daisy Creek prospect, located approximately 25 km north of Thompson Falls, Montana, consists of stratabound Cu–Pb–Ag mineralization hosted by Helikian quartzites of the Bonner Formation, Belt Supergroup. Hypogene mineralization occurs in zones containing disseminated galena, chalcopyrite, argentiferous bornite, and argentiferous chalcocite, which precipitated during middle diagenesis within apatite-rich, medium-grained, channel-facies quartzites. Oxidation of these sulfides occurred in two episodes, one during diagenesis under conditions of relatively low CO₂ and high Ba²⁺ activity, and the other during supergene weathering under conditions of higher CO₂ and lower Ba²⁺ activity. In the copper zones, cupriferous goethite, acanthite and barite occur as products of diagnostic oxidation, whereas native silver, limonite and malachite occur as products of supergene weathering. In the lead-rich zone, diagenetic barite replaces galena, and hinsdalite \((\text{Pb, Sr})_3\text{Al}_3\text{PO}_4\text{SO}_4\text{(OH)₅})\), a rare supergene mineral, fills vugs and locally replaces supergene cerussite and pyromorphite where the lead zone overlaps Pb-anomalous strata.

Keywords: stratabound copper, hinsdalite, oxidation products, Montana, Bonner Formation, Belt Supergroup.

INTRODUCTION

The Daisy Creek prospect, located approximately 25 km north of Thompson Falls, Montana, consists of stratabound Cu–Pb–Ag mineralization hosted by Helikian quartzites of the Bonner Formation, Belt Supergroup. Sulfides occur as disseminations, clouds, and ponds adjacent to siltite beds within a reduced (white to grey), epsilon-cross-bedded, fluvial channel (Stanley 1984). B-horizon soil samples, float-rock samples, and soil heavy-mineral concentrates were examined to determine the relationship between hypogene mineralization and the products of supergene alteration.

X-ray powder diffraction, scanning electron microscopy, X-ray spectroscopy (energy dispersion) and results of geochemical analyses were used to identify the various mineral phases. The products of oxidation of disseminated, quartzite-cementing galena, chalcopyrite, and argentiferous bornite and chalcocite consist of cupriferous goethite, barite, limonite, acanthite, native silver, cerussite, pyromorphite, malachite, chalcantihite and chrysocolla. In addition, hinsdalite \((\text{Pb, Sr})_3\text{Al}_3\text{PO}_4\text{SO}_4\text{(OH)₅})\), a rare product of supergene alteration, has been identified.

GEOLoGICAL SETTING

Within the Belt Basin of western Montana, two major quartzite formations are recognized. The younger of these quartzites, the Bonner Formation, is a fluvial, hematite-stained sandstone containing the Daisy Creek Cu–Ag–Pb prospect. Sedimentary facies within the Bonner Formation include alluvial-apron conglomerates, which grade into braid-plain, channel-facies quartzites and distributary, sheet- and overbank-facies siltite couplets in the Daisy Creek area (Fig. 1; Winston et al. 1977, Newton 1982, Stanley 1984).

At the Daisy Creek prospect, mineralization occurs within a grey to white, epsilon- and trough-cross-bedded, feldspathic, vitreous to micaceous, fine-
medium-grained, channel-facies orthoquartzite (informally, the upper cross-bedded member) interbedded with hematite-stained (pink, red, and purple), flat-laminated, coarse-grained, mud-cracked, overbank-facies siltite couplets (Fig. 2). The upper cross-bedded member averages 30 m in thickness and contains more disseminated ferroan carbonate cement and less ferric oxide cement than the surrounding red-beds.

