HINSDALITE AND OTHER PRODUCTS OF OXIDATION AT THE DAISY CREEK STRATABOUND COPPER–SILVER PROSPECT, NORTHWESTERN MONTANA

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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 CO_2 and high Ba^{2+} activity, and the other during supergene weathering under conditions of higher CO_2 and lower Ba^{2+} activity. In the copper zones, cupriferous goethite, acanthite and barite occur as products of diagenetic oxidation, whereas native silver, limonite and malachite occur as products of supergene weathering. In the lead-rich zone, diagenetic barite replaces galena, and hinsdalite $(Pb,Sr)Al_3PO_4SO_4(OH)_6$, a rare supergene mineral, fills vugs and locally replaces supergene cerussite and pyromorphite where the lead zone overlaps P-anomalous strata.

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

SOMMAIRE

L'indice minéralisé en Cu, Pb et Ag de Daisy Creek, situé environ 25 km au nord de Thompson Falls, au Montana, est conforme aux quartzites d'âge Hélikien de la formation Bonner, du supergroupe Belt. La minéralisation hypogène en zones est formée de galène, chalcopyrite, et bornite et chalcocite argentifères, espèces qui se sont formées pendant la diagenèse moyenne dans des quartzites d'un facies de chenal, riches en apatite et à grain moyen. L'oxydation de ces sulfures s'est faite en deux stades, le premier lors de conditions diagénétiques de faible activité de CO_2 et de forte activité de Ba^{2+}, et le second pendant le lessivage supergène, à forte activité de CO_2 et d'une activité réduite de Ba^{2+}. Dans les zones riches en cuivre, goethite cuprifère, acanthite et barytine sont les produits d'oxydation diagénétique, tandis que argent natif, limonite et malachite sont les produits du lessivage. Dans la zone riche en plomb, la barytine diagénétique remplace la galène, et la hinsdalite $(Pb,Sr)Al_3PO_4SO_4(OH)_6$, espèce supergène peu commune, remplit des cavités et remplace ici et là cerussite et pyromorphite supergènes, là où la zone riche en plomb coïncide avec les strates à teneur de phosphore anomale.

(Traduit par la Rédaction)

Mots-clés: gîte de cuivre stratiforme, hinsdalite, produits d'oxydation, Montana, formation Bonner, supergroupe Belt.

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, chalcanthite and chrysocolla. In addition, hinsdalite $(Pb,Sr)Al_3PO_4SO_4(OH)_6$, 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-flow- 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- to
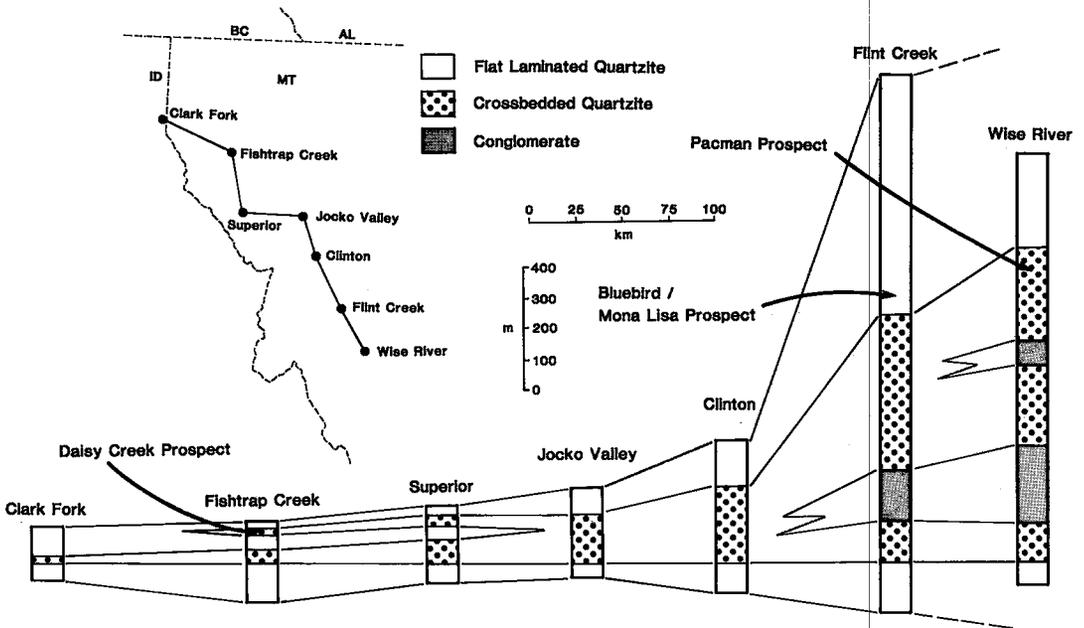
FIG. 1. Regional cross-section showing sedimentary facies relationships within the Bonner Formation, Belt Supergroup. At Fishtrap Creek, the approximate location of the Daisy Creek prospect, the Bonner Formation is divided into 5 informal members (lower, middle, and upper flat-laminated, fine-grained quartzites (Ybn_1, Ybn_3, and Ybn_5) and lower and upper cross-bedded, medium-grained quartzites (Ybn_2 and Ybn_4, respectively).