B-horizon soil samples collected at 15-m intervals over the upper cross-bedded member exhibit elevated concentrations of aqua-regia-soluble Ca, Sr, Mg, Ti and P (Fig. 3) with respect to the soils developed over the enclosing red-beds. These high concentrations are attributed to the abundance of 1) carbonate cement filling the voluminous pore-spaces of these quartzites, and 2) heavy minerals (specifically, apatite, ilmenite and leucoxene) concentrated within the lower 15 m of this member. Highly anomalous P concentrations (0.12 to 0.25 wt.% P₂O₅) from these strata contrast with lower concentrations from the surrounding red-beds (< 0.08 wt.% P₂O₅).

The concentrations of P in the soil samples are virtually identical to those found in float-rock samples from the upper cross-bedded member (up to 0.55 wt.% P₂O₅), and are extremely high for terrigenous sandstones relative to Pettijohn’s estimate of global average composition (0.02 wt.% P₂O₅ for orthoquartzites: Pettijohn 1963). Furthermore, nonmagnetic fractions of panned concentrates from B-horizon soils above this member contain up to 85% apatite, most of which consists of subrounded, frosted (abraded), translucent, detrital grains up to 1 mm in diameter (probably igneous fluorapatite detritally transported from granitic source-rocks to the south: Winston et al. 1977). The other 15% of the apatite grains are transparent, euhedral, acicular prisms and have an average width-to-length ratio of 5:1. These crystals probably are recently formed carbonate-hydroxyapatite, because they do not exhibit evidence of abrasion. This suggests that at least some of the apatite has recently precipitated in situ within the soil.

Float-rock samples of the coarsest quartzite facies from the upper cross-bedded member contain abundant grains of detrital apatite. They also commonly contain lag lamellae that consist of imbricated, subrounded, pale green, impure (significant amounts of Fe and Al), phosphatic mud-chips up to 1 cm in longest dimension. Subhedral grains of detrital monazite also occur within heavy-mineral lag laminae in the upper cross-bedded member. The monazite is not dissolved by the aqua regia digestion and thus does not contribute to the P concentrations determined.

The above evidence demonstrates that 1) the upper
The extent of the sulfide mineralization at the Daisy Creek prospect has been defined by anomalous concentrations of Cu, Pb and Ag in soil (Fig. 4). The overlapping geometry of these anomalous regions demonstrates that the deposit has a distinct geochemical zonation that cannot be related to differential hydromorphic dispersion or downslope creep because slope orientations are inconsistent with the zone offsets. In addition, several distinct forms of disseminated limonite gossans within the float-rock samples are recognizable as supergene products of galena, chalcopyrite, argentiferous bornite, and argentiferous chalcocite (Blanchard 1968). These have spatial distributions that precisely match the pedo-geochemically anomalous zones, suggesting that the zonation is controlled by the primary hypogene mineralogy (Stanley 1984).

The sulfide zonation (galena, chalcopyrite, argentiferous bornite, and argentiferous chalcocite, observed sequentially from SSW to NNE) is identical to that in zonation models for many other stratabound copper deposits (Brown 1971, Annels 1974, Hayes 1984), and can be attributed to a stable equilibrium assemblage of these sulfides across a range of Eh and pH conditions (Hayes 1984).
Paragenetic relationships of the sulfides, as observed in polished sections of float-rock samples, demonstrate that cubes of early diagenetic pyrite were replaced progressively by galena and chalcopyrite, bornite, and chalcocite (Fig. 5). This suggests that the metals migrated from north to south into a reduced zone within the quartzites, where they precipitated as sulfides during early-middle diagenesis (Stanley 1984).

**PRODUCTS OF OXIDATION**

After sulfide deposition, two episodes of oxidation occurred. The first is characterized by the oxidation of galena, chalcopyrite and argentiferous bornite, forming cupriferous goethite, barite and acanthite. Evidence for the breakdown of chalcocite during this episode of oxidation has not been observed.

Oxidation appears to have occurred sequentially, involving firstly Fe$^{2+}$ to Fe$^{3+}$, followed by S$^{2-}$ to SO$_4^{2-}$. The oxidation reactions that occurred at Daisy Creek can be summarized by the following balanced equilibria:

\[
\begin{align*}
\text{Ba}^{2+} + \text{PbS} + 2\text{O}_2 & \rightarrow \text{Pb}^{2+} + \text{BaSO}_4 \\
\text{CuFeS}_2 + 2\text{Ba}^{2+} + 4.75\text{O}_2 + 0.5\text{H}_2\text{O} + (2+2x)e^- & \rightarrow 2\text{BaSO}_4 + (1-x)\text{Cu}^{2+} + \text{Cu}_x\text{FeO-OH} \\
\text{Ag}_y\text{Cu}_x\text{FeS}_4 + 4-(y/2)\text{Ba}^{2+} + (8.75-y)\text{O}_2 + 0.5\text{H}_2\text{O} + (2x-y-2)e^- & \rightarrow \text{Cu}_x\text{FeO-OH} + (5-x)\text{Cu}^{2+} + (y/2)\text{Ag}_2\text{S} + 4-(y/2)\text{BaSO}_4 
\end{align*}
\]

**Fig. 4.** Soil-grid concentrations of Cu, Pb and Ag over the Daisy Creek prospect. The threshold values were selected from probability plots and demonstrate the overlapping relationships of anomalous areas.

**Fig. 5.** Van der Veer diagram (Robertson & Van der Veer 1952) of mineral paragenesis at the Daisy Creek prospect. Four periods of formation of economic minerals are recognized. These are: 1) ED, an early-diagenetic cubic pyrite, 2) MD–RED, middle-diagenetic replacement of pyrite by successively more copper-rich sulfide phases (galena, chalcopyrite, bornite and chalcocite) under relatively reducing conditions, 3) MD–OX, middle-diagenetic oxidation of these previously formed sulfides, producing acanthite, barite and cupriferous goethite, and 4) SG, supergene oxidation of the sulfide minerals and diagenetic oxidation-products. Abbreviations: PY pyrite, GN galena, CP chalcopyrite, BN bornite, CC chalcocite, BA barite, GO cupriferous goethite, AC acanthite, CH chrysocolla, CK chalcocite, MA malachite, LM limonite, AG native silver, HD hinsdalite, PM pyromorphite, and CE cerussite. Limonite annotated with one, two, or three stars refers to recognizable different morphologies of limonite, which can be related to the original galena, chalcopyrite or bornite–chalcocite mineralogy, respectively.
Evidence for these reactions can be seen in the textures of sulfide and oxide phases in Figure 6. Chalcopyrite, after cubic pyrite, generally is rimmed by argentiferous bornite, and these sulfide aggregates are oxidized to cupriferous goethite. Acanthite occurs at the goethite-chalcopyrite replacement boundary, probably because Ag from the bornite migrated along with the oxidation front and precipitated when encountering \( S^2^- \) released during oxidation of the chalcopyrite. Barite commonly rims the cupriferous goethite and fills cracks within the goethite created by a volume loss during oxidation. These products are considered to result from an oxidation event characterized by relatively low \( CO_2 \) (malachite is absent) and high activity of the barium ion (the oxidation of sulfide liberated sulfate, which reacted with \( Ba^{2+} \) and precipitated as barite), and which occurred after sulfide precipitation. Reaction products from this oxidation event are considered to have formed when an oxidized groundwater migrated into and reacted with the sulfide-bearing quartzites. These reaction products are mineralogically, geochemically, and texturally distinct from other products of oxidation.

A second, later oxidation event of supergene affinity, i.e., high (atmospheric) \( CO_2 \) and low \( Ba^{2+} \) activities (no barite is observed with limonite after sulfides) is characterized by the development of limonite, malachite, native silver, cerussite and pyromorphite (Fig. 5; Stanley 1984). Malachite generally occurs as flakes along bedding planes, defined by laminae of white mica within the chalcocite-bearing quartzites, and as coatings on fracture surfaces within the bornite-bearing quartzites. Native silver was observed in heavy-mineral concentrates from soils from both of these zones. Within chalcopyrite-bearing-quartzites, limonite and malachite in a symplectitic intergrowth replace cupriferous goethite along fractures and are the characteristic supergene phases. Minor chalcantlite and chrysocolla also occur sporadically within Cu-anomalous strata. Within the Pb-anomalous zone, cerussite and pyromorphite replace galena and fill carbonate-vacated voids as exotic gossans within float-rock samples.