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.% P_2O_5) from these strata contrast with lower concentrations from the surrounding red-beds (< 0.08 wt% P_2O_5).

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.% P_2O_5), and are extremely high for terrigenous sandstones relative to Pettijohn's estimate of global average composition (0.02 wt% P_2O_5 for ortho-

quartzites: 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
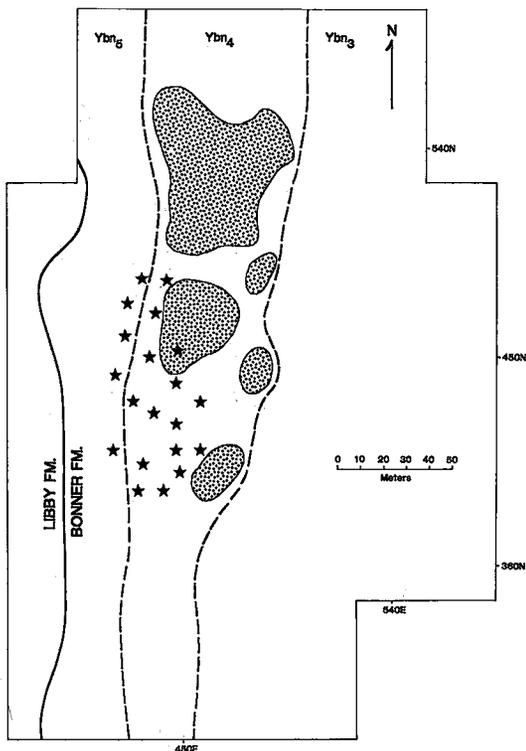
FIG. 2. Geological map of the Daisy Creek prospect. Shaded areas contain malachite oxidation products in float-rock chips within the Cu-anomalous zone. Stars represent prospect pits over the Pb-anomalous zone. Bonner Formation members Ybn$_3$ and Ybn$_5$ are flat-laminated, fine-grained quartzites that enclose the medium-grained, epsilon- and trough-cross-bedded Ybn$_4$ quartzite member. Regionally, bedding strikes approximately 165° and dips 40° SW.

FIG. 3. Soils with anomalous concentrations of phosphorus over the Daisy Creek prospect. The outer contour encloses areas with greater than 0.07 wt.% P$_2$O$_5$, whereas the shaded areas have concentrations greater than 0.10 wt.% P$_2$O$_5$. Threshold values were selected using probability plots. The P-anomalous zone approximately overlies the lower half of the upper cross-bedded member (Ybn$_4$).

cross-bedded member of the Bonner Formation, at least within the areal confines of the soil survey (22 soil lines traversing the stratigraphy across a strike length of 8 km), contains abundant apatite, both in mud chips and as individual detrital grains, in its lower 15 metres, and 2) supergene rock–water reactions have produced solutions with high concentrations of phosphate.

NATURE OF THE MINERALIZATION

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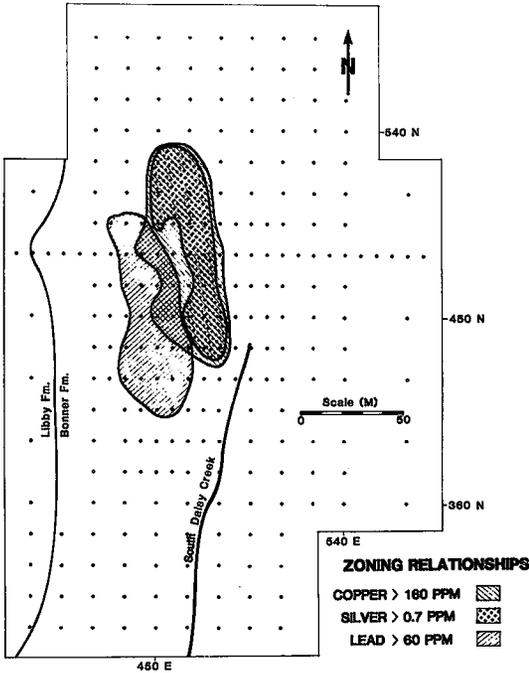
FIG. 4. Soil-grid concentrations of Cu, Pb and Ag over the Daisy Creek prospect. The threshold values were selected from probability plots and demonstrate the overlapping relationships of anomalous areas.

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 chalcanthite, MA malachite, LM limonite, AG native silver, HD hinsdalite, PM pyromorphite, and CE cerussite. Limonite annotated with one, two, or three stars refers to recognizably different morphologies of limonite, which can be related to the original galena, chalcopyrite or bornite–chalcocite mineralogy, respectively.

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:

$$Ba^{2+} + PbS + 2O_2 \rightarrow Pb^{2+} + BaSO_4$$

$$CuFeS_2 + 2Ba^{2+} + 4.75O_2 + 0.5H_2O + (2+2x)e^- \rightarrow 2BaSO_4 + (1-x)Cu^{2+} + Cu_x{}^0FeO{\cdot}OH$$

$$Ag_y{}^0Cu_5FeS_4 + 4-(y/2)Ba^{2+} + (8.75-y)O_2 + 0.5H_2O + (2x-y-2)e^- \rightarrow Cu_x{}^0FeO{\cdot}OH + (5-x)Cu^{2+} + (y/2)Ag_2S + 4-(y/2)BaSO_4$$
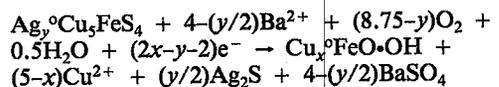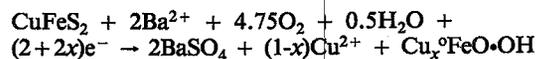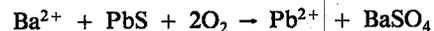
Evidence for these reactions can be seen in the textures of sulfide and oxide phases in Figure 6. Chalcopyrite, after cubic pyrite, generally is rimmed by argentiferous bornite, and these sulfide aggregates are oxidized to cupriferous goethite. Acanthite occurs at the goethite–chalcopyrite replacement 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 chalcanthite 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$_3$PO$_4$ SO$_4$(OH)$_6$, a rare supergene mineral, is also present.