The overlapping region of the Pb-anomalous zone of the mineral occurrence and the P-anomalous part of the upper cross-bedded member (the lower 15 m) contains abundant cerussite and pyromorphite. These minerals generally occur as a replacement of galena, and as exotic gossans filling vugs formed by the dissolution of a pre-existing carbonate cement. Gandolfi camera X-ray powder-diffraction patterns, scanning-electron photomicrographs (Fig. 7), and energy-dispersion X-ray spectra (Fig. 8) of float-rock samples indicate that hinsdalite \((Pb, Sr)Al_3PO_4\cdot SO_4(OH)_6\), a rare supergene mineral, is also present.

Hinsdalite is known to occur at only a few other localities worldwide. These include: 1) the Sylvester and Comet mines, Tasmania (Birch 1977), where it replaces pyromorphite, 2) the Mineral Park mine, Arizona (Wilkinson et al. 1980), where it occurs with supergene chalcocite replacing hypogene sphalerite, 3) the Butte mine, Montana (Roberts et al. 1974), where it occurs with supergene covellite replacing enargite, and 4) the Golden Fleece mine, near Hinsdale, Colorado (Palache et al. 1951), the type locality, where it occurs abundantly within a quartz vein containing barite, rhodochrosite and sulfides.

At Daisy Creek, hinsdalite commonly lines vugs left by the dissolution of carbonate cement within quartzites that contain the galena mineralization. It also occurs in a few samples coating and replacing pyromorphite and, less commonly, cerussite, both products of the supergene alteration of galena (Stanley 1984). The hinsdalite occurs in clusters of euhedral rhombohedra up to 10 micrometres long that grew into the open spaces of the vugs. Tabular, hexagonal prisms of hinsdalite, an abundant form at the Mineral Park mine, Arizona (Wilkinson et al. 1980) are not observed at Daisy Creek, but hinsdalite replacing pyromorphite is a common mode of occurrence at the Sylvester and Comet mines, Tasmania.
FIG. 7. Backscattered (A) and secondary (B) electron SEM photomicrographs of hinsdalite (HD). Rhombohedral form is evident in mass of hinsdalite rimming void in quartzite formed by dissolution of pre-existing carbonate cement. Scale bar 10 μm.

(Birch 1977). Energy-dispersion X-ray spectra (Fig. 8) indicate that the hinsdalite at Daisy Creek contains little or no Sr, a feature also observed for the hinsdalite at the Comet mine (Birch 1977).

CONCLUSIONS

Two periods of oxidation of the sulfides at the Daisy Creek prospect are observed. The first formed
cupriferous goethite, acanthite and barite, and probably occurred during middle diagenesis owing to the introduction of an oxidizing brine into the sulfide-bearing strata. The second, related to supergene processes, produced mainly limonite and malachite from the previously formed cupriferous goethite, as well as native silver, cerussite and pyromorphite.

The occurrence of hinsdalite at the Daisy Creek prospect, Montana, and its similarity to other occurrences worldwide, attest to its importance as a supergene mineral that commonly replaces previously formed products of oxidation. At the Daisy Creek prospect, the occurrence of hinsdalite in the zone of overlapping anomalous concentrations of Pb and phosphate suggests that the major limiting control on its precipitation may be the activity of phosphate and Pb species in meteoric waters. Finally, the typically microscopic size of hinsdalite at all localities leaves open the possibility that it is more common than has previously been considered.

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Fig. 8. Energy-dispersion X-ray spectrum (175,000 counts) for hinsdalite from sample DC-7547. No Sr peak is observable.


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