Hinsdalite is known to occur at only a few other
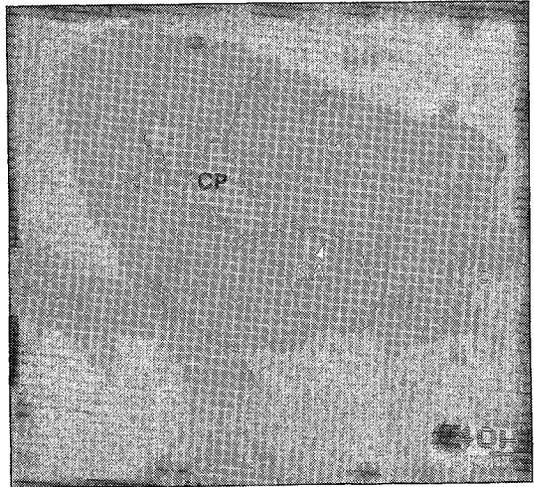
FIG. 6. SEM backscattered electron photograph of cupriferous goethite (GO) replacing chalcopyrite (CP). Note the rim of acanthite surrounding the replacement boundary, and the barite (BA) infilling cracks and rimming the cupriferous goethite. The thin dark band around the goethite consists of goethite with a higher concentration of Cu than the core, and is considered originally to have been bornite that replaced a chalcopyrite rim before oxidation took place. Scale bar 40 μm.

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
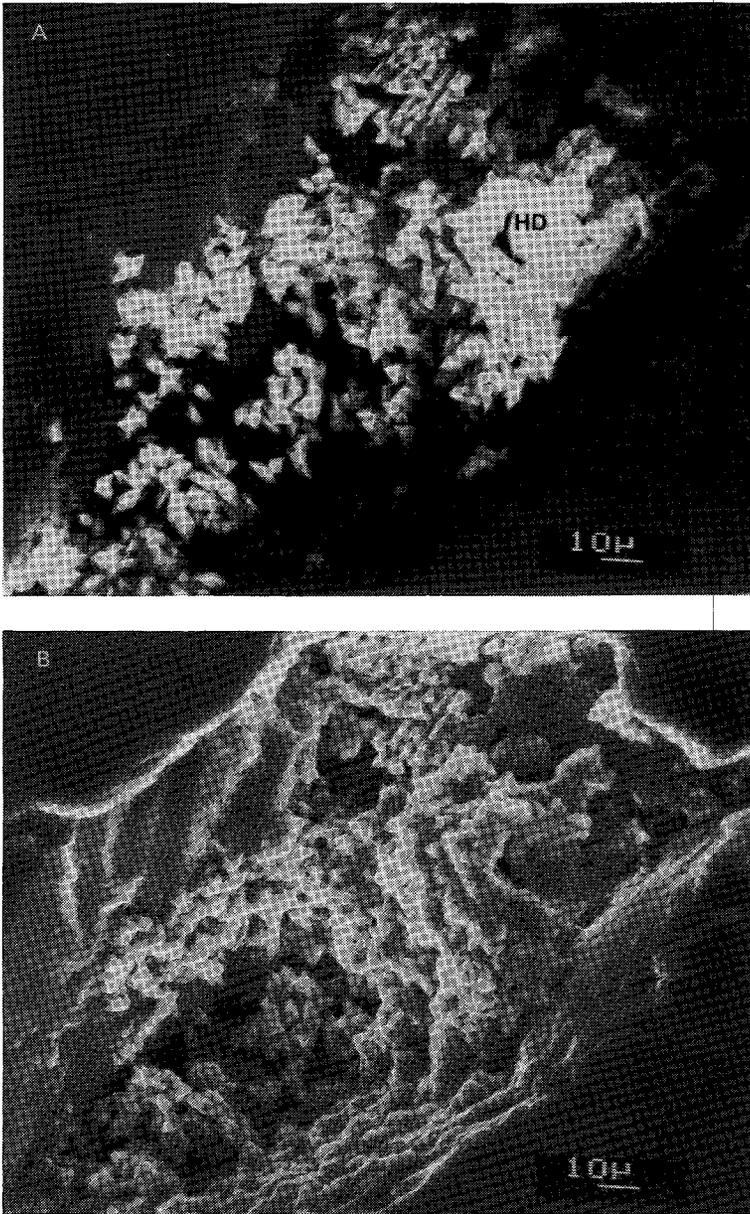
FIG. 7. Backscattered (A) and secondary (B) electron SEM photomicrographs of hinsdalite (HD). Rhombohedral form is evident in mass of hinsdalite rimming void in quartzite formed by dissolution of pre-existing carbonate cement. Scale bar 10 μm.

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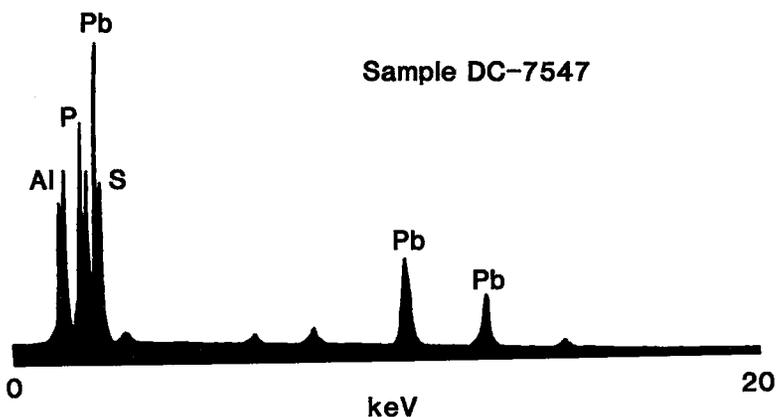
FIG. 8. Energy-dispersion X-ray spectrum (175,000 counts) for hinsdalite from sample DC-7547. No Sr peak is observable.

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.

REFERENCES

ANNELS, A.E. (1974): Some aspects of the stratiform ore deposits of the Zambian Copperbelt and their genetic significance. In Gisements Stratiformes et Provinces Cuprifères (P. Bartholomé, ed.). Centenaire de la Société Géologique de Belgique, Liège, Belgique, 235-254.

BIRCH, B. (1977): Hinsdalite from the Zeehan area, Tasmania. Mineral. Record 8, 391-392.

BLANCHARD, R. (1968): The interpretation of leached outcrops. Nevada Bur. Mines Bull. 66.

BROWN, A.C. (1971): Zoning in the White Pine copper deposit, Ontonagon County, Michigan. Econ. Geol. 66, 543-573.

HAYES, T.S. (1984): Geologic Studies on the Genesis of the Spar Lake Stratabound Copper-Silver Deposit, Lincoln County, Montana. Ph.D. thesis, Stanford Univ., Stanford, California.

NEWTON, E. (1982): A Petrographic Study of Cu-Ag Mineralization in the Bonner Formation of the Precambrian Belt Supergroup of Western Montana. A.B. thesis, Dartmouth College, Hanover, New Hampshire.

PALACHE, C., BERMAN, H. & FRONDEL, C. (1951): Dana's System of Mineralogy (7th ed., Vol. II). John Wiley and Sons, New York.

PETTIJOHN, F.J. (1963): Chemical compositions of sandstones – excluding carbonate and volcanic sands. In Data of Geochemistry (6th ed.). U.S. Geol. Surv. Prof. Pap. 440-S.

ROBERTS, W.L., RAPP, G.R., JR. & WEBER, J. (1974): Encyclopedia of Minerals. Van Nostrand Reinhold Co., New York.

ROBERTSON, F. & VAN DER VEER, P.L. (1952): A new diagrammatic scheme for paragenetic relations of ore minerals. Econ. Geol. 47, 101-109.

STANLEY, C.R. (1984): *The Geology and Geochemistry of the Daisy Creek Prospect, A Stratabound Copper–Silver Occurrence in Western Montana.* M.Sc. thesis, Univ. British Columbia, Vancouver, B.C.

WILKINSON, W.H., JR., ROE, A. & WILLIAMS, C. (1980): Some unusual secondary minerals from the Mineral Park mine, Mohave County, Arizona. *Mineral. Record* **11**, 243-245.

WINSTON, D., LANGE, I.M., BLEIWAS, D. & GODLEWSKI, D. (1977): Alluvial fan, shallow water, and sub-wave base deposits of the Belt Supergroup near Missoula, Montana. *Geol. Soc. Amer., Rocky Mountain Sect. Field Trip Guide* **5**.